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THEORETICAL STUDY OF THE SPIN-HAMILTONIAN OF A COMPLEX WITH PENTAVALENT MOLYBDENUM.

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1) Introduction:

The purpose of this paper is to explain the g-values and hyperfine structure constants observed in the paramagnetic resonance of one complex of Mo^{5+}. The resonance of Mo^{5+} has been observed in diluted crystals (1), and in liquid and frozen solutions (2), and the optical absorption spectrum of one complex is also available (3). Most of these references (1, 2, 3) deal with the complex of Mo^{5+} with chlorine in strongly concentrated hidrocloric acid, and in them, the formula $[Cl_5OMo]^{=}$ is assumed. It will be shown that the measured parameters can be explained under reasonable assumptions with this formula for the complex. As the paramagnetic resonance spectrum of this ion is axially symmetric, it will be assumed that the complex ion is a tetragonally distorted octahedron with Mo in the center. The formula assumed for the complex ion makes unlikely the axial trigonal distortion.

For octahedric symmetry and in the crystal field approximation, the orbital levels of the Mo^{5+} ion would split into a triplet and doublet. The triplet being of lower energy than the doublet for negatively charged ligands. The states of the triplet and doublet are designed as t_2 and e states respectively and their energy levels are further split by a tetragonal distortion of the octahedron. The triplet t_2 splits into a singlet and a doublet under this distortion, their separation in energy being proportional to $R^2\ 27\langle r^2\rangle - 25\langle r^4\rangle$ and to the amount of the tetragonal distortion. The sign of this expression is very sensitive to the details of the electronic distribution, and although it will be shown that the orbital singlet from t_2 is lower than the doublet, it is not possible to be sure of the sign of the tetragonal distortion from the expression above. When the electron spin is considered, the three orbital t_2 states become three spin doublets, and their g-values have been calculated (4) when the tetragonal distortion and spin-orbit

coupling between these six states are considered. As the measured $g_{||}$ and $g_{\perp}$ are very near the value 2, the spin doublet from the orbital singlet has the lower energy, because if the other t_2 states were of lower energy, the g values would be near zero. This deduction depends on the assumption that the spin orbit coupling constant ζ is smaller than the tetragonal splitting δ between the t_2 orbital singlet and orbital doublet. There is another possibility of having $g_{||}$ and $g_{\perp}$ near value 2, but in the present case it corresponds to $\zeta = 20\,\delta$, which is not reasonable as it will be presently seen.

The formulae already mentioned (4) fail to give an accurate agreement with the measured $g_{||}$, because $g_{||} = 2$ up to first order in ζ / δ while $g_{\perp} = 2 - 2\,(\zeta/\delta)$. This difficulty disappears when one considers the admixture of the (4d)e orbital states into the ground state through the spin-orbit coupling, and it can be shown that both $g_{||}$ and $g_{\perp}$ differ from 2 by a term of first order in λ. When the formulae so obtained are made to fit with the measured $g_{||}$ and $g_{\perp}$, the ratio of the spin-orbit matrix element of the energy separation between the t_2 and e states, turns out to be unreasonably small. To explain this discrepancy, one is forced to consider the covalency between the (4d) states of Mo and the p states of the ligand. It was not enough to choose convenient orbital factors (5), as these would have been too small, and it was necessary to take into account the fact that some excited states, that are not considered in the crystal field approximation, are mixed into the ground sate through the spin-orbit interaction. These states are those obtained from the ground state of the complex ion by excitation of electrons from the fully occupied orbitals into the empty orbitals. By this mechanism some orbitals that are essentially ligand states, give contributions to the g-values that are comparable to those orbitals that are essentially central ion states. This contribution does not appear in the crystal field approximation or in

theories where covalency is taken into account only by the use of convenient reduction coefficients.

One would expect that the introduction of all these excited states would make very difficult the calculation of g-values, but it was shown that under several restrictions most of the contributions became zero. Under those restrictions, most of the required results are obtained by making the calculation for a fictitious one-electron system, provided the energy levels and wave functions of this fictitious system are conveniently choosen. These results are generalized to the case when there is only one magnetic electron or hole besides empty or fully occupied orbitals.

When considering the covalency between the 4d electrons of the central ion and the p electrons of the ligand, the difference between the $O^{=}$ and the Cl^{-} is disregarded. To find a justification for this assumption it is assumed that the difference between $O^{=}$ and Cl^{-} can be described by the sum of two perturbations: one even and the other odd under inversion, taking Mo as center of inversion. The even perturbation only adds to the effects of the even tetragonality already considered. The odd perturbation would mix odd contributions to the wave function of the ground state, and their effect on the hyperfine and Zeeman terms would be of second order in the perturbation because the corresponding operators are even, If it is then assumed that the said odd perturbation is small, its effect on the hyperfine and Zeeman parameters can be disregarded.

Under all these assumptions the expressions for $g_{\parallel}$, $g_{\perp}$, A and B, have been obtained.

Although the formulae have too many parameters to be determined from the available data, the model assumed is justified by the reasonable values that can be given to those theoretical parameters.

From the theoretical expressions for the hyperfine constants A, B, sensible values for the parameter P and K, defined as usual (6), have been obtained.

2 The wave function of the complex

The way in which the ^4d, 5p, 5s states of Mo and the 3p states of the ligands would be occupied when covalency is assumed for octahedric symmetry is now considered. One should take 2p states for the oxygen ion, but that difference will be disregarded. Molecular orbitals will be formed from linear combination of the atomic orbitals mentioned above, not considering the inner shells. It is better to work with symmetry orbitals which are readily constructed for the central ion and for the ligands. They are denoted by $|(S)\ A,\ a_i\rangle$, with $S = d, p, s$ for the central ion, and $S = \sigma, \pi$ for the ligands, with the standard meaning for σ and π electrons. A denotes the irreducible representation of the cubic group, and a_i the particular state in that representation. All these states conform with the notation of Griffiths (7), and their transformation properties are those given in Table A16 of that reference.

From the five ^4d orbitals, three $(\pi)\ T_{2g}$ and two $(\sigma)\ E_g$ orbitals are obtained, and similarly, three (σ) T_{1u} orbitals from 5p and one $(\sigma)\ A_{1g}$ orbital from 5s are obtained. The eighteen 3p orbitals of the ligand are separated into six σ orbitals and twelve π orbitals. They give orbitals with A equal to A_{1g}, E_g and T_{1u} for the σ electrons and equal to T_{1g}, T_{1u}, T_{2g} and T_{2u} for the π electrons.

Therefore for octahedric symmetry (8), there are bonding and antibonding orbitals with A equal to A_{1g}, E_g, T_{1u} and T_{2g}, and non bonding orbitals with A equal to T_{1g}, T_{1u}, and T_{2u}.

Of the thirtyseven electrons that have to be accomodated into these orbitals, eighteen can be put into the bonding A_{1g}, E_g, T_{1u} and T_{2g} orbitals, eighteen into the non-bonding T_{1g}, T_{1u} and T_{2u} orbitals, and there is one magnetic electron left. From the hyperfine structure observed, it can be deduced that this electron is most of the time around the central ion.

In the crystal field approximation this electron should be a T_{2g}, and it is assumed that this state of affairs would not be changed by covalency.

The symmetry assumed for the complex ion is not cubic but tetragonal and molecular orbitals suited to D_{4h} symmetry are defined as linear combinations of the already defined symmetry orbitals $|(S)\ A,\ a_i\rangle$. The new molecular orbitals span the irreducible representation of the D_{4h} group, and they are denoted by $|\alpha\ ;\ A,\ a_i\rangle$, where $A,\ a_i$ corresponds to D_{4h}, and α is an integer that identifies each one of the several molecular orbitals that transform like $A\ a_i$.

In a tetragonal field the orbital triplet t_2 is split into an orbital singlet of symmetry B_2 in D_{4h} and an orbital doublet. It has been said before that in the crystal field approximation, the magnetic electron occupies the t_2 orbital singlet, so that the values of $g_{\parallel}$ and $g_{\perp}$ are very near two. Assuming that covalency does not alter this situation, the magnetic electron would occupy a molecular orbital of symmetry B_{2g} b_2 in D_{4h} when the spin-orbit interaction is equal to zero.

The two spin states of a spin one half transform under D^{*}_{4h} like E'_g and the ground states will have in this approximation two one-electron states available for the magnetic electron, their symmetry being $B_{2g} \times E'_g = E''_g$.

In the next paragraph, it will be swown that the g-values and hyperfine structure constants for this complex, are obtained by making the calculation for a fictitious system of only one electron. As the spin-orbit coupling is invariant under D^{*}_{4h}, the only molecular orbitals that will be required are all those belonging to irreducible representations A, such that $A \times E'_g$ contain E''_g, i.e.: B_{1g}, B_{2g} and E_g.

The following are all the possible orbitals that can be obtained from the $|\ (S)\ A, a_i\rangle$ considered:

$$|1;\ B_{1g},\ b_1\rangle = C_1\ |(\sigma)\ E_g, \varepsilon\rangle + D_1\ |(4d)\ E_g, \varepsilon\rangle \qquad 2.1$$

$$|2;\ B_{1g},\ b_1\rangle = C_2\ |(\sigma)\ E_g, \varepsilon\rangle + D_2\ |(4d)\ E_g, \varepsilon\rangle$$

$$|1;\ B_{2g},\ b_2\rangle = C_3\ |(\pi)\ T_{2g}, 0\rangle + D_3\ |(4d)\ T_{2g},\ 0\rangle$$

$$|2;\ B_{2g},\ b_2\rangle = C_4\ |(\pi)\ T_{2g}, 0\rangle + D_4\ |(4d)\ T_{2g},\ 0\rangle$$

$$|1;\ E_g,\ +1\rangle = C_5\ |(\pi)\ T_{2g}, -1\rangle + D_5\ |(4d)\ T_{2g}, -1\rangle + F_5\,|(\pi) T_{1g},\ +1\rangle$$

$$|1;\ E_g,\ -1\rangle = -C_5\ |(\pi)\ T_{2g}, +1\rangle - D_5\ |(4d)\ T_{2g}, +1\rangle + F_5\,|(\pi) T_{1g},\ -1\rangle$$

$$|2;\ E_g,\ +1\rangle = C_6\ |(\pi)\ T_{2g}, -1\rangle + D_6\ |(4d)\ T_{2g}, -1\rangle + F_6\,|(\pi) T_{1g},\ +1\rangle$$

$$|2;\ E_g,\ -1\rangle = -C_6\ |(\pi)\ T_{2g}, +1\rangle - D_6\ |(4d)\ T_{2g}, +1\rangle + F_6\,|(\pi) T_{1g},\ -1\rangle$$

$$|3;\ E_g,\ +1\rangle = C_7\ |(\pi)\ T_{2g},\ -1\rangle + D_7\ |(4d)\ T_{2g}, -1\rangle + F_7\,|(\pi) T_{1g},\ +1\rangle$$

$$|3;\ E_g,\ -1\rangle = -C_7\ |(\pi)\ T_{2g}, +1\rangle - D_7\ |(4d)\ T_{2g}, +1\rangle + F_7\,|(\pi) T_{1g},\ -1\rangle$$

The coefficients are choosen in such a way that for the B_{1g} and B_{2g} functions $a = 1$ are the bonding orbitals, and $a = 2$ the antibonding ones. For the E states there are three possibilities, because the states $|T_{2g},\ \pm 1\rangle$ and $|T_{1g};\ \pm 1\rangle$ belong to the same representation of the group D_4. In cubic symmetry the T_{1g} gives a non-bonding orbital while the two groups of T_{2g} states give bonding and antibonding orbitals. It will be assumed that the E states are essentially the same as their counterparts in cubic symmetry, taking $a = 1$ for the bonding, $a = 2$ for the antibonding and $a = 3$ for the non-bonding orbitals, i.e.: F_5, F_6, C_7, D_7 are much smaller than the others coefficients. Latter, as a rough approximation these coefficients are taken equal to zero, to reduce the number of parameters in the formulae.

The phase of the $|(S)\ A, a_i\rangle$ functions are chosen in such a way that D and C are positive for the bonding combination. Besides, a further restriction on all the states defined in 2.1 is assumed, namely: that they are all orthonormal, so that the usual formulae of perturbation theory apply.

As in the case of cubic symetry, the ground state wave funcions are assumed to be the two Slater determinants of 37 electrons, with 36 electrons in the bonding and non-bonding orbitals mentioned before. As it was already discussed the magnetic electron is in one of the two $|2;\ B_{2g},\ b_2\rangle$ states. The two Slater determinants are eigenfunctions of an unperturbed Hamiltonian H_o and the effect of the spin-orbit coupling remains to be considered, this being done in the next paragraph.

The inner electrons of central ions and ligands are not considered because it is assumed that the energy necessary to excite these states is too big, and that these excited states give a very small contribution to the g-values and hyperfine structure constants.

3 Reduction to a one-electron problem.

It has been assumed above, that the 37 electron Slater determinants are eigenfunctions of an unperturbed Hamiltonian, and the two ground states in this approximation will be called $|\alpha''\rangle$ and $|\beta''\rangle$. They behave under the group D_{4h}^{*} as the α'' and β'' basis vectors of the E_g'', irreducible representation (table A16 in ref. (7)), and it is assumed that the only important perturbation is the spin-orbit Hamiltonian H_{so}. In view of a latter generalization these two states are denoted by $|\eta_i\rangle$ for $i = 1, 2$. The perturbed states $|\bar{\eta}_i\rangle$ are to first order:

$$|\bar{\eta}_i\rangle = |\eta_i\rangle + \sum_{\gamma}{}' (E_o - E_\gamma)^{-1} \langle\gamma|H_{so}|\eta_i\rangle|\gamma\rangle \qquad 3.1$$

The excited states $|\gamma\rangle$ have zero-order energy E_γ,

and the summation excludes the ground states (their energy is E_o to zero order). For the matrix elements of any operator O between the functions 3.1/

$$\langle \bar{\eta}_i \mid O \mid \bar{\eta}_j \rangle - \langle \eta_i \mid O \mid \eta_j \rangle = \sum_{\gamma}{}' (E_o - E_\gamma)^{-1} \langle \eta_i \mid O \mid \gamma \rangle \langle \gamma \mid H_{so} \mid \eta_j \rangle + \qquad 3.2$$

$$+ \text{ cross terms}$$

where the "cross terms" are those obtained by exchanging O and H_{so} in the first summation.

For the problem under consideration, the operator O will be of the form

$$O = \sum_{i=1}^{N} O_i \qquad 3.3$$

where O_i is a one-electron operator acting on the coordinates of the i-the electron, and all the O_i are otherwise equal. The operator H_{so} is also assumed of this form. For these operators the matrix element between Slater determinants are equal to zero, unless they differ at most in one of the one-electron states. This property makes the contribution of many excited states to 3.2, equal to zero. The only excited states that contribute to 3.2 are divided in two categories: a) the magnetic electron of the ground state $|\eta_i\rangle$ is excited to a higher state; b) one of the 36 paired electrons is excited to a non-occupied higherstate.

In order to simplify the calculation the one-electron states have been chosen in such a way that they transform according to one of the two irreducible representations of D^*_{4h} . E' or E", and in particular, in the same way as $\alpha' \beta'$ or $\alpha'' \beta''$ respectively (table A16 in ref. 7). These two representations are the only ones allowed for one-electron states when the electronic spin is considered. The one-electron states are then grouped in

doublets, and symbolized with latin letters with a subscript e.g.: c_1 and c_2 for the partially occupied doublet of the ground states. For each term in 3.2, the one-electron states of all the doublets which are equally occupied in $|\eta_i\rangle, |\eta_j\rangle$ and $|\gamma\rangle$ will not be explicity written, and it is further assumed, that if two states belong to the same representation and have equal subscripts, they transform in the same way under D^*_{4h}. The excited states $|\gamma\rangle$ of type b) do not contribute to 3.2 unless the excited state is the unoccupied c_i state. For $c_i \neq c_j$ this is very simple to show because the two only possible $|\gamma\rangle$ when the electron in the a_s state of the $a_s\ a_t$ doublet is excited to the b_K state of an empty doublet, are $|a_t\ b_K\ c_i\rangle$ or $|a_t\ b_K\ c_j\rangle$. The first differs from $|\eta_j\rangle = |a_s\ a_t\ c_j\rangle$ and the second differs from $|\eta_i\rangle = |a_s\ a_t\ c_i\rangle$ in two electronic states, and one of the two matrix elements in each term of 3.1 is zero.

The proof of this property when $c_i = c_j$ is different: the contribution of all the $|\gamma\rangle$ obtained by exciting the states a_1 and a_2 into the states b_1 and b_2 of the empty doublet, is given by:

$$(E_o - E_\gamma)^{-1}\{\langle a_2|O|b_1\rangle\langle b_1|H_{so}|a_2\rangle + \langle a_1|O|b_1\rangle\langle b_1|H_{so}|a_1\rangle + \langle a_2|O|b_2\rangle\langle b_2|H_{so}|a_2\rangle + \langle a_1|O|b_2\rangle\langle b_2|H_{so}|a_1\rangle + \text{cross terms}\} \quad 3.4$$

From the transformation properties chosen for the one-electron states and the invariance of H_{so} under D^*_{4h}, the quantity 3.4 is equal to

$$(E_o - E_\gamma)^{-1}\{\left[\langle a_1|O|b_1\rangle + \langle a_2|O|b_2\rangle\right]\langle b_1|H_{so}|a_1\rangle + \langle a_1|H_{so}|b_1\rangle\left[\langle b_1|O|a_1\rangle + \langle b_2|O|a_2\rangle\right]\} \quad 3.5$$

Each term in 3.5 is proportional to an expression of the form

$$\sum_i \langle \alpha\ A\ a_t\ |O_K^B|\alpha'\ A'\ a_i\rangle \quad 3.6$$

where α and α' characterize two sets (α A) and (α' A) of ℓ_A one-electron wave functions each, that transform under G as a given basis of a unitary irreducible representation A of a group G, and the summation is over all the elements of this representation. In the present case $\ell_A = 2$, but later the generalization for any ℓ_A is made. The operator O_K^B is one of a set of operators that transform under G as the irreducible representation B. In Apendix I it is shown that unless B is the identity representation, 3.6 is equal to zero; therefore if the operator O has the required properties, the quantity 3.5 equals zero, and the property stated before follows for $c_i = c_j$.

The non-zero contribution of states of type b) to 3.2 comes from the intermediate $|\gamma\rangle$ states obtained by exciting any electron a_s of an occupied doublet $a_s\, a_t$ into the unoccupied c_i state. The only excited state of this type is then $|a_t\, c_i\, c_j\rangle$. For $c_i \neq c_j$, the contribution of a doublet $a_1\, a_2$ to 3.2 is equal to

$$-(E_o - E_\gamma)^{-1}\left\{\langle c_i|O|a_1\rangle\langle a_1|H_{so}|c_j\rangle + \langle c_i|O|a_2\rangle\langle a_2|H_{so}|c_j\rangle + \text{cross terms}\right\} \qquad 3.7$$

The negative sign comes from the different position of the one-electron wave functions in the Slater determinants, as they have to be placed in those determinants according to some fixed ordering, so as to define their phases uniquely.

For $c_i = c_j = c_1$, and with similar arguments as for 3.5, the contribution to 3.2 is equal to

$$(E_o - E_\gamma)^{-1}\langle c_2|H_{so}|a_2\rangle\langle a_2|O|c_2\rangle + \text{cross terms} \qquad 3.8$$

From the invariance of H_{so} under D^*_{4h}, it follows that $\langle c_2|H_{so}|a_2\rangle$ equals zero unless c_2 and a_2 belong to the same irreducible representation of D^*_{4h}, and in this case

$\langle a_2 | 0 | c_2 \rangle$ is one term of 3.6. Assuming as before that 0 belongs to an irreducible representation of D_{4h}^{*} different from the identity, it follows that 3.8 is equal to

$$- (E_o - E_\gamma)^{-1} \langle c_1 | H_{so} | a_1 \rangle \langle a_1 | 0 | c_1 \rangle + \text{cross terms} \qquad 3.9$$

In the same way, the contribution to 3.2 for

$$c_i = c_j = c_2$$

is equal to

$$- (E_o - E_\gamma)^{-1} \langle c_2 | H_{so} | a_2 \rangle \langle a_2 | 0 | c_2 \rangle + \text{cross terms} \qquad 3.10$$

The excited states of type a) give expressions equal to 3.7, 3.8 and 3.9, but without the negative sign.

The calculation of the matrix elements of the operator 0 between two Slater determinants $| \eta_i \rangle$ and $| \eta_j \rangle$ is simple because 0 satisfies 3.2. For $i \neq j$ it follows that

$$\langle \eta_i | 0 | \eta_j \rangle = \langle c_i | 0 | c_j \rangle \qquad 3.11$$

but for $i = j$, there is also the contribution of all the filled doublets. As it was assumed that 0 transforms under D_{4h}^{*} as an irreducible representation different from the identity, the expression 3.6 is equal to zero and the validity of 3.11 when $i = j$ is immediately deduced.

Looking at all the non-zero contributions to $\langle \bar{\eta}_i | 0 | \bar{\eta}_j \rangle$, it follows that its value can be obtained by making a similar calculation for a fictitious one-electron system.

To state this result in a precise way, a more general property, (derived in Apendix II) is given here. The following property includes the results just derived.

Let an operator 0 and a Hamiltonian $H = H_o + H'$ be given for a system of N particles, with the following properties:

i) The operator 0 is of the form 3.3, and the O_i have the properties stated after that equality.

ii) The operator O is one of a set of operators that transform under the group G that leaves H_o invariant, as the irreducible representation K of G.

iii) There is an orthogonal set of one-electron wave functions denoted by $|\alpha\ A\ a_i\rangle$, such that the Slater determinants of order N obtained from them, are eigenfunctions of H_o. These Slater determinants are denoted by a k e t with a greek letter, with or without subscript, e.g. $|\gamma\rangle$ or $|\eta_i\rangle$.

iv) The one-electron wave functions $|\alpha\ A\ a_i\rangle$ are sorted into sets $(\alpha\ A)$ of ℓ_A elements each, such that the elements of each set span the irreducible representation A of the group G. The integer α identifies each one of the several sets with a given A.

v) The several Slater determinants that have all the sets $(\alpha\ A)$ equally occupied, have equal eigenvalues of H_o.

vi) The number N of electrons is such, that in the several ground states $|\eta_i\rangle$ all the sets $(\alpha\ A)$ are full or empty with the excepcion of set $(\gamma\ C)$, which has only the state $|\gamma\ G\ a_i\rangle$ occupied.

vii) The perturbation Hamiltonian H', has the same property i) as the operator O.

viii) The operator H' is a linear combination of operators that span irreducible representations of G, all different from K (see ii). A fictitious one-electron system is now defined with stationary states equal to the $|\alpha\ A\ a_i\rangle$ of iii). When $|\alpha\ A\ a_i\rangle$ belong to a set $(\alpha\ A)$ completely occupied in the ground state of the real system, its energy in the unperturbed fictitious system is $\Delta E_{\alpha A} = -(E_\gamma - E_o)$, where E_γ is the energy of the state of the real system that is obtained from the ground state by exciting the

electron in $|\alpha A\ a_i\rangle$ to any available state of the set (γC), partially occupied in the ground state: when $|\alpha A\ a_i\rangle$ belong to a set (αA) that is empty in the ground states of the real system, its energy in the unperturbed fictitious system is $E_{\alpha A} = (E_\gamma - E_o)$, where E_γ is the energy of the state of the real system, that is obtained from the ground state by exciting an electron of the set (γC) to the state $|\alpha A\ a_i\rangle$. The energy of any state $|\gamma C\ c_i\rangle$ of the set partially occupied in the real ground state is equal to zero in the fictitious system. The energy E_o is that of the ground states of the real system.

Defining

$$|\overline{\gamma C\ c_i}\rangle = |\gamma C\ c_i\rangle + \sum_{\alpha A_j} (E_{\alpha A} - E_{\gamma C})^{-1} \langle \alpha A\ a_j | H_1' | \gamma C\ c_i\rangle |\alpha A\ a_j\rangle \qquad 3.12$$

where H_1' is the one-electron operator that corresponds to H', it follows for $i \neq j$

$$\langle \bar{\eta}_i | O | \bar{\eta}_j \rangle = \langle \overline{\gamma C\ c_i} | O_1 | \overline{\gamma C\ c_j} \rangle \qquad 3.13$$

where O_1 is the one-electron operator that corresponds to O. This equality holds for $i = j$, only when the irreducible representation K (see ii)) is not the identical representation. When O is invariant under G, the two members in 3.13 differ by a constant independent of c_i times the Kronecher δ_{ij}.

A very similar property is obtained for a system with all the properties i) to viii), but using instead of vi) the property vi'): in the ground states, all the sets (αA) are fully occupied or empty, with the exception of set (γC), for which the state $|\gamma C\ c_i\rangle$ is the only one unoccupied. These ground states will be denoted with $|(\eta_i)\rangle$, and instead of 3.12 the following equation holds:

$$|(\overline{\eta_i})\rangle = |(\eta_i)\rangle + \sum_{\gamma}{}' (E_\gamma - E_o)^{-1} \langle \gamma | H' | (\eta_i)\rangle |\gamma\rangle \qquad 3.14$$

For $i \neq j$, it is shown in Apendix II

$$\langle(\overline{n_i}) \mid 0 \mid (\overline{n_j})\rangle = (-1)^{n_{ij}} \langle \overline{\gamma C\ c_j} \mid O_1 \mid \overline{\gamma C\ c_i}\rangle \qquad 3.15$$

where n_{ij} is the number of states between c_i and c_j in the ordering selected for states of the (γC) set, using the convention $n_{ii} = -1$ (For a doublet, $n_{12} = 0$). The equality 3.15 holds for $i = j$ when K (see ii)) is different from the identical representation. When O is invariant under G, the two members in 3.15 differ by a constant independent of c_i times δ_{ij}. The same definition is used for the energies of the fictitious system when there is only one electron in (γC) or only one hole.

The generalization stated in this paragraph, makes possible the calculation of the g-values and hyperfine structure constants, up to first order perturbation theory, with one-electron functions like 3.12, instead of using the more cumbersome many-electron functions 3.1. The orbital functions in 2.1 are written with a + or - sign to denote the two possible spin states, transforming under D^*_{4h} as $E'\alpha'$ or $E'\beta'$ respectively (table A16 in ref. (7)). Instead of the two ground states of the many electron system, the following states of the fictitious system will be used:

$$\begin{aligned}
\mid \overline{2;\ B_{2g},\ b_2^{+}} \rangle = {} & \mid 2;\ B_{2g},\ b_2^{+}\rangle + X_1 \mid 1;\ B_{2g},\ b_2^{+}\rangle + \\
& + X_2 \mid 1;\ B_{1g},\ b_1^{+}\rangle + X_3 \mid 2;\ B_{1g},\ b_1^{+}\rangle + \\
& + Y_1 \mid 1;\ E_g, -1^{-}\rangle + Y_2 \mid 2;\ E_g, -1^{-}\rangle + \\
& + Y_3 \mid 3;\ E_g, -1^{-}\rangle \\
\mid \overline{2;\ B_{2g},\ b_2^{-}} \rangle = {} & -\mid 2;\ B_{2g},\ b_2^{-}\rangle - X_1 \mid 1;\ B_{2g},\ b_2^{-}\rangle + \\
& + X_2 \mid 1;\ B_{1g},\ b_1^{-}\rangle + X_3 \mid 2;\ B_{1g},\ b_1^{-}\rangle + \\
& + Y_1 \mid 1;\ E_g, +1^{+}\rangle + Y_2 \mid 2;\ E_g, +1^{+}\rangle + \\
& + Y_3 \mid 3;\ E_g, +1^{+}\rangle
\end{aligned}$$

The two states $|\overline{2;\ B_{2g},\ b_2^{+}}\rangle$ and $|\overline{2;\ B_{2g},\ b_2^{-}}\rangle$ behave under D_{4h}^{*} as E" α" and E" β" respectively, and will be denoted by $|\alpha''\rangle$ and $|\beta''\rangle$ for convenience.

4 Spin-Hamiltonian parameters.

It is now straightforward to obtain $g_{\parallel}$ and $g_{\perp}$ to first order from the Zeeman term: $\beta H.\ (\underline{L} + 2\ \underline{S})$. From 3.16 and their symmetry properties

$$g_{\parallel} = 2 + 4\ \mathrm{Re}\Big\{ X_2 \langle 2;\ B_{2g},\ b_2 \mid L_z \mid 1;\ B_{1g},\ b_1\rangle + X_3\langle 2;\ B_{2g}, b_2 \mid L_z \mid 2;\ B_{1g},\ b_1 \Big\}$$

$$g_{\perp} = -2 + 4\ \mathrm{Re}\Big\{ \sum_{a=1}^{3} Y_a \langle 2;\ B_{2g},\ b_2 \mid L_x \mid a;\ E_g,\ +1\rangle \Big\} \qquad 4.1$$

The matrix elements of L_z and L_x between (4d) states were immediately obtained; those between a (4d) state and a ligand state were obtained with the technique of Stevens (5); those between two ligand states were obtained neglecting the contribution of matrix elements between two 3p states centered around different ions. The final formulae are:

$$g_{\parallel} = 2 + 4\ \mathrm{Re}\Big\{ X_2\Big[2D_4^{*}\ (D_1 + C_1\ S_\xi) + C_4^{*}\ (-C_1 + 2D_1\ S_\xi^{*})\Big] + X_3\Big[2D_4^{*}\ (D_2 + C_2\ S_\xi) + C_4^{*}\ (-C_2 + 2D_2\ S_\xi^{*})\Big]\Big\}$$

$$g_{\perp} = -2 - \sqrt{2}\ \mathrm{Re}\Big\{ Y_1\Big[2D_4^{*}\ (D_5 + C_5\ S_\zeta) + C_4^{*}\ (C_5 - F_5 + 2D_5\ S_\zeta)\Big] + Y_2\Big[2D_4^{*}\ (D_6 + C_6\ S_\zeta) + C_4^{*}\ (C_6 - F_6 + 2D_6\ S_\zeta)\Big] + Y_3\Big[2D_4^{*}\ (D_7 + C_7\ S_\xi) + C_4^{*}\ (C_7 - F_7 + 2D_7\ S_\zeta)\Big]\Big\} \qquad 4.2$$

where

$$S_\xi = \langle (4d)\ E_g\ \xi \mid (\sigma)\ E_g, \xi\rangle$$

$$S_\zeta = \langle (4d)\ T_{2g}, \zeta \mid (\pi)\ T_{2g}, \zeta\rangle \qquad 4.3$$

The hyperfine parameters A and B are obtained from states 3.16 and the usual perturbation term (6):

$$H_n = 2\gamma\beta\beta_N\left\{\frac{1}{r^3}(\underline{\ell} - \underline{S})\cdot\underline{I} - \frac{3}{r^5}(\underline{r}\cdot\underline{S})(\underline{r}\cdot\underline{I}) + \right.$$

$$\left. + \frac{8\pi}{3}\delta(r)\,\underline{S}\cdot\underline{I}\right\} \qquad 4.4$$

where $\underline{r}$ is the distance from the magnetic electron to the central ion, $\underline{\ell}$ is the orbital angular momentum of an electron, $\underline{S}$ its spin, β the Bohr magneton, β_N the nuclear magneton and γ the nuclear gyromagnetic factor.

The quadrupole interaction has not been considered as the quadrupole moments of Mo^{95} and Mo^{97} have not been observed, so they are presumably small.

The dependence of H_N on r goes as r^{-3}, and it can be expected that its matrix elements between any two states of the ligands, or between a state of a ligand and a state of the central ion, are much smaller than those between two states of the central ion. It can also be seen that when one considers covalency, the contributions of $r^{-3}\,\underline{\ell}$ and $r^{-3}\,\underline{S}$ are not proportional to $g^{(L)}$ or $g^{(S)}$, as happens when the one electron states are the product of a radial function times a function of the polar angle. (cf. formulae 12.14 in ref. (7) or formulae 5.3 and 5.4 in ref.(9)).

Considering only the matrix elements of H_N between any two central ion states,

$$A = P\left\{-\frac{4}{7}\left[D_4^* D_4 + 2\,\mathrm{Re}\,(X_1 D_4^* D_3)\right] + \mathrm{Re}\left[D_4^*\,8(X_2 D_1 + X_3 D_2) + \right.\right.$$

$$\left.\left.\frac{6\sqrt{2}\,D_4^*}{7}(Y_1 D_5 + Y_2 D_6 + Y_5 D_7)\right] - K\right\}$$

$$B = P\left\{-\frac{2}{7}\left[D_4^* D_4 + 2\,\mathrm{Re}\,(X_1 D_4^* D_3) - \frac{11\sqrt{2}}{7}\mathrm{Re}\left[D_4^*\,(Y_1 D_5 + \right.\right.\right.$$

$$\left.\left.\left. + Y_2 D_6 + Y_3 D_7)\right] + K\right\} \qquad 4.5$$

where $P = 2\gamma\beta\beta_N \langle r^{-3} \rangle$ and K comes from the Fermi contact term in 3.4.

5 Spin-Orbit interaction.

Before formulae 4.2 and 4.5 are compared with experiment, it is necessary to estimate the coefficients X_i and Y_i in 3.16; the spin-orbit interaction H_{so} is assumed to give these coefficients in first order perturbation theory.

To estimate the spin orbit matrix elements between the $|\alpha A a_i\rangle$ states it is assumed that the matrix elements of H_{so} between two free-ion states centered around different ions are zero, but those between two states centered around the same ion give the free ion value. This assumption gives a sufficient approximation (10) for the estimation of X_i and Y_i. Therefore, only ζ_p, the 3p spin orbit parameter of the free chlorine ion; and ζ_d, the 4d, spin orbit parameter of the free molybdenum ion are needed.

After some calculations the following formulae

$$X_1 = 0$$

$$X_2 = \left(D_4^* D_1 \zeta_d - \frac{1}{2} C_4^* C_1 \zeta_p \right) / \delta_4 \qquad 5.1$$

where $\delta_4 = E_{2B2} - E_{1B1}$ and the same formulae hold for X_3 with D_2, C_2 and $\delta_5 = E_{2B_2} - E_{2B1}$ instead of D_1, C_1, δ_4.

$$Y_1 = \frac{1}{2\sqrt{2}} \left(2 D_4^* D_5 \zeta_d + C_4 (C_5 - F_5) \zeta_p \right) \delta_1 \qquad 5.2$$

where $\delta_1 = E_{2B2} - E_{1E}$ and the same formulae hold for Y_2 and Y_3 with D_6, C_6, F_6 $\delta_2 = E_{2B2} - E_{2E}$ or D_7, C_7, F_7, $\delta_3 = E_{2B2} - E_{3E}$ respectively instead of D_5 C_5, F_5, δ_1. The $E_{\alpha A}$ are the energies of the states $|\alpha ; A, a_i\rangle$ in the fictitious one-electron system, and have been defined in § 3.

6 Comparison with experimental g-values.

Formulae 4.2 and 4.5 depend on several kinds of parameter: i) coefficients like D_4, that are related to the amount of covalency between central ion and ligands, ii) coefficients like X_1, given in 5.1 and 5.2 as function of the coefficients i), the spin-orbit parameters of the free ions ζ_p and ζ_d, and the energy difference between the ground state and the other states; iii) parameters P and K. Values of the same order as those given by Owen (8) for similar ions, will be assumed for all the coefficients of type i). To simplify the analysis it will be assumed $S_\varepsilon = S_\zeta = 0$, as they only appear explicity in the first order corrections, and pressumably give small changes in 4.2. In 4.2 it has been already assumed that F_5, F_6, C_7, D_7 are small, and they are now set equal to zero, so it follows from normalization that $F_7 = 1$.

There are still too many coefficients in 2.1, but their number will be reduced by assuming that the amount of covalency is the same for all bonding π orbitals, i.e.: $D6 = D_4$. All D_i are chosen real and positive, and from the phases assumed in 4.2 for the orbitals $|(S)\ A, a_1\rangle$ and the orthogonality of the functions in 2.1, it follows that

$$D_4 = D_6 = C_3 = C_5 \qquad D_2 = C_1$$

$$D_3 = D_5 = -C_4 = -C_6 = \sqrt{1 - D_4^2} \qquad D_1 = -C_2 = \sqrt{1 - D_2^2} \qquad 6.1$$

With all these assumptions it would be possible to obtain D_2 and D_4 from 4.2 if the energy levels of the states in 2.1 where known, as ζ_p and ζ_d can be estimated reasonably well. Unfortunately the only two energy differences that have been identified (3) are: $-\delta_2 = 14050\ cm^{-1}$ that corresponds to the splitting of the ground T_{2g} triplet, due to the tetragonal field; and $22500\ cm^{-1}$, that corresponds to the transition between the ground state and the lowest of the two excited

states with orbital symmetry E_g (under O_h). Although it is known that the ground state corresponds to B_{2g} (under D_{4h}), it has been already said that the sign of the tetragonal distortion can not be deduced with certainty, and therefore the equality - $\delta_5 = 22500$, is not necessarily true. Nevertheless, it will be assumed that this equality holds, but it must be born in mind that - δ_5 can be much greater, perhaps around 50000 cm^{-1}.

It is necessary to estimate ζ_p and ζ_d, and the value $\zeta_p = 550\ cm^{-1}$ will be assumed. In Apendix A. 6.2 of reference (4), ζ_d is given for Mo for several degrees of ionization. Although the simple crystal field theory assumes Mo^{5+}, the covalency with the ligands increases the negative charge around the nucleus. It has been already assumed that there are eightenn electrons in bonding orbitals, twelve in σ orbitals and six in π orbitals. (The remaining eighteen electrons besides the magnetic electron are in non-bonding ligand states). The probability of finding the electron in the molybdenum atomic orbital will be later taken as approximately 0.3 and 0.2 for the σ and π bonding orbitals respectively, and this gives an extra charge around Mo^{5+} equal to 4.8, assuming that the non-bonding orbitals do not give any charge to Mo^{5+}. The value $\zeta_d = 600\ cm^{-1}$ that corresponds to an ionic charge slightly greater than zero has been accordingly chosen. This estimate of ζ_d will not be altered under small changes of the covalency, as these small corrections are not justifiable after all the rough approximations made.

With all the above mentioned approximations, the formulae 4.2 will be fitted to the values

$g_{\parallel} = 1.970 \pm 0.005$; $g_{\perp} = 1.940 \pm 0.005$

measured in frozen solution (2). These values are very similar to those given in reference (1) for the two magnetic complexes of Mo^{5+} in a diluted crystal, and in particular $g_\perp$ is nearly the same in all cases.

With the values assumed for $g_\perp$, ζ_d, ζ_p and δ_2, one can write an implicit function of δ_1, δ_3 and $D_4^2 = \xi$. For simplification it is assumed that $\delta_1 = \delta_3$, and this energy difference is calculated as a function of ξ; typical values are: 3300 cm^{-1} for $\xi = 0.9$; 12000 cm^{-1} for $\xi = 0.8$ and 135000 for $\xi = 0.7$. As one can expect that $\delta_1 > \delta_3$ they have been both calculated for $\xi = 0.8$ when they are different. Typical pairs of values measured in cm^{-1} are: 7000 and 48600; 8000 and 25100; 10000 and 15100 for δ_3 and δ_1 respectively. The value $\xi = 0.8$ gives a reasonable order or magnitude for δ_1, and δ_3, and it will be used in future calculations.

With the expression for $g_{||}$, and the values assumed for ζ_p, ζ_d and $g_{||}$ an implicit function of δ_4, δ_5, ξ and $\eta = D_2^2$ may be written. The value of δ_4 has been calculated with $\delta_5 = -22500$ cm^{-1} for several values of η and for $\xi = 1$, 0.9, 0.8, 0.7; typical values for $\xi = 0.8$ being; $\delta_4 = 11300$ cm^{-1} for $\eta = 0.9$, $\delta_4 = 22200$ cm^{-1} for $\eta = 0.8$, $\delta_4 = 39000$ cm^{-1} for $\eta = 0.7$ and $\delta_4 = 70900$ cm^{-1} for $\eta = 0.6$. From the values calculated, it seems that $\xi = 0.8$ and $\eta = 0.7$ are the best guesses when $\delta_5 = -22500$ cm^{-1} is assumed, i.e.: that the antibonding B_{1g} state is of lower energy than the antibonding A_{1g} state. If the opposite situation is assumed for this pair of levels one should have a larger value for $-\delta_5$, probably around 50000 cm^{-1}. For this value of δ_5, one should take a value of η closer to one, and assuming that the degree of covalency is larger in the σ- bonds than in the π - bonds, i.e.:

$\xi > \eta$, the value of ξ would also be nearer to one.

If one had better values of the energy differences involved, one would be able to test the present theory in a more satisfactory way. Nonetheless, two points be stressed: i) For $X_2 = 0$, i.e.: when the contribution to $g_{\parallel}$ of states that do not appear in the crystal field thoery is not taken into account and the contribution of ζ_p to the spin orbit interaction is disregarded (as is usually done), one obtains the formulae:

$$g_{\parallel} = 2 - \frac{8\,\zeta_d}{\delta_5}\,k$$

where k corresponds to the orbital reduction factor. For $\delta_5 = -22500\ cm^{-1}$ follows $k = 0.14$, and for $\delta_5 = -50000\ cm^{-1}$ the value $k = 0.31$. Both values of k seem unreasonably small, and it was this difficulty that led the author to make this theory. ii) The difference $g_{\parallel} - 2$, is obtained as the difference of two larger cuantities. This could be the reason for the larger variation of $g_{\parallel}$ with respect to $g_{\perp}$ in the several systems measured (1,2), as small differences in the energy levels produce larger variations of $g_{\parallel}$ than those of $g_{\perp}$.

7 Comparison with the experimental hyperfine structure constants.

The parameters P and K will now be deduced from the measured values of A and B, and their expressions in 4.5. Replacing the values $\zeta = 0.8$; $\eta = 0.7$; $\zeta_d = 600\ cm^{-1}$ and $\zeta_p = 550\ cm^{-1}$ in 4.5

$$A = P\{-0.457 - K + (1560/\delta_4) + (2250/\delta_5) + (45/\delta_1) + (367/\delta_2)\}$$

$$B = P\{-0.229 + K - (82/\delta_1) - (673/\delta_2)\} \qquad 7.1$$

From the spectra measured in the frozen solution it has been deduced:

$$|A| = (0.0074 \pm 0.0002)\ cm^{-1}$$
$$|B| = (0.0034 \pm 0.0002)\ cm^{-1} \qquad 7.2$$

It is known (12) that by a simple numerical transformation and redefining $\underline{S}$, it is possible to obtain other Spin-Hamiltonians that describe the energy levels of the system equally well, but have two of the g-factors with signs opposite to those which appear in the original Spin-Hamiltonian (the sign of $g_{xx}\ g_{yy}\ g_{zz}$ is the same in all these Spin-Hamiltonians). The fact that it might turn out that $g_{xx} = -g_{yy}$ in a system of axial symmetry is not forbidden in principle, because the redefined S_x, S_y and S_z have transformation properties different from the original ones under the symmetry group of the system, and the axial symmetry of the system is maintained. In spite of all this argument it is always preferable to have $g_{xx} = g_{yy}$ for a system with axial symmetry, and $g_{xx} = g_{yy} = g_{zz}$ for a system with cubic symmetry. The wave functions used in the theoretical calculation of this paper give $g_{xx} = g_{yy}$. In these formal changes of the Spin-Hamiltonian, the values of the hyperfine structure constants change values in the same way as the g-values do, when the operators I_x I_y and I_z are not redefined.

Similar arguments apply to the operators I_x, I_y and I_z appearing in the Spin-Hamiltonian. One can choose these operators and their corresponding wavefunctions, as the usual one for the free-ion, because one does not have to mix any excited nuclear states into the ground states. It is apparent from the theoretical calculations that the operators I_x, I_y, I_z used in this paper, are the free ion ones, and the value of the parameter $P = 2\beta\beta_N\ \gamma \langle r^{-3} \rangle$ has the sign of γ

this being the value measured for he free ion. An average of the values (13) for Mo^{95} and Mo^{97}; $\gamma = -0.3746$ will be used, and it follows:

$$(P/hc) = -0.001192\ cm^{-1}\ a_o^3 \langle r^{-3} \rangle \qquad 7.3$$

For $\delta_1 = 25100\ cm^{-1}$, $-\delta_2 = 14050\ cm^{-1}$, $\delta_4 = 39000\ cm^{-1}$ and $\delta_5 = -22500\ cm^{-1}$, one deduces from 7.1:

$$P = -1.375\ (A + B)$$
$$PK = -0.253\ A + 0.747B \qquad 7.4$$

and from 7.2 it is known that $|A| > |B|$. From 7.3 is known that P is negative, and it follows that A is positive for the wave functions and operators used in the present calculations. From 7.4 follows that one still has two sets of values of P and K that give the same $|B|$. For B positive: $P/hc = -0.0149\ cm^{-1}$, $K = .045$ and for B negative $P/hc = -0.0055\ cm^{-1}$, $K = 0.80$. From 7.3 follows $\langle r^{-3} \rangle = 12.46\ a_o^{-3}$ in the first case, and $\langle r^{-3} \rangle = 4.61\ a_o^{-3}$ in the second.

The values of P and K depend on those assumed for ζ, η, ζ_d, ζ_p and the energy differences δ_i. The first term in 7.1 is the most sensitive, and is proportional to ζ; reasonable changes in all the other coefficients will alter the two expressions in 7.4 only by a few percent, so one expects that the error in the values obtained for $\langle r^{-3} \rangle$ will be at most 30%. These values will be compared with reasonable estimates of $\langle r^{-3} \rangle$ to see whether it is possible to predict the sign of B that corresponds to the wave function and operators used in this paper. The approximation of Elliot and Stevens (14) namely, to calculate $\langle r^{-3} \rangle$ using the Hydrogenic wave function, with the same n and ℓ atributed to the one-electron wave function, but with an effective charge that gives the known value of ζ is the first considered. In this problem: $n = 4$, $\ell = 2$ and $\zeta = 600\ cm^{-1}$ and one obtains $\langle r^{-3} \rangle = 6.37\ a_o - 3$.

This value is intermediate between the two possible values deduced from the measured spectrum, but the author believes that the value $\langle r^{-3} \rangle = 4.61\ a_o^{-3}$, corresponding to negative B, is the correct one. This assumption is based on the fact that in other cases, the approximation of Elliot and Stevens gives values of the ratio $\langle r^{-3} \rangle / \zeta$ higher than those obtained in a more accurate calculation. As an example the 5f electrons of transuranic-ions are considered; for $\zeta = 2200\ cm^{-1}$: $\langle r^{-3} \rangle = 10.05\ a_o^{-3}$ from the formulae of Elliot and Stevens. For these ions, the value of ζ and $\langle r^{-3} \rangle$ have been calculated (15) from the solution of the one-electron Schrodinger equation, obtaining the potential from the Thomas-Fermi model of an ion with the right number of electrons. With this model, one obtains a given value of ζ for several pairs of values of the atomic number Z and the ionic charge n'; i.e.: $\zeta = 2210\ cm^{-1}$ for Z = 96, n' = 1.119 and also for Z = 95, n' = 5.164, and the values for $\langle r^{-3} \rangle$ are $5.78\ a_o^{-3}$ and $5.87\ a_o^{-3}$ respectively. It is seen that the ratio $\langle r^{-3} \rangle / \zeta$ is fairly constant in this range, and rather smaller than the one obtained from the formulae of Elliot and Stevens. A similar calculation for 4d electrons was not available, but it is reasonable to expect a lower value for $\langle r^{-3} \rangle$ than the $6.37\ a_o^{-3}$ calculated before, so the value $\langle r^{-3} \rangle = 4.61\ a_o^{-3}$ was the one chosen from the two possible ones.

With regard to the signs of A and B, one finds in the first reference (2) the statement that as the average value of the hyperfine constant measured in the liquid solution, is very near $(|A| + 2|B|)/3$, both A and B are positive. But it has been seen before, that the sign of $g_\perp$ and B are changed by altering the phases of the spin wave-function 3.16 and redefining the Spin-Hamiltonian operators S_x and

S_y, and that all the descriptions of the system obtained after those formal changes are equelly good. It seem strange that the value measured should give preference to any one of those descriptions of the system over all the other possible ones.

This apparent contradiction is solved when one looks at the derivation (16,17) of the formulae that, in first approximation, describe the microwave obsorption in liquids by an isotropic Hamiltonian with

$$\bar{g} = \frac{1}{3}(g_{\parallel} + 2\,g_{\perp}) \quad \text{and} \quad \bar{A} = \frac{1}{3}(A + 2\,B)$$

In these references, the spin hamiltonian of a microcrystal, arbitrarily oriented in the laboratory system is written as function of operators S'_x, S'_y, S'_z, I'_x, I'_y, I'_z, expressed as a linear combination of the operators S_x, S_y, S_z, I_x, I_y, I_z (the unprimed operators are defined in the usual way in the molecular system). The coefficients that relate both sets of operators are given functions of the Euler angles α, β, γ that transform the Molecular System into the Laboratory System of coordinates. A canonical transformation depending on α, β, γ is then made for each microcrystal. It must be so defined that the matrix elements of the primed operators between the states of the basis in the new representation are equal to the matrix elements of the unprimed operators between the corresponding states of the basis in the old representation. By this procedure, the Spin-Hamiltonian of each microcrystal is expressed in terms of operators with matrix elements independent of the orientation of the microcrystal. The angular dependence is now shifted to the parameters of the Spin-Hamiltonian.

This Spin-Hamiltonian separates in a natural way:

$$H = H_o + H_1 \qquad 7.5$$

where H_o is independent of the Euler Angles, and H_1 depends on them. For the system under study:

$$H_o = \bar{g}\ S_z\ H + \bar{A}\ (\ \underline{S} \cdot \underline{I}) \qquad 7.6.$$

if the Laboratory z axis is taken along the magnetic field. The operator H_1 is a rather complicated function of α, β, γ, with $(g_{\parallel} - g_{\perp})$ and $(A - B)$ appearing as coefficients of the different terms; its time average is zero for a liquid.

When the matrix elements of H_1 are much smaller than those of H_o, a perturbation calculation may be done, and the line width of the resonat absorption is obtained. The position of rthe resonant absorption lines is given by H_o, which is the isotropic Hamiltonian of 7.6. When the assumption on the relative values of the matrix elements of H_o and H_1 is not valid, the perturbation calculation breaks down, and H_o is not any more a good approximation to the observed spectrum.

The usual procedure does not give a convenient separation 6.5 when $g_{\parallel}$ and $g_{\perp}$ are of opposite sign, because the matrix elements of H_1, will be larger or of the same order than those of H_o. In this case, one should define the primed operators as a different linear combination; employing the usual formulae but with $\alpha + \pi$ instead of α. (The Euler Angle α is the first rotation around the Z axis). After that, a canonical transformation with the same property as in the previous case is made for each microcrystal, and the separation 7.5 is obtained as before, but in all the formulae, $-g_{\perp}$ and $-B$ appear instead of $g_{\perp}$ and B respectively. As $g_{\perp}$ is of opposite sign to $g_{\parallel}$, we now have $\bar{g} = (g_{\parallel} - 2\ g_{\perp})/3 \gg g_{\parallel} + g_{\perp}$, when $|g_{\parallel}|$ and $|g_{\perp}|$ differ very little.

If the signs of $g_{\parallel}$ and $g_{\perp}$ are opposite, and those of A and B are not, (or viceversa), the linear combinations that give I'_x, I'_y, I'_z should be different from those giving S'_x, S'_y, S'_z, so that the two Euler Angles α that appear in

the coefficients of both sets of linear combinations differ by π . In that way one can make sure that the separation 6.5 is the best possible. From all these arguments one concludes that the measured values of $\bar{g}$ and $\bar{A}$, are

$$\bar{g} = \pm \frac{1}{3} \left(|g_{\parallel}| + 2 |g_{\perp}| \right)$$

and

$$\bar{A} = \pm \left(|A| + 2 |B| \right)$$

It is well known that one can not distinguish between the two signs from the obsorption spectrum of paramagnetic resonance.

Conclusions

The g-values and hyperfine structure constants of Mo^{5+} in a complex ion with six ligands that occupy the vertices of a tetragonally distorted octahedrum with Mo in its center have been calculated. It is assumed that the outermost occupied electronic shell of each of the six ligands is $S^2 p^6$ and covalent effects are considered, by taking molecular orbitals that are linear combinations of these six sets of six p-states with the Mo 4d, 5 S and 5 p states. For simplicity the twelve S electrons of the ligands are not taken into account, as one would expect that they will only introduce contributions similar to those of the twelve p electron of type σ .

This model has 37 electrons to consider, and to simplify the calculations, it has been shown that the g-values and hyperfine structure constants in this model are equal to those of a conveniently chosen one-electron system. In this fictitious one-electron system, the eigenstates are the molecular orbitals of the 37 electron model, and their energy eigenvalues are directly related to those of the original model. In the following discussion, the fictitious

one-electron system is used but it has to be born in mind that their states and energies are directly related to those of the 37 electron model.

In the calculation of g-values and hyperfine structure constants, the contribution of molecular orbitals that are essentially ligand orbitals was included. This is a contribution that does not appear in the crystal field approximation, and is not usually taken into account in this type of calculation. It turns out that the contribution of these states to the orbital part of theg-values and hyperfine structure constants (appearing through the spin-orbit coupling) can be of the same order as that of the central ion molecular orbitals. It is the energy separation between these two kinds of states and the ground state, which decides their relative contributions to the Spin-Hamiltonian parameters: the smaller this energy separation, the greater the contribution.

In the calculation of the hyperfine structure constants, only the contribution of the $4d$ electrons was considered, as there is a dependence of the relevant operators on the electronic radius proportional to r^{-3}, surely making the contribution of the ligand states much smaller than that of the $4d$ electrons. The contribution of the ligand nuclei to the hyperfine structure, was also disregarded.

The contributions of the ligand states to the spin-orbit matrix elements was taken into account by making crude assumptions about the properties of these matrix elements. The formulae 3.2 and 3.5 obtained under the said assumptions have a great number of parameters and to reduce it, several additional assumptions were made: i) the overlap integrals appearing explicity in 3.2 and in the scalar products of the 2.1 functions were set equal to zero. ii) wave functions of different ligands were assumed orthogonal to each other.

iii) the molecular orbitals where assumed to form an orthogonal system. iv) the (π) T_{1g} ligand orbitals were assumed not to mix with the (π) T_{2g} ligand orbitals nor with the (4d) T_{2g} states of the central ion, i.e.: $C_7 = D_7 = F_5 = F_6 = 0$. This is true only for cubic symmetry. v) the probability of finding a 4d electron in all the bonding π-type molecular orbitals of 2.1 is the same. With all these assumptions, 5.1 was obtained.

It is possible the make reasonable estimates for the one electron parameter of the spin-orbit interaction. If the energy difference between the states in 2.1 were known, it would now be possible to determine the two independent parameters in 5.1, namely D_2 and D_4, their squares η and ζ respectively being a measure of the covalency in the σ and π bonds respectively. From the few data available it was found that with the values $D_2^2 = 0.7$ and $D_4^2 = 0.8$ it is possible to fit the measured $g_{||}$ and $g_{\perp}$ with reasonable values of the unknown energy differences. In the present model, $(2 - g_{||})$ is equal to the difference of two quantities several times, larger than itself and this is not so for $2 - g_{\perp}$. This might explain why the changes of $g_{||}$ are larger than those of $g_{\perp}$ in the several measurements available (1.2).

Using $D_4^2 = 0.8$ and $D_2^2 = 0.7$ and the measured values of A and B, it has been deduced that:

$$\langle r^{-3} \rangle = 4.6 \ a_o^{-3} \quad \text{and} \quad K = 0.80$$

It was also discussed why the other possible values $\langle r^{-3} \rangle = 12.5 \ a_o^{-3}$ and $K = 0.95$ seem unlikely.

The possibility of deciding the relative signs of A and B (or $g_{||}$ and $g_{\perp}$) from the paramagnetic absorption spectrum in liquid solutions was discussed, and the conclusion was, that it is not possible to derive these signs from the paramagnetic resonance spectrum in liquid solution.

Appendix I

In this appendix two properties are derived that are direct consequence of the symmetry properties of the system.

It is known that when the system is invariant under all the operations R of a group G of transformations of the spatial coordinates, it is possible to define (18) a set of operators P_R, acting on the state vectors of the system, that is a representation of G. The wave functions can be so chosen (18) that the P_R are unitary operators and the vector space of the state vectors therefore, can be reduced into irreducible subspaces. A basis of vectors in each of these irreducible subspaces of dimension ℓ_A, will be denoted by a set of ℓ_A state vectors $|\alpha; A, a\rangle$ with $a = 1,2,\ldots, \ell_A$. To each irreducible subspace there are two symbols associated: α and A; A gives the irreducible representation, and α identifies one subspace from all those with the same A. The state obtained by operating P_R on $|\alpha; A, a\rangle$ will be denoted with $|P_R(\alpha; A, a)\rangle$: and the basis of the irreducible subspaces is chosen in such a way that:

$$|P_R(\alpha; A, a_i)\rangle = \sum_{a\,a'} T^A_{a'a}(R)\,|\alpha; A, a'\rangle \qquad \text{I.1}$$

The $T^A_{a'a}$ is a unitary matrix with the property

$$\sum_R (T^A_{a'a}(R))^* T^{A'}_{a''',a''}(R) = (h/\ell_A)\,\delta_{AA'}\,\delta_{aa''}\,\delta_{a'a'''} \qquad \text{I.2}$$

Where the summation is over all the h elements of the group G. Each operator P_R defines a canonical transformation, and any operator O, is given in the new representation by $P_R\,O\,P_R^{-1}$. A set of Hermitian operators O^B_b is now considered. They have the property that:

$$P_R\,O^B_b\,P_R^{-1} = \sum_{b'} T^B_{b'b}(R)\,O^B_{b'} \qquad \text{I.3}$$

for any R of G. Some properties of the matrix elements of these operators O^B_b between states $|\alpha; A, a\rangle$ will be derived. From I.1 and I.2:

$$\sum_{a\,R} \langle P_R(\alpha; A, a)|\, O^B_b\,|\, P_R(\alpha', A, a)\rangle =$$

$$= \sum_{a\,a'\,a''} \langle \alpha; A, a' | O^B_b | \alpha' A\, a''\rangle \sum_R (T^A_{a'a}(R))^* T^A_{a''a}(R) =$$

$$= (h/\ell_A) \sum_{a\,a'} \langle \alpha A\, a' | O^B_b | \alpha' A\, a'\rangle \qquad \text{I.4}$$

Therefore

$$\sum_a \langle \alpha; A, a | O^B_b | \alpha'; A, a\rangle =$$

$$= h^{-1} \sum_{a\,R} \langle P_R(\alpha; A\, a) | O^B_b | P_R(\alpha'; A, a)\rangle \qquad \text{I.5}$$

As the operator P_R^{-1} is unitary:

$$\langle \alpha; A, a | O | \alpha'; A, a\rangle = \langle P_R^{-1}(\alpha; A, a) | P_R^{-1} O^B_b P_R | P_R^{-1}(\alpha'; A, a)\rangle \qquad \text{I.6}$$

Using I.5, I.6 and I.3 in that order:

$$\sum_a \langle \alpha; A, a | O^B_b | \alpha'; A, a\rangle = h^{-1} \sum_{a\,R} \langle P_R(\alpha; A, a) | O^B_b | P_R(\alpha'; A, a)\rangle$$

$$= h^{-1} \sum_{a\,R} \langle \alpha; A, a | P_R^{-1} O^B_b P_R | \alpha'; A, a\rangle$$

$$= h^{-1} \sum_{a\,b'} \langle \alpha; A, a | O^B_{b'} | (\alpha'; A, a)\rangle \sum_R T^B_{b'b}(R^{-1}) \qquad \text{I.7}$$

As $T^I_{1\,1}(R) = 1$ for all R, is a representation of any group, it follows from I.2 that I.7 equals zero unless the irreducible representation B is equal to I. In that case, it is well known that

$$\langle \alpha; A, a | O^I | \alpha'; A, a\rangle = \delta_{AA'} \delta_{aa'} \langle \alpha; A, a | O^I | \alpha'; A, a\rangle \qquad \text{I.8}$$

and with $\ell_I = 1$, :

$$\sum_a \langle \alpha; A, a | O^B_b | \alpha'; A, a \rangle = \delta_{BI}\, \ell_A \langle \alpha; A, a | O^I | \alpha'; A, a \rangle \qquad 1.9$$

Another property will be derived using the unitarity of P_R i.e.:

$$\sum_a (T^A_{a'a}(R))^* T^A_{a''a}(R) = \delta_{a'a''} \qquad 1.10$$

A set of operators Q^B_b, with the same property I.3 as the O^B_b is introduced.

From I.6

$$\sum_{a\,c} \langle \alpha; A, a | O^B_b | \gamma; C, c \rangle \langle \gamma'; C, c | Q^D_d | \alpha'; A, a \rangle =$$

$$= \sum_{a\,c} \langle P_R(\alpha; A, a) | P_R O^B_b P_R^{-1} | P_R(\gamma; C, c) \rangle$$

$$\langle P_R(\gamma'; C, c) | P_R Q^D_d P_R^{-1} | P_R(\alpha'; A, a) \rangle \qquad I.11$$

As all O^D_d are Hermitian, and all P_R are unitary, writing A^+ for the Hermitian conjugate of A it follows that

$$(P_R Q^D_d P_R^{-1})^+ = P_R Q^D_d P_R^{-1} \qquad I.12$$

and taking the Hermitian conjugate of I.3:

$$P_R Q^D_d P_R^{-1} = \sum_{d'} (T^D_{d'd}(R))^* Q^D_{d'} \qquad I.13$$

Replacing I.1, I.3 and I.12 into I.11, the first term of I.11 equals

$$\sum_{a'a''} \sum_{c'c''} \sum_{b'd'} \left\{ \sum_a (T^A_{a'a}(R))^* T^A_{a''a}(R) \right\}$$

$$\left\{ \sum_c (T^C_{c''c}(R))^* T^C_{c'c}(R) \right\} T^B_{b'b}(R) (T^D_{d'd}(R))^*$$

$$\times \langle \alpha; A, a' | O^B_{b'} | \gamma; C, c' \rangle \langle \gamma'; C, c'' | Q^D_{d'} | \alpha'; A, a'' \rangle \qquad I.14$$

Using I.10 it follows that:

$$\sum_{a\,c} \langle \alpha; A, a | O^B_b | \gamma; C, c \rangle \langle \gamma'; C, c | Q^D_d | \alpha'; A, a \rangle = \qquad I.15$$

$$= \sum_{b'd'} T^B_{b'b}(R) (T^D_{d'd}(R))^* \sum_{a'c'} \langle \alpha; A, a' | O^B_{b'} | \gamma; C, c' \rangle \langle \gamma'; C, c' | Q^D_{d'} | \alpha'; A, a' \rangle$$

Summing both terms of I.15 over all R of G, and using I.2,

$$\sum_{a\,c} \langle \alpha;\, A,\, a \,|\, O_b^B \,|\, \gamma;\, C,\, c\rangle \langle \gamma;\, C,\, c \,|\, Q_d^D \,|\, \alpha;\, A,\, a\rangle =$$

$$= \delta_{BD}\, \delta_{bd}\, \ell_B^{-1} \sum_{abc} \langle \alpha;\, A,\, a \,|\, O_b^B \,|\, \gamma;\, C,\, c\rangle \langle \gamma';\, C,\, c \,|\, Q_b^B \,|\, \alpha';\, A,\, a\rangle \qquad \text{I.16}$$

Appendix II

In this appendix the property stated in 3 is derived as an extension of the proof given in that paragraph. The main difference is that the sets $(\alpha\ A)$ of one-electron wave functions $|\alpha; A, a_i\rangle$ that span the irreducible representations of G, have dimension ℓ_A instead of two. From vi) in § 3, there are ℓ_c ground states denoted by $|\eta_i\rangle$, and the basic formula is again 3.2, but with H' instead of H_{so}. The notation in this Appendix is the same as in § 3 unless otherwise stated. Instead of assuming viii) of § 3, it is assumed that H' is one of a set that spans a given irreducible representation of G, different from K. The extension to the case when viii) holds, is trivial. The different contributions to 3.2 will be considered one by one, as it was done in § 3. To avoid repetition, $(\alpha\ A)$ denotes any set completely occupied in the ground state; $(\beta\ B)$ a set empty in the ground state and $(\gamma\ C)$ the set incompletely occupied in the ground state.

1) Contribution of excited states obtained by exciting an electron from any state a_s of a set $(\alpha\ A)$, to any state of a set $(\beta\ B)$ when $|\eta_i\rangle \neq |\eta_j\rangle$. The only possible $|\gamma\rangle$ states are $|\alpha;\, A,\, (a_s)\beta;\, B,\, b_t,\, \gamma;\, C,\, c_K\rangle$, where only the electrons of sets whose occupation is different in $|\eta_i\rangle$, $|\eta_j\rangle$ or $|\gamma\rangle$ are written down explicitly, together with the electrons of the set $(\gamma\ C)$; by $\alpha;\, A\ (a_s)$ it is meant that the state a_s is the only unoccupied one in the set (αA). It is easily seen that the contribution of these states is zero: for $c_K = c_i$,

the state differs from $|\eta_j\rangle$ in the occupation of two states; for $c_K = c_j$ it differs from $|\eta_i\rangle$ in two states; for the other c_K it differs at least in the occupation of two electrons with both $|\eta_i\rangle$ and $|\eta_j\rangle$

From i) and vii) it follows that these states give zero contribution to 3.2.

2) Contribution of states obtained by exciting one electron from any state a_s of the set $(\alpha\ A)$ to the state c_K of $(\gamma\ C)$, when $|\eta_i\rangle \neq |\eta_j\rangle$. The states $|\gamma\rangle$ are $|\alpha;\ A\ (a_s),\ \gamma; C, c_K\ c_i\rangle$ or $|\alpha;\ A\ (a_s),\ \gamma\ C\ c_K\ c_j\rangle$, and when $c_K \neq c_i$ or c_j, they again give zero contribution to 3.2, because they differ in the occupation of two one-eletron states with $|\eta_i\rangle$ or $|\eta_j\rangle$. To calculate the non-zero contribution, it is assumed that in the ordering chosen for the one-electron states, c_j goes to the right of c_i. This contribution equals

$$(E_o - E_\gamma)^{-1} \sum_{s=1}^{\ell_A} \{\langle \alpha;\ A,\ a^{\ell_A};\ \gamma\ C\ c_i | O | \alpha;\ A\ (a_s),\ \gamma\ C\ c_i\ c_j\rangle \times$$

$$\times \langle \alpha;\ A,\ (a_s),\ \gamma;\ C;\ c_i\ c_j | H' | \alpha;\ A,\ a^{\ell_A};\ \gamma;\ C,\ c_j\rangle + \text{cross terms} \qquad \text{II.1}$$

where $\alpha;\ A,\ a^{\ell_A}$ means that the set $(\alpha\ A)$ is fully occupied, and the "cross terms" are obtained by exchanging H' with O. The contribution to 3.2 is then

$$-(E_o - E_\gamma)^{-1} \sum_{s=1}^{\ell} \{\langle \gamma;\ C,\ c_i | O_1 | \alpha;\ A,\ a_s\rangle \langle \alpha;\ A,\ a_s | H' | \gamma;\ C,\ c_j\rangle +$$

$$+ \text{cross terms} \qquad \text{II.2}$$

and the matrix elements in this formula are between one-electron states.

3) Contribution of states obtained by exciting one electron from any state of $(\alpha\ A)$ to any state of $(\beta\ B)$, when

$$|\eta_i\rangle = |\eta_j\rangle$$

The states $|\gamma\rangle$ are $|\alpha\,;\ A\ (a_s),\ \gamma\ ;\ C,\ c_i, \beta\ ;\ B,\ b_t\rangle$ and their contribution to 3.2 is

$$(E_o - E_\gamma)^{-1} \sum_s \sum_t \{\langle \alpha;\ A\ a^{\ell_A};\ \gamma\ ;\ C,\ c_i\ |\ 0|\alpha;\ A(a_s);\gamma\ ;\ C,\ c_i;\beta\ ;\ B,\ b_t\rangle *$$

$$x\alpha;\ A,\ (a_s);\gamma\ ;\ C,\ c_i;\beta\ ;\ B,\ b_t|H'|\alpha;\ A,\ a^{\ell_A};\gamma\ ;\ C,\ c_i\rangle + \text{cross terms}\} =$$

$$= (E_o - E_\gamma)^{-1} \sum_s \sum_t \{\langle \alpha;\ A,\ a_s|\ O_1|\ \beta;\ B,\ b_t\rangle\langle\beta;\ B,\ b_t|H_1'|\ \alpha\ ;\ A,\ a_s\rangle *$$

$$+ \text{cross terms}\} \qquad \text{II.3}$$

but from viii) and I.16 this contribution is zero.

4) Contribution of states obtained by exciting one electron from any state a_s of $(\alpha\ A)$ to any state of $(\gamma\ C)$ when $|\eta_i\rangle = |\eta_j\rangle$. The excited states are $|\gamma\rangle = |\alpha,\ A(a_s);\gamma\ ;\ C,\ c_i\ c\cdot\rangle$ and they contribute to 3.2 the amount:

$$(E_o - E_\gamma)^{-1} \sum_{s=1}^{\ell_A} \sum_{\substack{t=1 \\ t\neq i}}^{\ell_c} \{\langle \alpha;\ A,\ a^{\ell_A};\gamma\ ;\ C,\ c_i|\ 0|\alpha;\ A,(a_s);\gamma;\ C,\ c_i c_t\rangle x$$

$$\langle \alpha\ A\ (a_s);\gamma C\ c_i\ c_t\ |\ H'|\ \alpha;\ A,\ a^{\ell_A};\gamma\ ;\ C,\ c_i\rangle + \text{cross terms}\} =$$

$$= (E_o - E_\gamma)^{-1} \sum_{s=1}^{\ell_A} \sum_{\substack{t=1 \\ t\neq i}}^{\ell_c} \{\langle \alpha;\ A,\ a_s|\ O_1|\ \gamma\ ;\ C,\ c_t\rangle x$$

$$x\langle\gamma;\ C,\ c_t\ |\ H_1'|\ \alpha;\ A,\ a_s\rangle + \text{cross terms}\}$$

and from I.16

$$= -(E_o - E_\gamma)^{-1}\{\langle\gamma\ ;\ C,\ c_i\ |\ O_1|\ \alpha;\ A,\ a_s\rangle\langle\alpha;\ A,\ a_s|H_1'|\ \gamma\ ;\ C,\ c_i\rangle +$$

$$+ \text{cross terms}\} \qquad \text{III.4}$$

5) Contribution from all $|\gamma\rangle$ obtained by exctiting the electron in $(\gamma\ C)$ to any state of $(\beta\ B)$. It is straight forward to obtain

$$(E_o - E_\gamma)^{-1} \sum_{t=1}^{\ell_B}\{\langle\gamma;\ C,\ c_i|\ O_1|\ \beta B,\ b_t\rangle\langle\beta;\ B,\ b_t|\ H_1'|\gamma;\ C,\ c_j\rangle +$$

$$+ \text{cross terms}\} \qquad \text{III.5}$$

From 1), 2), 3), 4), 5), 3.2 and 3.12 and the definition of $E_{\alpha A}$ for the one-electron fictitious system:

$$\langle \bar{\eta}_i | o | \bar{\eta}_j \rangle - \langle \eta_i | o | \eta_j \rangle = \langle \gamma; \overline{C, c_i} | o_1 | \overline{\gamma; C, c_j} \rangle - \langle \gamma; C, c_i | o_1 | \gamma; C, c_j \rangle$$

III.6

when O is invariant under G, the electrons of all the sets (αA) give a contribution to $\langle \eta_i | o | \eta_j \rangle$ independent of i, and this contribution is not necessarily zero. When the irreducible representation K (see ii) in § 3) is different from the identical representation the equality

$$\langle \eta_i | o | \eta_j \rangle = \langle \gamma; C, c_i | o_1 | \gamma; C, c_j \rangle$$

follows from 1.9. From this and II.6 the formulae 3.13 follows with the qualifications written after that equality.

In § 3, there is another generalization of property 3.13, to states $|(\eta_i)\rangle$ which are just like $|\eta_i\rangle$, but instead of having only the state $|\gamma; C, c_i\rangle$ from the set (γC) occupied, they have a hole in that state i.e. all the states of (γC) are occupied with the exception of state c_i. The derivation is very similar to that of 3.13, and only the arguments which are different in both cases will be stated.

1') The same type of contributions as in 1) give also zero by the same arguments.

2') Contribution of states obtained by exciting one electron from any state a_s from (αA) to the hole in (γC) when $|(\eta_i)\rangle \neq |(\eta_j)\rangle$. The only $|\gamma\rangle$ for each a_s is $|\alpha; A(a_s); \gamma; C, c^{\ell_c}\rangle$ and the contribution of (αA) to 3.2 is

$$(E_o - E_\gamma)^{-1} \sum_{s=1}^{\ell_A} \Big\{ \langle \alpha; A, a^{\ell_A}, \gamma; O(c_i) | o | \alpha; A, (a_s), \gamma; C, c^{\ell_c} \rangle \times$$

$$\times \langle \alpha; A(a_s); \gamma; C, c^{\ell_c} | H' | \alpha; A, a^{\ell_A}; \gamma; C, (c_j) \rangle +$$

$$+ \text{ cross terms} \Big\} \qquad \text{II.7}$$

Defining n_{ij} as the number of states between c_i and c_j in the ordering selected for the states of the $(\gamma\, C)$ set, and using the convention that $n_{ii} = -1$ (for a doublet: $n_{12} = 0$), the contribution II.7 is written:

$$- (E_o - E_\gamma)^{-1} (-1)^{n_{ij}} \sum_{s=1}^{\ell_A} \langle \alpha;\, A,\, a_s | O_i | \gamma;\, C,\, c_i \rangle \times$$

$$\times \langle \gamma;\, C,\, c_j | H_1' | \alpha;\, A,\, a_s \rangle + \text{cross term} \qquad \text{II.8}$$

3') The same type of contribution as in 3) gives

$$(E_o - E_\gamma)^{-1} \sum_{s\,t} \Big\{ \langle \alpha;\, A,\, a^{\ell_A};\, \gamma;\, C\,(c_i) | O | \alpha;\, A\,(a_s);\, \gamma;\, C(c_i);$$

$$\beta;\, B,\, b_t \rangle \times$$

$$\times \langle \alpha;\, A\,(a_s);\, \gamma;\, C\,(c_i);\, \beta;\, B,\, b_t | H' | \alpha;\, A,\, a^{\ell_A};\, \gamma,\, C\,(c_i) \rangle +$$

$$+ \text{cross terms} \Big\} =$$

$$= (E_o - E_\gamma)^{-1} \sum_{s\,t} \Big\{ \langle \alpha;\, A,\, a_s | O_1 | \beta;\, B,\, b_t \rangle$$

$$\langle \beta;\, B,\, b_t | H_1' | \alpha;\, A,\, a_s \rangle + \text{cross terms} \Big\} \qquad \text{II.9}$$

and this contribution is equal to zero by viii) and I.16.

4') Contribution of states obtained by exciting one electron from any state a_s of $(\alpha\, A)$ to the hole in $(\gamma\, C)$, when $|(\eta_i)\rangle = |(\eta_j)\rangle$. This is equal to:

$$(E_o - E_\gamma)^{-1} \sum_{s=1}^{\ell_A} \Big\{ \langle \alpha;\, A,\, a^{\ell_A};\, \gamma;\, C\,(c_i) | O | \alpha;\, A(a_s);\, \gamma;\, C,\, c^{\ell_c} \rangle \times$$

$$\langle \alpha A\,(a_s);\, \gamma\, C\, c^{\ell_c} | H' | \alpha;\, A,\, a^{\ell_A};\, \gamma;\, C\,(c_i) \rangle + \text{cross terms} \Big\} =$$

$$= - (-1)^{n_{ii}} (E_o - E_\gamma)^{-1} \sum_{s=1}^{\ell_A} \Big\{ \langle \alpha;\, A,\, a_s | O_1 | \gamma;\, C\, c_i \rangle$$

$$\langle \gamma;\, C,\, c_i | H_1' | \alpha;\, A,\, a_s \rangle + \text{cross terms} \Big\} \qquad \text{II.10}$$

because $- (-1)^{n_{ii}} = 1$

5') Contribution from all $|\gamma\rangle$ obtained by exciting any state in $(\gamma\, C)$ to any state in (βB), when $|(\eta_i)\rangle \neq |(\eta_j)\rangle$. It is equal to

$$(E_o - E_\gamma)^{-1} \sum_{t=1}^{\ell_B} \sum_{\substack{s=1 \\ s\neq i}}^{\ell_c} \langle \gamma\,;\, C\,(c_i)|\, O|\gamma\,;\, C\,(c_i\, c_s), \beta\,;\, B,\, b_t\rangle \times$$

$$\times\langle \gamma\,;\, C\,(c_i\, c_s)\,, \beta\,;\, B,\, b_t|H'|\,\gamma\,;\, C\,(c_j)\rangle + \text{cros terms} \qquad \text{II.11}$$

where $\gamma\, C\,(c_i\, c_s)$ means that only the two states c_i and C_s are missing from $(\gamma\, C)$. When $c_s \neq c_j$, the intermediate state differs in two one-electron states from $|\gamma\,;\, C\,(c_j)\rangle$, and their contribution is zero. It follows that II.11 equals:

$$(E_o - E_\gamma)^{-1}(-1)^{nij} \sum_{t=1}^{\ell_B} \Big\{ \langle \beta;\, B,\, b_t|\, O_1|\,\gamma\,;\, C,\, c_i\rangle$$

$$\langle \gamma\, C\, c_j\,|\, H_1'|\,\beta B\, b_t\rangle + \text{cross terms}\Big\} \qquad \text{II.12}$$

6') Contribution of the same $|\gamma\rangle$ as in 5') when

$$|(\eta_i)\rangle = |(\eta_j)\rangle$$

It is equal to

$$(E_o - E_\gamma)^{-1} \sum_{t=1}^{\ell_B} \sum_{\substack{s=1 \\ s\neq i}}^{\ell_c} \Big\{ \langle \gamma\,;\, C\,(c_i)|\, O|\gamma\,;\, C\,(c_i\, c_s);\beta\,;\, B,\, b_t\rangle \times$$

$$\times\langle \gamma\,;\, C\,(c_i\, c_s);\beta\,;\, B,\, b_t\,|\,H'|\,\gamma\,;\, C\,(c_i)\rangle + \text{cross terms} =$$

$$= (E_o - E_\gamma)^{-1} \sum_{t=1}^{\ell_B} \sum_{\substack{s=1 \\ s\neq i}}^{\ell_c} \Big\{ \langle \gamma\,;\, C,\, c_s|\, O_1|\,\beta\,;\, B,\, b_t\rangle$$

$$\langle \beta\,;\, B,\, b_t\,|\, H_1'|\,\gamma\,;\, C\, c_s\rangle + \text{cross terms}\Big\} \qquad \text{II.13}$$

and by I.16 it is equal to

$$(-1)^{nii}\,(E_o - E_\gamma)^{-1} \sum_{t=1}^{\ell_B} \langle \gamma\,;\, C,\, c_i|\, O_1|\,\beta\,;\, B,\, b_t\rangle$$

$$\langle \beta\,;\, B,\, b_t\,|\, H_1'|\,\gamma\,;\, C,\, c_i\rangle + \text{cross terms}\Big\} \qquad \text{II.14}$$

From 1'), 2'), 3'), 4'), 5'), 6'), and 3.2. and 3.12, the definition of $E_{\alpha A}$

$$\langle(\overline{\eta_i})|O|(\overline{\eta_j})\rangle - \langle(\eta_i)|O|(\eta_j)\rangle = \qquad \text{II.15}$$

$$= (-1)^{nij}\left\{\langle\gamma;\, \overline{C\, c_j}\,|\,O_1|\,\gamma;\, C,\, c_i\rangle - \langle\gamma;\, C,\, c_j|O_1|\,\gamma;\, C,\, c_i\rangle\right\}$$

The equality

$$\langle(\eta_i)|O|(\eta_j)\rangle = (-1)^{nij}\,\langle\gamma;\, C\, c_j|O_1|\,\gamma\, C\, c_i\rangle \qquad \text{II.16}$$

is trivial for $i \neq j$. When $i = j$, it is only true when the irreducible representation K (see ii) in § 3) is different from the identical one. When O is invariant under G, both members in II.16 differ by the contribution of the diagonal matrix elements of all the one-electron states in all the sets (αA) and in the set (γC) (formulae I.9 is used to derive this property). Formula 3.15 is now proved, with the qualifications that follows that equality.

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