THE EFFECTS OF COVALENT BONDING

20.1. Summary of the foregoing theory

IN the theory of paramagnetic ions described in the previous chapters we have assumed throughout that the magnetic electrons were strictly localized on the paramagnetic ion itself.

The neglect of configuration interaction (with one exception, see § 17.5) resulted in the even more restrictive assumption that, apart from closed shells, the one-electron wave-functions, from which the wave-function of the ion was built, were f or d Hartree–Fock wave-functions with the same radial function as in the free ion. Many-electron wave-functions, eigenstates of (L, S, L_z, S_z) or (L, S, J, J_z), can be built as linear combinations of Slater determinants constructed using these one-electron wave-functions. Finally the low-lying states of the bound ion were represented as linear combinations of states $|L, S, L_z, S_z\rangle$ or $|L, S, J, J_z\rangle$, the former representation being more convenient for the iron group and the latter for the rare-earth group. In first approximation a single set of values was required for L, S in the iron group and for L, S, J in the rare-earth group. The amplitudes of the component states $|L, S, L_z, S_z\rangle$ or $|L, S, J, J_z\rangle$ were obtained by solving a secular equation whose coefficients were matrix elements

$$\langle L, S, M_L, M_S| \ V \ |L', S', M_L', M_S'\rangle \ \text{or} \ \langle L, S, J, M_J| \ V \ |L', S', J', M_J'\rangle$$

of a certain crystal potential $V = \sum_i V(\mathbf{r}_i)$ which was intended to represent the influence of the surroundings of the paramagnetic ion. The number of independent constants in V was severely limited by symmetry considerations and even more so by the neglect of configuration interaction.

The fact that a wealth of magnetic resonance data could be made to agree with calculated values, simply by adjusting these few constants to 'reasonable' values, might be considered as a justification of the crystal field model. The fact that a single set of (L, S) values was generally sufficient in the iron group and a single set of (L, S, J) values in the rare-earth group pointed further to the approximate correctness of the hypothesis of 'intermediate crystal field' and 'weak crystal field' respectively. There are, however, serious reasons for believing that for $3d$ electrons (and even more so for $4d$ and $5d$) the above picture is

incomplete. Among the evidence pointing in this direction we can list the following facts.

(a) Some paramagnetic compounds such as cyanides have anomalous values of spin and magnetic moment which contradict Hund's rule. Thus, for instance, $K_3Fe(CN)_6$ and $K_3Co(CN)_6$, where in an ionic model the iron should be Fe^{3+} and the cobalt Co^{3+}, would be expected through Hund's rule to have in their ground states respectively spins $S = \frac{5}{2}$ and $S = 2$, but turn out to have an effective spin $\frac{1}{2}$ for $K_3Fe(CN)_6$ and 0 for $K_3Co(CN)_6$.

(b) In compounds with 'normal' values of the spin the orbital contribution to the magnetic moment turns out to be systematically smaller than the theoretical value calculated by using the crystal field model.

(c) While crude calculations of the magnitude of the crystal field using the point-charge model can give values in qualitative agreement with those extracted from the analysis of resonance and spectroscopic data, attempts to improve the model by taking into account the spatial extension of neighbouring ions and the overlap of their wave-functions with those of the central ion, destroy the agreement, leading to values for the crystal field wrong in magnitude or in sign or in both.

(d) The most cogent argument against the purely ionic model is the observation in the resonance spectrum of hyperfine structure with neighbouring nuclei, demonstrating unambiguously the presence of unpaired electrons on these ligand ions.

While some of the discrepancies above can be explained away by suitable modifications of the purely ionic crystal field picture, the molecular orbital model appears to provide a consistent explanation for them all and will be discussed next.

20.2. The molecular orbitals model for covalent bonding

We shall describe this model using the specific example of an octahedral complex XY_6 where the central atom X is surrounded by six identical atoms Y, called ligands, each at the apex of a regular octahedron. In the purely ionic picture X is a paramagnetic ion and the ligands are six diamagnetic ions with closed shells. The complex NiF_6 constitutes a good example. The central ion Ni^{++} has $3d^8$ electrons outside closed shells and each surrounding ion F^- has the closed-shell configuration $1s^2 2s^2 2p^6$. In the ionic picture we study the $3d$ electrons of the central ion under the influence of the crystal potential created by the neighbouring fluorines (and also by ions further removed). The next step is to treat the XY_6 complex as a single isolated molecule.

In principle we could conceive of a generalized self-consistent field

method where one-electron orbitals are determined in a self-consistent field that has the octahedral symmetry of the molecule rather than the full rotational symmetry of the isolated atom. In practice this is neither possible nor indeed necessary. Instead we assume first that the wave-functions of the inner electrons, $1s^2$ through $3p^6$ of the central atom X, and of the inner electrons $1s^2$ of the surrounding atoms Y, do not participate in the bonding and are correctly described by the Hartree–Fock functions of the corresponding atoms. For the external or valence orbitals of X and Y we make the drastic approximation that they are linear combinations of the atomic Hartree–Fock orbitals of these atoms. The number and nature of these combinations is pre-determined to a large extent by symmetry considerations. Once these combinations have been written down, the remaining independent amplitudes can be determined either from experiment by adjusting them to fit the observed data, or from theory by a variational method: the molecular orbitals, consisting of linear combinations of atomic Hartree–Fock orbitals are considered as trial functions and the amplitudes are determined from the usual condition that the energy be stationary. The two sets of values can be compared to provide a test of the validity of the model.

We begin by examining the symmetry limitations on the linear combinations of atomic orbitals to be used as molecular orbitals. The three C_4 axes of the octahedron are chosen as coordinate axes Ox, Oy, Oz. We label respectively 1 and 4 the ligands on the positive and negative side of Ox, 2 and 5 those on Oy, 3 and 6 those on Oz. Each ligand has a $2s$ orbital which we label $\sigma_{1,s}$ through $\sigma_{6,s}$. It also has 3 p-orbitals. The p-orbitals with zero orbital momentum along the direction towards the central atom, we label $\sigma_{1,p}$ through $\sigma_{6,p}$. Since each function $\sigma_{i,p}$ has a positive and a negative lobe we adopt the convention that all the positive (we could choose all the negative) lobes of the $\sigma_{i,p}$ point towards the central ion. There are twelve other p-orbitals on the ligands, the so-called π-orbitals. We call Y_1 and Z_1 the two π-orbitals of ligand 1, whose angular momentum components are zero along axes parallel to Oy and Oz respectively and passing through the nucleus of ligand 1. The other orbitals will be Y_4, Z_4; X_2, Z_2; X_5, Z_5; X_3, Y_3; X_6, Y_6. Their relative signs can be defined by the convention that the symbols X, Y, Z in X_i, Y_i, Z_i transform under the operation of the full cubic group O_h (that includes the inversion I through the centre of the octahedron) in the same way as the coordinates x, y, z, the transformation of the indices i being obvious. Thus for instance a rotation of $90°$ around Oz will turn Y_4 into $-X_5$ while the inversion

operation I turns Y_4 into $-Y_1$. In either case,

$$(Y_1 - Y_4 + X_2 - X_5) \rightarrow -(Y_1 - Y_4 + X_2 - X_5).$$

We could have labelled the σ_p functions: X_1, X_4; Y_2, Y_5; Z_3, Z_6; however, if we applied to their transformation the rules outlined for the π-functions, we would contradict the earlier convention that all positive lobes point towards the centre.

Different sign conventions may be adopted, and are sometimes used in the literature. Since we are going to use definite linear combinations of the σ_s, σ_p, and π-orbitals, the signs of the coefficients in these combinations depend on the sign conventions made for the σ_s, σ_p, π and the latter must therefore be clearly specified.

Returning for a moment to the central atom we recall that its d-orbitals provide a basis for the irreducible representations Γ_3 and Γ_5 of the cubic group. Since the d-functions are even under inversion these representations are customarily written as e_g and t_{2g} (g stands for 'gerade' or 'even' in German). Similarly the orbital $4s$ provides the even representation Γ_1 or a_{1g} and $4p$ the odd representation Γ_4 or t_{1u} (u for 'ungerade' which means 'odd'). Similarly the orbitals of the ligands, which transform into each other under operations of O_h, provide representations of this group which are reducible and can be reduced by the usual methods using the character tables of O_h. In these transformations ($\sigma_{i,s}$, $\sigma_{i,p}$) and π-orbitals clearly do not mix and the representations they span can be reduced separately. It is also clear that $\sigma_{i,s}$ and $\sigma_{i,p}$ transform in the same way (thanks to our sign convention for the $\sigma_{i,p}$) and will give rise to the same irreducible representations. It is easy to verify that the reduction of the representations spanned by the six functions σ_s (or σ_p) yields $a_{1g} + e_g + t_{1u}$, whereas the reduction of that spanned by the π-functions yields $t_{1u} + t_{2u} + t_{1g} + t_{2g}$. The corresponding proper linear combinations can be calculated by the method outlined in § 14.4 for the reduction of the rotation group.

The results are given in Table 23 for the representations a_{1g}, e_g, t_{1u}, t_{2g}, which are the only ones that can be coupled by a Hamiltonian of octahedral symmetry to orbitals $3d$, $4s$, $4p$ of the central ion. The representation t_{2u} would couple to f-electrons on the central atoms.

20.3. Bonding and anti-bonding orbitals, overlap, and covalency

We consider for the sake of definiteness an orbital of the complex XY_6, belonging to the representation t_{2g} and denoted by

$$\psi_\zeta = \alpha\varphi_\zeta + \beta\chi_\zeta, \tag{20.1}$$

where φ_ζ is the usual d-function of the central ion

$$\varphi_\zeta = d_{xy} = \frac{1}{i\sqrt{2}}\{|2\rangle - |-2\rangle\} \tag{20.2}$$

and χ_ζ is the linear combination, given in Table 23, of p_π functions belonging to the ligands 1, 2, 4, 5,

$$\chi_\zeta = \tfrac{1}{2}(Y_1 - Y_4 + X_2 - X_5). \tag{20.3}$$

We use (20.1) as a trial function where the 'best' values must be selected for the amplitudes α and β. It is important to notice that since the functions φ_ζ and χ_ζ which belong to different atoms are not orthogonal, the normalization condition for (20.1) is not $\alpha^2 + \beta^2 = 1$ but rather

$$\alpha^2 + \beta^2 + 2\alpha\beta S = 1, \tag{20.4}$$

where $S = \langle\varphi_\zeta \mid \chi_\zeta\rangle$ is an overlap integral. If h is an approximate one-electron Hamiltonian that contains both the kinetic energy of the electron and its electrostatic interactions (including exchange terms) with the electrons on the central ion and on the ligands, the energy W of the orbital ψ_ζ is

$$W = (\psi_\zeta| \, h \, |\psi_\zeta) = \alpha^2(\varphi_\zeta| \, h \, |\varphi_\zeta) + \beta^2(\chi_\zeta| \, h \, |\chi_\zeta) + 2\alpha\beta(\varphi_\zeta| \, h \, |\chi_\zeta). \tag{20.5}$$

By varying α and β in order to make (20.5) stationary, under the subsidiary normalization condition (20.4) we find two sets of values (α_a, β_a), (α_b, β_b) for (α, β) and two values W_a and W_b for the energy W. Writing $W_1 = (\varphi_\zeta| \, h \, |\varphi_\zeta)$, $W_2 = (\chi_\zeta| \, h \, |\chi_\zeta)$, $W_{12} = (\varphi_\zeta| \, h \, |\chi_\zeta)$, the equations for α and β can be written

$$\begin{aligned}
\alpha W_1 + \beta W_{12} &= W(\alpha + \beta S), \\
\alpha W_{12} + \beta W_2 &= W(\alpha S + \beta).
\end{aligned} \tag{20.6}$$

The secular equation $(W_1 - W)(W_2 - W) - (W_{12} - WS)^2 = 0$ has clearly two roots, W_a and W_b, with $W_a > W_1, W_2$; $W_b < W_1, W_2$. Let α_a, β_a and α_b, β_b be the amplitudes of φ_ζ and χ_ζ in the orbitals whose energies are W_a and W_b. If we assume $W_1 > W_2$ we can extract from (20.6) the following expressions for W_a and W_b:

$$\begin{aligned}
W_a &= W_1 + \frac{(\beta_a/\alpha_a)^2}{1 - (\beta_a/\alpha_a)^2}(W_1 - W_2), \\
W_b &= W_2 - \frac{(\alpha_b/\beta_b)^2}{1 - (\alpha_b/\beta_b)^2}(W_1 - W_2).
\end{aligned} \tag{20.7}$$

It is clear from (20.7) that since $W_a > W_1 > W_2 > W_b$ we must have

$(\alpha_a/\beta_a)^2 > 1$, $(\alpha_b/\beta_b)^2 < 1$. The two orbits with energies W_a and $W_b < W_a$ are called respectively anti-bonding and bonding. The anti-bonding orbital contains a greater admixture α_a^2 of the orbital of higher energy φ_ζ, and the bonding orbital a greater admixture β_b^2 of the orbital of lower energy, χ_ζ.

It is convenient to rewrite eqn (20.1) for the anti-bonding and bonding orbitals in the form

$$\psi_\zeta^a = N_i^{-\frac{1}{2}}(\varphi_\zeta - \lambda\chi_\zeta),$$
$$\psi_\zeta^b = N_t'^{-\frac{1}{2}}(\chi_\zeta + \gamma\varphi_\zeta),$$
$$\text{(20.8)}$$

where $\lambda = -\beta_a/\alpha_a$, $\gamma = \alpha_b/\beta_b$, and the normalization conditions are

$$N_t = 1 - 2\lambda S + \lambda^2,$$
$$N_t' = 1 + 2\gamma S + \gamma^2.$$
$$\text{(20.9)}$$

So far no assumption has been made about the magnitudes of λ and γ. For instance $\lambda = \gamma = 1$ corresponds to a complete sharing of the electron between the two atomic orbitals φ and χ. However a complex XY_6 such as, say, NiF_6 is still mainly ionic and we expect the electrons to stay mainly either on the central ion or on the ligands. This implies that the overlap $S = (\varphi \mid \chi)$ is small compared to unity and that the coupling matrix element $W_{12} = (\varphi| h |\chi)$ is small compared to the difference $(W_1 - W_2) = (\varphi| h |\varphi) - (\chi| h |\chi)$. If we treat S, $W_{12}/(W_1 - W_2)$, λ, and γ as small quantities of first order and neglect terms of higher order the formulae become much simpler. From the orthogonality of ψ_ζ^a and ψ_ζ^b as given in (20.8) we get

$$\lambda = S + \gamma. \qquad \text{(20.10)}$$

The value of $\gamma = \alpha_b/\beta_b$, extracted from (20.6), takes the simple form

$$\gamma = -\frac{(\varphi| h |\chi) - S(\chi| h |\chi)}{(\varphi| h |\varphi) - (\chi| h |\chi)}. \qquad \text{(20.11)}$$

The expression (20.11) resembles the usual first-order perturbation formula except for the term $S(\chi| h |\chi)$ which takes into account the lack of orthogonality of φ and χ. Similarly,

$$\lambda = -\frac{(\varphi| h |\chi) - S(\varphi| h |\varphi)}{(\varphi| h |\varphi) - (\chi| h |\chi)}. \qquad \text{(20.12)}$$

It is reasonable to assume that the unperturbed orbitals χ of the ligands constructed from $2s$ and $2p$ electrons lie much deeper than the $3d$ orbitals (and *a fortiori* than $4s$ and $4p$) of the central atom, and

to assign the bonding orbitals ψ_b to the ligands and the anti-bonding orbitals to the central ion.

Since the overlap $S = (\varphi \mid \chi)$ is not zero, the definition of covalency needs to be sharpened. We shall agree to call the complex purely ionic if the surrounding ions Y carry no charge transferred from the central ion, that is if in the bonding orbitals (20.8), $\gamma = 0$. But from (20.10) it follows that $\lambda = \gamma + S = S$ is *not* zero for the anti-bonding orbitals.

From a knowledge of the Hartree–Fock wave-functions of the atoms X and Y it is possible to calculate from first principles, using (20.7), (20.10), and (20.11), the admixture coefficients λ and γ, the overlaps S, and the energies W_a of the various anti-bonding orbitals. The description of such a calculation is outside of the scope of this book. Performed for the complex NiF_6 by Sugano and Shulman (1963) it has led, for the admixtures λ and γ and the anti-bonding energies W_a, to values in excellent agreement with most of the observed data, contrasting with earlier calculations based on the ionic model (even when generalized to take into account the overlap between orbits of the central atoms and of the ligands). Some of the results of this calculation will be mentioned in a later discussion (§ 20.6).

We have so far considered the case when an orbit φ of the central ion was coupled by the Hamiltonian to a single orbit χ of the ligands. The generalization is straightforward. With the functions $\varphi_e = d\gamma$ belonging to the representation e_g we have an example of a coupling with two orbitals $\chi^e_{\sigma,s}$ and $\chi^e_{\sigma,p}$ of the ligands. We now have three orbitals, one which is mainly $\chi_{\sigma,s}$ with admixtures from φ_e, a second $\chi_{\sigma,p}$ which is mainly $\chi_{\sigma,p}$ and a third anti-bonding orbital

$$\psi_e = N_e^{-\frac{1}{2}}(\varphi_e - \lambda_s \chi^e_{\sigma,s} - \lambda_p \chi^e_{\sigma,p}) \qquad (20.13)$$

where

$$N_e = 1 + \lambda_s^2 + \lambda_p^2 - 2\lambda_s S_s - 2\lambda_p S_p, \qquad (20.14)$$

which is mainly $\varphi_e = d\gamma$ and is primarily localized on the central ion. Finally, on the ligands there are non-bonding orbitals which transform according to t_{1g} and t_{2u} and which have no counterpart on the central ion.

20.4. The ground states in weakly covalent compounds

We now pass on to the description of the magnetic behaviour of the central ion by means of anti-bonding molecular orbitals, adopting therefore a 'strong field' representation. Let $3d^n$ be the configuration of the central ion in the ionic picture. In this picture, since we have

assumed that all the orbits $2s$ and $2p$ of the ligands lie much lower in energy than the orbits $3d$ (and *a fortiori* lower than $4s$ and $4p$) of the central ion, the number of bonding and non-bonding orbitals will be exactly equal to the number of ligand orbitals $2s$ and $2p$, i.e. $6 \times (1+3) = 24$. The corresponding $6 \times 8 = 48$ electrons, which fill these $2s$ and $2p$ orbitals in the ionic picture, will be housed in the bonding and non-bonding orbitals. The n remaining electrons that are purely $3d$ in the ionic picture, will be housed in the anti-bonding orbitals whose wave-functions are listed in Table 24.

The model we use to construct the ground state of a many-electron ion is the following. The effects of covalency are taken into account by using the orbitals (20.13) as basis one-electron wave-functions and by assigning a different energy to the orbits t_{2g} and e_g. The splitting $W(e_g) - W(t_{2g})$ is not here considered to arise from a classical crystal field but now represents the difference

$$\Delta = (\psi_{e_g}^a | \, h \, | \psi_{e_g}^a) - (\psi_{t_{2g}}^a | \, h \, | \psi_{t_{2g}}^a), \tag{20.15}$$

computed by means of the formalism outlined in the last section, a straightforward calculation in principle but very heavy in practice. In the case of NiF_6 where such a calculation has actually been carried out completely (Sugano and Shulman 1963) it turns out that probably most of the splitting Δ is due to terms proportional to the covalency coefficients γ, thus explaining why the best calculations based on the ionic model have led to values of Δ which are an order of magnitude too small. (For further discussion see Owen and Thornley (1966).)

The eigenstates of the ion are obtained by filling the various orbitals t_2 and e with electrons and constructing from these orbitals many-electron wave-functions that transform according to irreducible representations of O_h. If at the first stage we neglect spin-orbit coupling, these functions must be eigenstates of the total spin S and belong to one of the five single-valued representations of O: Γ_1, Γ_2, Γ_3, Γ_4, Γ_5, also called A_1, A_2, E, T_1, T_2. We may by analogy with free ions call these states cubic terms. Very many cubic terms can be built in this fashion which are needed for the interpretation of optical absorption spectra of the transition elements. In magnetic resonance we may take a narrower view of the problem by concentrating on the cubic term of lowest energy, and possibly one or two low-lying excited cubic terms.

The assumption of weak covalency means that the nature of the cubic term is the same as in the ionic picture, given in § 19.1. To illustrate this point consider, for instance, the configuration $3d^5$ which in the ionic

model gives the sextet term ^6S, which is also the cubic term $(t_2^3 e^2)^6 A_1$. By placing five electrons in five t_2 orbitals we are able to form the doublet cubic term $(t_2^5)^2 T_1$. With little or no covalency this doublet is well above the sextet in energy, but with increasing covalency the separation $\Delta = W(e) - W(t_2)$ may increase to such an extent that it becomes energetically more advantageous to place five electrons in t_2 orbitals giving a doublet spin state, rather than to decrease their electrostatic repulsion by having their spins parallel. If we were to plot the energy of the ion as a function of Δ, the two levels would cross for a certain value of Δ and the doublet would come below the sextet (cf. Fig. 7.13). This is the situation that prevails in the $4d$, $5d$ groups and in the complex cyanides of the $3d$ group (see Chapter 8).

We return now to the case of weak covalency for which the ground cubic terms for the various ions are listed in Table 25. The weak covalency assumption implies that they are the same as in the purely ionic picture as given in § 19.1, but their expression in terms of one-electron orbitals has a somewhat different form.

We see from Table 25 that the cubic term $^3T_1$ which is the ground state for the configuration $3d^2$ can be built from either one of the *two* cubic configurations t_2^2 or $t_2 e$. Similarly the cubic term $^4T_1$ which is the ground state for seven electrons $3d^7$ (equivalent to three holes $3d^3$) can be built from either one of the two 3-hole configurations $t_2 e^2$ or $t_2^2 e$. This shows that the simple-minded argument that we used in § 19.1 to predict the structure of the ground states in cubic symmetry had only approximate validity. For instance, for $3d^2$ we had argued that by putting two electrons with parallel spins into two orbits t_2 of lower energy we minimized both the cubic field energy and the electrostatic electron-electron repulsion. Actually, by allowing one electron to spend some time in an upper orbit e, that is by using a combination of the two configurations t_2^2 and $t_2 e$, it is possible further to lower the overall energy of the cubic term $^3T_1$. The same is true for the cubic term $^4T_1$ with three holes. In fact $^3T_1(3d^2)$ and $^4T_1(3d^3)$ are the only cubic terms of maximum spin for which the state $S_z = S$ is not a single Slater determinant. This is related to the fact that in the weak-field representation they are respectively mixtures of $(^3F, {}^3P)$ and $(^4F, {}^4P)$. As an illustration we discuss in some detail the form of the wave-function of $^4T_1(3d^7 \equiv 3d^3)$ which applies to Co^{2+} in octahedral environment. We use the formalism of the fictitious orbital momentum introduced in § 14.2 where the one-electron functions η_x, η_y, η_z that span the triplet t_2 are related to the eigenstates $|m\rangle$ of $\tilde{l}_z$ by the formulae (14.5) which we

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rewrite here for convenience:

$$|\pm \tilde{1}\rangle = \mp \frac{\eta_x \pm i\eta_y}{\sqrt{2}}, \ |\tilde{0}\rangle = \eta_z. \tag{20.16}$$

If η_x, η_y, η_z are purely d-functions (which they are not if covalent bonding is allowed) the states $|\tilde{m}\rangle$ are related to the states $l_z = m$ of the *true* orbital-momentum by the formulae given in Table 4,

$$|\tilde{1}\rangle = |2, -1\rangle; \ |-\tilde{1}\rangle = -|2, 1\rangle; \ |\tilde{0}\rangle = \frac{1}{\sqrt{2}}\{|2, 2\rangle - |2, -2\rangle\}, \tag{20.16a}$$

where the symbol $|2, -1\rangle$ represents the state $l = 2$, $l_z = -1$.

The functions θ and ε that span $\Gamma_3 = E$ transform like $3z^2 - r^2$ and $\sqrt{(3)}(x^2 - y^2)$. Their transformation law under permutation of the coordinates is given by eqns (14.4).

For the cubic term T_1 we use the symbols

$$|\overline{\pm 1}\rangle = \mp \frac{\bar{X} \pm i\bar{Y}}{\sqrt{2}}, \ |\bar{0}\rangle = \bar{Z}, \tag{20.17}$$

to represent again eigenstates of the fictitious orbital momentum. Equations (20.16) and (20.17) differ in two respects: the former represent one-electron wave-functions belonging to the cubic triplet t_2; the latter deal with many-electron wave-functions spanning a cubic triplet term T_1.

If now we single out the state $S = \frac{3}{2}$, all electrons have spin $+\frac{1}{2}$. The three orbital states of $^4T_1(t_2e^2)$ are then simply

$$\begin{cases} |^4T_1(t_2e^2), \ \bar{1}\rangle = \{\tilde{1}, \ \theta, \ \varepsilon\}, \\ |^4T_1(t_2e^2), \ \bar{0}\rangle = \{\tilde{0}, \ \theta, \ \varepsilon\}, \\ |^4T_1(t_2e^2), \ -\bar{1}\rangle = \{-\tilde{1}, \ \theta, \ \varepsilon\}. \end{cases} \tag{20.18}$$

The cubic term $^4T_1(t_2^2e)$ is less simple since from t_2^2e we can also construct a term $^4T_2(t_2^2e)$. We give the result first and then explain how to obtain it simply.

$$\begin{cases} |^4T_1(t_2^2e), \ \bar{1}\rangle = -\tfrac{1}{2}\{\tilde{1}, \ \tilde{0}, \ \theta\} + \dfrac{\sqrt{3}}{2}\{-\tilde{1}, \ \tilde{0}, \ \varepsilon\}, \\ |^4T_1(t_2^2e), \ \bar{0}\rangle = \{\tilde{1}, \ -\tilde{1}, \ \theta\}, \\ |^4T_1(t_2^2e), -\bar{1}\rangle = \tfrac{1}{2}\{-\tilde{1}, \ \tilde{0}, \ \theta\} - \dfrac{\sqrt{3}}{2}\{\tilde{1}, \ \tilde{0}, \ \varepsilon\}. \end{cases} \tag{20.19}$$

The expression $\{\tilde{1}, \ -\tilde{1}, \ \theta\} = i\{\eta_x, \ \eta_y, \ \theta\}$ for $|^4T_1(t_2^2e), \ \bar{0}\rangle$ is obvious;

it is the only Slater determinant unchanged by a rotation of $\pm\pi/2$ around Oz. To find the expressions for $|\bar{1}\rangle$ and $|-\bar{1}\rangle$ in (20.19) we notice that $|\bar{X}\rangle = -(|\bar{1}\rangle - |-\bar{1}\rangle)/\sqrt{2}$ and $\bar{Y} = i(|\bar{1}\rangle + |-\bar{1}\rangle)/\sqrt{2}$ are deduced from $\bar{Z} = |\bar{0}\rangle$ by the cyclic permutations R and R^2 of $\{x, y, z\}$. We can then write

$$\begin{cases} |\bar{X}\rangle = R\,|\bar{Z}\rangle = iR\{\eta_x,\ \eta_y,\ \theta\} = i\{\eta_y,\ \eta_z,\ R\theta\} \\ |\bar{Y}\rangle = R^2\,|\bar{Z}\rangle = i\{\eta_z,\ \eta_x,\ R^2\theta\} \end{cases} \tag{20.20}$$

and on replacing $R\theta$ and $R^2\theta$ by the expressions (14.4) we get $|\bar{X}\rangle$ and $|\bar{Y}\rangle$ and then $|\bar{1}\rangle$ and $|-\bar{1}\rangle$ in (20.19).

In general we can write the cubic term of the ground state as

$$\cos\alpha\ {}^4T_1(t_2e^2) + \sin\alpha\ {}^4T_1(t_2^2e). \tag{20.21}$$

For Co^{2+} where the hole orbitals e are below the hole orbitals t_2 we expect the configuration to be mainly t_2e^2, and α to be small. To determine the amplitudes $\cos\alpha$ and $\sin\alpha$ we must know the matrix elements of the electrostatic energy between the two states ${}^4T_1(t_2e^2)$ and ${}^4T_1(t_2^2e)$. These can be found by going back to the weak-field representation and expressing the states ${}^4T_1(t_2^2e)$ and ${}^4T_1(t_2e^2)$, where we assume that the orbitals t_2 and e are pure d-orbitals, as linear combinations of the free ion states, ${}^4P$ and ${}^4F$, using (20.18) and (20.19). A simple calculation gives

$$\begin{cases} {}^4T_1(t_2^2e) = \dfrac{2}{\sqrt{5}}|{}^4P\rangle - \dfrac{1}{\sqrt{5}}|{}^4F\rangle, \\[2ex] {}^4T_1(t_2e^2) = \dfrac{1}{\sqrt{5}}|{}^4P\rangle + \dfrac{2}{\sqrt{5}}|{}^4F\rangle. \end{cases} \tag{20.22}$$

Since the electrostatic interaction has no off-diagonal matrix elements between ${}^4F$ and ${}^4P$ the secular matrix can be written as

$$\begin{pmatrix} \dfrac{4\delta}{5}+\Delta, & \dfrac{2\delta}{5} \\[2ex] \dfrac{2\delta}{5}, & \dfrac{\delta}{5} \end{pmatrix} \tag{20.23}$$

where we have taken the electrostatic energy as zero in ${}^4F$ and δ in ${}^4P$ and denote by Δ the cubic splitting $W(t_2) - W(e)$ (which is positive for holes). The parameter δ is related to a certain radial integral B, known

in the literature as a Racah parameter, by $\delta = 15B$. Then from (20.23) we get

$$\tan 2\alpha = \frac{12B}{9B+\Delta}. \tag{20.24}$$

When B/Δ goes to infinity we are back to the purely ionic case where the admixture from ^4P is negligible and our state $^4T_1$ is pure ^4F. In this case $\tan 2\alpha = -\frac{4}{3}$, $\cos \alpha = 2/\sqrt{5}$, $\sin \alpha = -1/\sqrt{5}$. In the opposite case when $B/\Delta \to 0$ we find $\alpha = 0$ and the configuration is pure $(t_2 e^2)$.

For the sake of completeness we also consider the other cubic term of Table 25 which has components belonging to two different strong field configurations, namely $^3T_1(t_2^2, t_2 e)$ where the orbitals t_2 and e are either electrons or holes, depending on whether there are two or eight electrons outside of closed shells. We use a notation similar to that for the term $^4T_1(t_2 e^2, t_2^2 e)$ in (20.18) and (20.19) and obtain the formulae

$$\left\{ \begin{array}{l} |^3T_1(t_2^2), \bar{1}\rangle = (\tilde{1}, \tilde{0}), \\[2mm] |^3T_1(t_2^2), \bar{0}\rangle = (1, -1), \\[2mm] |^3T_1(t_2^2), -\bar{1}\rangle = (\tilde{0}, -\tilde{1}); \end{array} \right. \tag{20.18a}$$

$$\left\{ \begin{array}{l} |^3T_1(t_2 e), \bar{1}\rangle = \dfrac{\sqrt{3}}{2}(-\tilde{1}, \theta) - \dfrac{1}{2}(\tilde{1}, \varepsilon), \\[3mm] |^3T_1(t_2 e), \bar{0}\rangle = (\tilde{0}, \varepsilon), \\[3mm] |^3T_1(t_2 e), -\bar{1}\rangle = \dfrac{\sqrt{3}}{2}(\tilde{1}, \theta) - \dfrac{1}{2}(-\tilde{1}, \varepsilon). \end{array} \right. \tag{20.19a}$$

The wave-functions (20.18a) can be written down at once: they are the same as those of a ^3P term constructed from two p-electrons. The relations (20.19a) are obtained in the same manner as (20.19): we start from the expression $|\tilde{0}, \tilde{\varepsilon}\rangle$ for $|^3T_1(t_2 e), \bar{0}\rangle$ as the only Slater determinant unchanged by a rotation $\pm\pi/2$ around Oz, and then use a cyclic permutation to generate the two other states of (20.19a), as explained for (20.19). A calculation similar to that which gave (20.22) yields

$$\left\{ \begin{array}{l} ^3T_1(t_2 e) = \dfrac{2}{\sqrt{5}}|^3P\rangle - \dfrac{1}{\sqrt{5}}|^3F\rangle, \\[3mm] ^3T_1(t_2^2) = \dfrac{1}{\sqrt{5}}|^3P\rangle + \dfrac{2}{\sqrt{5}}|^3F\rangle. \end{array} \right. \tag{20.22a}$$

The signs in (20.22a), as in (20.22), are not completely determined since there is a certain freedom in the choice of the phases of the

different states. We have made the choice that gives the same coefficients and thus the same secular equation as (20.22) (cf. § 7.3).

20.5. Orbital momentum and spin-orbit coupling in the presence of covalent bonding

In a uniform external magnetic field the fact that the electron spin may no longer be localized on the central ion does not affect its contribution to the magnetic moment. The situation is different for the orbital momentum and we now show that covalent bonding leads to a reduction of the matrix elements of the orbital momentum.

The matrix elements of the orbital momentum taken between the anti-bonding orbitals of Table 24 are somewhat different from those taken between pure d-functions. Using (20.16) we rewrite the formulae of Table 24 in the self-evident form

$$|+\tilde{1}\rangle = N_t^{-\frac{1}{2}}\{|\tilde{1}_d\rangle - \lambda_t \,|\tilde{1}_\pi\rangle\}, \quad \text{etc.},$$

$$|\theta\rangle = N_\sigma^{-\frac{1}{2}}\{|\theta_d\rangle - \lambda_{\sigma s}\,|\theta_s\rangle - \lambda_{\sigma p}\,|\theta_p\rangle\}, \tag{20.25}$$

$$|\varepsilon\rangle = N_\sigma^{-\frac{1}{2}}\{|\varepsilon_d\rangle - \lambda_{\sigma s}\,|\varepsilon_s\rangle - \lambda_{\sigma p}\,|\varepsilon_p\rangle\}.$$

There are two types of matrix elements of $\mathbf{L}$: those inside the manifold t_2 and those between t_2 and e. (We have shown in § 14.2 that they all vanish within e.)

If the λ in (20.25) are all zero, the matrix elements of $\mathbf{L}$ within t_2 are those of a fictitious angular momentum $\tilde{\mathbf{l}} = \alpha\mathbf{L}$ with $\alpha = -1$. Between e and t_2 a typical matrix element is

$$\langle \tilde{0}_d|\, L_z\, |\varepsilon_d\rangle = \langle \eta_{zd}|\, L_z\, |\varepsilon_d\rangle = 2. \tag{20.26}$$

Use of the augmented orbitals (20.25) results in multiplication of the $\langle t_{2d}|\, \mathbf{L}\, |t_{2d}\rangle$ matrix elements by a certain numerical factor, written in the literature as $k_{\pi\pi}$, and the $\langle t_{2d}|\, \mathbf{L}\, |e_d\rangle$ matrix elements by another factor $k_{\pi\sigma}$.

The calculation of $k_{\pi\pi}$ is straightforward:

$$k_{\pi\pi} = \frac{\langle \tilde{1}|\, L_z\, |\tilde{1}\rangle}{\langle \tilde{1}_d|\, L_z\, |\tilde{1}_d\rangle} = -\langle 1|\, L_z\, |\tilde{1}\rangle$$

$$= -N_t^{-1}\{\langle \tilde{1}_d|\, L_z\, |\tilde{1}_d\rangle - 2\lambda_t\langle \tilde{1}_d|\, L_z\, |\tilde{1}_\pi\rangle + \lambda_t^2\langle \tilde{1}_\pi|\, L_z\, |\tilde{1}_\pi\rangle\}. \tag{20.27}$$

The first two terms in the curly bracket give $-1+2\lambda_t S_t$, where $S_t = \langle \tilde{1}_d \,|\, \tilde{1}_\pi\rangle = (\varphi_t \,|\, \chi_t)$ is the overlap integral for π-bonding. To calculate the last term, we get from Table 24,

$$|\tilde{1}_\pi\rangle = \frac{1}{2}\left\{\frac{Z_1 - Z_4 - i(Z_2 - Z_5)}{\sqrt{2}} + \frac{(X_3 - iY_3)}{\sqrt{2}} - \frac{(X_6 - iY_6)}{\sqrt{2}}\right\}. \tag{20.28}$$

We introduce the vector operators,

$$\mathbf{L}(3) = \mathbf{L} - \frac{1}{\hbar}(\mathbf{a_3} \wedge \mathbf{p}),$$

$$\mathbf{L}(6) = \mathbf{L} - \frac{1}{\hbar}(\mathbf{a_6} \wedge \mathbf{p}),$$

(20.29)

where $\mathbf{L}(i)$ is the orbital momentum operator with respect to the position $\mathbf{a}_i$ of the ligand i. Clearly $L_z(3) = L_z(6) = L_z$; $(X_3 - iY_3)/\sqrt{2}$ and $(X_6 - iY_6)/\sqrt{2}$ are normalized eigenstates of respectively $L_z(3)$ and $L_z(6)$ with eigenvalue -1. Then in the expansion of $\langle + \tilde{1}_\pi | L_z | + \tilde{1}_\pi \rangle$ all terms can be seen to vanish except the expectation values of $L_z(3)$ and $L_z(6)$ in these two states, whence,

$$\langle \tilde{1}_\pi | L_z | \tilde{1}_\pi \rangle = -\tfrac{1}{2}$$

(20.30)

and

$$k_{\pi\pi} = N_t^{-1}\left\{1 - 2\lambda_t S_t + \frac{\lambda_t^2}{2}\right\} = \frac{\left(1 - 2\lambda_t S_t + \dfrac{\lambda_t^2}{2}\right)}{1 - 2\lambda_t S_t + \lambda_t^2} = 1 - \frac{\lambda_t^2}{2}N_t^{-1} \approx 1 - \frac{\lambda_t^2}{2}.$$

(20.31)

The calculation of

$$k_{\pi\sigma} = \frac{\langle \tilde{0} | L_z | \varepsilon \rangle}{\langle \tilde{0}_d | L_z | \varepsilon_d \rangle}$$

(20.32)

is more involved and its details are outlined below. From (20.26) we have

$$k_{\pi\sigma} = \tfrac{1}{2}\langle \tilde{0} | L_z | \varepsilon \rangle$$

(20.33)

or, using (20.25),

$$k_{\pi\sigma} = \frac{N_t^{-\frac{1}{2}}N_\sigma^{-\frac{1}{2}}}{2} \langle \tilde{0}_d - \lambda_t \tilde{0}_\pi | L_z | \varepsilon_d - \lambda_{\sigma s}\varepsilon_s - \lambda_{\sigma p}\varepsilon_p \rangle$$

$$= N_t^{-\frac{1}{2}}N_\sigma^{-\frac{1}{2}}\left(1 - \lambda_t S_t - \lambda_{\sigma s}S_s - \lambda_{\sigma p}S_p + \right.$$

$$\left. + \frac{\lambda_t \lambda_{\sigma s}}{2} \langle \tilde{0}_\pi | L_z | \varepsilon_s \rangle + \frac{\lambda_t \lambda_{\sigma p}}{2} \langle \tilde{0}_\pi | L_z | \varepsilon_p \rangle\right).$$

(20.34)

To compute the last two terms of (20.34) we replace ε_s, ε_p and $|\tilde{0}_\pi\rangle$ by their expressions from Table 24. We now encounter terms such as $\langle \chi_{\pi j} | L_z | \chi_{\sigma i} \rangle$ where $\chi_{\pi j}$ and $\chi_{\sigma i}$ are orbitals located on ligands i and j. Replacing L_z by $L_z(i) + (\mathbf{a}_i \wedge \mathbf{p})_z/\hbar$ (cf. eqn (20.29)), we get

$$\langle \chi_{\pi j} | L_z | \chi_{\sigma i} \rangle = \delta_{ij}\left\{\langle \chi_{\pi i} | L_z(i) | \chi_{\sigma i} \rangle + \langle \chi_{\pi i} | \frac{(\mathbf{a}_i \wedge \mathbf{p})_z}{\hbar} | \chi_{\sigma i} \rangle\right\}.$$

(20.35)

The first term on the right-hand side of (20.35) vanishes if $\chi_{\sigma i}$ is a σ_s orbital that carries zero orbital momentum, and the second vanishes if $\chi_{\sigma i}$ is a σ_p orbital because of parity conservation.

We thus find

$$\frac{\langle \tilde{0}_\pi | \, L_z \, | \varepsilon_s \rangle}{2} = -\frac{a}{2} \langle p_y | \, \frac{\partial}{\partial_y} \, | s \rangle, \qquad (20.36)$$

where p_y and s are wave-functions $2p$ and $2s$ of a ligand and a its distance from the origin. Also

$$\frac{\langle \tilde{0}_\pi | \, L_z \, | \varepsilon_p \rangle}{2} = -\tfrac{1}{2}, \qquad (20.37)$$

whence

$$k_{\pi\sigma} = N_t^{-\frac{1}{2}} N_\sigma^{-\frac{1}{2}} \left(1 - \lambda_t S_t - \lambda_{\sigma s} S_s - \lambda_{\sigma p} S_p - \tfrac{1}{2} \lambda_t \lambda_{\sigma p} - \frac{\lambda_t \lambda_{\sigma s}}{2} a \langle p_y | \, \frac{\partial}{\partial_y} \, | s \rangle \right). \qquad (20.38)$$

From the equations for N_σ and N_t in Table 24 we have approximately,

$$(N_t N_\sigma)^{-\frac{1}{2}} = 1 + \lambda_t S_t + \lambda_{\sigma s} S_s + \lambda_{\sigma p} S_p - \tfrac{1}{2} (\lambda_t^2 + \lambda_{\sigma s}^2 + \lambda_{\sigma p}^2) \qquad (20.39)$$

and in the same approximation we have, from (20.38),

$$k_{\pi\sigma} = 1 - \tfrac{1}{2} \left(\lambda_t^2 + \lambda_{\sigma s}^2 + \lambda_{\sigma p}^2 + \lambda_t \lambda_{\sigma p} + \lambda_t \lambda_{\sigma s} a \langle p_y | \, \frac{\partial}{\partial_y} \, | s \rangle \right). \qquad (20.40)$$

The dimensionless quantity $a \langle p_y | \, \partial / \partial_y \, | s \rangle$ in the last term of (20.40) must be computed numerically.

For instance, for $Ni^{2+}F_6^-$, Owen and Thornley (1966) find it has the value $-1 \cdot 6$, using analytical Hartree–Fock functions for the $2s$ and $2p$ orbitals of F^-, and taking $a = 0 \cdot 21$ nm. For $Ni^{2+}F_6^-$ (20.40) can then be rewritten as

$$k_{\pi\sigma} = 1 - \tfrac{1}{2} \{ \lambda_t^2 + \lambda_{\sigma s}^2 + \lambda_{\sigma p}^2 + \lambda_t (\lambda_{\sigma p} - 1 \cdot 6 \lambda_{\sigma s}) \}. \qquad (20.41)$$

Spin-orbit coupling

It is sometimes said that the spin-orbit constant ζ is reduced by covalent bonding. In this form the statement is misleading and needs to be clarified.

The introduction of covalent bonding modifies the spin-orbit coupling in a way which is related to, but not identical with, the reduction of the orbital momentum through the coefficients $k_{\pi\pi}$ and $k_{\pi\sigma}$ of (20.31) and (20.40). The covalent bonding does not affect the form of the operator

L in the x-representation and the change in its matrix elements is solely due to the change in the one-electron wave-functions that are the augmented orbitals of Table 24 rather than pure d-functions. On the other hand the spin-orbit coupling operator is already changed in the x-representation. We recall that the spin-orbit coupling is represented in the Pauli approximation by the operator

$$\frac{1}{2}\left(\frac{\hbar}{mc}\right)^2\left(\frac{\nabla V \wedge \mathbf{p}}{\hbar}\right) . \mathbf{s}, \tag{20.42}$$

where V is the potential energy of the electron moving in a self-consistent field. It could only be cast into the familiar form (11.19) of $\zeta \mathbf{l} . \mathbf{s}$ with $\zeta = \frac{1}{2}(\hbar/mc)^2(1/r)(dV/dr)$ because V was assumed to have spherical symmetry. We can write quite generally the spin-orbit coupling operator in the form **U . s**. The vector **U**, like all vectors, has matrix elements within t_2 proportional to those of **L**, and others between t_2 and e also proportional to those of **L** but with a different proportionality constant. We can then write

$$\langle t_2| \mathbf{U} |t_2\rangle = \zeta_{\pi\pi}\langle t_2| \mathbf{L} |t_2\rangle = \zeta_{\pi\pi}k_{\pi\pi}\langle t_{2d}| \mathbf{L} |t_{2d}\rangle \tag{20.43}$$

and

$$\langle t_2| \mathbf{U} |e\rangle = \zeta_{\pi\sigma}\langle t_2| \mathbf{L} |e\rangle = \zeta_{\pi\sigma}k_{\pi\sigma}\langle t_{2d}| \mathbf{L} |e_d\rangle, \tag{20.44}$$

where $k_{\pi\pi}$ and $k_{\pi\sigma}$ are given by (20.31) and (20.40).

The actual matrix elements of the spin-orbit coupling between t_2 and e, responsible for the orbital contribution $g-2$ of the orbital momentum for ions of type A (see § 19.2), are thus reduced in the ratio $\zeta_{\pi\sigma}k_{\pi\sigma}/\zeta_0$ where ζ_0 is the spin-orbit coupling constant for the free ion. On the other hand, the matrix elements of the spin-orbit coupling inside t_2 that occur for ions of type B such as, say, Co^{2+} considered in § 19.3, are reduced in the ratio $\zeta_{\pi\pi}k_{\pi\pi}/\zeta_0$.

It is sometimes argued that the main contribution to the matrix elements of the spin-orbit coupling comes from the region near the nucleus of the central ion where (a) the potential energy $V(r)$ is practically equal to that $V_0(r)$ of the free ion and (b) the values of the wave-functions from the ligands, admixed into the augmented orbitals of Table 24, are small. In that case one should have

$$\langle t_2| \mathbf{U} |t_2\rangle = N_t^{-1}\langle t_{2d}| \mathbf{U_0} |t_{2d}\rangle \tag{20.45}$$

and

$$\langle t_2| \mathbf{U} |e\rangle = N_t^{-\frac{1}{2}}N_\sigma^{-\frac{1}{2}}\langle t_{2d}| \mathbf{U_0} |e_d\rangle, \tag{20.46}$$

where $\mathbf{U_0} = \zeta_0\mathbf{L}$. In practice there is considerable uncertainty about

the actual value of the matrix elements of the spin-orbit coupling and it is preferable to consider $\zeta_{\pi\pi}/\zeta_0$ and $\zeta_{\pi\sigma}/\zeta_0$ as adjustable parameters. (For a discussion of these points see Owen and Thornley (1966).)

20.6. Ligand hyperfine structure for ions of type A

As we have already stated, the presence in the resonance spectrum of hyperfine structure due to the coupling of the electronic spins with the nuclei of the ligands is the most clear-cut evidence for the transfer of spin density onto the ligands.

If the ground state of the central ion has a spin S (real or fictitious), in cubic symmetry we shall expect the hyperfine structure of say ligand 3 placed on the positive side of the z-axis to have a hyperfine structure of the form

$$A_{\parallel}I_zS_z + A_{\perp}(I_xS_x + I_yS_y). \qquad (20.47)$$

Here we use $A_{\parallel}$ for the value along the bond axis, that is the line joining the nucleus of the ligand ion to the nucleus of the central ion. Thus for the ligand 1, for instance, (20.47) becomes obviously $A_{\parallel}I_xS_x + A_{\perp}(I_zS_z + I_yS_y)$.

Here our problem is clearly that of calculating the coefficients $A_{\parallel}$ and $A_{\perp}$. As we shall see, these coefficients are directly correlated to the admixture coefficients λ of Table 24 and their measurement affords the most direct information on the amount of covalent bonding. In this and following sections the more detailed formulae (in particular those where specific reference is made to $2s$-, $2p$-orbitals) assume that the ligand ions are fluorines.

We consider first the case when the central ion is of type A, that is effectively without orbital degeneracy in its ground state, as in Cr^{3+}, $V^{2+}(d^3)$; Cr^{+}, Mn^{2+}, $Fe^{3+}(d^5)$; $Ni^{2+}(d^8)$. If in a first approximation we neglect admixtures from higher cubic terms through the spin-orbit coupling, the substate of the ground state with $S_z = S$ is a single Slater determinant of molecular orbitals, and the expectation value of the operator $\mathscr{H}(3)$, describing the hyperfine structure coupling with the nucleus of ligand 3, will be a sum of expectation values of $\mathscr{H}(3)$ taken over the orbitals composing the ground term. Let ψ be one of the orbitals of Table 24. It can be written as

$$\psi = \alpha\varphi_d + \sum_{\lambda,i} \beta_{\lambda,i}\chi_\lambda(i), \qquad (20.48)$$

where the index i refers to the ligand i, the coefficient α is of the order of unity, and the $\beta_{\lambda,i}$ are small. The hyperfine structure operator $\mathscr{H}$ (3)

decreases rapidly with the distance from the nucleus of ligand 3 and it is reasonable to keep in the expectation value $(\psi|\ \mathscr{H}(3)\ |\psi)$, only the terms

$$\sum_{\lambda,\mu} \beta^*_{\lambda 3}\beta_{\mu 3}\{(\chi_\lambda(3)|\ \mathscr{H}(3)\ |\chi_\mu(3))+|\alpha|^2(\varphi_d|\ \mathscr{H}(3)\ |\varphi_d)\}. \qquad (20.49)$$

We have retained the second term because $|\alpha|^2$ is of order unity, but even so it is often small compared to the first and will be disregarded for the time being. We rewrite (20.48) as $\psi = F(3)+\psi'$, where $F(3)$ is the part of ψ constructed from orbitals of ligand 3, and we wish to calculate $(F(3)|\ \mathscr{H}(3)\ |F(3))$.

From Table 24 we extract the $F(3)$ that differ from zero; these are

$$F_{\eta_x}(3) = -\frac{\lambda_t}{2}N_t^{-\frac{1}{2}}Y_3,$$

$$F_{\eta_y}(3) = -\frac{\lambda_t}{2}N_t^{-\frac{1}{2}}X_3, \qquad (20.50)$$

$$F_\theta(3) = -\frac{\lambda_{\sigma s}}{\sqrt{3}}N_\sigma^{-\frac{1}{2}}\sigma_{s3}+\frac{\lambda_{\sigma p}}{\sqrt{3}}N_\sigma^{-\frac{1}{2}}Z_3.$$

Note that in $F_\theta(3)$ our sign convention for the σ_p leads to $\sigma_{p3} = -Z_3$. Also it is customary in the literature to introduce the so-called spin-densities

$$f_t = \frac{\lambda_t^2}{4}N_t^{-1}, \qquad f_{\sigma s} = \frac{\lambda_{\sigma s}^2}{3}N_\sigma^{-1}, \qquad f_{\sigma p} = \frac{\lambda_{\sigma p}^2}{3}N_\sigma^{-1}, \qquad (20.51)$$

which are the squares of the amplitudes in (20.50).

For p-ligand orbitals we take as magnetic hyperfine operator the form (17.45) with $L = 1$, $S = \frac{1}{2}$, and ξ given by (17.46) $= \frac{2}{5}$. For s-ligand orbitals we take $(16\pi/3)\beta\gamma_n\hbar\delta(r)(\mathbf{I}.\mathbf{s})$. Omitting as usual the electron-spin operator from the expectation value we obtain

$$\langle Z_3|\ \mathscr{H}(3)\ |Z_3\rangle = a_p\{2I_zS_z-(I_xS_x+I_yS_y)\}, \qquad (20.52)$$

with

$$a_p = \tfrac{4}{5}\beta\gamma_n\hbar\langle r^{-3}\rangle_{2p}. \qquad (20.53)$$

Clearly $\langle X_3|\ \mathscr{H}(3)\ |X_3\rangle$ and $\langle Y_3|\ \mathscr{H}(3)\ |Y_3\rangle$ are deduced from (20.52) by cyclic permutation of x, y, z.

Similarly

$$\left\langle \sigma_{s3}\left|\frac{16\pi}{3}\beta\gamma_n\hbar\delta(r)\right|\sigma_{s3}\right\rangle(\mathbf{I}.\mathbf{S}) = a_s(\mathbf{I}.\mathbf{S}) \qquad (20.54)$$

with

$$a_s = \frac{16\pi}{3}\beta\gamma_n\hbar\ |\psi_{2s}(0)|^2. \qquad (20.55)$$

Disregarding the second term in (20.49), we find

$$\langle \eta_x | \mathscr{H}(3) | \eta_x \rangle \approx \langle F_{\eta_x}(3) | \mathscr{H}(3) | F_{\eta_x}(3) \rangle = f_t a_p (2 I_y S_y - I_x S_x - I_z S_z),$$

$$\langle \eta_y | \mathscr{H}(3) | \eta_y \rangle \approx \langle F_{\eta_y}(3) | \mathscr{H}(3) | F_{\eta_y}(3) \rangle = f_t a_p (2 I_x S_x - I_y S_y - I_z S_z),$$

$$\langle \theta | \mathscr{H}(3) | \theta \rangle \approx \langle F_\theta(3) | \mathscr{H}(3) | F_\theta(3) \rangle$$
$$= f_{\sigma s} a_s (\mathbf{I} \cdot \mathbf{S}) + f_{\sigma p} a_p (2 I_z S_z - I_x S_x - I_y S_y). \quad (20.56)$$

Let us apply (20.56) to our three ions of type A which have singlet ground states.

(1) V^{2+}, Cr^{3+} (d^3)

The ground cubic term is $^4A_2(t_2^3)$, and the substate $S_z = S = \tfrac{3}{2}$ is $\Psi = (\eta_x^+, \eta_y^+, \eta_z^+)$ for which

$$\langle \Psi | \mathscr{H}(3) | \Psi \rangle = \langle \eta_x | \mathscr{H}(3) | \eta_x \rangle + \langle \eta_y | \mathscr{H}(3) | \eta_y \rangle$$
$$= (f_t a_p (2 I_y S_y^{(1)} - I_x S_x^{(1)} - I_z S_z^{(1)}) + f_t a_p (2 I_x S_x^{(2)} - I_y S_y^{(2)} - I_z S_z^{(2)}),)$$
$$(20.57)$$

where $S^{(1)}$, $S^{(2)}$ are the spins of the two electrons in the orbits $|\eta_x\rangle$ and $|\eta_y\rangle$.

Within the manifold $S = \tfrac{3}{2}$ of $^4A_2(t_2^3)$, the expectation value of a component of the spin of each electron is a fraction $(1/2S)$ (that is for $S = \tfrac{3}{2}$, one-third), of that of the total spin $\mathbf{S}$. Hence in (20.47) we find from (20.56), (20.57) expressions for $A_{\parallel}$ and $A_{\perp}$:

$$A_{\parallel} = -2A_{\perp} = -\frac{2f_t}{2S} a_p = -2A_\pi \quad (20.58)$$

where

$$A_\pi = \frac{f_t a_p}{2S}. \quad (20.59)$$

(2) Cr^+, Mn^{2+}, Fe^{3+} (d^5)

The ground cubic term is $^6A_1(t_2^3 e^2)$ and the substate $S_z = S = \tfrac{5}{2}$ is $(\eta_x^+, \eta_y^+, \eta_z^+, \theta^+, \varepsilon^+)$. We find by the same method as before

$$A_{\parallel} = \frac{2}{2S}(f_{\sigma p} - f_t) a_p + f_{\sigma s}\frac{a_s}{2S} = 2(A_\sigma - A_\pi) + A_s, \quad (20.60)$$

$$A_{\perp} = \frac{-1}{2S}(f_{\sigma p} - f_t) a_p + f_{\sigma s}\frac{a_s}{2S} = -(A_\sigma - A_\pi) + A_s,$$

where

$$A_\sigma = \frac{f_{\sigma p} a_p}{2S}; \qquad A_s = \frac{f_{\sigma s} a_s}{2S}. \quad (20.61)$$

(3) Ni^{2+} (d^8)

The ground cubic term expressed by means of holes is $^3A_2(e^2)$ and the ground substate $S_z = S = 1$ is $(\theta^+\varepsilon^+)$. We find

$$A_\parallel = \frac{2}{2S}f_{\sigma p}a_p + \frac{1}{2S}f_{\sigma s}a_s = 2A_\sigma + A_s,$$

$$A_\perp = \frac{-1}{2S}f_{\sigma p}a_p + \frac{1}{2S}f_{\sigma s}a_s = -A_\sigma + A_s. \qquad (20.62)$$

From a measurement of $A_\parallel$ and $A_\perp$ and from a Hartree–Fock calculation of a_{2p} and a_{2s} for the fluorine ligand ions we can obtain the spin densities $f_t, f_{\sigma p}, f_{\sigma s}$.

It is reasonable to assume that since the orbits $2s$ of the ligands lie well below the orbits $2p$, they must have a smaller amplitude λ_s in the anti-bonding orbitals and the corresponding spin density $f_{\sigma s} = (\lambda_{\sigma s}^2/3)N_\sigma^{-1}$ must be a good deal smaller than $f_{\sigma p}$ and f_t. (This is not to say that $A_s = f_{\sigma s}a_{2s}/2S$ should be much smaller than A_σ or A_π for the smallness of $f_{\sigma s}$ is more than compensated by the fact that $a_{2s} \gg a_{2p}$.) On the other hand, it had generally been assumed that the σ_p orbitals of the ligands, directed towards the central ion, were much more strongly bound to it than π-orbitals and that $f_{\sigma p}$ should correspondingly be much larger than f_t. It came therefore as a great surprise that in the first experiment on $Mn^{2+}(d^5)$ in $KMnF_3$ by Shulman and Knox (1960) the value of $f_{\sigma p} - f_t$ (attributed for the larger part to $f_{\sigma p}$) turned out to be ~ 0.3 per cent, whereas $f_{\sigma s}$ was of the order of 0.5 per cent.

One possible explanation was that actually $f_{\sigma p}$ and f_t were comparable and that the small value observed for $f_{\sigma p} - f_t$ resulted from a near compensation between two larger quantities. Striking confirmation of this explanation and of the general correctness of the model was provided by the study of d^3 compounds, for which $f_{\sigma p} = 0$, and d^8 compounds, for which $f_t = 0$. For $Cr^{3+}(d^3)$ in K_2NaCrF_6 it was found that $f_t = 4.90$ per cent whereas values of $f_{\sigma p} = 4.95$ per cent and $f_{\sigma s} = 0.5$ per cent were found for $Ni^{2+}(d^8)$ in $KNiF_3$ establishing that $f_{\sigma p} \approx f_t \gg f_{\sigma s}$.

Finally, further evidence that the bulk of the isotropic hyperfine structure on the ligands does indeed result from covalent σ_s bonds and not from some other mechanism, such as fluorine core-polarization, has been provided by the small value of the isotropic spin density $f_{\sigma s}$ in d^3 compounds where σ_s bonds cannot be formed. Values of $f_{\sigma s} \sim 0.02$ per cent, which is some twenty times smaller than for d^5 and d^8 compounds, have been observed for $V^{2+}(d^3)$ and $Cr^{3+}(d^3)$. The reader is

referred to the review article of Owen and Thornley (1966) for further discussion of the experimental evidence.

20.7. Orbital singlets: correction terms for the ligand hyperfine structure

Direct coupling with the central ion

We have so far neglected the interaction of the nuclear moment μ_I of the ligand with the distribution of magnetization carried by the d-part of the anti-bonding orbitals of the central ion, which is described by the second term of (20.49). If the distance R from the ligand nucleus to the nucleus of the central ion is large compared to the mean radius of d-orbitals, we can argue that the field H_μ created by μ_I is uniform all over the ion and that its coupling with the central ion is given by $H_\mu \cdot \mathbf{g} \cdot \beta S$, where $-\beta\mathbf{g} \cdot S$ is the magnetic dipole moment of the central ion. Even if R is not very large compared to the ionic radius we can still treat the central ion as a point dipole if its charge distribution has spherical symmetry as for d^5 compounds (Cr^+, Mn^{2+}, Fe^{3+}). Under these conditions for, say, the ligand 3, the corresponding coupling can be written

$$A_{\mathrm{d}}(2I_z S_z - I_x S_x - I_y S_y), \qquad (20.63)$$

with

$$A_{\mathrm{d}} = \frac{2\beta\hbar\gamma_{\mathrm{n}}}{R^3}. \qquad (20.64)$$

For $R = 0{\cdot}2$ nm, a typical distance in fluorine compounds, we find $A_{\mathrm{d}} \approx 3 \times 10^{-4}$ cm^{-1}. This is to be compared with values of A_s of the order of 15×10^{-4} cm^{-1} observed in d^5 fluorine compounds.

The comparison of A_{d} with values of $A_\sigma - A_\pi$ observed for d^5 compounds is not very instructive since, as we mentioned earlier, the fact that $(A_\sigma - A_\pi)$ is experimentally found to be small does not necessarily imply that A_σ, A_π taken separately are small. For d^3 fluorine compounds, values of A_π of the order of 7×10^{-4} cm^{-1}, and for d^8 compounds values of A_σ of the order of 10×10^{-4} cm^{-1}, have been observed.

Multipole corrections to the coupling with the central ion

For d^3 and d^8 compounds small corrections arising from higher multipole moments of the distribution of magnetization of the central ion have to be introduced. These corrections have different forms for the distributions of magnetization due to spin and to unquenched orbital momentum. We quote only the results (Marshall (1963)).

For the *spin magnetization* the spin constant $A_d = 2\beta\gamma_n\hbar/R^3$ has to be multiplied by the following correction factors in which $\langle r^4 \rangle$ is the mean fourth power of a $3d$ wave-function:

$$3d^8(^3F): \quad \left(1 + \frac{5}{2}\frac{\langle r^4 \rangle}{R^4}\right), \tag{20.65}$$

$$3d^3(^4F): \quad \left(1 - \frac{5}{2}\frac{\langle r^4 \rangle}{R^4}\right). \tag{20.66}$$

For the unquenched *orbital magnetization* the constant

$$\frac{(g-2)\beta\gamma_n\hbar}{R^3} = A_d'' \tag{20.67}$$

must be multiplied by a correction factor (which has the same form for d^3 and d^8)

$$\left(1 - \frac{5}{28}\frac{\langle r^2 \rangle}{R^2}\right). \tag{20.68}$$

A second correction is a small scalar coupling

$$A_d'''(\mathbf{I} \cdot \mathbf{S}) = -\tfrac{1}{2}A_d''(\langle r^2 \rangle/R^2)(\mathbf{I} \cdot \mathbf{S}), \tag{20.69}$$

which must be added to the overall dipolar coupling.

Such multipole corrections are usually quite small.

Effects of the spin-orbit coupling on the ligand hyperfine structure

We saw in § 19.2 how in second order the spin-orbit coupling modifies the hyperfine structure on the central nucleus by adding to the hyperfine structure operator (17.30), where $\mathbf{n}_i$ is a unit vector along $\mathbf{r}_i$,

$$\mathscr{H} = \sum_i \frac{2\beta\gamma_n\hbar}{r^3}\mathbf{I} \cdot \{\mathbf{l}_i - \mathbf{s}_i + 3\mathbf{n}_i(\mathbf{s}_i \cdot \mathbf{n}_i)\}, \tag{20.70}$$

the operator

$$\mathscr{H}' = \mathscr{H}C(\lambda\mathbf{L} \cdot \mathbf{S}) + (\lambda\mathbf{L} \cdot \mathbf{S})C \cdot \mathscr{H} \tag{20.71}$$

with

$$C = \sum_n{}' \frac{|n\rangle\langle n|}{W_0 - W_n}. \tag{20.72}$$

The same procedure yields correction terms to the hyperfine structure of the ligands (Marshall 1963). We quote the results only for $3d^3(^4F)$ and $3d^8(^3F)$.

The orbital part $(2\beta\gamma_n\hbar/r^3)(\mathbf{l} \cdot \mathbf{I})$ of (20.70) adds through (20.71) a

contribution of the same form for $(3d^3, {}^4F)$ and $(3d^8, {}^3F)$, namely

$$\frac{\beta\hbar\gamma_n(g-2)}{12}\langle r^{-3}\rangle\lambda_{\sigma p}\lambda_t\{3(\mathbf{S}\cdot\mathbf{n})(\mathbf{I}\cdot\mathbf{n})-(\mathbf{I}\cdot\mathbf{S})-2(\mathbf{I}\cdot\mathbf{S})\}. \quad (20.73)$$

This represents a contribution to $(A_\sigma - A_\pi)$ equal to

$$\delta_l(A_\sigma-A_\pi) = \frac{\beta\hbar\gamma_n(g-2)}{12}\langle r^{-3}\rangle\lambda_{\sigma p}\lambda_t \approx \frac{\beta\hbar\gamma_n}{2\sqrt{3}}\langle r^{-3}\rangle(f_{\sigma p}f_t)^{\frac{1}{2}}(g-2) \quad (20.74)$$

and a contribution to A_s equal to

$$\delta_l A_s = -\frac{\beta\hbar\gamma_n}{\sqrt{3}}\langle r^{-3}\rangle(f_{\sigma p}f_t)^{\frac{1}{2}}(g-2). \quad (20.75)$$

Similarly the spin part of (20.70) adds to $(A_\sigma - A_\pi)$ the following corrections:

$$(3d^8, {}^3F) \quad \delta_s(A_\sigma-A_\pi) = \tfrac{3}{80}\beta\hbar\gamma_n(g-2)\langle r^{-3}\rangle\lambda_{\sigma p}\lambda_t$$

$$\approx \frac{3\sqrt{3}}{40}\beta\hbar\gamma_n\langle r^{-3}\rangle(f_{\sigma p}f_t)^{\frac{1}{2}}(g-2); \quad (20.76)$$

$$(3d^3, {}^4F) \quad \delta_s(A_\sigma-A_\pi) = \tfrac{1}{40}\beta\hbar\gamma_n(g-2)\langle r^{-3}\rangle\lambda_{\sigma p}\lambda_t$$

$$\approx \frac{\sqrt{3}}{20}\beta\hbar\gamma_n\langle r^{-3}\rangle(f_{\sigma p}f_t)^{\frac{1}{2}}(g-2). \quad (20.77)$$

Effects of the fluorine 1s wave-functions on the ligand hyperfine structure (Marshall and Stuart 1961)

In our model of covalent bonding we had assumed that the augmented anti-bonding orbitals did not contain any admixtures from the $1s$ orbitals of the ligands. Although such admixtures are undoubtedly small their contribution to the ligand hyperfine structure may not be negligible, for $a_{1s} = (16\pi/3)\beta\gamma_n\hbar\,|\varphi_{1s}(0)|^2$ is very much larger than a_{2s}. If instead of a single admixture coefficient λ_s we introduce two, namely λ_{1s} and λ_{2s}, into the anti-bonding σ-orbitals we find that the isotropic hyperfine structure constant A_s instead of being proportional to $\lambda_{2s}^2\,|\varphi_{2s}(0)|^2$ is now proportional to

$$\lambda_{2s}^2\varphi_{2s}^2(0)\left\{1+\frac{\lambda_{1s}\varphi_{1s}(0)}{\lambda_{2s}\varphi_{2s}(0)}\right\}^2. \quad (20.78)$$

The magnitude of the second term in the curly bracket is difficult to estimate: $\varphi_{1s}(0)/\varphi_{2s}(0)$ in F^- is of the order of $-4\cdot5$. For λ_{2s}, assuming that the effect of φ_{1s} is a small correction, we can take the value extracted from the measurement of $A_s \approx (\lambda_{2s}^2/3)(a_{2s}/2S)$.

For λ_{1s} we could tentatively take the overlap integral

$$S_{1s} = (3d_\sigma \mid \chi_{\sigma,1s}),$$

which is equivalent to taking the covalent bonding constant

$$\gamma_{1s} = \lambda_{1s} - S_{1s} = 0.$$

Unfortunately this integral depends very critically on the shape of the $3d$ wave-function near the fluorine ion, which may be quite different from that of the $3d$ wave-function of the free ion. For instance, with $S_{1s} = \lambda_{1s} = 0.0045$, calculated using $3d$ functions of the free ion Mn^{2+}, and with $\lambda_{2s} \simeq 0.12$ compatible with $A_s = 16 \times 10^{-4}$ cm^{-1} in $KMnF_3$, we get $\{1 + (S_{1s}\varphi_{1s}(0)/\lambda_{2s}\varphi_{2s}(0))\}^2 \approx 0.70$, which is a sizeable reduction. The correction is negative because φ_{2s} has a node whereas φ_{1s} has not. If we choose φ_{1s} and φ_{2s} to have the same sign in the overlap region with $3d$, they will have opposite signs at the fluorine nucleus, in accordance with the sign convention we have chosen. However in view of the uncertainty in the magnitude of the correction some authors prefer to omit it altogether.

20.8. Ligand hyperfine structure for ions of type B

When the ground cubic term of the central ion is degenerate the calculation of the hyperfine interaction for the ligands is much more complicated than for orbital singlets. The spin-orbit coupling, which now acts in first order, scrambles orbital and spin states in a way that makes each substate of the ground level a sum of many Slater determinants, and the expectation value of the hyperfine coupling with the nuclear moment of a ligand is a sum of many terms. To illustrate the principle of the calculation we shall take the specific example of Co^{2+} (Thornley, Windsor, and Owen 1965).

To start with, the ground cubic term $^4T_1$ of Co^{2+}, composed of three holes, must be described in the strong-field formalism, which is suitable for the study of covalent bonding, using the formulae (20.18), (20.19), (20.21). On introducing the spin-orbit coupling, its effect in first approximation is to split the ground level which has a degeneracy of $3(2S+1) = 12$ into three $\tilde{\mathscr{J}}$ multiplets, $\tilde{J} = \frac{5}{2}, \frac{3}{2}, \frac{1}{2}$, resulting from the vector coupling of the fictitious orbital momentum $\tilde{l} = 1$ with the spin $S = \frac{3}{2}$. It also mixes into the ground cubic term $^4T_1$ the excited cubic term $^4T_2$ but we shall disregard this smaller effect to keep our treatment as simple as possible. The ground level is $\tilde{J} = \frac{1}{2}$, for which the states

$\tilde{J}_z = \frac{1}{2}$ and $\tilde{J}_z = -\frac{1}{2}$ are given by the vector coupling formulae

$$|\pm\rangle = \frac{1}{\sqrt{6}}\,|\pm\tilde{1}\rangle\,|\mp\tfrac{1}{2}\rangle - \frac{1}{\sqrt{3}}\,|\tilde{0}\rangle\,|\pm\tfrac{1}{2}\rangle + \frac{1}{\sqrt{2}}\,|\mp\tilde{1}\rangle\,|\pm\tfrac{3}{2}\rangle. \quad (20.79)$$

The notation in this equation requires some clarification. Let $|A\rangle$ be an orbital state which is a single Slater determinant $\{a, b, c\}$. The combined orbit-spin state $|A\rangle\,|\tfrac{3}{2}\rangle$ will be the Slater determinant $\{a^+b^+c^+\}$ and can be written symbolically

$$|A\rangle\{+, +, +\} = \{a, b, c\}[+, +, +].$$

The state $|A\rangle\,|\tfrac{1}{2}\rangle$ can similarly be written symbolically $\{a, b, c\}$ $[+, +, -]$ where $[+, +, -]$ is a symmetrized spin Slater determinant $(1/\sqrt{3})[\{+, +, -\}+\{+, -, +\}+\{-, +, +\}]$. Thus $(a, b, c)[+, +, -]$ means $(1/\sqrt{3})\{(a^+b^+c^-)+(a^+b^-c^+)+(a^-b^+c^+)\}$.

This factorization of orbit and spin variables is a special feature of Hund's states with maximum spin. The state $|+\rangle$ of (20.79) can now be rewritten in detail using (20.18), (20.19), and (20.21),

$$|+\rangle = \frac{1}{\sqrt{6}}\Big\{C(\tilde{1}, \theta, \varepsilon) - \frac{S}{2}(\tilde{1}, \tilde{0}, \theta) + \frac{S\sqrt{3}}{2}(-\tilde{1}, \tilde{0}, \varepsilon)\Big\}[-, -, +] - $$

$$- \frac{1}{\sqrt{3}}\Big\{\{C(\tilde{0}, \theta, \varepsilon) + S(\tilde{1}, -\tilde{1}, \theta)\}[+, +, -] + $$

$$+ \frac{1}{\sqrt{2}}\Big\{C(-\tilde{1}, \theta, \varepsilon) + \frac{S}{2}(-\tilde{1}, \tilde{0}, \theta) - \frac{S\sqrt{3}}{2}(\tilde{1}, \tilde{0}, \varepsilon)\Big\}[+, +, +], \quad (20.80)$$

with a similar formula for $|-\rangle$. In this formula C and S are the amplitudes $\cos\alpha$ and $\sin\alpha$ (see eqn (20.21)) of the cubic configurations $(t_2 e^2)$ and $(t_2^2 e)$ in the ground term $^4T_1$. The one-electron orbital states $|\tilde{1}\rangle, |\tilde{0}\rangle, |-\tilde{1}\rangle$ (not to be confused with the many-electron states $|\tilde{1}\rangle, |\tilde{0}\rangle,$ $|-\tilde{1}\rangle$) are defined in (20.16) where η_x, η_y, η_z and also θ and ε are the augmented antibonding orbitals of Table 24.

The calculation of the hyperfine structure with, say, the nucleus of ligand 3 is now straightforward in principle. The result can again be written in the form $A_{\parallel}I_z\tilde{S}_z + A_{\perp}(I_x\tilde{S}_x + I_y\tilde{S}_y)$ where the fictitious spin $\tilde{S}$ is the fictitious total angular momentum $\tilde{J} = \frac{1}{2}$. The values of $A_{\parallel}$ and $A_{\perp}$ are given by

$$\tfrac{1}{2}I_z A_{\parallel} = \langle+|\,\mathcal{H}(3)\,|+\rangle,$$
$$\tfrac{1}{2}I_x A_{\perp} = \langle+|\,\mathcal{H}(3)\,|-\rangle, \quad (20.81)$$

where $\mathcal{H}(3)$ is the Hamiltonian for the hyperfine coupling with the nucleus of ligand 3. In order to evaluate (20.81) we must replace the

orbitals $|\tilde{1}\rangle$, $|\tilde{0}\rangle$, $|-\tilde{1}\rangle$, $|\theta\rangle$, $|\varepsilon\rangle$ in (20.80) by their expansions given in Table 24, using (20.16). The calculation is lengthy but offers no special difficulties. To illustrate it we consider in $\mathscr{H}(3)$ the contact interaction part

$$\mathscr{H}_c(3) = \frac{16\pi}{3}\beta\gamma_n\hbar\delta(r_3)\,(\mathbf{I_3 \cdot s}). \tag{20.82}$$

The only orbital in (20.80) that gives a non-vanishing contribution to $\langle +|\,\mathscr{H}_c(3)\,|+\rangle$ and $\langle +|\,\mathscr{H}_c(3)\,|-\rangle$ is the orbital $|\theta\rangle$, which contains the wave-function $\varphi_{2s}(3)$ with an amplitude $(-\lambda_s/\sqrt{3})(N_\sigma^{-\frac{1}{2}}) = -f_s^{\frac{1}{2}}$. From (20.79) we obtain

$$\tfrac{1}{2}I_zA_\parallel^s = \langle +|\,\mathscr{H}_c(3)\,|+\rangle = \tfrac{1}{6}\langle\bar{1},\,-\tfrac{1}{2}|\,\mathscr{H}_c(3)\,|\bar{1},\,-\tfrac{1}{2}\rangle +$$
$$+\tfrac{1}{3}\langle\bar{0},\,\tfrac{1}{2}|\,\mathscr{H}_c(3)\,|\bar{0},\,\tfrac{1}{2}\rangle+\tfrac{1}{2}\langle-\bar{1},\,\tfrac{3}{2}|\,\mathscr{H}_c(3)\,|-\bar{1},\,\tfrac{3}{2}\rangle \tag{20.83}$$

which, using (20.80), becomes

$$A_\parallel^s = \frac{16\pi}{3}\,\beta\gamma_n\hbar f_{\sigma s}\,|\varphi_{2s}(0)|^2\left\{-\frac{1}{6}\Big(C^2+\frac{S^2}{4}\Big)\frac{1}{3}+\frac{1}{3}(C^2+S^2)\frac{1}{3}+\frac{1}{2}\Big(C^2+\frac{S^2}{4}\Big)\right\}$$

$$= a_{2s}f_{\sigma s}\frac{5C^2+2S^2}{9}\,. \tag{20.84}$$

Similarly

$$\tfrac{1}{2}I_xA_\perp^s = \langle +|\,\mathscr{H}_c(3)\,|-\rangle$$
$$= \frac{1}{\sqrt{12}}\langle\bar{1},\,-\tfrac{1}{2}|\,\mathscr{H}_c\,|\bar{1},\,-\tfrac{3}{2}\rangle+\frac{1}{3}\langle\bar{0},\,\tfrac{1}{2}|\,\mathscr{H}_c\,|\bar{0},\,-\tfrac{1}{2}\rangle+$$
$$+\frac{1}{\sqrt{12}}\langle-\bar{1},\,\tfrac{3}{2}|\,\mathscr{H}_c\,|-\bar{1},\,\tfrac{1}{2}\rangle, \tag{20.85}$$

whence

$$A_\perp^s = a_{2s}f_{\sigma s}\Big(\frac{5C^2}{9}+\frac{11S^2}{36}\Big). \tag{20.86}$$

A feature of this result, which we have not met before, is that the contact interaction is not perfectly isotropic. The anisotropy, as measured by $(A_\parallel^s-A_\perp^s)/A_\parallel^s = (-\tfrac{3}{20})(\tan^2\alpha)/(1+\tfrac{2}{5}\tan^2\alpha)$ which is quite small. For a vanishing splitting $\Delta = W(t_{2g})-W(e)$ the ground cubic term is pure ^4F and $\tan^2\alpha = \tfrac{1}{4}$ (see after eqn (20.24)) giving an anisotropy of about -3 per cent. It is actually much less because experimentally $\tan^2\alpha$ turns out to be of the order of $0\cdot08$.

The calculation of $A_\parallel^p$ and $A_\perp^p$ follows the same principle but is more involved, in particular because the p-hyperfine structure Hamiltonian

$\mathscr{H}_p$, in contrast with $\mathscr{H}_c$, can have off-diagonal matrix elements between two different antibonding orbitals.

Since α is small, it is not a bad approximation and a great simplification to take in (20.80) $C = 1$, $S = 0$. Then the part of (20.80) that contains p-orbitals of ligand 3, which we need to calculate the expectation value of the p-hyperfine structure Hamiltonian $\mathscr{H}_p(3)$, can be written

$$|+\rangle = \frac{1}{\sqrt{6}}\{-f_t^{\frac{1}{2}}(-1_p,\ \theta,\ \varepsilon)-f_{\sigma p}^{\frac{1}{2}}(0_p,\ \tilde{1},\ \varepsilon)\}\ [-,\ -,\ +]+$$

$$+\ \frac{1}{\sqrt{3}}f_{\sigma p}^{\frac{1}{2}}(0_p,\ \tilde{0},\ \varepsilon)[+,\ +,\ -]+$$

$$+\ \frac{1}{\sqrt{2}}\{f_t^{\frac{1}{2}}(1_p,\ \theta,\ \varepsilon)-f_{\sigma p}^{\frac{1}{2}}(0_p,\ -\tilde{1},\ \varepsilon)\}[+,\ +,\ +], \qquad (20.87)$$

where $|-1_p\rangle$, $|0_p\rangle$, $|1_p\rangle$ are p-orbitals of ligand 3, eigenstates of $l_z(3)$ with eigenvalues -1, 0, 1. A similar formula can be written for the Kramers conjugate state $|-\rangle$.

The one-electron p-hyperfine structure Hamiltonian $\mathscr{H}_p(3)$ can be written

$$\begin{cases} \mathscr{P}(\mathbf{I} \cdot \mathbf{N}), \text{ where} \\ \mathscr{P} = 2\beta\hbar\gamma_\mathrm{n}\langle r^{-3}\rangle \text{ and} \\ \mathbf{N} = 1+\tfrac{4}{5}\mathbf{s}-\tfrac{3}{5}\{\mathbf{l}(\mathbf{l} \cdot \mathbf{s})+(\mathbf{l} \cdot \mathbf{s})\mathbf{l}\}-\kappa\mathbf{s}. \end{cases} \qquad (20.88)$$

Here the last term in $\mathbf{N}$ allows phenomenologically for possible core polarization on the fluorine ion.

The hyperfine structure coefficients $A_\parallel^p$ and $A_\perp^p$ are given by

$$A_\parallel^p = 2\mathscr{P}\langle+|\ N_z\ |+\rangle,\ A_\perp^p = 2\mathscr{P}\langle+|\ N_x\ |-\rangle$$

and, using (20.87), (20.88), we obtain

$$\begin{cases} A_\parallel = \mathscr{P}\left\{f_{\sigma p}\left(\dfrac{4}{9}-\dfrac{5\kappa}{9}\right)+f_t\left(\dfrac{22}{45}-\dfrac{4\kappa}{9}\right)\right\}, \\ A_\perp = \mathscr{P}\left\{f_{\sigma p}\left(-\dfrac{2}{9}-\dfrac{5\kappa}{9}\right)+f_t\left(\dfrac{1}{15}-\dfrac{\kappa}{3}\right)\right\}. \end{cases} \qquad (20.89)$$

The complete expressions for $A_\parallel$ and $A_\perp$ for $\alpha \neq 0$ can be found in Thornley et al. (1965), where finer effects such as spin-orbit mixing of $^4T_1$ and $^4T_2$ are also considered.

We have outlined this calculation of ligand hyperfine structure in some detail because it is the first example of a situation where we

could not use the Wigner–Eckart theorem generalized for the cubic group and have had to write out the Slater determinants explicitly. The reason for this state of affairs is clear: the hyperfine structure with *one given* ligand is *not* invariant under cubic symmetry.

20.9. Ligand quadrupole hyperfine structure

If the ligand nuclei have spins $I \geq 1$ there exists, besides the hyperfine magnetic coupling, an electric quadrupole coupling between the nuclear quadrupole moments and the electronic field gradients at the nuclear sites. Since most studies of transferred hyperfine couplings have been performed on compounds where the ligands are fluorine ions with nuclear spin $I = \frac{1}{2}$, the experimental evidence on quadrupole effects is scarce. Furthermore, the relationship between these couplings and covalency is somewhat more complicated than in the case of magnetic hyperfine coupling. One obvious difference between magnetic and quadrupole couplings with the nuclei of the ligands is that s-orbitals, so important for the former, do not contribute to the latter. Another essential difference is the fact that in contrast to magnetic hyperfine structure, bonding orbitals do contribute to the quadrupole couplings. In order to minimize the total energy of the complex, each bonding orbital is filled with two electrons with opposite spins whose contributions to the magnetic hyperfine structure of a ligand nucleus cancel each other. On the other hand, their contributions to the quadrupole coupling of a ligand are spin independent and *add*.

Let us again consider ligand 3, and the contributions from its orbitals to the anti-bonding orbitals of the complex given by (20.50). The quadrupole hyperfine interaction will have axial symmetry around the z-axis. If $\mathscr{H}_Q$ is the quadrupole Hamiltonian we know that for a p-electron

$$\langle Z_3 | \mathscr{H}_Q | Z_3 \rangle = -2\langle X_3 | \mathscr{H}_Q | X_3 \rangle = -2\langle Y_3 | \mathscr{H}_Q | Y_3 \rangle$$
$$= -\frac{12}{5} \frac{e^2 Q \langle r^{-3} \rangle}{4I(2I-1)} \{ I_z^2 - \tfrac{1}{3}I(I+1) \}, \quad (20.90)$$

where $\langle r^{-3} \rangle$ is of course the value for a p-orbital on the ligand ion. Using (20.50) and (20.51) we find the following contributions to the quadrupole couplings from the antibonding orbitals of ions in singlet states:

$$3d^3 \quad \langle \mathscr{H}_Q \rangle = -f_t \langle Z_3 | \mathscr{H}_Q | Z_3 \rangle,$$
$$3d^5 \quad \langle \mathscr{H}_Q \rangle = (f_{\sigma p} - f_t)\langle Z_3 | \mathscr{H}_Q | Z_3 \rangle, \quad (20.91)$$
$$3d^8 \quad \langle \mathscr{H}_Q \rangle = (f_{\sigma p} - 2f_t)\langle Z_3 | \mathscr{H}_Q | Z_3 \rangle.$$

To these we must add the contribution of the filled bonding orbitals. If these orbitals were exactly p-orbitals of the ligand their contribution to the quadrupole interaction would be that of a closed shell and therefore vanish. Actually each bonding p-orbital contains admixtures from $3d$ orbitals of the central ion (and possibly admixtures from other orbitals) which behave like holes in the p-shell. This remark makes possible an estimate of the quadrupole interaction of the ligands if the following simplifying assumptions are made (Owen and Thornley 1966): bonding ligand p-orbitals contain admixtures from central $3d$-orbitals which have the *same* magnitude as the corresponding admixtures from ligand p-orbitals in the central antibonding $3d$-orbitals (this assumption is equivalent to taking the overlap S as much smaller than the covalency coefficient γ in eqn (20.10)).

With these assumptions the contribution of an electron in a bonding p-orbital to the quadrupole interaction is equal and *opposite* to that of an electron in the corresponding anti-bonding orbital. The contribution of the bonding orbitals to the quadrupole interaction is thus, using (20.50), (20.51),

$$-2\langle Z_3| \mathscr{H}_Q |Z_3\rangle\{f_{\sigma p}-f_t\}. \tag{20.92}$$

Adding (20.91) and (20.92) we find the following approximate expressions for the quadrupole interaction:

$$
\begin{aligned}
3d^3 &\quad \langle Z_3| \mathscr{H}_Q |Z_3\rangle(f_t-2f_{\sigma p}), \\
3d^5 &\quad \langle Z_3| \mathscr{H}_Q |Z_3\rangle(f_t-f_{\sigma p}), \\
3d^8 &\quad -\langle Z_3| \mathscr{H}_Q |Z_3\rangle f_{\sigma p}.
\end{aligned}
\tag{20.93}
$$

These expressions should be compared to the eqns (20.58), (20.60), and (20.62), which give the magnetic hyperfine structure due to p-electrons. It will be noticed that while for $3d^5$ and $3d^8$ the magnetic hyperfine structure contains the same admixture coefficients, namely $f_t-f_{\sigma p}$, and $f_{\sigma p}$, the situation is different for $3d^3$ where the magnetic hyperfine structure is proportional to f_t.