Theory of the spin Hamiltonian of a complex with pentavalent molybdenum

PROC. PHYS. SOC., 1967, VOL. 91. PRINTED IN GREAT BRITAIN

Theory of the spin Hamiltonian of a complex with pentavalent molybdenum

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MS. received 6*th October* 1966, *in revised form* 24*th January* 1967

Abstract. The g values and hyperfine structure constants of $[\mathrm{Cl_5OMo}]^{2-}$ have been studied theoretically, and it has been found necessary to include the contribution of excited states that are not usually taken into account. The values 2 Å and 2.3 Å have been used for the Mo–O and Mo–Cl distances respectively, and it was possible to fit the measured g values into the formulae derived, on the assumption of reasonable values for the unknown parameters. It was not possible to fit the measured g values into the formulae of previous theories for the vanadyl ion if we assume the same interatomic distances.

From the hyperfine structure constants A and B, two sets of values of $\langle r^{-3}\rangle$ have been obtained as a function of the unknown parameters, one set for each sign of B. The set that gives values smaller than those predicted by the formulae of Elliot and Stevens was chosen. In that set the value of $\langle r^{-3}\rangle$ is between $3a_0{}^{-3}$ and $4a_0{}^{-3}$ when the unknown parameters are within the expected range of variation.

1. Introduction

The purpose of this paper is to explain the g values observed in the paramagnetic resonance of a complex of Mo^{5+}, and to discuss the contribution of some excited states that are not usually considered in this type of calculation.

The resonance of Mo^{5+} has been observed in dilute crystals (Owen and Ward 1956) and in liquid and frozen solutions (Garif'yanov and Fedotov 1962, Abraham *et al.* 1966, Hare *et al.* 1962); the optical spectrum is also available (Jorgensen 1957, Gray and Hare 1962). All these references but the first one deal with the complex of Mo^{5+} with chlorine in strongly concentrated hydrochloric acid where the formula $[\mathrm{Cl_5OMo}]^{2-}$ is assumed with the ligands in the vertices of a distorted octahedron: the Mo–O distance is taken to be 2 Å and the Mo–Cl distance is taken to be 2·3 Å, and the symmetry group that leaves the complex invariant is C_{4v}. The theory for complexes of V^{4+} with the same structure has been developed (Ballhausen and Gray 1962, Kivelson and Lee 1964), and it was possible to find reasonable agreement with the experimental results.

Using the theory of Ballhausen and Gray (1962) and the measured value of $\bar{g}$, the values $g_{\parallel} = 1{\cdot}915$, $g_{\perp} = 1{\cdot}965$ and $\zeta = 240\ \mathrm{cm}^{-1}$ were predicted for $[\mathrm{Cl_5OMo}]^{2-}$ (Hare *et al.* 1962), where ζ is the spin–orbit parameter. These values disagree with the recently measured $g_{\perp} = 1{\cdot}942 \pm 0{\cdot}005$ and $g_{\parallel} = 1{\cdot}972 \pm 0{\cdot}004$ (Abraham *et al.* 1966) and with the previous values $g_{\parallel} \simeq 1{\cdot}96$, $g_{\perp} = 1{\cdot}938 \pm 0{\cdot}005$ (Garif'yanov and Fedotov 1962). The value assumed for ζ is considerably smaller than the Mo^{5+} value $\zeta = 1030\ \mathrm{cm}^{-1}$ (Dunn 1961), and one would rather expect something around the free-ion value $550\ \mathrm{cm}^{-1}$ (Griffith 1961). It was found very difficult to fit the measured values of $g_{\parallel}$, $g_{\perp}$ and the energy of the optical transitions into the formulae of the existing theories for the vanadyl ion. Studying this problem, we have found that the contribution to the orbital part of $g_{\parallel}$ and $g_{\perp}$ of some charge-transfer states (one electron is promoted from the ground state to an essentially ligand state) is of the same order as that of the states considered in the previous theories (one electron is promoted from the ground state to an essentially central ion state). The only important difference between the present theory and the previous ones is the inclusion of these excited states.

One would expect that the introduction of all the charge-transfer states into the theory would make the calculation of g values very difficult, but we have been able to show that, under several approximations, most of the contributions become zero.

Of these approximations, the following two will be mentioned:

(i) The excited states are described by Slater determinants made with conveniently chosen molecular orbitals (with spin up or down); these molecular orbitals are grouped into sets of equal one-electron energies and symmetry properties.

(ii) The excited states that have all these sets equally occupied are degenerate. This second assumption is not generally true and the departures from it give rise to an extra contribution to the g values. This contribution is proportional to the ratio of the energy splitting between the states that we assume degenerate and the energy difference between these states and the ground state. As this ratio is in general much smaller than one, we have disregarded this extra contribution to g values because it would be rather difficult to calculate it.

The number of parameters that appear in the formulae for $g_{\parallel}$ and $g_{\perp}$ is rather large, but the number of unknowns can be reduced to five. If we impose reasonable restrictions to these parameters, and use the measured values of $g_{\parallel}$ and $g_{\perp}$, only two independent parameters are left, and the remaining three have been plotted as a function of them.

The formulae that give the hyperfine structure constants A and B are also given, but it is not possible to obtain extra information about the unknown parameters discussed above, because two extra unknowns appear. From one of them, the value of $\langle r^{-3}\rangle$ for the magnetic electron was obtained as a function of the two independent parameters.

2. The molecular orbitals for the complex

As discussed in the previous paragraph, the excited states will be approximated by Slater determinants, the one-electron wave functions being molecular orbitals obtained by linear combination of atomic orbitals. Three atomic orbitals will be used for each ligand: two π orbitals and one σ orbital; they are linear combinations of the 3p and 3s states for chlorine and of the 2p and 2s states for oxygen. The π orbitals are pure p states; the σ orbitals are linear combinations of one p and the s state of each atom. The coefficient of the p state in the σ orbitals is $\pm m$ (the sign depends on the relative phases of the p and s states) and these orbitals are directed towards the central ion; in our case, we have $m = 1/\sqrt{2}$ for sp hybridization.

There are, therefore, eighteen different ligand orbitals that combine to give symmetry orbitals for the C_{4v} group; they will be denoted by $|(s)\alpha, A, a_i\rangle$. The A corresponds to the irreducible representation of C_{4v}, a_i to the particular state in that representation, $s = \sigma, \pi$ indicates the type of orbital, and α is a number that identifies the different orbitals with the same s, A and a_i; α is omitted when unnecessary. The same notation will be used for the Mo atomic orbitals but using s = d for the 4d orbitals and A, a_i refer to the irreducible representations of O_h. We use adequate values for all the undefined phases of the symmetry orbitals; unless otherwise stated, the symbols and transformation properties used for the irreducible representations are those given by Griffith (1961).

From the atomic orbitals considered, twenty-seven molecular orbitals are obtained: the seventeen orbitals used in previous theories (Gray and Hare 1962) plus those obtained from the extra two π orbitals for each of the five chlorine atoms. Correspondingly, there are twenty extra electrons, and we assume that eighteen of them are in the five non-bonding A_1, A_2, B_1, E orbitals and in the two pairs of weakly bonding E orbitals. The other new orbital is $|(\pi)B_2b_2\rangle$ and it mixes with the Mo orbital of the same symmetry; the remaining two extra electrons are in the bonding orbital of this symmetry, and the magnetic electron is in an antibonding orbital, instead of being in a non-bonding orbital as in the previous theory (Gray and Hare 1962).

Of the ten extra orbitals, only $|(\pi)B_2b_2\rangle$ appears in the calculation of $g_{\parallel}$, and the two pairs of weakly bonding E orbitals $|(\pi)2Ea\rangle$ and $|(\pi)3Ea\rangle$ (with a = x, y) in that of $g_{\perp}$. The ligand symmetry orbitals $|(\sigma)B_1b_1\rangle$ and $|(\pi)1Ea\rangle$ are essentially the same as those with the same symmetry used in the paper by Gray and Hare (1962).

For the molecular orbitals, the notation $|\alpha Aa_i\rangle$ will be used; the meaning of A, a_i and α is the same as for the ligand symmetry orbitals. The notation $|\alpha Aa_i\rangle$ must not be confused with $|(s)\alpha Aa_i\rangle$ used for symmetry orbitals of the ligands and atomic orbitals of the central ion. The following molecular orbitals are necessary for this calculation:

$$|\alpha B_1b_1\rangle = D_\alpha|(d)E_g\epsilon\rangle + D_\alpha'|(\sigma)B_1b_1\rangle \qquad (2.1)$$

$$|\alpha B_2b_2\rangle = F_\alpha|(d)T_{2g}0\rangle + F_\alpha'|(\pi)B_2b_2\rangle \qquad (2.2)$$

where $|(\mathrm{d})\mathrm{T}_{2\mathrm{g}}0\rangle = i|(\mathrm{d})\mathrm{T}_{2\mathrm{g}}\zeta\rangle$ (Griffith 1961) and $\alpha = 1, 2$;

$$|\alpha\mathrm{Ex}\rangle = i\{C_\alpha|(\mathrm{d})\mathrm{T}_{2\mathrm{g}}\eta\rangle + C_\alpha'|(\pi)1\mathrm{Ex}\rangle + C_\alpha''|(\pi)2\mathrm{Ex}\rangle + C_\alpha'''|(\pi)3\mathrm{Ex}\rangle\} \tag{2.3}$$

where $\alpha = 1, 2, 3, 4$. For the case of $|\alpha\mathrm{Ey}\rangle$ the atomic orbital $|(\mathrm{d})\mathrm{T}_{2\mathrm{g}}\xi\rangle$ appears instead of $|(\mathrm{d})\mathrm{T}_{2\mathrm{g}}\eta\rangle$ and $|(\pi)\alpha\mathrm{Ey}\rangle$ instead of $|(\pi)\alpha\mathrm{Ex}\rangle$.

In § 4 we shall disregard the contribution of $|(\pi)2\mathrm{Ea}\rangle$ and $|(\pi)3\mathrm{Ea}\rangle$ to $g_\perp$, by taking $C_\alpha'' = C_\alpha''' = 0$ and using only $\alpha = 1, 2$ for the molecular orbitals $|\alpha\mathrm{Ea}\rangle$. The coefficients of these two molecular orbitals, and also those of the orbitals defined in (2.1) and (2.2), will be taken in such a way that $\alpha = 1$ is the bonding orbital and $\alpha = 2$ is the antibonding orbital.

3. The spin-Hamiltonian parameters

In previous theories the only states mixed by the spin–orbit interaction into the unperturbed ground states were those obtained by promoting the magnetic electron (in the antibonding b_2 state according to the present description) into molecular orbitals of higher energy, which are essentially localized in the central ion. In the present theory we also include the excited states obtained by promoting a non-magnetic electron (in a molecular orbital of less energy than the magnetic one) to a vacant molecular orbital of the unperturbed ground state. Not all of these excited states contribute to the g values, but only those obtained from the unperturbed ground state by promoting a non-magnetic electron into the antibonding b_2 molecular orbital half occupied by the magnetic electron, i.e. filling this molecular orbital. The proof of this property is based on group theory; it is rather long but straightforward, and only approximately valid as discussed in § 1.

The expressions for $g_\parallel$ and $g_\perp$ have been calculated by neglecting the matrix elements of the orbital angular momentum between two atomic orbitals centred around different ligands, and using the techniques of Stevens (1953) for all other cases:

$$g_\parallel - 2{\cdot}002 = 8\mathscr{R}\sum_{\alpha=1}^{2} X_\alpha[F_2^*(D_\alpha + D_\alpha'S) + (F_2')^*\{D_\alpha\Pi^* + \tfrac{1}{2}D_\alpha'T(-m)\}] \tag{3.1}$$

$$g_\perp + 2{\cdot}002 = 2\sqrt{2}\,\mathscr{R}\sum_{\alpha=1}^{4} Y_\alpha\left\{F_2^*\left(C_\alpha + C_\alpha'\Pi_0 + \frac{1}{\sqrt{2}}C_\alpha''\Pi - \tfrac{1}{2}C_\alpha'''\Pi\right) + (F_2')^*\left(C_\alpha\Pi^* + \frac{1}{\sqrt{2}}C_\alpha''\right)\right\} \tag{3.2}$$

where

$$\begin{aligned} S &= \langle(\mathrm{d})\mathrm{E}_{\mathrm{g}}\epsilon|(\sigma)\mathrm{B}_1\mathrm{b}_1\rangle \\ \Pi &= \langle(\mathrm{d})\mathrm{T}_{2\mathrm{g}}0|(\pi)\mathrm{B}_2\mathrm{b}_2\rangle \\ \Pi_0 &= \langle(\mathrm{d})\mathrm{T}_{2\mathrm{g}}\eta|(\pi)1\mathrm{Ex}\rangle \end{aligned} \tag{3.3}$$

and

$$T(m) = m - \{\tfrac{1}{3}(1-m^2)\}^{1/2} R\int_0^\infty r^2 R_{3\mathrm{p}}(r)R_{3\mathrm{s}}'(r)\,dr. \tag{3.4}$$

In this formula R is the Mo–Cl distance, $R_{3\mathrm{p}}(r)$ is the radial function for the chlorine 3p state and $R_{3\mathrm{s}}'(r)$ the radial derivative of the radial function for the 3s state of the same atom.

To calculate the coefficients X_α, Y_α, only the matrix elements of the spin–orbit interaction between pairs of atomic orbitals centred around the same ion have been considered, and the corresponding free-ion values have been used (Misetich and Buch 1964). The result obtained was

$$X_\alpha = \frac{F_2D_\alpha^*\zeta_{\mathrm{d}} - F_2'(D_\alpha')^*\frac{1}{2}m\zeta_{\mathrm{p}}}{\delta_\alpha'} \tag{3.5}$$

$$Y_\alpha = -\frac{(1/\sqrt{2})F_2C_\alpha^*\zeta_{\mathrm{d}} + \frac{1}{2}F_2'(C_\alpha'')^*\zeta_{\mathrm{p}}}{\delta_\alpha}. \tag{3.6}$$

In these formulae ζ_d is the spin–orbit parameter of the free molybdenum ion, and ζ_p that of the free chlorine ion, both for adequately chosen ionic charges. The parameters δ_2' and δ_2 are negative; they are minus the energy necessary to promote the electron in the orbital $|2B_2b_2\rangle$ from the ground state to the orbitals $|2B_1b_1\rangle$ and $|2Ex\rangle$ respectively. For all the other cases, δ_1' and δ_α are positive, and equal to the energy necessary to promote the electron in the orbitals $|1B_1b_1\rangle$ and $|\alpha Ex\rangle$ respectively from the ground state to the empty $|2B_2b_2\rangle$ orbital. All the δ's with positive sign appear in the contribution due to the charge-transfer excited states introduced in this theory.

The hyperfine parameters A and B were easily obtained from the nuclear Hamiltonian (Abragam and Pryce 1951 a); the quadrupole interaction was not considered, since the quadrupole moments of ^{95}Mo and ^{97}Mo have not been observed and they are presumably small.

When only the contribution of matrix elements between pairs of states of the central ion is considered, the following expressions are obtained:

$$A = P\left\{-\frac{4}{7}F_2F_2{}^* - K + \mathscr{R}\left(8F_2{}^* \sum_{\alpha=1}^{2} D_\alpha X_\alpha - \frac{6\sqrt{2}}{7}F_2{}^* \sum_{\alpha=1}^{4} C_\alpha Y_\alpha\right)\right\} \tag{3.7}$$

$$B = P\left\{-\frac{2}{7}F_2F_2{}^* + K + \mathscr{R}\left(\frac{11\sqrt{2}}{7}F_2{}^* \sum_{\alpha=1}^{4} C_\alpha Y_\alpha\right)\right\} \tag{3.8}$$

where $P = 2\gamma\beta\beta_N\langle r^{-3}\rangle$ and K comes from the Fermi contact term in the nuclear Hamiltonian. As usual r is the distance from the magnetic electron to the central ion, β the Bohr magneton, β_N the nuclear magneton and γ the nuclear gyromagnetic factor.

It can be seen from (3.7) and (3.8) that, when covalency is present, the contribution of the terms $r^{-3}\mathbf{L}$ and $r^{-3}\mathbf{S}$ of the nuclear Hamiltonian is not proportional to $g^{(L)}$ or $g^{(S)}$ as is the case when the one-electron states are the product of a radial function times a function of the angle (Abragam and Pryce 1951 b).

4. Comparison with the experimental values

Formulae (3.1) and (3.2) give $g_\parallel$ and $g_\perp$ as a function of several parameters: (i) the energies δ_α and δ_α' and the spin–orbit parameters ζ_d and ζ_p, (ii) C_α, D_α, F_α introduced in (2.1), (2.2) and (2.3), and (iii) the overlap integrals S, Π and Π_0 defined in (3.3) and $T(-m)$ defined in (3.4). Of the energies δ_α, δ_α' the values $\delta_1 = 26\,700$ cm^{-1}, $\delta_2 = -13\,800$ cm^{-1} and $\delta_2' = -23\,000$ cm^{-1} are known (Gray and Hare 1962); as the values of δ_3 and δ_4 will not be necessary (cf. below), only δ_1' remains unknown. The results are not too sensitive to ζ_p (the spin–orbit parameter for the chlorine 3p electron), and the value $\zeta_p = 550$ cm^{-1} (Blume and Watson 1963) will be used without further corrections; the values of the molybdenum spin–orbit parameter ζ_d for a 4d electron are also known for several degrees of ionization (Griffith 1961), and an ionic charge consistent with all the other parameters will be used to determine ζ_d.

The coefficients C_α, D_α, F_α are unknown and a rather long calculation (as the one performed by Ballhausen and Gray (1962) for the vanadyl ion) would be necessary to obtain them independently. The perturbation method used in this work requires all the molecular orbitals used to be orthonormal, and this restriction reduces the number of undetermined coefficients: it is enough to know D_2 and F_2 to obtain all the other D_α and F_α respectively. From the sixteen coefficients C_α only four independent ones are left when the orthonormality conditions are used, but the energies δ_3 and δ_4 are also unknown. Although the four orbitals in (2.3) contribute to $g_\perp$, it was possible to obtain good agreement with the experimental values by taking only the contribution of the two molecular orbitals in (2.3) with $\alpha = 1, 2$ and also taking $C_\alpha'' = C_\alpha''' = 0$: this is equivalent to disregarding the two sets of symmetry orbitals $|(\pi)2Ea\rangle$ and $|(\pi)3Ea\rangle$ throughout the calculation. This procedure was adopted for simplicity, and because one could not obtain more information by keeping the contribution of these states; small changes in C_α and C_α' would compensate for the effect of C_α'' and C_α'''. As a consequence of this approximation, the values of δ_3 and δ_4 are not required, and the knowledge of C_2 is enough to obtain all the necessary C_α.

To calculate the values of S, Π and Π_0, we used tables of overlap integrals (Jaffe and Doak 1953, Jaffe 1953) and one-electron wave functions available in the literature. For oxygen, the radial functions were in the required form (Ballhausen and Gray 1962), but for molybdenum (Roothaan and Synek 1964) and chlorine (Bagus 1965) we had to express them in terms of the Slater functions appearing in the tables available to us. If we use 2·0 Å for the Mo–O distance and 2·3 Å for the Mo–Cl distance (Gray and Hare 1962) and assume sp hybridization for the σ orbitals (i.e. $m = 1/\sqrt{2}$), the values $S = 0{\cdot}360$, $\Pi = 0{\cdot}378$, $\Pi_0 = 0{\cdot}129$ were obtained.

The value $-0{\cdot}3732/a_0$ was calculated for the integral in (3.4) using the 'less accurate wave functions' given by Bagus (1964) (a_0 is the Bohr radius). Taking $m = 1/\sqrt{2}$, the value $T(-1/\sqrt{2}) = -0{\cdot}0449$ was obtained.

After all the above assumptions, five unknown parameters are left: δ_1', ζ_d, D_2, F_2 and C_2 in the two relations (3.1) and (3.2); the experimental g values are known: $g_{\parallel} = 1{\cdot}972$ and $g_{\perp} = 1{\cdot}942$ (Abraham *et al.* 1966). As too many degrees of freedom are left, the following restrictions on the parameters will be imposed.

(i) The quantities $D_2(D_2+SD_2')$, $F_2(F_2+\Pi F_2')$ and $C_2(C_2+\Pi_0 C_2')$ are larger than 0·5. These quantities are respectively the 'partial gross populations' for the orbitals $|2B_1b_1\rangle$, $|2B_2b_2\rangle$ and $|2Ea\rangle$ in the central atom (Mulliken 1955) and measure the probability of finding an electron in that atom when it is in the corresponding molecular orbital.

(ii) The value of ζ_d corresponds to an electronic charge of the molybdenum ion equal to the 'total net atomic populations', i.e. we assume that the 'overlap populations' (Mulliken 1955) do not affect the value of ζ_d, because most of their contributions are due to charges located far from the atomic nucleus. As there are many σ bonding orbitals that do not contribute to the g values, it will be assumed that they all give the same contributions as $|1B_1b_1\rangle$ to the 'net atomic populations'.

(iii) The value of δ_1' is larger than $|\delta_2'|$ and its probable value about 40 000 cm^{-1}.

With the two relations for $g_{\parallel}$ and $g_{\perp}$ and the restriction (ii) on the value of ζ_d, only two independent parameters are left: for example δ_1' and D_2. In figure 1, the full lines represent the value of C_2 as a function of D_2 for a constant value of δ_1' (given at the bottom left of each curve); the broken lines give C_2 as a function of D_2 for a constant value of F_2 (given at the bottom right of each curve).

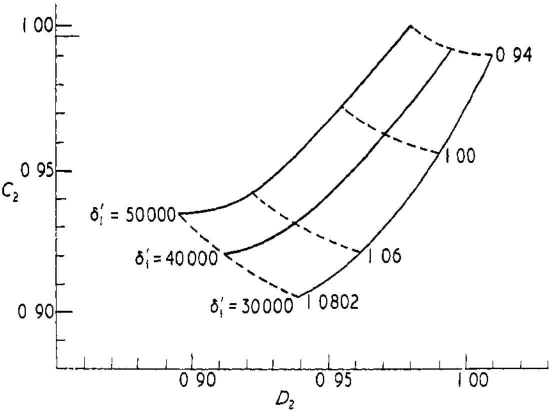

Figure 1.

Values of the coefficients D_2, F_2, C_2 greater than one are due to the non-orthogonality of the atomic wave functions, their maximum values being respectively 1·0719, 1·0802 and 1·0084.

For $D_2 < 0{\cdot}9$ the value of $D_2(D_2+SD_2')$ is smaller than 0·53 and does not satisfy the condition (i); on the other hand, the value $D_2 = 1{\cdot}0719$ is not reached for all δ_1' because it is not possible to satisfy condition (ii) beyond a certain D_2 for each δ_1'. The values of D_2 are therefore restricted to a small interval and consequently the values of ζ_d are also restricted. In figure 2 the values of ζ_d are given as a function of D_2 for given values of

δ_1', and they fall between 600 cm^{-1} and 800 cm^{-1}; the dependence with δ_1' for constant D_2 is rather weak in the region of interest.

Because of all the approximations made to derive the curves drawn in figures 1 and 2, they have only a qualitative value, but they show that it is possible to fit the measured $g_{\parallel}$ and $g_{\perp}$ using perfectly reasonable values for all the parameters appearing in formulae (3.1) and (3.2). The situation is different in previous theories: we considered the formulae derived by Kivelson and Lee (1964) for the vanadyl ion, because they can be applied in the present case and are more elaborate than those of Hare *et al.* (1962). Our formulae for $g_{\parallel}$ and $g_{\perp}$ coincide with those given by Kivelson and Lee (1964) when only the term $\alpha = 2$ is left in the two summations of (3.1) and (3.2). Using the same values for S, Π, Π_0 and $T(-m)$ as in figures 1 and 2, it was not possible to find values of D_2, C_2 and F_2 such that they give the experimental values of $g_{\parallel}$ and $g_{\perp}$ and also satisfy condition (i).

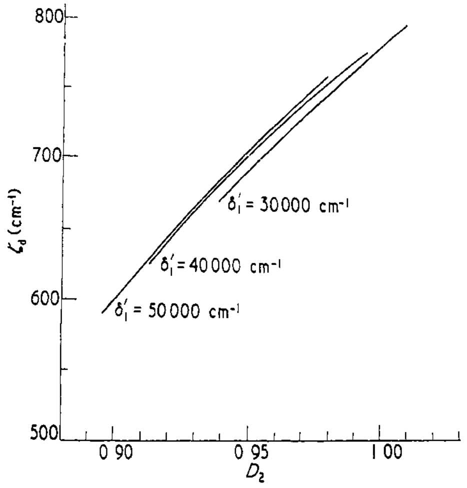

Figure 2.

From the values of A and B (81 G and 39 G, respectively, as given by Abraham *et al.* (1966)) one cannot obtain extra information about the unknowns in (3.1) and (3.2) because two extra parameters appear in (3.7) and (3.8): they are $P = 2\gamma\beta\beta_N\langle r^{-3}\rangle$ and K (related to the Fermi contact term).

Assuming values for δ_1' and F_2, one obtains D_2, C_2 and ζ_d, from figures 1 and 2, and by substitution in (3.7) and (3.8), the values of P and PK are given as a function of A and B. As an example, for the values corresponding to the vertex determined by $\delta_1' = 30\,000$ cm^{-1} and $F_2 = 1{\cdot}0802$ in figure 2

$$P = -0{\cdot}009\,02(A+B). \qquad (4.1)$$

The signs of A and B are not known, but the value $\gamma = -0{\cdot}3746$ is given in the table of Strominger *et al.* (1958), and by substitution into the definition of P, it follows that $P/hc = -0{\cdot}001\,192\ \mathrm{cm}^{-1} \times a_0^3\langle r^{-3}\rangle$; therefore, A is positive. It is not possible from the measurements available (Abraham *et al.* 1966) to give B a sign, and the two possibilities must be considered. From (4.1) the values of $\langle r^{-3}\rangle a_0^3$ are derived: 7·57 for B positive and 3·14 for B negative. To decide between the two possibilities the method of Elliot and Stevens (1953, formula (3.2)) was used, and the value 6·30 was obtained. In the transuranic series this method gives values of $\langle r^{-3}\rangle/\zeta$ larger than those obtained with a more exact method (Foglio and Pryce 1962); on the assumption that the same is true for the 4d group, the value $\langle r^{-3}\rangle = 3{\cdot}14\ a_0^{-3}$ must be chosen (for $\delta_1' = 30\,000\ \mathrm{cm}^{-1}$ and $F_2 = 1{\cdot}0802$).

The value calculated for $\delta_1' = 50\,000\ \mathrm{cm}^{-1}$ and $F_2 = 0{\cdot}94$ is $\langle r^{-3}\rangle = 3{\cdot}96 a_0^{-3}$ and those obtained for the other two vertices in figure 2 are between the two values given; therefore, the quantity $\langle r^{-3}\rangle a_0^3$ is in the neighbourhood of 3·5 and probably between 3 and 4.

5. Summary and conclusions

The formulae that give the g values and hyperfine structure constants for complexes similar to $[Cl_5OMo]^{2-}$ with C_{4v} symmetry have been derived. The molecular orbitals used here are practically the same as those used by Kivelson and Lee (1964) in a similar calculation for the vanadyl ion, but the contribution of excited states that are not usually considered in such theories has been included. These states are obtained by promoting an electron from one of the occupied bonding orbitals of the ground state into the b_2 molecular orbital that is half occupied by the magnetic electron in that state. Under approximations discussed in the text, it can be shown by the use of group theory that all the other charge-transfer states do not contribute to the g values.

Taking the distance 2 Å for the Mo–O bond and 2·3 Å for the Cl–Mo bond (Gray and Hare 1962) and using one-electron wave functions obtained from the literature, the relevant overlap integrals have been calculated. With those values it can be shown that it is possible to fit the measured values of the complex using reasonable values for all the unknown parameters. Using restrictions given in § 4 on the values of these parameters, it is possible to express them as a function of only two independent ones, and a plot of these relations is given in figures 1 and 2. In these figures it is shown that the values of ζ_d and those of the coefficients D_2, F_2 and C_2 are restricted to a rather limited range.

It was not possible to fit the measured g values into the formulae obtained by neglecting the contribution of the charge-transfer excited states in (3.1) and (3.2) (this procedure gives the formulae of Kivelson and Lee (1964)) when the same values of the relevant overlap integrals as before were used.

It can be concluded that the contribution to the g values of the charge-transfer states mentioned above is important for $[Cl_5OMo]^{2-}$, and is sufficient to explain the measured g values of that complex.

The only extra information given by the hyperfine structure constants A and B concerns the two parameters P and K that appear in (3.7) and (3.8). Two values of $\langle r^{-3}\rangle$ can be obtained from each P, according to the sign selected for B. Comparison with the values of $\langle r^{-3}\rangle$ obtained by using the method of Elliot and Stevens (1953, formula (3.2)) indicates that B is negative for the wave functions used in the present paper; it is easy to show that A is positive. For B negative the value of $\langle r^{-3}\rangle a_0^3$ is around 3·5 and, because of the limited range of variation of the unknown parameters, it is presumably between 3 and 4.

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