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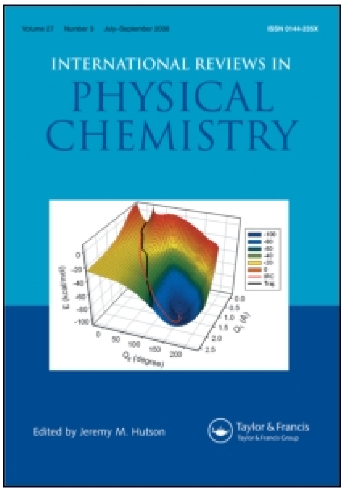

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Ligand-field analysis of transition-metal complexes

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Ligand-field analysis of transition-metal complexes

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The aim of this review is to give an account of recent theoretical work ('Ligand-Field Analysis') that has both led to clarification of the basic structure of ligand-field theory and has facilitated the acquisition of information about chemical bonding in paramagnetic transition-metal complexes that form insulating crystals. The review begins with a justification in modern terms for the classical crystal-field approach based on a well defined d^n-configuration for the metal ion; the central idea is that the ground and low-lying electronic states are based on *localized electron wavefunctions* because the interelectron repulsion energy is so important in these systems. The ligand-field theory is developed in two stages; first, the group product wavefunction method is used to construct a physically important subspace of many-electron wavefunctions for a transition-metal complex. The full n-electron hamiltonian is then studied in this basis using Löwdin partitioning and the chain formalism of Haydock; a full theoretical characterization of the Ligand-Field hamiltonian, which refers explicitly to only the d-electrons, is given. The paper describes the parametrization of the ligand-field based on the Cellular Ligand Field (CLF) model which explicitly introduces the notion of the chemical functional group to ligand-field theory. The $\{e_k^l\}$-parameters associated with the local interactions of the metal ion and its individual ligands (l) are discussed, and the review includes some general remarks about these quantities for the ligand-fields of some typical transition-metal complexes. A short introduction to the modern electronic structure theory of materials is given as a postlude to the main review.

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1. Introduction

This article is concerned with the application of quantum mechanical theory to the description of the spectral and magnetic properties of transition-metal complexes that form electrically insulating crystals—the 'ligand-field problem'. Much progress has been made recently with chemical aspects of ligand-field theory and the aim of the article is to give an account of theoretical work that has both lead to clarification of the basic structure of ligand-field theory and facilitated the acquisition of information about chemical bonding in transition-metal complexes.

Ligand-Field Analysis is a comprehensive approach to the ligand-field problem that emphasizes chemical features (Gerloch and Woolley 1984, Gerloch 1984). It has three interrelated aspects:

(1) The use of various experimental techniques to provide an extensive data of 'ligand-field' properties for a transition-metal complex, for example:
   (*a*) visible/U.V. spectroscopy, preferably using polarized radiation;
   (*b*) magnetic susceptibility tensor, χ, measurements with temperature dependence;
   (*c*) *g*-value measurements by e.s.r.

   For all three types of measurement, single-crystal studies are highly desirable.

(2) A quantum mechanical formalism to describe the experiments referred to in (1); this involves the development of a suitably parametrized many-electron theory together with a *chemical bonding* interpretation of the resulting parametrization, based on what we now refer to as the Cellular Ligand Field (CLF) model.

(3) A powerful computational package implementing the quantum mechanical model to carry out the analysis of the experimental data base, and so generate the ligand-field parameter set $[P_\alpha]$ on which the chemical interpretation is based.

Figures (1) and (2) show schematically how the three aspects of Ligand-Field Analysis are brought together. In addition to the spectroscopic and magnetic data, we also require the molecular geometry, which can be obtained from X-ray crystallography, and the d^n-configuration, which is obtained from chemical knowledge (Jørgensen 1969). The parameter set $[P_\alpha]$ is optimized by comparison between calculated and experimentally determined observables. Given an adequate data base, Ligand-Field Analysis can tackle essentially any transition-metal complex that forms an insulating crystal and is a magnetically dilute paramagnet, without recourse to special assumptions or crude simplifications. This allows some confidence in comparisons *between* parameter sets for related materials, a requirement of any chemically interesting theory.

While the whole procedure is much more sophisticated than the early work with crystal-field theory, none of the experimental techniques are particularly demanding of time or money, so Ligand-Field Analysis is of wide applicability. A few illustrative examples will be presented at the end of the article after the theoretical status of the CLF has been examined. Thinking in terms of local interactions of functional groups is *really the key to the whole enterprise; it allows the facile construction of the ligand-field* potential matrix **V** for transition-metal complexes that have little or no global point-group symmetry and, at the same time, the resulting parametrization can be given a chemical bonding interpretation that seems to make good chemical sense. This article concentrates on aspect (2) of Ligand-Field Analysis—the quantum mechanical

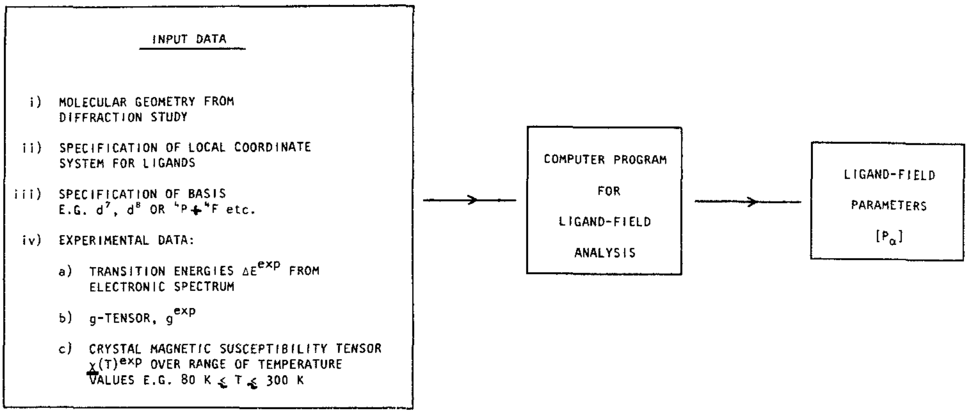

Figure 1. Schematic showing input for Ligand-Field Analysis. A basis set may be specified as either a d^n-configuration or as a particular set of terms (e.g. of given spin multiplicity) arising from a configuration.

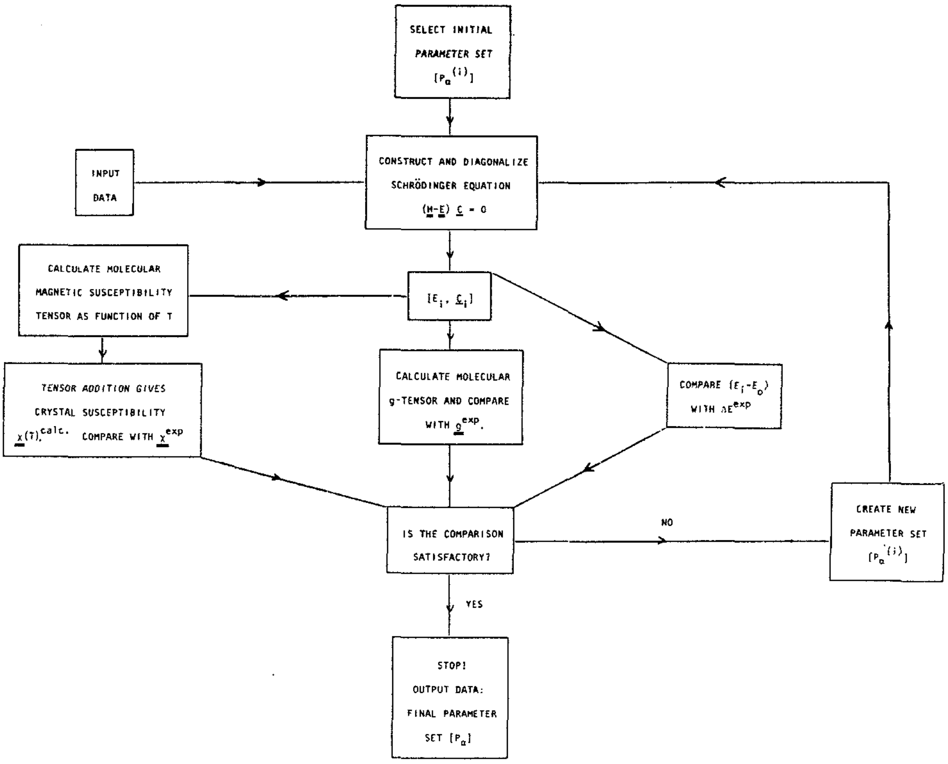

Figure 2. Block diagram showing the relationship between the input (experimental data), the quantum mechanical model, and the output ('best-fit' parameters) in Ligand-Field Analysis.

formalism—and is intended to complement a recent survey of applications (Gerloch and Woolley 1984). Throughout the review it may be helpful for the reader to keep in mind that the ligand-field parametrization, which by and large is very successful, is bases on a Schrödinger equation that has a well known structure (Griffith 1961, Ballhausen 1962) and has to be regarded as the *fixed* end-point of the theoretical analysis. This crucial fact determines the whole thrust of the theory described here.

The plan of the article is as follows: Section 2 introduces the physical properties that characterize the ligand-field regime and their interpretation in terms of *localized electrons*. Section 3 is an attempt to present a modern view of the ligand-field theory of transition-metal complexes (Stevens 1976, 1985, Woolley 1981, Gerloch *et al.* 1981), points of connection with *ab initio* quantum chemistry are identified, and the close relationship between the methods used here and those used by solid-state physicists in their studies of 'magnetic insulators' is emphasized. Some of the quantum-mechanical analysis has come from recent theoretical physics and does not seem yet to be well known in physical/theoretical chemistry; accordingly, the main features of the 'chain formalism' of quantum mechanics are summarized and then applied to the ligand-field problem; section 3.4 has been developed in the course of the preparation of this article, and hopefully represents further progress in tightening up the theoretical framework.

Section 4 is devoted to a full discussion of the ligand-field parametrization based on the Cellular Ligand-Field (CLF) model which explicitly introduces the notion of the chemical *functional group* to ligand-field theory (Deeth *et al.* 1986). A chemical bonding interpretation of the ligand-field parameters is shown to emerge from the many-electron theory described in section 3; this demonstration relies heavily on the chain formalism (section 3.4) and eliminates some technical shortcomings of our earlier discussion (Woolley 1985). The $\{\tilde{e}_k^l\}$-parameters associated with the local interactions of the metal ion and its individual ligands (l) are discussed (section 4.3), and some general remarks about the $\{\tilde{e}_k^l\}$-parameters for the ligand-fields of typical transition-metal complexes are presented in section 4.4; much more detailed discussions will be found in the recent primary, review, and monograph literatures concerned with Ligand-Field Analysis (Deeth and Gerloch 1984 a, b, 1985 a, b, Gerloch and Woolley 1984, Gerloch 1984). The article ends with an outline of the electronic structure theory of solids (section 5) which it is hoped will be useful background material.

2. The ligand-field regime

The materials belonging to the ligand-field regime are typically stoichiometric transition-metal and lanthanide-metal complexes; in the solid-state physics literature such materials are often referred to as 'magnetic insulators'. They form one of the three canonical types of electronic structures identified in section 5. We shall begin by reviewing their characteristic physical properties which reflect the large interelectron repulsion energies in these systems.

2.1. *Characteristic physical properties of the ligand-field regime*

2.1.1 *Magnetism*

The metal complexes of interest are *paramagnetic*; the temperature (T) variation of their average magnetic susceptibility, χ, is typically found to obey Curie's law over a wide range of temperatures above a few degrees kelvin,

$$\chi^{\text{molar}} \approx \mu_0 N_{\text{A}} \left(\frac{\mu_{\text{exp}}^2}{3k_{\text{B}}T} \right) \tag{1}$$

where, to a first approximation, the magnetic moment μ_{exp} is given by the usual atomic formula for an ion with total angular momentum quantum number J,

$$\mu_{\text{exp}} = g\sqrt{\{J(J+1)\}}, \tag{2}$$

g is the electron g-value and μ_0, k_B and N_A are the usual fundamental constants. For lanthanide complexes the value of J depends on the occupancy (n) of the f-electron shell: $J = L + S$ for $n \geqslant 7$, $J = |L - S|$ for $n \leqslant 7$, where L and S are the usual Russell–Saunders quantum numbers for the total electronic orbital and spin angular momentum. In transition-metal complexes the crystalline environment quenches the orbital contribution (effectively $L = 0$) and $J = S$ is the appropriate value in equation (2). The correct predictions of the orbital and spin degeneracy of the ground states of transition-metal and lanthanide-metal complexes, classified according to their geometry and the electronic configuration of the metal ion and confirmed by magnetic susceptibility measurements, were among the first considerable successes of the quantum theory of condensed matter (Ballhausen 1979). Ligand-field theory is not applicable to the more complex and varied magnetic behaviour found at very low temperatures ($\lesssim 10$ K)† which signals the occurrence of 'exchange phenomena' caused by electronic coupling *between* the metal ion centres (Interrante 1974).

2.1.2. *Spectroscopy*

These materials show characteristic weak absorption bands in the visible and ultraviolet regions of the electromagnetic spectrum. A convenient numerical scale for comparing intensities is provided by the oscillator strength, f, of a transition $k \leftarrow i$

$$f_{k \leftarrow i} = \frac{2m_e}{3e^2\hbar^2}(E_k - E_i)|\mathbf{d}_{ki}|^2 \tag{3}$$

$$\mathbf{d}_{ki} = \langle k|\hat{\mathbf{d}}|i\rangle \tag{4}$$

where $\hat{\mathbf{d}}$ is the electric dipole operator, and the states i, k involved in the transition have energies E_i, E_k respectively. For 'fully allowed' electric dipole transitions in electronic spectroscopy ($(E_k - E_i) = h\nu \gtrsim O(10^4\,\text{cm}^{-1})$),‡ the oscillator strength is typically ≈ 1; for 'forbidden' transitions, $f \ll 1$. Figure 3 shows a schematic energy level diagram for a transition-metal complex in an insulating crystal. The characteristic low-energy weak transitions in Cu(II) complexes, for example, have f values $\approx 10^{-4}$, whereas for Mn(II) complexes f is even smaller, typically $\approx 10^{-6}$ (Cotton and Wilkinson 1980).

In the theoretical spectroscopy of atoms it is convenient to choose a representation such that the atomic stationary states are labelled by energy (E_i), angular momentum (J, M_J) and parity (P) quantum numbers, and a typical key may be written as e.g. $|E_i, N, J, M_J, P\rangle$ where N refers to any other quantum numbers required to specify completely the representation. The electric dipole transition moment then becomes

$$\langle E_k, N', J', M'_{J'}, P'|\hat{\mathbf{d}}|E_i, N, J, M_J, P\rangle \tag{5}$$

---

† At these very low temperatures ordered magnetic structures responsible for e.g. antiferromagnetism are formed.

‡ Throughout this review the symbols '$\lesssim$', '$\gtrsim$' are to be interpreted as 'less than about', 'greater than about'; they are used with quantities (mainly ligand-field parameters) for which strict inequalities seem inappropriate.

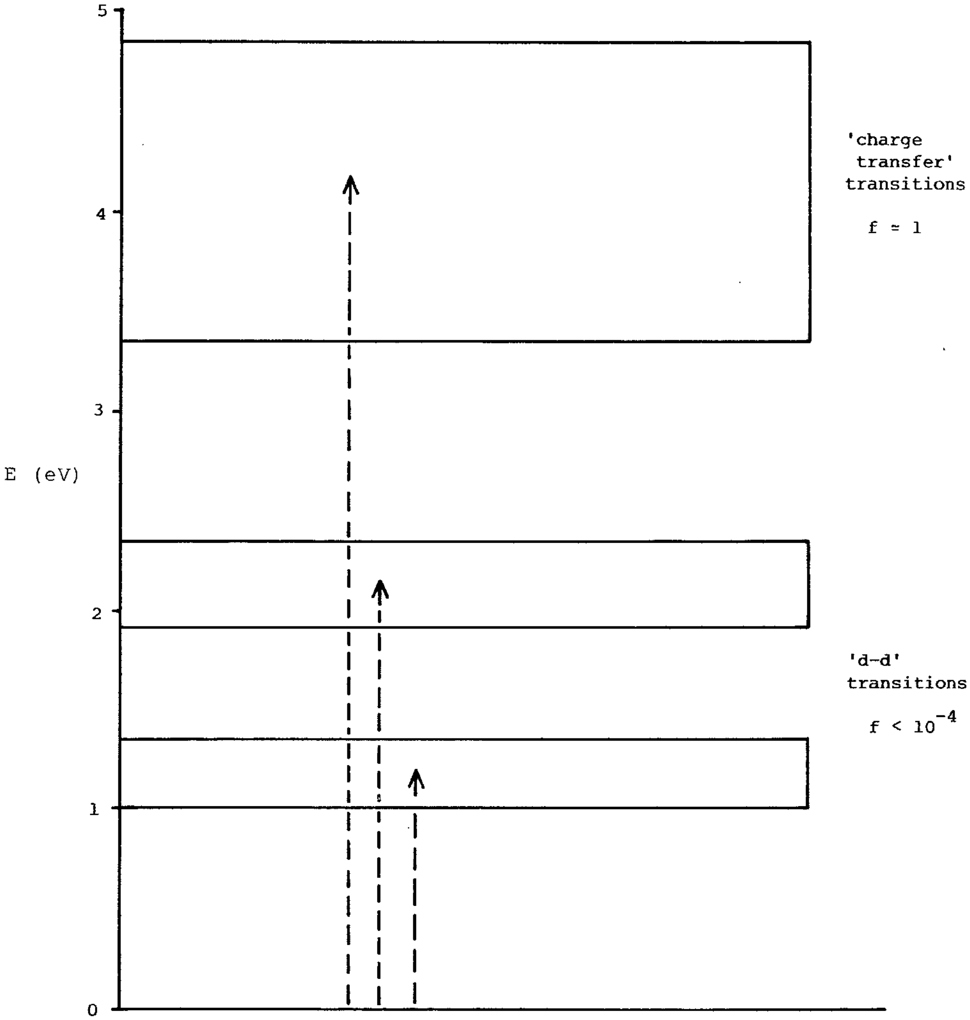

Figure 3. Energy-level diagram for the electronic spectroscopy of a transition metal complex in an insulating crystal.

and its non-zero values satisfy the selection rules (Landau and Lifshitz 1979) for angular momentum (the 'triangle rule')

$$|J-J'| \leqslant 1 \leqslant J+J' \tag{6}$$

$$\therefore \ \Delta J = 0, \pm 1, \ 0 \leftrightarrow 0 \text{ forbidden} \tag{7}$$

and for parity (the 'Laporte Rule')

$$PP' = -1 \tag{8}$$

$$\therefore \text{ only odd} \leftrightarrow \text{even transitions allowed.} \tag{9}$$

In the present context it is an important observation that the parity selection rule valid for the gas-phase spectra of atoms and ions is useful for understanding the intensity patterns of the spectra of metal complexes in condensed phases.

2.1.3. *Electrical conductivity*

Although transition-metal ions have only *partially filled* shells of valence electrons, many transition-metal complexes behave as electrical insulators in the solid state. The theoretical significance of this experimental observation rests on the following result for the conductivity. Let the electron wavefunctions $\{\psi_E(\mathbf{r})\}$ at energy E be normalized to one electron in a volume Ω, and consider what current may flow when an electric field is applied to the crystal in, say, the x-direction. The static conductivity $\sigma(0)$ is given by the Kubo–Greenwood formula (Mott and Davis 1979)

$$\left.\begin{aligned} \sigma(0) &= -\frac{2\pi e^2\hbar}{m_e^2}\Omega\,|D_E|^2_{\text{av}}N(E_{\text{F}})^2 \\ D_{\text{E}} &= \langle\psi_{E'}|\hat{p}_x|\psi_E\rangle,\; E=E' \end{aligned}\right\} \qquad (10)$$

where $N(E_{\text{F}})$ is the density of electron states evaluated at the Fermi energy, $\hat{p}_x$ is the x-component of the momentum operator, and the current matrix element squared $(|D_E|^2)$ must be averaged over all states at the Fermi surface. Evidently, electrical conduction requires two conditions to be met. Firstly there must be a non-zero density of states at E_{F}; in a band model this corresponds to an incompletely filled band of one-electron levels. Secondly, these electron levels must give a non-zero current matrix element. Now, for *localized* electron states with energy E $\int d^3x\psi_E^*(-i\hbar\,\partial/\partial x)\,\psi_E$ is zero because ψ_E can be chosen as a *real* wavefunction and the hermitian operator $\hat{p}_x$ is pure imaginary; furthermore two overlapping localized *eigenfunctions* ψ_1, ψ_2 with the *same* energy cannot occur. Thus $\sigma(0)$ can only be non-zero for extended (delocalized) electron wavefunctions in the crystal. In more physical terms, this analysis shows that a necessary condition for electrical conduction is the presence of free charge-carriers; such are not found in *insulating materials* which have electronic structures characterized by *localized electron states* (see section 5).

2.2. *The interelectron repulsion energy and electron localization*

The fact that we are dealing with paramagnetic insulators has important implications for the theoretical description of the ligand-field regime; it is as well to be clear about these at the outset. The most important conclusion is that what has always been the main quantum chemistry approach to electronic structure theory, namely the independent-electron (SCF-MO) model, is of little practical use. An example will help to make the point: $CuSO_4\cdot 5H_2O$ is a familiar blue crystalline material formally built up from Cu(II) ions and sulphate counterions, with water of hydration. The cupric ion, Cu(II), has a d^9 configuration; accordingly a SCF calculation of the one-electron levels in hydrated copper sulphate in its equilibrium crystal structure necessarily gives rise to a partially filled energy band because of the incomplete valence d-shells of the Cu(II) ions. The corresponding one-electron eigenfunctions are Bloch functions that extend throughout the periodic crystal. This result, in conjunction with the Kubo–Greenwood conductivity formula (10), leads to the prediction that $CuSO_4\cdot 5H_2O$ should behave electrically as a metal because both D_E and $N(E_{\text{F}})$ are non-zero in such a calculation. In fact copper sulphate crystals are excellent insulators. The band theory results are equally poor for the magnetic† and spectroscopic properties. The same argument can

---

† The delocalized band electrons of the independent electron model exhibit temperature-independent (Pauli) paramagnetism which is much weaker than the Curie paramagnetism of atomic species; this is because the Pauli Exclusion Principle suppresses the alignment of the electron spins with the magnetic field much more effectively than does the thermal disorder (Ashcroft and Mermin 1976).

be made for any other transition-metal complex and it implies that a SCF description of the electronic structure cannot even be qualitatively correct unless the complex behaves electrically as a metal.

The theoretical interpretation of these findings is well known (Mott 1949, 1974). In the ground state and thermally accessible excited electronic states, the valence d-electrons (i.e. the electrons at or near the Fermi energy) remain localized about individual metal ions and cannot move freely from ion to ion throughout the crystal without a considerable net increase in energy because to do so costs considerable interelectron repulsion energy that is not compensated by the lowering of kinetic energy associated with delocalization. Physically, our knowledge of the crystal structure and understanding of chemical bonding interactions suggests that the d-electrons of individual ions are only weakly coupled to those of neighbouring ions or even their diamagnetic environment (the ligands); this is reflected in the SCF band-structure by the occurrence of very narrow bands for these electrons. Narrow bands always indicate the necessity for going beyond the independent-electron model because, for such bands, interelectron repulsion effects are very important (Cox 1985).

Within a *one-electron model*, a simple (and useful) description of such a situation can be given within a *localized orbital* picture; even though the one-electron (molecular orbital of SCF) part of the (many-electron) hamiltonian is not diagonalized by a basis of localized orbitals, placing the d-electrons in such orbitals leads to an energetically more favourable distribution in space for them because it reduces the total interelectron repulsion energy by keeping electrons out of each other's way; this more than compensates for the loss of electron mobility throughout the crystal. In chemical valency terms we are close to the Heitler–London valence bond limit, and far from the molecular orbital limit.

The reference to electron correlation here signals that the many-electron ground state and low-lying excited states of the crystal cannot be constructed in a simple way† out of the independent-electron model orbitals populated in accordance with the Pauli Exclusion Principle. The crystal however is the object on which the experiments are performed and to which the quantum theory is properly addressed. Since there is no question of an *ab initio* calculation of the many-electron electronic structure of the crystal, we must perforce turn to heuristics.

Stevens (1976, 1985) has given the following argument to characterize the low-lying, many-electron levels in a crystalline magnetic insulator. The individual metal ions have a set of discrete energy levels (terms) which are characteristic of their d^n configuration and often have a high degree of degeneracy; for example the ground and first excited levels of the Co^{2+} ion (d^7) comprise the forty levels of $^4F + {}^4P$. When these ions are brought altogether in the diamagnetic environment of the crystal their energy levels broaden out into bands. One's first intuition is that the bands will be narrow and separated by substantial gaps; the intuition has some validity as we shall see, but strictly speaking it is erroneous. The energy levels of *any* macroscopic system (macroscopic matter, electromagnetic field) form a *continuum* that starts from the ground-state energy. Even if the average interaction energies ΔE of the ion terms are tiny compared

---

† The lack of straightforward correspondence between the orbitals of the SCF independent-electron model and the many-electron states of molecules has been demonstrated in extensive *ab initio* SCF-Hartree–Fock and configuration interaction (C.I.) calculations on transition-metal atoms and their complexes; see recent discussions of species such as Ni, $Ni(CO)_4$, $Fe(CO)_5$, ferrocene (Faegri and Almlöf 1984, Lüthi *et al.* 1984, Rohlfing and Martin 1985, Blomberg *et al.* 1985, Widmark *et al.* 1985) as well as earlier calculations of Hillier *et al.* (1976 a, b) and Hillier and Kendrick (1976).

with typical term separation energies, the bands formed from individual terms by bringing together N ions have widths that scale as $N\Delta E$ so that in the limit of a large system, such as a crystal ($N \rightarrow \infty$), the end result is inevitably a continuum of energy levels with the states originating from the ground term merging into or even overlapping those of the first excited state, and all higher terms of the d^n configuration up to the series limit. This continuum has a high degree of degeneracy inherited from the atomic terms.

This result may seem a surprise, conflicting as it does with our intuitions about the spectroscopy of the crystal (cf. figure 3); the paradox is resolved by noting that how this continuous spectrum of many-electron states translates into physical properties depends on the transition matrix elements to which it gives rise. This observation suggests an interpretation of the gaps between the bands of energy levels in figure 3: the figure refers to excitations induced by the electric dipole operator (or some other multipolar operator) and an external electromagnetic field, that are recognizable *one-electron* in character. Such excitations must be in accordance with the Pauli Exclusion Principle and qualitatively can still be understood in terms of a suitably chosen set of one-electron orbitals (not the molecular orbitals); transitions to electronic states with energies lying in the gaps in figure 3 involve the reorganization of several or many electrons simultaneously, and simply lack intensity in optical spectroscopy. Equally, there are no transitions to states near the ground-state taking an electron from a localized orbital to an unoccupied delocalized orbital, and the resistivity is therefore high.

The success of the ‘spin-only’ formula in the Curie Law for the magnetic susceptibility of transition-metal complexes, equation (2), and the continued relevance of the Laporte rule for their absorption spectra, suggests that the localized orbitals for the d-electrons should be *atomic-like* orbitals centred on the metal ions. A description in terms of electrons localized on fragments (atoms, bonds, molecules etc.) is valid for any *insulating material* and accounts in a physically immediate way for the absence of free charge-carriers. The notion of localized electron states in an insulating material is a key insight that has ramifications far beyond the description of the ligand-field regime (Mott and Davis 1979, Kaveh and Mott 1985, Elliott 1983; Anderson 1984).

We noted earlier that the Hartree–Fock SCF-M0 model must be supplemented by substantial configuration interaction (C.I.) if we are to obtain anything like a quantitative description of the electronic energy levels of transition-metal complexes (Lüthi *et al.* 1984). For this reason the methods of *ab initio* quantum chemistry are of limited utility, being feasible for only rather special molecular models (for example, complexes involving simple ligands). Where the C.I. methods have been used they appear to confirm the picture of localized d-electrons assumed by ligand-field models. Perhaps the hardest lesson they teach us is that as far as spectra and magnetism are concerned, molecular orbital theory for transition-metal complexes must be viewed with considerably more circumspection than has often been the case in the inorganic chemistry literature. The C.I. calculations of Hillier *et al.* (1976a, b, Hillier and Kendrick 1976) on tetrahalide species MX_4 (M = Ti, Co, V; X = Cl), for example, are consistent with localized d-electrons, and suggest that ‘evidence’ for d-orbital participation in ‘covalency’ is exaggerated by simple m.o. models of these species. From the physical point of view, the effect of the C.I. is to bring about destructive interference between delocalized orbitals (m.o.s or Bloch orbitals) so as to give the result described above in terms of localized orbitals; at the same time, considerable alterations can occur in the order of low-lying energy levels when explicit account is taken of the interelectron repulsion energy (c.f. footnote page 00). The conclusion to be drawn from this discussion is that for most materials in the ligand-field regime a parameterized or semi-empirical quantum theory is the order of the day. Even so, although our main concern cannot be with *ab initio* computation, the ligand-field model must be grounded in reasonable electronic structure theory—what we are doing must not be arbitrary—and it must be subject to quantitative tests.

One major ingredient of theoretical treatments of the ligand-field regime is the assumption that the electrons move under the influence of a rigid lattice of ions; this assumption is sometimes found to fail, and we then deal with so-called Jahn–Teller systems for which we explicitly recognize coupling between electronic and nuclear motion and/or spin–lattice relaxation effects, for example 'spin-crossover' phase transitions (Gütlich 1981). The considerable complications in a quantum theory of solids (or macroscopic matter in general) in which electrons and nuclei are treated on an equal footing would take us too far afield, and this review will make the adiabatic assumption (Born and Huang 1954) that the nuclei are only weakly coupled to the electron states. We also assume that the nuclear orbitals are strongly localized about the classical equilibrium structure; that is, just as in the electron case, the spectrum of energy levels for the nuclei in the crystal is continuous, but a large excitation energy is assumed to be required for any one nucleus to be moved into a delocalized nuclear orbital, for then we shall achieve the mechanical property we call solidity (Anderson 1984). General arguments suggest that vibronic coupling is likely to be more important for *localized* electron states than for delocalized (Bloch or 'metallic') states (Anderson 1972, 1974) so perhaps we ought to be more surprised that the rigid-lattice model works well in ligand-field theory, rather than it fails on occasion; however, its use may be more a conventional step than an essential feature. The incorporation of the nuclei as quantum-mechanical entities in the ligand-field formalism—electron–phonon coupling may be introduced by perturbation theory, for example—has been discussed by Stevens (1973).

2.3. *The crystal-field parametrization—old and new*

Section 2.2 is a justification, in modern terms, for the early *crystal-field* and *ligand-field* models of Bethe (1929), Pauling (1931, 1932) and Van Vleck (1935). The electronic structure of a spherical metal ion, with d-electron configuration fixed by the ion's chemical oxidation state, is taken as a reference system; the assumption is that the metal ion valence s and p-orbitals are substantially involved in chemical bonding interactions with the ligands, leaving the metal ion with a specified d^n-configuration that is relatively independent of these chemical bonding effects. Thus crystal-field theory is concerned only with low-lying electronic states of pure valence d-orbital parentage; it focuses attention on how the crystal environment about an individual ion (the 'crystal-field') perturbs the ion's originally degenerate set of valence d-orbitals. This perturbation is described by the 'crystal-field' matrix or 'ligand-field potential' matrix—**V**; for a transition-metal ion, **V** is a 5 × 5 matrix that can be labelled by the metal's five valence d-orbitals.

Electron-electron repulsion interactions and spin–orbit coupling are also important perturbations for the d-electrons and an essential aspect of the ligand-field problem is that it involves an *atomic* C.I. calculation leading to many-electron states for the d-electrons of each ion. In the crystal-field limit, i.e. with neglect of interion exchange interactions or other couplings, antisymmetrized products of these states approximate the low-lying, many-electron states of the crystal with sufficient accuracy to account for the ligand-field experiments—magnetic measurements and absorption spectroscopy. One of the questions addressed by this review is how such a model should be related to general electronic structure theory.

Within a rigid-lattice model, the global point-group symmetry of the equilibrium crystal structure about each magnetic ion is carried† by the matrix **V** and this led to much of the early work being directed towards metal complexes with structures that could be idealized in terms of relatively high point-group symmetries (O_h, T_d, D_{4h} and so on) because symmetry reduces the number of independent matrix elements in **V**. The majority of metal complexes of interest to chemists have structures with little, if any, point-group symmetry, so that, even at this early stage, the differing concerns and interests of chemists and physicists, which persist today, had become apparent. It is important to recognize however that there has been considerable convergence in the theoretical methods used by these communities.

The recent progress in ligand-field theory which is of interest to chemists is the development of a quantum-mechanical formalism that meets three criteria (Gerloch 1984):

(i) It is capable of accounting for experimental data obtained from investigations of magnetism and spectroscopy.

The transitions observed in optical spectroscopy involve many-electron states, and a *quantitative* interpretation of the spectroscopy cannot generally be based on one-electron orbital energies. We mentioned above that a many-electron theory is essential.

(ii) It allows a tractable parametrization scheme for the matrix elements involved in the theory required for (i).

The ligand-field potential matrix, **V**, is normally known only to the extent that it can be obtained by parametrization of the experimental data. Similarly, the interelectron repulsion energies are described by the Slater–Condon–Shortley parameters A, B, C (or Racah's F_0, F_2, F_4) and these again are to be parametrized. Finally, there are the d-electron spin–orbit coupling constant and Steven's orbital reduction factor, ζ_d and k respectively, both of which are important quantities in studies of magnetism. This leads to a parameter set $[P_\alpha] = [\mathbf{V}, F_0, F_2, F_4, \zeta_d, k]$.

(iii) The formalism promises a *chemical* interpretation of the parameter set $[P_\alpha]$ described under (ii), more or less irrespective of the point-group symmetry of the crystal-field.

Criterion (iii) is important because the ligand-field theory parametrization is very different from the parametrized models familiar in molecular and nuclear spectroscopy. The hermitian 5×5 matrix **V** contains 15 independent matrix elements, a number that may be reduced by the occurrence of symmetries in the physical system which it describes. We must confront the fact that the total number of ligand-field parameters ($\lesssim 20$) may be comparable to the number of quantities required to represent the experimental data—evidently even a purely utilitarian argument for parametrization as a means of data reduction is not possible here.

The key to achieving criterion (iii) is the recognition that a change in point of view is possible. The matrix **V** must carry the global point-group symmetry of the crystal-field;

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† This conclusion remains valid when the nuclei are allowed to move if electron-phonon interactions are allowed for by perturbation theory (Stevens 1973, 1976).

by its nature, therefore, **V** can only give an indirect, averaged view of the *individual* chemical bonds in the complex. For example, there is no clear-cut separation of metal ion–ligand σ and π-bonding effects. A chemically more interesting theory results when these conventional ideas are integrated with a much older chemical tradition in which attention is focused on the role of *functional groups*, i.e. parts of individual ligands. This is the promise of the Cellular Ligand-Field model—CLF for short—(Deeth *et al.* 1986). Before describing the CLF, which is concerned with the interpretation of **V** only, it is essential to describe the general quantum mechanical formalism that gives rise to the parameter set $[P_\alpha]$ and this is the concern of section 3.

3. Ligand-field theory

3.1. *The many-electron theory—general structure*

In Heisenberg's version (1927) of quantum mechanics there are only matrix elements and the rules for manipulating them, and a quantum mechanical system can always be described in a Heisenberg representation by specifying the hamiltonian matrix **H** on an infinite-dimensional Hilbert space $\mathbb{H}$. What we are aiming at as a quantum mechanical basis for Ligand-Field Analysis is the specification of a hamiltonian matrix, **H**, such that the solution of the eigenvalue equation

$$(\mathbf{H}-E_i\mathbf{1})C=0,\ \mathbf{H}=\mathbf{H}^* \tag{11}$$

yields eigenvalues and eigenvectors for the ground state and low-lying excited electronic states that reproduce the optical spectrum and magnetic properties of a transition-metal complex. However, we also want to have a direct connection between *ab initio* electronic structure theory and the ligand-field model, and for this it is more convenient to set up the quantum theory in a Schrödinger representation in terms of operators acting on a Hilbert space labelled by functions, and derive the corresponding matrix elements that give **H**.

Two similar general treatments have been given (Stevens 1976, Gerloch *et al.* 1981). A detailed analysis using the second quantization formalism and treating both the single-ion ('crystal-field') problem and exchange interactions *between* ions has been given by Stevens (1976) for a magnetic insulator; this work shows how the conventional 'spin-hamiltonians' of solid-state physics can be related to the full many-electron theory by exploiting a well known correspondence between annihilation/creation operators and angular momentum operators. A less complete analysis, restricted to the case where the individual molecules of a transition-metal complex are magnetically dilute and based on the use of Slater determinants with the group product wavefunction idea (Lykos and Parr 1956, McWeeny and Sutcliffe 1976) has been given by Gerloch *et al.* (1981). This presentation is more closely tied to a coordinate wavefunction description in accordance with the chemist's traditional view of local interactions in real space. The two approaches seem to be largely equivalent (Stevens 1985).

An essential feature of the ligand-field theory is the requirement that the low-lying electronic energy levels of the crystal be described in terms of a *fixed* number of electrons associated with distinct fragments in the crystal; as discussed in section 2, this is intimately connected with the circumstance that we are dealing with an insulating crystal. On this basis it is possible to obtain these low-lying levels from an effective hamiltonian for the crystal written in the form of a cluster expansion (Stevens 1976),

$$\mathscr{H}=\sum_{A}\hat{H}_A+\sum_{AB}\hat{H}_{AB}+\sum_{ABC}\hat{H}_{ABC}+\dots \tag{12}$$

where $A, B, C, \dots$ are distinct fragments having a definite number of electrons; more explicitly, each fragment consists of a paramagnetic (open-shell) metal ion in a diamagnetic (closed-shell) environment. If we ignore the coupling terms $\hat{H}_{AB}$, $\hat{H}_{ABC}, \dots$ in this expansion, the sum we are left with leads directly to the classical 'crystal-field' or 'ligand-field' theories; the coupling terms in (12) describe exchange phenomena. Stevens derived the hamiltonian (12) using the fermion second quantization formalism; this has the great advantage of automatically taking account of the requirement that electrons throughout the crystal should be indistinguishable. His results for the crystal-field problem seem to be equivalent to those obtained by Gerloch *et al.* (1981) for a single fragment, and since the latter used methods closer to traditional quantum chemistry I have chosen to describe it here.

The basic idea of both approaches is that the ligand-field problem involves a hamiltonian matrix constructed by projection of the full many-body hamiltonian onto the many-electron states associated with a subset of the electrons of each metal ion. Before giving an account of how this may be accomplished with the use of group product wavefunctions, it is helpful to review the *structure* of ligand-field theory. Although parametrized ligand-field calculations have been carried out for many years, it is only recently that attempts to relate its working equations to rigorous quantum mechanics have been carried through to completion. To appreciate the theoretical development described below it is vital to understand that these investigations have necessarily been directed towards achieving the *known* working equations of ligand-field theory, which can be specified concisely by the following two groups of statements:

(i) Quite generally, a fragment hamiltonian $\hat{H}_A$ in a many-electron basis gives rise to the structure

$$\mathbf{H}=\underbrace{\underset{\substack{\text{spin-independent}\\ \text{kinetic energy and nuclear}\\ \text{attraction interactions}}}{\mathbf{V}_1}+\underset{\substack{\text{spin-orbit}\\ \text{coupling}}}{\mathbf{V}_{\text{s.o.}}}}_{\text{sums of one-electron matrix elements}}+\underbrace{\underset{\substack{\text{interelectron}\\ \text{repulsion}}}{\mathbf{V}_{\text{ee}}}}_{\substack{\text{sums of two-electron}\\ \text{matrix elements}}} \tag{13}$$

(ii) The Ligand-Field hamiltonian is expected to account only for the magnetism of the complex and its low-lying set of spectroscopic transitions in the visible/U.V. region of the spectrum that have weak intensity; ligand-field theory is *not* concerned with quantitative aspects of the energetics of chemical bond formation. Guided by the Laporte rule of atomic spectroscopy, we restrict the orbital matrix elements to be diagonal in l. For each l value there are $2(2l+1)\equiv N^l$ spin-orbitals.

(iii) We wish to describe a small range of excitation energies, a few eV at most, which in accordance with (ii) involve excitations that are *atomic* in character. Given the typical scale of energy separations of atomic orbitals with different values of l and the same, or adjacent, principal quantum numbers, we achieve this restriction by allowing only one value of l. For transition-metal complexes, $l=2$.

(iv) The number of electrons, n, associated with atomic orbitals of given l at each metal ion must be specified; for a transition-metal ion this is given by the d^n configuration which is related directly to the chemical oxidation state.

As a result of combining restrictions (ii)–(iv) with (i), we obtain a matrix defined on a subspace of dimension given by the combinatorial number ${}^{N'}C_n$; this matrix is an obvious candidate to be considered as the ligand-field hamiltonian $\mathbf{H}_{\text{L.F.}}$, but then we are lead to the question: how must the ligand-field matrix $\mathbf{H}_{\text{L.F.}}$, so defined, be related to the infinite-dimensional matrix, $\mathbf{H}$, expected according to rigorous quantum theory applied to one of the fragment hamiltonians $\hat{H}_A$ appearing in equation (12)? The completion of the characterization of the ligand-field model is achieved through answering this question.

The first part of the answer is easy; the partitioning technique (Löwdin 1966) can always be used to rewrite the infinite dimensional eigenvalue equation (11) as an implicit eigenvalue problem on a finite-dimensional space. If we partition the Hilbert space $\mathbb{H}$ as $\mathbb{H}=\mathbb{H}_1\oplus\mathbb{H}_2$, where $\mathbb{H}_1$ is finite-dimensional, we have the decomposition

$$\mathbf{H}=\begin{pmatrix}\mathbf{H}_1 & \mathbf{V}\\ \mathbf{V}^+ & \mathbf{H}_2\end{pmatrix};\quad \mathbf{1}=\begin{pmatrix}\mathbf{1}_1 & 0\\ 0 & \mathbf{1}_2\end{pmatrix};\quad C=\begin{pmatrix}C_1\\ C_2\end{pmatrix}, \tag{14}$$

and the original Schrödinger eigenvalue equation (11), becomes

$$(\mathscr{H}(E)-E_i\mathbf{1}_1)C_1=0 \tag{15}$$

where

$$\mathscr{H}(E)=\mathbf{H}_1+\mathbf{V}^+(E\mathbf{1}_2-\mathbf{H}_2)^{-1}\mathbf{V} \tag{16}$$

is a finite-dimensional effective hamiltonian. The matrix $\mathbf{H}_1$ is simply the projection of the full hamiltonian onto the subspace $\mathbb{H}_1$. The second part of $\mathscr{H}(E)$, equation (16), contains all other interactions that couple the two subspaces folded back onto the subspace $\mathbb{H}_1$. The complete solution of (15) and (16) gives all solutions of (11) for which $C_1\neq 0$, It is to be noted that the matrix $\mathscr{H}$ is energy-dependent and corresponds to an operator involving $1,2,\ldots n$-body interaction terms.

As a consequence of (i)–(iv) we now have

(v) The direct truncation of the matrix $\mathbf{H}$, specified by statements (ii)–(iv), is related to the term $\mathbf{H}_1$ in equation (16)—the projection of the hamiltonian $\hat{H}_A$ on the subspace of d-electron states, We show this explicitly with the group-product wavefunction formalism (section 3.3).

(vi) The Ligand-Field hamiltonian, $\mathbf{H}_{\text{L.F.}}$, that is actually parametrized, must be related to an effective hamiltonian $\mathscr{H}(E)$, equation (16), for we seek a subset of eigenvalues of the full matrix $\mathbf{H}$, rather than simply its projection $\mathbf{H}_1$.

(vii) In practice the complete 'd–d' excitation manifold is described with sufficient accuracy by a *single* set of ligand-field parameters (=orbital matrix elements). This corresponds to working with a mean energy $\bar{E}$ in the effective hamiltonian

$$\mathscr{H}(E)\rightarrow\mathscr{H}(\bar{E})\equiv\mathbf{H}_{\text{L.F.}} \tag{17}$$

where $\mathbf{H}_{\text{L.F.}}$ is the matrix that is parametrized.

(viii) Some n'-body interactions ($n \geqslant n' \geqslant 2$) introduced by the partitioning procedure must be neglected. Freed's work (1974) on the foundations of semi-empirical quantum chemistry shows that some, but not all, of the contributions of the additional n'-electron operators can be included in the 1 and 2-electron matrix elements specified in statement (i) when $\mathbf{H}$ is transformed into $\mathbf{H}_{\mathrm{L.F.}}$.

Statements (i)–(viii) give a formal specification of the ligand-field model which will be put into more concrete terms in the following sections. Equations (14)–(16) are exact and hold for an arbitrary decomposition of $\mathbb{H}$. The essential physical content of ligand-field theory lies in its claim that there is a choice of subspace $\mathbb{H}_1$ such that an averaged effective hamiltonian $\mathscr{H}(\bar{E})$, or, equivalently, a perturbation approach to the corrections to $\mathbf{H}_1$ can account for the magnetism and spectroscopy of a paramagnetic insulator: the physics reviewed in section 2 is the heuristic basis for this choice of $\mathbb{H}_1$. It is worth remarking that an analytical investigation of this kind should not be compromised by approximations that are necessary to make numerical calculations possible with currently available computational resources because the latter are subject to much more rapid change than the underlying theoretical structure; such approximations should be dealt with as a separate matter. Equally it is essential that there be a clear path from the full many-electron formalism to the Ligand-Field hamiltonian $\mathbf{H}_{\mathrm{L.F.}}$ and this is the subject of the remainder of section 3. There are two stages to the development. First, we must characterize the subspace $\mathbb{H}_1$; the group product wavefunction formalism to be described in section 3.3 is one way of explicitly constructing $\mathbb{H}_1$. Subsequently, we must investigate the consequences of the partitioning based on this choice of $\mathbb{H}_1$.

3.2. *The Schrödinger equation for a molecular fragment*

Under the assumption of negligible coupling between fragments, the energy levels of the crystal are simply a sum of fragment energies, and the corresponding crystal wavefunctions can be expressed as the antisymmetric components of products of fragment wavefunctions:

$$\Phi_\alpha^{\mathrm{crystal}} = \mathscr{A} \prod_A \phi_i^A$$
$$E_\alpha^{\mathrm{crystal}} = \sum_i E_i^A. \tag{18}$$

Here the energies and wavefunctions for the fragment A are the solutions of the Schrödinger equation

$$(\hat{H}_A - E_i^A)\phi_i^A = 0. \tag{19}$$

Interfragment interactions are responsible for the continuous spectrum above E_0^{crystal} described in section 2. As explained there, equation (18) can be expected to be useful for understanding the physical properties characteristic of the ligand-field regime, and with this assumption the analysis can be confined to a single-fragment hamiltonian, which from now on we shall refer to as $\hat{H}$ with no subscript.

The typical fragment described by $\hat{H}$ is a first-row, transition-metal ion coordinated to several ligands, very commonly 4 or 6, although other coordination numbers are not unusual. Ligands vary widely in complexity: atomic species such as the halogens and oxygen, simple inorganic diatomic and polyatomic species (OH^-, CN^-, H_2O, NH_3,

N_3^-, NCS$^-$, etc.), heterocyclic organic species coordinated through N, O or S (pyridine, quinoline, phenol, thiophene and derivatives), chelates and macrocyclic ligands, are all of interest. Many ligands carry substituents, often bulky alkyl or aromatic groups, far from the site of metal–ligand bond formation. Ligand-Field Analyses of a representative set of such species were reviewed by Gerloch and Woolley (1984).

The n-electron hamiltonian for a metal ion and its ligands can be written in the fixed-nucleus approximation in the form

$$\hat{H} = \sum_{\alpha=1}^{n} \hat{H}_N(\alpha) + \frac{1}{2} \sum_{\alpha,\beta}^{n}{}' 1/r_{\alpha\beta} \tag{20}$$

$$\hat{H}_N(\alpha) = -\tfrac{1}{2}\nabla_\alpha^2 - \sum_\sigma Z_\sigma/r_{\sigma\alpha} + \hat{h}(\alpha)^{\mathrm{Rel}} \tag{21}$$

where Z_σ is the charge on the nucleus σ (in units of $+e$), $r_{\sigma\alpha}$ is the distance of electron α from nucleus σ, and $\hat{h}(\alpha)^{\mathrm{Rel}}$ describes any additional relativistic corrections, for example the Darwin and mass-velocity corrections which become increasingly important for heavy elements, and the spin–orbit coupling operator which is always important in magnetism. All the complexity of solving equations (19)–(21) is hidden in the summation limit n. From the description of the range of ligands of interest just given, we can make a conservative estimate that the number of electrons per fragment, n, will typically be several hundred. Ligand-Field Analysis is less ambitious than an *ab initio* quantum chemistry approach to the Schrödinger equation based on the n-electron hamiltonian, equation (19). *Ab initio* quantum chemistry has the goal of describing the ground electronic state (and possibly some excited states) of the whole fragment; it must therefore achieve a good description of parts of the ligands stereochemically remote from the metal ion, as well as the local electronic structure about the metal ion. The latter is notoriously difficult to do well because of the correlation energy of the valence d-electrons; molecular C.I. calculations on small transition-metal complexes with configurations counted in millions have been carried out in pursuit of this goal (Lüthi *et al.* 1984).

Such calculations can give detailed information about the energetics of chemical bonding as well as a quantitative account of excited-state energies. While it would be desirable to have a quantitative account of the molecular electronic structure, such an approach is out of the question for the majority of transition-metal complexes of interest to chemists. Chemistry and studies of chemical bonding will not be confined by such a bind; with a combination of powerful quantum theoretical techniques guided by physico-chemical intuitions, Ligand-Field Analysis succeeds in cutting through this complexity. There results a general description of the properties of materials in the ligand-field regime based on parametrized matrix elements. The cost of this approach is that no direct account of the *process* of chemical bond formation can be given; the magnetic ion is described *in situ* after all chemical bonds between it and its ligands have been formed, and after all associated charge redistributions have occurred in accordance with the Electroneutrality Principle (Pauling 1939).† Nevertheless, its claim is, that having obtained a satisfactory parametrization of the magnetism and spectroscopy of more or less any paramagnetic transition metal complex, qualitative information about the metal–ligand bonding in the complex can be derived from the

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† The Electroneutrality Principle (Pauling 1939) states that 'Stable molecules and crystals have electronic structures such that the electric charge of each atom is close to zero'. Here 'close to zero' means between -1 and $+1$, in units of the proton charge.

parameters of the model because *the model is well based theoretically*. The present writer believes that both these two approaches are worthwhile and will remain complementary for the foreseeable future.

The calculations of Hillier *et al.* (1976 a, b, Hillier and Kendrick 1976) on tetrahedral metal halide complexes $TiCl_4$ (d^0), VCl_4 (d^1) and $CoCl_4^{2-}$ (d^7) and the oxocation CrO^{3+} (d^1) provide general points of convergence between the *ab initio* and semi-empirical procedures. Firstly, the calculations used a procedure in which the basis orbitals were determined by the SCF calculation so that the orbitals were related directly to the problem at hand. Next, the order of the low-lying excited states did not correlate with the SCF one-electron orbital energies and C.I. with single and double excitations out of orbitals intimately associated with the metal ion was needed to obtain an accurate account of the first few excited states. These calculations also showed little hybridization between the metal d-orbitals and either other metal valence orbitals or ligand orbitals. Such a picture is more in keeping with classical crystal-field theory than molecular orbital theory; it is encouraging to see it made explicit in these *ab initio* C.I. calculations. Perhaps the most important result of these calculations is the relative independence of the metal ion d-orbitals from all other orbitals; this is the key to the construction of the subspace $\mathbb{H}_1$ introduced at the start of this section, and to which we now turn.

3.3. *Group product wavefunctions for the subspace* $\mathbb{H}_1$

Guided by the ideas just described, and the physics of magnetic insulators reviewed in section 2, we divide the n electrons in the fragment into *two* groups, which we label M and L, namely the N_d d-electrons corresponding to the presumed oxidation state (d^n configuration) of the metal ion (group M), and the remaining N_L electrons (group L) such that $n=N_d+N_L$, and we stipulate that N_d and N_L will be taken separately as constant. The specification of a well defined d^n-configuration for the transition-metal ion in the complex is perhaps the most characteristic feature of ligand-field theory (Jørgensen 1969, 1981) and, as discussed by Stevens (1976), is an essential step towards the construction of the lowest-energy electronic states in the crystal.

Each subset of electrons is described by a set of many-electron wavefunctions, to be discussed further below, and we construct a trial wavefunction for the n-electron fragment using the group product form (Lykos and Parr 1956, McWeeny and Sutcliffe 1976)

$$\phi_k^{N_d}(\mathbf{x}_1,\dots \mathbf{x}_n)=C\mathbb{A}^n[\Psi_{Mm}(\mathbf{x}_1,\dots \mathbf{x}_{N_d})\Psi_{Ll}(\mathbf{x}_{N_d+1},\dots \mathbf{x}_n)] \tag{22}$$

where C is a normalization constant, $\mathbb{A}^n$ makes the product antisymmetric for all permutations of the n electrons, the $\{\mathbf{x}_i\}$ are combined space ($\mathbf{r}_i$) and spin (s_i) coordinates, Ψ_{Mm} and Ψ_{Ll} are normalized antisymmetrized wavefunctions for the groups of electrons M and L with quantum numbers m and l respectively, and k is an index that picks out the combination (m, l).

A further condition on the many-electron group wavefunctions ensures that the two groups of electrons are 'independent' of each other in a sense made precise below. This condition is the *strong orthogonality* property which expresses the fact that the wavefunctions for the groups of electrons belong to disjoint subspaces. Although the wavefunctions Ψ_{Mm} and Ψ_{Ll} contain different numbers of electronic coordinates, they can always be manipulated so as to bring a common label (say 1) to the first position;

strong orthogonality is the condition that integration over this variable must give zero, i.e.

$$\int d\mathbf{x}_1 \bar{\Psi}^*_{\mathrm{M}m}(\mathbf{x}_1, \ldots \mathbf{x}_i, \mathbf{x}_j \ldots)\ \bar{\Psi}_{\mathrm{L}l}(\mathbf{x}_1, \ldots \mathbf{x}_k, \mathbf{x}_p \ldots) = 0 \tag{23}$$

It seems likely that the use of *disjoint* sets of orthogonal spin-orbitals is a necessary condition for strong orthogonality to be ensured (it is obviously sufficient).

As a result of the above we are lead to defining a basis of orthonormal spin-orbitals which is divided into two disjoint sets. For the ligand-field theory of transition-metal complexes we choose a set of five degenerate atomic d-orbitals to describe the M-group of electrons $\{\chi_i;\ i=1, \ldots 5\}$, and so write the basis as

$$\begin{array}{c|c} \mathrm{M} & \mathrm{L} \\ \chi_1, \cdots\cdots\cdots \chi_5 & \chi_6, \cdots\cdots\cdots\cdots\cdots \chi_N \\ \bar{\chi}_1, \cdots\cdots\cdots \bar{\chi}_5 & \bar{\chi}_6, \cdots\cdots\cdots\cdots\cdots \bar{\chi}_N \end{array} \tag{24}$$

where χ_i, $\bar{\chi}_i$ refer to α and β spins respectively. The choice of these atomic orbitals will be deferred until later (see after equation (31)). The remaining orbitals in the basis need not be characterized explicitly since all that is needed for the present discussion is the knowledge that such a basis can be constructed, and that Slater determinants constructed out of the M and L subsets of spin-orbitals are automatically strong-orthogonal. The basis (24) is needed explicitly only if a numerical all-electron calculation is to be attempted.

If the wavefunctions in equation (22) are constructed from the basis (24) if follows that the expectation value of $\bar{H}$ for a wavefunction of this type may be written in 'separable' form (McWeeny and Sutcliffe 1976)

$$\mathscr{E}_k = \langle \phi_k^{N_\mathrm{d}} | \hat{H} | \phi_k^{N_\mathrm{d}} \rangle = E_{\mathrm{M}m} + E_{\mathrm{L}l} \tag{25}$$

where,

$$E_{\mathrm{M}m} = \int d\tau_\mathrm{M} \bar{\Psi}^*_{\mathrm{M}m} \hat{\mathscr{H}}_\mathrm{M} \bar{\Psi}_{\mathrm{M}m} \tag{26 a}$$

$$E_{\mathrm{L}l} = \int d\tau_\mathrm{L} \bar{\Psi}^*_{\mathrm{L}l} \hat{\mathscr{H}}_\mathrm{L} \bar{\Psi}_{\mathrm{L}l} \tag{26 b}$$

$$\hat{\mathscr{H}} = \sum_{\mu=N_\mathrm{d}+1}^{n} \hat{H}_N(\mu) + \frac{1}{2} \sum_{\mu,\nu=N_\mathrm{d}+1}^{n} 1/r_{\mu\nu} \tag{26 c}$$

$$\hat{\mathscr{H}}_\mathrm{M} = \sum_{\kappa=1}^{N_\mathrm{d}} \hat{\mathscr{H}}(\kappa)_{\mathrm{core}} + \frac{1}{2} \sum_{\kappa,\lambda=1}^{N_\mathrm{d}}{}' 1/r_{\kappa\lambda} \tag{26 d}$$

where

$$\hat{\mathscr{H}}(\kappa)_{\mathrm{core}} = \hat{H}_\mathrm{N}(\kappa) + \hat{J}^{\,l}_\mathrm{L}(\kappa) - \hat{K}^l_\mathrm{L}(\kappa). \tag{26 e}$$

$\hat{J}^l_\mathrm{L}$ and $\hat{K}^l_\mathrm{L}$ are Coulomb and exchange operators respectively, which are defined by formulae specifying their action on a one-electron spin-orbital ψ,

$$\hat{J}^l_\mathrm{L} \psi(\mathbf{x}_1) = \int d\mathbf{x}_2 1/r_{12}\, \rho^\mathrm{L}_1(ll : \mathbf{x}_2, \mathbf{x}_2) \psi(\mathbf{x}_1) \tag{27 a}$$

$$\hat{K}^{l}_{\mathrm{L}}\psi(\mathbf{x}_1)=\int d\mathbf{x}_2 1/r_{12}\,\rho^{\mathrm{L}}_1(ll:\mathbf{x}_1,\mathbf{x}_2)\psi(\mathbf{x}_2); \tag{27b}$$

$\rho^{\mathrm{L}}_1(ll:\mathbf{x}_1,\mathbf{x}_2)$ is a general matrix element of the first-order reduced density operator constructed from the many-electron wavefunction $\Psi_{\mathrm{L}l}$.

In equation (26), $E_{\mathrm{L}l}$ is the energy of the N_{L} electrons of the L subset, described by the wavefunction $\Psi_{\mathrm{L}l}$, *excluding* any interaction with the M group of electrons, while $E_{\mathrm{M}m}$ is the energy of the N_{d} electrons of the M subset described by the wavefunction $\Psi_{\mathrm{M}m}$ under an effective field due to the L electrons. A well defined variational procedure, that leads to a self-consistent choice of the $\{\Psi_{\mathrm{M}m},\Psi_{\mathrm{L}l}\}$ minimizing the energy $\mathscr{E}_k$, can be based on the above equations provided only that the condition of strong orthogonality is preserved in the variations. The wavefunctions $\{\Psi_{\mathrm{M}m}\}$ will be optimized functions for the N_{d} d-electrons in the effective field provided by the *ground state* of the L group electrons, Ψ_{Lo} (the diamagnetic environment of the metal ion). Similarly the $\{\Psi_{\mathrm{L}l}\}$ can be assumed to be optimized functions for the L group of electrons in the average potential field of the d-electrons described by Ψ_{Mo}. The optimization of the many-electron fragment wavefunction $\phi^{N_{\mathrm{d}}}_k$ is constrained by the condition that N_{d}, N_{L} remain separately constant and the interactions *between* the two groups of electrons are thus treated in a self-consistently averaged way. Nevertheless, if the division of electrons into the two groups is physically realistic, the procedure can be expected to lead to wavefunctions for the ground state and low-lying excited states of the fragment that incorporate a good description of the chemical bonding between the metal ion and its ligands.

Once the density matrix ρ^{L}_1 is obtained from the optimized wavefunction Ψ_{Lo}, the effective hamiltonian $\mathscr{H}_{\mathrm{M}}$, equation (26 d) is completely specified. The wavefunctions $\{\Psi_{\mathrm{M}m}\}$ can be expanded in terms of Slater determinants constructed from the M subset of spin-orbitals $\{\chi\}$,

$$||\Omega_u|\rangle=\mathscr{A}^{N_{\mathrm{d}}}|\chi_1,\ldots\ldots\ldots\bar{\chi}_5\rangle \tag{28}$$

$$|\Psi_{\mathrm{M}m}\rangle=\sum_u C^{\mathrm{M}}_{mu}||\Omega_u|\rangle. \tag{29}$$

The corresponding eigenvalues, the energies of the d-electron states in this approximation, are the solutions of the secular problem

$$(\mathbf{H}_{\mathrm{M}}-E_{\mathrm{M}m}\mathbf{1})\mathbf{C}^{\mathrm{M}}_m=0 \tag{30}$$

where

$$(\mathbf{H}_{\mathrm{M}})_{uu'}=\langle|\Omega_u||\mathscr{H}_{\mathrm{M}}||\Omega_{u'}|\rangle. \tag{31}$$

The reduction of these determinantal matrix elements to combinations of orbital matrix elements is described by Gerloch *et al.* (1981). The matrix elements of the two-electron operator in $\hat{\mathscr{H}}_{\mathrm{M}}$ give rise to the usual Slater–Condon F_k integrals ($k=0,2,4$) for the d^n configuration, while the one-electron terms give rise to 'ligand-field' potential and spin–orbit coupling matrices. Terms, including relativistic ones, that are rotationally invariant with respect to the metal nucleus as origin can be used to define the atomic d-orbitals, i.e. the d-orbitals in the basis (24) should be thought of as referring to a given d^n configuration for a transition-metal ion *in its diamagnetic* environment. In a fairly obvious sense this is an optimal choice of the d-orbitals, and their construction parallels the method of calculation reported by Hillier *et al.* (1976 a).

The group product function method amounts to a choice of a set of trial wavefunctions motivated by physical considerations; if we set $k=(m, 0)$, i.e. restrict the L electrons to their spin singlet ground state, the resulting finite set of wavefunctions $\{\phi_k^{N_d}: k=m, 0\}$ spans a finite-dimensional subspace that can be identified with the subspace $\mathbb{H}_1$ introduced in section 3.1. Furthermore, the hamiltonian matrix $\mathbf{H}_M$ in equation (31) must be identified with the matrix $\mathbf{H}_1$ in equation (16); it is the projection of the full n-electron hamiltonian (20), (21) on the subspace of wavefunctions $\{\phi_k^{N_d}\}$ that cover $\mathbb{H}_1$. In order to make a satisfactory identification of the *theoretical* form of the ligand-field hamiltonian $\mathbf{H}_{\text{L.F.}}$ we must next investigate the coupling between the functions $\{\phi_k^{N_d}\}$ and the complementary subspace $\mathbb{H}_2$ under the action of the full n-electron hamiltonian, $\hat{H}$, and this is the concern of the next section.

3.4. *Partitioning and the chain formalism*

The functions $\{\phi_k^{N_d}: k=m, 0\}$ constructed according to the procedure of section 3.3 form an orthonormal basis for the subspace $\mathbb{H}_1$,

$$\langle \phi_k^{N_d} | \phi_{k'}^{N_d} \rangle = \delta_{kk'}. \tag{32}$$

These wavefunctions describe a manifold of degenerate, or near-degenerate, electronic states associated with the different arrangements of the d-electrons on the transition-metal ion in its diamagnetic environment; we refer to them as 'ligand-field states'. A basis for the subspace complementary to $\mathbb{H}_1$ can be defined as the set of functions of group product type specified by equation (22) with either $N_M = N_d$, $l \neq 0$, or all possible values of $N_M \neq N_d$. The former correspond to many-electron wavefunctions describing excitations of the diamagnetic environment of the metal ion, whereas the latter describe either charge-transfer states involving exchanges between the d-electron subset (M) and the ligand electrons, or states involving interactions between the metal core and valence s, p-electrons and the metal d-electrons. For the moment we choose them as an orthonormal set $\{\Delta_i\}$ orthogonal to the ligand-field states,

$$\langle \phi_k^{N_d} | \Delta_i \rangle = 0 \tag{33}$$

$$\langle \Delta_i | \Delta_j \rangle = \delta_{ij}. \tag{34}$$

A general matrix element of the effective hamiltonian $\mathscr{H}(E)$, equation (16), written out in full, is then

$$[\mathscr{H}(E)]_{kk'} = \langle \phi_k^{N_d} | \left\{ \hat{H} + \sum_{i,j} \hat{H} | \Delta_i \rangle G(E)_{ij} \langle \Delta_j | \hat{H} \right\} | \phi_{k'}^{N_d} \rangle \tag{35}$$

where

$$G(E)_{ij} = \left\langle \Delta_i \left| \frac{1}{E\hat{1} - \hat{H}} \right| \Delta_j \right\rangle \tag{36}$$

is the (i,j) matrix element of the resolvent of $\hat{H}$ evaluated in the subspace $\mathbb{H}_2$. To make progress with these formidable expressions we need to develop some appreciation of the orthonormal set $\{\Delta_i\}$. If our choice of the space of ligand-field states is reasonable, most of the wavefunctions belongings to $\mathbb{H}_2$ should be irrelevant since our concern is purely with the effect these wavefunctions have on the *low-lying* electronic states associated with the d-electrons. Thus we need a procedure that imposes an ordering on the set $\{\Delta_i\}$ determined by the strength of interaction with $\mathbb{H}_1$ under the influence of the n-electron hamiltonian.

The analysis proposed here is based on the following observation (Haydock *et al.* 1972, 1975, Haydock 1980, Heine 1980): given any hamiltonian $\hat{H}$ and a trial wavefunction $|u_0\rangle$ it is always possible to construct a 'chain' representation of the quantum mechanics of the system. By this we mean that we can construct an orthonormal sequence of states $\{|u_n\rangle\}$ such that they satisfy a three-term recurrence relation, generated by $\hat{H}$, starting from $|u_0\rangle$,

$$\hat{H}|u_n\rangle = a_n|u_n\rangle + b_{n+1}|u_{n+1}\rangle + b_{n-1}|u_{n-1}\rangle \tag{37}$$

with $b_{-1}=0$, $b_0=1$. One can interpret this equation by saying that the coefficients $\{a_n, b_n\}$ give a matrix representation of $\hat{H}$ that is *tridiagonal* (Jacobi form), the $\{a_n\}$ being the diagonal elements, and the $\{b_n\}$ the off-diagonal ones; it is also the basis of the Lanczos method of finding the eigenvalues of a hermitian matrix (Paige 1972).

Let us take $\hat{H}$ to be the full n-electron hamiltonian for the transition-metal complex, equations (20), (21) and set $|u_0\rangle = |\phi_k^{N_d}\rangle$ for some quantum number k, and consider the first step of the recurrence. We have

$$\hat{H}|\phi_k^{N_d}\rangle = a_{0k}|\phi_k^{N_d}\rangle + b_{1k}|u_{1k}\rangle \tag{38}$$

where a_{0k}, b_{1k} and $|u_{1k}\rangle$ are to be determined. These quantities are given by (Haydock 1980)

$$a_{0k} = \langle\phi_k^{N_d}|\hat{H}|\phi_k^{N_d}\rangle \tag{39}$$

$$|u_{1k}\rangle = b_{1k}^{-1}(\hat{H} - a_{0k})|\phi_k^{N_d}\rangle \tag{40}$$

$$b_{1k} = \langle u_{1k}|\hat{H}|\phi_k^{N_d}\rangle. \tag{41}$$

Thus a_{0k} is the average energy of the wavefunction $|\phi_k^{N_d}\rangle$ under the action of the hamiltonian $\hat{H}$. If the starting state is chosen as the optimized solution of the equations described in section 3.3, $a_{0k} = \mathscr{E}_k$, equation (25); in this case, the wavefunctions $\{\phi_k^{N_d}\}$ satisfy the analogue of Brillouin's theorem for the SCF-Hartree–Fock one-electron molecular orbitals (McWeeny and Sutcliffe 1976)

$$\langle\phi_k^{N_d}|\hat{H}|\phi_{k'}^{N_d}\rangle = 0 \begin{cases} k = m, 0 \text{ and} \\ k' = m', 0 \text{ or } m, l \end{cases} \tag{42}$$

essentially because they are solutions of a self-consistent problem. For such starting wavefunctions $|u_0\rangle$, we obtain a particularly transparent chain representation.

When we operate with the hamiltonian $\hat{H}$ on a wavefunction $|\phi_k^{N_d}\rangle$ we obtain a new state that can be thought of as a linear combination of wavefunctions that are coupled to $|\phi_k^{N_d}\rangle$ under the action of $\hat{H}$, including obviously $|\phi_k^{N_d}\rangle$ itself. The subtraction of the term $a_{0k}|\phi_k^{N_d}\rangle$ in equation (40) eliminates this contribution and, *if equation (42) is valid*, the resulting wavefunction $|u_{1k}\rangle$ *belongs purely to the subspace* $\mathbb{H}_2$; its normalization constant b_{1k}, equation (41), is the matrix element connecting $|\phi_k^{N_d}\rangle$ to this unique wavefunction in $\mathbb{H}_2$. On the other hand, requiring normalization to unity of $|u_{1k}\rangle$ in equation (40) shows that

$$\begin{aligned} b_{1k}^2 &= \langle(\hat{H} - a_{0k})\phi_k^{N_d}|(\hat{H} - a_{0k})\phi_k^{N_d}\rangle \\ &= \langle\phi_k^{N_d}|\hat{H}^2|\phi_k^{N_d}\rangle - \mathscr{E}_k^2 \end{aligned} \tag{43}$$

which identifies the matrix element b_{1k}^2 as the variance of the hamiltonian $\hat{H}$ in the state $|\phi_k^{N_d}\rangle$.

The mean energy of the wavefunction $|u_{1k}\rangle$, and all further chain states $|u_{nk}\rangle$, are calculated in an exactly analogous fashion to a_{0k} by putting

$$a_{nk}=\langle u_{nk}|\hat{H}|u_{nk}\rangle;\ n=1,2,\ldots\ldots\,; \tag{44}$$

a_{1k} is expected to be *significantly different* from $a_{0k}=\mathscr{E}_k$ because equation (42) shows that the wavefunctions $|u_{1k}\rangle$ constructed from optimized ligand-field states $\{\phi_k^{N_d}\}$ by this method must describe either excitations of the diamagnetic environment coupled with changes in the electronic state of the d-electrons and/or changes in the d^n configuration of the metal ion. The many-electron wavefunction $|u_{1k}\rangle$ is coupled to a new wavefunction $|u_{2k}\rangle$ by the chain equation, (37), and in general the recursion continues indefinitely linking any chain state $|u_n\rangle$ to (only) its immediate neighbours $|u_{n\pm 1}\rangle$; however, the essential point is that the influence of the wavefunctions $|u_{nk}\rangle$ on the starting state $|u_{0k}\rangle=|\phi_k^{N_d}\rangle$ becomes progressively less as n increases, so that the recursion is a highly efficient way of selecting the significant states in the complementary subspace $\mathbb{H}_2$. This method could offer significant advantages for future *ab initio* computational investigations of the ligand-field regime.

It will be appreciated from the foregoing discussion that all the chain parameters $\{a_{nk}, b_{nk}\}$ are calculated by operating with the full n-electron hamiltonian, $\hat{H}$, on the optimized ligand-field state $|\phi_k^{N_d}\rangle$; they may in fact be interpreted in terms of the *power moments* of the hamiltonian, $\mu_{r,k}$, evaluated with respect to our chosen starting wavefunction,

$$\mu_{r,k}=\langle\phi_k^{N_d}|\hat{H}^r|\phi_k^{N_d}\rangle \tag{45}$$

for example,

$$\mu_{0,k}=1,\ \mu_{1,k}=a_{0k} \tag{46 a}$$

$$\mu_{2,k}-\mu_{1,k}=b_{1k}^2 \tag{46 b}$$

$$\mu_{1,k}+\frac{\mu_{1,k}\mu_{2,k}-\mu_{3,k}}{\mu_{2,k}-\mu_{1,k}^2}=a_{1k} \tag{46 c}$$

and these formulae again show how the restriction of the trial wavefunction to the subspace $\mathbb{H}_1$ forces us to deal with the multi-electron operators that arise from powers of the hamiltonian. From the calculational point of view the chain parameters are to be greatly preferred because moments grow very rapidly and easily lead to numerically ill-conditioned equations.

The chain wavefunction $|u_{1k}\rangle$ describes completely the many-electron environment of the ligand-field state $|\phi_k^{N_d}\rangle$ in the transition metal complex; the *strength* of the coupling between the two states is measured by the magnitude of the matrix element b_{1k} relative to their energy separation, $|a_{0k}-a_{1k}|$. When this ratio is small compared to unity, a perturbation theory argument shows that a good estimate of the energy of the eigenstate of $\hat{H}$ corresponding† to $|\phi_k^{N_d}\rangle$ is given by

$$E_k\approx\mathscr{E}_k+\frac{b_{1k}^2}{(a_{0k}-a_{1k})} \tag{47}$$

where $\mathscr{E}_k$ is obtained from (25), and the perturbation term (which need not be small compared to $\mathscr{E}_k$) is expressed in terms of the chain parameters $\{a_{0k}, a_{1k}, b_{1k}\}$. A comparison of equation (35) and equation (47) written out in full is in order here;

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† This is the eigenstate with the *largest* overlap with $|\phi_k^{N_d}\rangle$.

equation (47) shows that, to this accuracy, the matrix $\mathscr{H}(E)$ is diagonal with eigenvalues given by

$$E_k \approx \langle \phi_k^{N_d} | \hat{H} | \phi_k^{N_d} \rangle + \langle \phi_k^{N_d} | \hat{H} | u_{1k} \rangle G(a_{0k})_{11} \langle u_{1k} | \hat{H} | \phi_k^{N_d} \rangle \tag{48}$$

where $|\phi_k^{N_d}\rangle$ is optimized ligand-field state (section 3.3), $|u_{1k}\rangle$ is the unique wavefunction in $\mathbb{H}_2$ that is coupled directly to $|\phi_k^{N_d}\rangle$ (selected by the chain equation (37)) and we have evaluated the resolvent matrix element

$$G(E)_{11} = \left\langle u_{1k} \left| \frac{1}{E\hat{1} - \hat{H}} \right| u_{1k} \right\rangle \tag{49}$$

at energy $E = a_{0k} (= \mathscr{E}_k)$ with the approximation

$$G(a_{0k})_{11} \approx \frac{1}{(a_{0k} - a_{1k})} \tag{50}$$

where $a_{1k} \equiv \langle u_{1k} | \hat{H} | u_{1k} \rangle$, equation (44), (Haydock 1980, Woolley 1985).

Equation (48) has something of the appearance of the 'crystal-field' formulae derived by Stevens (1976); the difference is that (48) refers to a particular eigenvalue E_k, whereas Stevens obtained a hamiltonian that is to be diagonalized to yield all low-lying eigenvalues simultaneously. This of course must be the 'ligand-field' hamiltonian $\mathbf{H}_{\mathrm{L.F.}}$ that we aim to derive from equation (35); to do this we need to relax the condition (42) and investigate the matrix $\mathscr{H}(E)$, equation (35), in a more general basis.

When equation (42) is relaxed there are off-diagonal matrix elements of $\hat{H}$ between group-product wavefunctions with $l=0$, and we need the following generalization of the chain idea. The functions in equation (22) with $l=0$, $\bar{\Psi}_{\mathrm{L0}}$ the optimized ground-state wavefunction for the diamagnetic environment of the metal ion, and the $\{\bar{\Psi}_{\mathrm{M}m}\}$ constructed as in equation (29), form an orthonormal basis $\{|\phi_k^0\rangle\}$ for the subspace $\mathbb{H}_1$ of dimension $d = {}^{N'}C_n$ (section 3.1). Instead of a starting state for the chain as in equation (37), we now select this subspace as a starting subspace $[\mathbb{O}]$ for a generalized ('vector') chain; the effect of the hamiltonian $\hat{H}$ on the subspace $[\mathbb{O}]$ is to create another subspace, with the same dimensionality, which we denote symbolically by [1],

$$\hat{H}[\mathbb{O}] \rightarrow [1]. \tag{51}$$

In terms of the basis $\{|\phi_k^0\rangle\}$ of $[\mathbb{O}]$ we see that for each k, $\hat{H}|\phi_k^0\rangle$ is an unnormalized combination, say $|\psi_k^1\rangle$, of wavefunctions that interact with $|\phi_k^0\rangle$. Having given up the condition (42), $|\psi_k^1\rangle$ will contain wavefunctions in $[\mathbb{O}]$ other than purely $|\phi_k^0\rangle$ itself. Guided by the chain formalism reviewed above however, we can construct the subspace so that it is orthogonal to $[\mathbb{O}]$; this means that we construct an orthonormal basis for [1], say $\{|\psi_1^1\rangle, \ldots |\psi_{\mathrm{d}}^1\rangle\}$, that is orthogonal to each basis wavefunction for $[\mathbb{O}]$. We let

$$\hat{H}|\phi_k^0\rangle = (\mathbf{a}_{[\mathbb{O}]})_{kn} |\phi_n^0\rangle + (\mathbf{b}_{[1]})_{kn} |\phi_n^1\rangle \tag{52}$$

where $\mathbf{a}_{[\mathbb{O}]}$ and $\mathbf{b}_{[1]}$ are matrices that are determined as follows. We may rearrange (52) to give

$$|\psi_k^1\rangle \equiv (\mathbf{b}_{[1]})_{kn} |\phi_n^1\rangle = \hat{H}|\phi_k^0\rangle - (\mathbf{a}_{[\mathbb{O}]})_{kn} |\phi_n^0\rangle \tag{53}$$

and then require

$$\langle \phi_m^0 | \phi_k^1 \rangle = 0 \text{ for all } m \text{ and } k \tag{54}$$

so that we must have

$$(\mathbf{a}_{[\mathbb{O}]})_{mn} = \langle \phi^0_m | \hat{H} | \phi^0_n \rangle \tag{55}$$

which is the matrix representation of the hamiltonian in the subspace $[\mathbb{O}]$. On the other hand, from equations (52), (54) we have,

$$(\mathbf{b}_{[1]})_{mn} = \langle \phi^1_m | \hat{H} | \phi^0_n \rangle \tag{56}$$

so that the elements of the $d \times d$ matrix $\mathbf{b}_{[1]}$ are the matrix elements describing the coupling between the subspaces $[\mathbb{O}]$ and $[1]$. The subspace $[1]$ is coupled to $[\mathbb{O}]$ and to another orthogonal subspace $[2]$, and this 'vector' chain can be extended in an obvious fashion,

$$[\mathbb{O}] \leftrightarrow [1] \leftrightarrow [2] \leftrightarrow [3] \leftrightarrow \ldots\ldots\ldots \leftrightarrow [\mathbb{N}] \leftrightarrow \ldots$$

The result of these operations is that the hamiltonian is given a tridiagonal block matrix representation, each diagonal block $\mathbf{a}_{[\mathbb{N}]}$ referring to the matrix elements of the hamiltonian within the subspace $[\mathbb{N}]$, and the off-diagonal blocks describing the coupling between adjacent subspaces

$$\mathbf{H} = \begin{bmatrix} \mathbf{a}_{[\mathbb{O}]} & \mathbf{b}_{[1]} & & \\ \mathbf{b}_{[1]} & \mathbf{a}_{[1]} & \mathbf{b}_{[2]} & \mathrm{O} \\ & \mathbf{b}_{[2]} & \mathbf{a}_{[2]} & \mathbf{b}_{[3]} \\ & & \mathbf{b}_{[3]} & \mathbf{a}_{[3]} \\ & \mathrm{O} & & \end{bmatrix} \tag{57}$$

On the other hand the Hilbert space is given the decomposition

$$\mathbb{H}_1 = [\mathbb{O}]$$
$$\mathbb{H}_2 = [1] \oplus [2] \oplus [3] \oplus \ldots [\mathbb{N}] \oplus \ldots$$

such that increasing values of $\mathbb{N}$ are associated with decreasing indirect perturbations of the subspace $[\mathbb{O}]$. By analogy with the argument leading to (48), an approximate form for the effective hamiltonian (35) can now be written down by partitioning $\mathbf{H}$ and truncating the expansion,

$$\mathscr{H}(E) \simeq \mathbf{a}_{[\mathbb{O}]} + \mathbf{b}_{[1]}(E\mathbf{1}_d - \mathbf{a}_{[1]})^{-1}\mathbf{b}_{[1]} + \ldots. \tag{58}$$

Without any loss of generality we may take the matrix $\mathbf{a}_{[1]}$ in a diagonal representation,

$$(\mathbf{a}_{[1]})_{nn'} = \mathbf{a}_{1n}\delta_{nn'} \tag{59}$$

so that if (58) is evaluated at some average energy $\bar{E}^0$ (cf. section 3.1 (vii)) calculated from the energies of the ligand-field states, we have an expression that is strictly analogous to the 'crystal-field' hamiltonian discussed by Stevens (1976, 1985):

$$(\mathscr{H}(\bar{E}^0))_{kk'} = \left\langle \phi^0_k \middle| \left\{ \hat{H} + \sum_n^d \hat{H} \frac{|\phi^1_n\rangle\langle\phi^1_n|}{\bar{E}^0 - a_{1n}} \hat{H} \right\} \middle| \phi^0_{k'} \right\rangle \tag{60}$$

expressed in terms of the ligand-field states and the most important contribution from $\mathbb{H}_2$. $\bar{E}^0$ could be taken as the mean of the eigenvalues of $\mathbf{a}_{[\mathbb{O}]}$, i.e.

$$\bar{E}^0 = d^{-1}\,\mathrm{Tr}\,(\mathbf{a}_{[\mathbb{O}]}) \tag{61}$$

where d is the dimensionality of the matrix $\mathbf{a}_{[O]}$. If we bring $\mathbf{a}_{[O]}$ to diagonal form, we shall also diagonalize $\mathscr{H}(\bar{E}^0)$ because any given wavefunction $|\phi_k^0\rangle$ in $[\mathbb{O}]$ will then give its own scalar chain as in equation (37), so that $|\phi_n^1\rangle = |u_{1k}\rangle\delta_{nk}$, and (60) reduces essentially to the expression (47) obtained earlier. In general, the wavefunctions $\{|\phi_n^1\rangle\}$ can be expressed as linear combinations of the wavefunctions $\{|u_{1n}\rangle\}$ obtained from such scalar chains, and hence the $\{|\phi_n^1\rangle\}$ in equation (60) have the same physical interpretation as the $\{|u_{1n}\rangle\}$ (see after (44)).

3.5. *The Ligand-Field hamiltonian*

In the discussion so far we have referred to the matrix representation of the full n-electron hamiltonian projected onto the subspace $\mathbb{H}_1$ as the 'crystal-field' or 'ligand-field' hamiltonian. This is not quite standard terminology since the conventional ligand-field hamiltonian involves explicitly only the metal ion d-electrons, but there should be no real confusion. This practice has been followed so as to demonstrate the relationship between *ab initio* electronic structure theory and the ligand-field model.

We pass to 'ligand-field theory' proper by integrating out the dependence on the L set of electrons; it is evident from both (35) and (60) that since $|\phi_k^{N_d}\rangle$ and $|\phi_{k'}^{N_d}\rangle$ involve the ground-state wavefunction Ψ_{L_0}, the resulting effective hamiltonian for the d-electrons is again a functional of the ground-state density matrix $\rho_1^L(0\,0:\mathbf{x}_1,\mathbf{x}_2)$ as in section 3.3. Thus we can still write an eigenvalue equation in the form of equation (30) with a modified matrix $\tilde{\mathbf{H}}_M$ labelled by the Slater determinants $\{|\Omega_u|\}$ constructed from the metal ion d-orbitals

$$(\tilde{\mathbf{H}}_M)_{uu'} = \langle|\Omega_u|\,|\mathscr{H}_M + \hat{h}_M|\,|\Omega_{u'}|\rangle. \tag{62}$$

For comparison with section 3.4, it may be noted that $\mathbf{H}_M$, equation (31), is equivalent to the matrix $\mathbf{a}_{[O]}$, equation (55), while the additional term in (62), $\hat{h}_M$, is derived from the second factor in (35), or (60), and contains $1-,\ldots N_d$-electron operators (Gerloch *et al.* 1981).

It is helpful to recall how Ligand-Field Analysis is carried out in practice. A convenient choice of the labels for the matrix elements of $\tilde{\mathbf{H}}_M$ are the angular momentum quantum numbers L, S, J, M_J referring to the d^n-configuration; these are what are actually used in the computational package described by Gerloch (1984). The many-electron matrix elements can then be reduced by standard vector-coupling techniques to combinations of d-orbital matrix elements labelled by the atomic orbital quantum numbers l, m_l, with $l=2$. The orbital matrix elements are the quantities we parametrize. In this reduction it is conventionally *assumed* that the Slater determinants labelled by u and u' in (62) *differ by no more than two spin-orbitals* because the ligand-field hamiltonian $\hat{H}_{\mathrm{L.F.}}$, which is restricted to terms referring only to the electrons of the d^n-configuration (Griffith 1961), is thought to have a structure like (26), e.g.

$$\text{“}\hat{H}_{\mathrm{L.F.}}\text{”} = \sum_{i=1}^{N_d} \hat{V}(i)_{\mathrm{L.F.}} + \sum_{i=1}^{N_d} \hat{V}(i)_{\mathrm{s.o.}} + \sum_{i>j}^{N_d} 1/r_{ij} \tag{63}$$

The matrix representation of (26) in the group product wavefunction basis, $\mathbf{H}_M$, equation (31), has precisely the form expected of ligand-field theory based on (63). In the light of the foregoing discussion however it wll be clear that equation (63) is a simplification of the full many-electron theory of the transition-metal ion in its diamagnetic environment; having analysed the latter in detail in sections 3.3 and 3.4, we are in a position to characterize the approximations involved in setting up a ligand-field model.

The effective hamiltonain ($\mathscr{H}_M + \hat{h}_M$) generated by the partitioning procedure, and hence the matrix $\tilde{\mathbf{H}}_M$, equation (62), has a more complicated structure than equation (63) because of the term $\hat{h}_M$. The conventional approach need not imply that the contributions of the additional multi-electron operators to (62) are simply neglected, for as shown by Freed in a different context (Freed 1974), matrix elements of many-electron operators can be partially subsumed in the matrix elements of *effective* one- and two-electron operators. Several consequences follow from this interpretation.

(i) The conventional ligand-field hamiltonian can be given an explicit form by reference to the *ab initio* theory which justifies the *structure* of (63) in terms of sums of *effective one- and two-electron operators.*

(ii) More explicitly, the Coulomb operator in (63) must be modified to take account of the fact that the electrostatic interaction between the d-electrons takes place in the presence of the L set of electrons (the diamagnetic environment); this can be described in terms of a spatially varying dielectric constant, and thought of in more physical terms as *screening*. The effective interelectron repulsion operator should still depend on interelectron separations and so can be treated by the Slater–Condon–Shortley theory.

(iii) The effective one-electron 'ligand-field' potential, $\hat{V}(i)_{\mathrm{L.F.}}$ contains the expected electrostatic terms due to the ligands as in equation (26) together with additional terms that originate from matrix elements of the electronic kinetic energy operator and the exchange-correlation potential (Stevens 1976, 1985). The 'mixed' nature of these one and two-electron effective operators can be inferred from the occurrence of the power moments (45), (46) of the full n-electron hamiltonian in the chain formalism used to calculate the corrections to the group product wavefunction calculation in section 3.3. If we write this hamiltonian as a sum of kinetic ($\hat{T}$) and potential ($\hat{V}$) energy operators, $\hat{H} = \hat{T} + \hat{V}$, then clearly the binomial expansion of $\hat{H}^r$ contains cross-terms between powers of $\hat{T}$ and $\hat{V}$.

(iv) Freed's argument (Freed 1974) also implies that the orbital matrix elements should, in principle, acquire a dependence on the particular electron configuration from which they were derived; that is, every low-lying electronic state of the complex described by the effective hamiltonian $\mathscr{H}(E)$ should have its own set of ligand-field parameters. Such a scheme, if strictly implemented, would have no value in practice as far as parametrization is concerned.

This discussion leads to the view that the relationship of the effective hamiltonian theory described above to the conventional ligand-field model is necessarily approximate because the latter *describes the complete manifold of d-electron states with a single set of parameters* for *effective* one and two-electron operators. The success of ligand-field theory is therefore seen to depend on

(*a*) an assumption of anonymous configuration parentage for the ligand-field parameters (Gerloch *et al.* 1981), and
(*b*) the neglect of some multi-electron interactions.

On these grounds, the ligand-field hamiltonian in the basis of Slater determinants $\{|\Omega_u|\}$ can be written

$$[\mathbf{H}_{\mathrm{L.F.}}]_{uu'} = [\mathbf{V}_{\mathrm{L.F.}} + \mathbf{V}_{\mathrm{s.o.}} + \mathbf{V}_{\mathrm{ee}}]_{uu'} \tag{64}$$

where u and u' differ by no more than *two* spin-orbitals, and the contributions to (64) have to be interpreted in the light of (i)–(iv) above rather than being taken directly from equation (63).

4. Parametrization of the Ligand-Field hamiltonian

In the previous section (section 3) we saw that the ligand-field hamiltonian, $\hat{H}_{\mathrm{L.F.}}$, can be taken to involve effective one- and two-electron operators such that the result is equation (64) when we calculate the matrix elements of $\hat{H}_{\mathrm{L.F.}}$ in a basis of Slater determinants $\{|\Omega_u|\}$ constructed from the metal-ion valence d-orbitals. In applications of Ligand-Field Analysis, the ligand-field hamiltonian $\mathbf{H}_{\mathrm{L.F.}}$ is constructed through parametrization of *orbital* matrix elements which are then combined into the determinantal many-electron matrix elements using standard vector coupling techniques (Gerloch 1984). The main features of the orbital matrix element structure derived from the operator $\hat{\mathscr{H}}_{\mathrm{M}}$ were summarized in section 3.3 (see after equation (31)) and apply to the ligand-field hamiltonian related to the effective operator $\hat{\mathscr{H}}_{\mathrm{M}}+\hat{h}_{\mathrm{M}}$ discussed in section 3.5; the d-orbital basis referred to in section 3.5 (and in the following) is the *same* as in section 3.3.

The modified interelectron repulsion operator in section 3.5 is again parametrized in terms of the Slater–Condon F_k integrals ($k=0,2,4$). These quantities must be expected to be different from the corresponding 'free-ion' values for the same d^n-configuration of the metal ion because (*a*) the radial parts of the d-orbitals in the complex differ from those in the isolated ion, and (*b*) the 'interelectron repulsion' operator is an effective operator that refers to the d-electrons of the ion in a specific diamagnetic environment of ligands. Both factors contribute to Jørgensen's *nephelauxetic effect* (Jørgensen 1971). The spin–orbit coupling is parametrized in terms of a spin–orbit coupling constant for the d-electrons and this too will be different from the 'free-ion' value for much the same reasons. Finally, the one-electron ligand-field potential operator $\hat{V}_{\mathrm{L.F.}}$ (which hereafter we write as $\hat{V}$) gives rise to a 5×5 hermitian matrix, $\mathbf{V}$, in the d-orbital basis, and the 15 independent matrix elements of this matrix must be parametrized. This is the 'ligand-field potential' matrix referred to in section 2; its parametrization is the main concern of this section. After introducing the Cellular Ligand-Field (CLF) model, the structure of $\mathbf{V}$ is studied using the chain formalism developed in section 3.4; then the cellular decomposition of the matrix $\mathbf{V}$ leads to the introduction of the $\{e_k^l\}$-parameters on which the chemical bonding interpretation is based.

4.1. *The Cellular Ligand-Field model*

The Cellular Ligand-Field model (CLF) is a descendent of Schäffer and Jørgensen's Angular Overlap Model (AOM). Both are concerned with the construction and chemical interpretation of the matrix $\mathbf{V}$. The early crystal-field approach, which was concerned mainly with octahedral and tetrahedral species, aimed to parametrize the matrix elements $V_{kk'}$ directly. For highly symmetrical transition-metal complexes the point-group symmetry reduces the number of independent matrix elements required; for octahedral ML_6 complexes, there is only one independent matrix element, Δ_{oct}. The majority of modern chemical studies however involve transition-metal complexes with little or no point-group symmetry, for which the traditional approach is scarcely feasible. Moreover, as noted in section 2, the global parametrization conveys little information about the chemical bonding between the metal ion and its ligands, something of central interest to chemists. By contrast the AOM, and its descendant the CLF model, aim to incorporate chemical bonding ideas in the ligand-field formalism by focusing on individual metal–ligand interactions in the complex. Such an approach utilizes the local pseudosymmetry of the metal–ligand bond, classifying interactions as

σ or π, and does not rely on the presence of any particular global point-group symmetry in the complex.

In the original formulation of the AOM (Jørgensen *et al.* 1963, Schäffer and Jørgensen 1958, 1965) it was assumed that the matrix $\mathbf{V}$ could be formed by simple addition of contributions $\{\mathbf{v}^l\}$ from each ligand l considered separately; if due regard is paid to the geometrical disposition of the ligands in the complex, the matrices $\{\mathbf{v}^l\}$ can be taken to be diagonal with eigenvalues $\{e_k^l\}$, referred to as 'the e-parameters' for the complex. The practical implementation of the AOM scheme is usually consistent with this assumption, although there are complexes, for example planar 4-coordinate species, which cannot be satisfactorily treated in this way.

Recent theoretical work has sought to characterize the *theoretical structure* of the matrix $\mathbf{V}$ by relating it to a properly formulated quantum-mechanical theory, and it is this theoretical approach which we now refer to as the CLF model (Woolley 1981, 1985, Gerloch *et al.* 1981, Gerloch and Woolley 1984, Deeth *et al.* 1986). In the main, the theoretical analysis confirms the validity of the *practice* followed by users of the AOM in ligand-field studies; however, it shows why the original model apparently 'breaks down' for planar complexes (Smith 1977) and it also shows what modifications must be made to rescue it in such anomalous cases. Most importantly, the CLF makes the transition from empirical parametrization to a well founded theoretical structure that can be parametrized.

The CLF model described here must not be confused with another form of the AOM based on molecular orbital theory that has been popularized in recent inorganic chemistry texts as offering a rationalization of thermodynamic and structural properties of both transition-metal and main-group species (Purcell and Kotz 1977, Burdett 1980, Cotton and Wilkinson 1980). Although the empirical record suggests that this other approach has proved to be a valuable heuristic for qualitative chemical arguments, its theoretical basis remains unclear. While the CLF and AOM models share a common concern with the *local* interactions between a central atom and its ligands, the decisive distinction between them follows from the recognition that the *molecular orbital model has no role in the ligand-field theory of transition-metal complexes.* This categorical statement may seem disturbing, conflicting as it does with what generations of chemistry students have been taught; it is justified by the observations that (*a*) molecular orbital theory at the SCF level does not give anything like a quantitative description of the magnetism and spectroscopy of paramagnetic transition-metal complexes, and (*b*) the *theoretical* basis for ligand-field theory reviewed here (sections 2 and 3) and elsewhere (Stevens 1976, 1985) is *not* developed in the independent-electron molecular orbital framework. This is not to say that a molecular orbital model supplemented by extensive C.I. cannot do the job†—it *is* a plea for recognition that the ligand-field and molecular orbital models are quite distinct schemes in electronic structure theory with their own regimes of validity. Nothing is gained by confusion between them.

Throughout this review emphasis has been placed on the essentially many-electron nature of ligand-field theory. Such an approach has the virtue of keeping the theoretical discussion in close correspondence with the actual practice of ligand-field studies, but may seem rather far from familiar chemical bonding notions which rely on one-electron models of the molecular orbital type. How, then, shall we give a *chemical* interpretation

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† Even so, there are doubts whether the electronic structure of a *crystal* of a magnetic insulator can be obtained starting from a molecular orbital viewpoint.

to the ligand-field parametrization? In previous discussions (Woolley 1981, Gerloch and Woolley 1984) we interpreted the ligand-field potential matrix, **V**, (section 2) in terms of a one-electron hamiltonian for the complex, $\hat{h}$, that differs from the usual m.o. hamiltonian by the mission of the self-consistently averaged terms describing the interactions *between the d-electrons* (which are treated fully by the Slater–Condon formalism in the ligand-field theory). Moreover, perhaps overly influenced by the widespread view among inorganic chemists that the AOM $\{e_k^l\}$-parameters used to construct **V** should be related to squares of overlap integrals involving metal ion d-orbitals and 'suitable' ligand donor atom valence orbitals, we utilized a *non-orthogonal* orbital basis.

Several technical criticisms can be made of this one-electron analysis of the matrix **V**. Firstly, it is not obvious that the use of a *non-orthogonal basis* is consistent with the many-electron, ligand-field theory formalism in which the matrix **V** is to be used; the group product wavefunction formalism described here is based on the demanding condition of strong orthogonality (equation (23), section 3.3), while fermion second quantization in a non-orthogonal basis is problematic (Stevens, personal communication 1982, 1985). Secondly, the results involve a set of 'localized bond-orbitals' to mediate the ligand interactions with the d-electrons. The non-orthogonal basis of d-orbitals and bond-orbitals introduces overlap integrals which disappear from the partitioning equations only if an average-energy approximation involving the unperturned energy of the d-orbitals in the complex is made.

The present writer showed how these objections could be avoided by using the chain formalism (cf. section 3.4) with the one-electron hamiltonian $\hat{h}$ and choosing the metal-ion d-orbitals as the starting wavefunctions $|u_0\rangle$; all quantities in the theory are then well defined and constructed recursively from $\hat{h}$ and $|u_0\rangle$, and the resulting orbital basis is automatically orthonormal (Woolley 1985). One final criticism is that the one-electron hamiltonian $\hat{h}$ used in these studies was related only implicitly to the many-electron theory that underlies the ligand-field theory. This objection can be disposed of by studying the ligand-field potential matrix, **V**, and its associated $\{e_k^l\}$-parameters, directly in the many-electron framework.

4.2. *The ligand-field potential matrix*, V

The spin–orbit coupling, $\mathbf{V}_{\mathrm{s.o.}}$, is a small perturbation additional to the ligand-field and electron repulsion interactions and can be dropped as far as concerns the present discussion.† The interelectron repulsion matrix, $\mathbf{V}_{\mathrm{ee}}$, in equation (64), vanishes for d^1 and d^9 configurations; on the assumption that the parametrization of $\mathbf{V}_{\mathrm{ee}}$ for d^n configurations, $2 \leqslant n \leqslant 8$, can be dealt with separately from the optimization of $\mathbf{V}_{\mathrm{L.F.}}$ we can confine our attention to the d^1 configuration for a discussion fof the matrix **V**.

In the d^1 case, the set of Slater determinants $\{|\Omega_u|\}$, equation (28), reduces to just the simple products of α- and β-spin-wavefunctions with the five metal-ion d-orbitals; since we use the d-electron wavefunctions $\{\Psi_{Mm}\}$ variationally with the ground-state

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† For first-row transition metal ions the exchange energy, P, varies between 20 000 and 30 000 cm^{-1}, while in octahedral complexes the ligand-field splitting, Δ_{oct}, varies from 5000 to over 30 000 cm^{-1}. The spin–orbit coupling energy is these systems is much smaller, normally a few hundred wavenumbers. For ions from the second and third transition series, the interelectron repulsion energy is reduced while the ligand-field splitting is usually enhanced; the spin–orbit coupling energy can be as much as an order of magnitude bigger, as compared with first-row transition metal ions. As a result, *diamagnetism* is much more commonly encountered with complexes of the heavier metal ions; ligand-field theory is not applicable to such cases.

wavefunction for the L set of electrons, Ψ_{Lo}, we may write a typical ligand-field state as

$$|\phi_k^{N_d=1}\rangle = \mathbb{A}^n\{|\Psi_{Lo}\rangle|d_k\rangle\},\ k, \ldots 5; \tag{65}$$

$|d_k\rangle$ is a d-orbital calculated from the rotationally invarient part of $\hat{\mathscr{H}}_M$ (section 3.3) and may be taken with either spin wavefunction. If we use a wavefunction of the form of (65) in equation (60), and integrate out the dependence on the L set of electrons, the resulting matrix $\tilde{\mathbf{H}}_M$, equation (62), is labelled by the five d-orbitals and can be identified directly with the 'ligand-field potential' matrix $\mathbf{V}$,

$$\left.\begin{array}{c}d^1\ (d^9)\text{ case;}\\ \text{spin-orbit coupling}\\ \text{neglected (equation (62))}\end{array}\right\}\ \tilde{\mathbf{H}}_M \Leftrightarrow \mathbf{V}\ \left\{\begin{array}{c}\text{ligand-field}\\ \text{potential}\\ \text{matrix.}\end{array}\right. \tag{66}$$

The eigenvalues of $\mathbf{V}$ (or equivalently of $\tilde{\mathbf{H}}_M$ in this case) are the energy levels of the d-electron in the diamagnetic environment provided by the remainder of the complex—these energies have exactly the *same* interpretation as the 'ligand-field orbital' (LFO) energies, E_k^*, we defined previously (see especially III.B in Gerloch and Woolley (1984)).

If, purely for simplicity, we suppose that the transition-metal complex has sufficiently high point-group symmetry that it is possible to choose d-orbitals such that no two of them belong to the same row of the same irreducible representation, we may use directly the chain formulae derived earlier to describe the eigenvalues of (66). For a starting state $|u_{0k}\rangle$ of the form of (65), the assumed high symmetry of the complex implies that the d-orbitals are not mixed by $\hat{H}$ and we may write down directly the chain approximation (47), or equivalently (48), for the corresponding eigenvalue of $\hat{H}$,

$$E_k \approx E_{Lo} + E_{Mk} + \frac{b_{1k}^2}{(a_{0k} - a_{1k})}. \tag{67}$$

The eigenvalues of $\mathbf{V}$(i.e. $\tilde{\mathbf{H}}_M$) are given by $(E_k - E_{Lo})$, so

$$E_k^* \approx E_{Mk} + \frac{b_{1k}^2}{(a_{0k} - a_{1k})},\ k = 1, \ldots 5. \tag{68}$$

In this expression we have,

$$E_{Mk} = \langle d_k|\hat{\mathscr{H}}_M|d_k\rangle,\ a_{0k} = E_{Lo} + E_{Mk} \tag{69}$$

where $\hat{\mathscr{H}}_M$ is now the one-electron operator specified in equations (26 d), (26 e) for $N_d = 1$ (with the Coulomb operator $(r_{\kappa\lambda})^{-1}$ omitted). E_{Mk} may be written as the sum of the d-orbital energy ε calculated from the rotationally invariant part of $\hat{\mathscr{H}}_M$, and the expectation value of the purely non-spherical part of $\hat{\mathscr{H}}_M$ which acts on the d-orbitals as a static 'crystal-field'-like potential,

$$E_{Mk} = \varepsilon + \langle d_k|(\hat{\mathscr{H}}_M)_{\text{Non-sph}}|d_k\rangle. \tag{70}$$

As for the interpretation of the second term in equation (68), this hinges on the nature of the chain state $|u_{1k}\rangle$ coupled to the ligand-field state $|\phi_k^{N_d=1}\rangle$ by the full n-electron hamiltonian $\hat{H}$. It is plausible to argue that the physically important contributions to $|u_{1k}\rangle$ will be many-electron wavefunctions obtained from the starting ligand-field state by substitution of ligand valence orbitals in place of the metal ion d-orbital (see the comments after equation (44)). If only single substitutions are considered we can write

$$|u_{1k}\rangle \approx \mathbb{A}^n\{|\Psi_{\mathrm{Lo}}\rangle|\phi_{1k}\rangle\} \tag{71}$$

where $|\phi_{1k}\rangle$ is a spin-orbital that is orthogonal to $|d_k\rangle$ *and* to the orbitals used in the construction of $|\Psi_{\mathrm{Lo}}\rangle$ (to maintain strong orthogonality); for such functions we can integrate out the dependence on the L set of electrons and write

$$\begin{aligned} a_{1k} \equiv \langle u_{1k}|\hat{H}|u_{1k}\rangle &= E_{\mathrm{Lo}} + \langle\phi_{1k}|\hat{\mathscr{H}}_{\mathrm{M}}|\phi_{1k}\rangle \\ &= E_{\mathrm{Lo}} + \bar{e}_{1k} \end{aligned} \tag{72}$$

$$b_{1k} \equiv \langle\phi_k^{N_d=1}|\hat{H}|u_{1k}\rangle = \langle d_k|\hat{\mathscr{H}}_{\mathrm{M}}|\phi_{1k}\rangle \tag{73}$$

where $\hat{\mathscr{H}}_{\mathrm{M}}$ is the *same* one-electron operator as specified in equation (69).

To the extent that the separability implied by (71) is valid, it seems correct to choose the orbital $|\phi_{1k}\rangle$ as the orthonormal chain orbital constructed from the one-electron hamiltonian $\hat{\mathscr{H}}_{\mathrm{M}}$ with $|d_k\rangle$ as the starting orbital, since this construction gives a complete description of the *orbital* environment of $|d_k\rangle$ under the effective hamiltonian $\hat{\mathscr{H}}_{\mathrm{M}}$ (Woolley 1985). Combining equations (68)–(73) we finally obtain the ligand-field orbital energies as

$$E_k^* \approx \varepsilon + \langle d_k|\hat{\mathscr{H}}_{\mathrm{M}})_{\mathrm{Non\text{-}sph}}|d_k\rangle + \frac{|\langle d_k|(\hat{\mathscr{H}}_{\mathrm{M}})_{\mathrm{Non\text{-}sph}}|\phi_{1k}\rangle|^2}{E_{\mathrm{M}k} - \bar{e}_{1k}} \tag{74}$$

in close correspondence with our earlier purely one-electron analyses. Clearly this is an heuristic argument; in particular the ansatz (71) requires scrutiny to verify that wavefunctions of this form do make large contributions to $|u_{1k}\rangle$.

The results given here are equivalent to those in Woolley (1985) provided that the one-electron hamiltonian discussed there is replaced by the one-electron effective hamiltonian, $\hat{\mathscr{H}}_{\mathrm{M}}$, defined here for the d^1 configuration. Accordingly we have the same interpretation for the ligand-field orbital energies $\{E_k^*\}$ as before; they consist of three types of contribution. Firstly, all E_k^* contain the d-orbital energy ε which is uninteresting and, as we shall see, can be eliminated completely from the ligand-field parametrization. Secondly, there is the mean *static potential* due to the non-spherical perturbation of the metal ion in its crystalline environment, $(\hat{\mathscr{H}}_{\mathrm{M}})_{\mathrm{Non\text{-}sph}}$. Thirdly, there is the term involving the square of the resonance integral b_{1k} and an energy denominator that measures the *coupling* of the orbital $|d_k\rangle$ to this environment under the action of $(\hat{\mathscr{H}}_{\mathrm{M}})_{\mathrm{Non\text{-}sph}}$; we refer to this contribution to E_k^* as the mean *dynamical potential*, so

LFO energy E_k^*	=	d-orbital energy ε	+	mean *static potential* for orbital $\lvert d_k\rangle$	+	mean *dynamic potential* for orbital $\lvert d_k\rangle$

What of the relative magnitudes of these two mean potentials for the d-orbitals $\{|d_k\rangle\}$? One can make the following qualitative argument (Woolley 1981). Both mean potentials depend on matrix elements of the non-spherical perturbation $(\hat{\mathscr{H}}_{\mathrm{M}})_{\mathrm{Non\text{-}sph}}$ which we can think of as *integrals over all space*; experience with SCF band-structure and molecular calculations of the X_α-type suggests that this perturbation should (*a*) be small *within* the atomic volume of the metal ion, and (*b*) increase with distance from the metal nucleus. Furthermore we know from such calculations that $|r\phi_{\mathrm{d}}(r)|^2$ for the valence d-orbitals is strongly localized about the metal nucleus which, as just noted, is the region of space where $(\hat{\mathscr{H}}_{\mathrm{M}})_{\mathrm{Non\text{-}sph}}$ is expected to be small; hence the integrand for the mean *static potential* is nowhere large. On the other hand, the orbital $|\phi_{1k}\rangle$ is expected to resemble a superposition of metal–ligand bond-orbitals with valence electron energies; thus the mean *dynamic potential* receives contributions from a much larger region of space that includes the bond overlap regions where $(\hat{\mathscr{H}}_{\mathrm{M}})_{\mathrm{Non\text{-}sph}}$ is most important. On this basis we may usually expect the mean dynamic potential (the third term in (74)) to make the dominant contribution to the LFO energy E_k^*, measured with respect to ε. Ultimately, the chemical bonding interpretation of the ligand-field formalism depends on this claim.

One other aspect of the ligand-field potential matrix, $\mathbf{V}$, that has emerged from recent Ligand-Field Analyses as a quantity of chemical interest (Deeth and Gerloch 1984 a, b, 1985 a, b) is the trace, $\sum^{\mathrm{exp}}$, of the experimentally determined matrix, $\mathbf{V}^{\mathrm{exp}}$,

$$\sum{}^{\mathrm{exp}}=\mathrm{Tr}\,(\mathbf{V}^{\mathrm{exp}}). \tag{75}$$

The theoretical expression for $\sum=\mathrm{Tr}\,(\mathbf{V})$ can be calculated formally from (74) by summing over the index k,

$$\sum=\sum_k E_k^*=5\varepsilon+\sum_k\frac{|\langle d_k|(\hat{\mathscr{H}}_{\mathrm{M}})_{\mathrm{Non\text{-}sph}}|\phi_{1k}\rangle|^2}{E_{\mathrm{M}k}-\bar{e}_{1k}}=\sum{}_0+\sum{}_1 \tag{76}$$

in an obvious notation; the trace of the wholly non-spherical potential $(\hat{\mathscr{H}}_{\mathrm{M}})_{\mathrm{Non\text{-}sph}}$ in the d-orbital basis vanishes. $\sum_1$ is expressed as a *sum of rational fractions* with positive numerators and can therefore vanish only accidentally; thus there is no barycentre rule for the splitting of the d-orbital energy levels (Gerloch and McMeeking 1975). We shall return to further discussion of $\sum$ after the $\{e_k^l\}$-parameters associated with $\mathbf{V}$ have been introduced; this is the concern of the next section.

4.3. *The local cellular potential and the* $\{e_k^l\}$*-parameters*

In the previous section we discussed the matrix $\mathbf{V}$ starting from the many-electron theory, and in particular studied its eigenvalues which are interpreted as the d-electron orbital energies ('ligand-field orbital energies') arising from a d^1-configuration calculation, a standard part of Ligand-Field Analysis (Gerloch and Woolley 1984). We now wish to change our point of view and concentrate on the *local* functional group interactions between the metal ion and the ligands in the complex. One of the key ideas of the CLF model is the representation of the matrix $\mathbf{V}$ as a superposition of disjoint contributions $\{\mathbf{e}^l\}$ that can be associated with N non-overlapping 'cells' (regions of space) into which the molecular coordination sphere can be divided. Formally, this can be related to a cellular decomposition of the ligand-field potential operator $\hat{V}(\equiv\hat{V}_{\mathrm{L.F.}}$ in equation (64)).

The metal-ion d-orbitals $\{|d_i\rangle\}$ are taken initially as quantized with respect to a global coordinate frame attached to the ion; in terms of these orbitals we may write

$$\langle d_i|\hat{V}|d_j\rangle=(\mathbf{V})_{ij},\quad i,j=1,\ldots 5. \tag{77}$$

In general $\hat{V}$ will contain both local and non-local operators (cf. the coulomb and exchange terms in equations (26) and (27)), but physical arguments based on the localized nature of the d-orbitals and the dielectric screening expected in the true, effective operator $\hat{V}(i)_{\text{L.F.}}$, equation (64), provide a justification for writing it in a cellular form (Gerloch and Woolley 1984),

$$\hat{V} = \sum_{l=1}^{N\,\text{cells}} \hat{v}^l. \tag{78}$$

The choice of cells is discussed further below.

Combining (77) and (78) we have a corresponding cellular decomposition of the matrix $\mathbf{V}$,

$$(\mathbf{V})_{ij} = \sum_{l=1}^{N\,\text{cells}} \langle d_i|\hat{v}^l|d_j\rangle = \sum_{l=1}^{N\,\text{cells}} (\mathbf{v}^l)_{ij}. \tag{79}$$

Each of the hermitian matrices $\mathbf{v}^l$ can be brought to diagonal form by a unitary transformation,

$$\mathbf{R}^l\mathbf{v}^l\mathbf{R}^{l\dagger} = \mathbf{e}^l;\ \mathbf{R}^l\mathbf{R}^{l\dagger} = \mathbf{R}^{l\dagger}\mathbf{R}^l = \mathbf{1} \tag{80}$$

where $\mathbf{e}^l$ is a 5×5 diagonal matrix with diagonal elements $\{e_k^l\}$. On the other hand if, for each cell l, we explicitly construct the d-orbitals that diagonalize the cellular potential $\hat{v}^l$, through the transformation

$$\langle d_k^l| = \sum_i (\mathbf{R}^l)_{ki}\langle d_i| \tag{81}$$

we see that the eigenvalues $\{e_k^l\}$ for cell l are just the expectation values of the cellular potential in the *local* d-orbital basis (81),

$$e_k^l = \langle d_k^l|\hat{v}^l|d_k^l\rangle. \tag{82}$$

Collecting all these formulae together enables us to write (Woolley 1981, Gerloch and Woolley 1984)

$$(\mathbf{V})_{ij} = \langle d_i|\hat{V}|d_j\rangle = \sum_{l=1}^{N\,\text{cells}} \sum_{k}^{5\,\text{modes}} (\mathbf{R}^l)^\dagger_{ik}(\mathbf{R}^l)_{kj}e_k^l; \tag{83}$$

the notation of writing the second summation over five 'bonding modes' anticipates the fact that the eigenvalues $\{e_k^l\}$ will normally be symmetry classified as σ, π_x, ... with respect to the metal-ion–ligand l bond-vector.

We define a local coordinate system for each ligand by taking a vector $\mathbf{Q}_l$ along the transition-metal-ion–ligand donor-atom bond as the local polar axis so that $\mathbf{Q}_l$ has coordinates $(|\mathbf{Q}_l|, \theta_l, \phi_l)$ in the global coordinate frame in which the orbitals $\{|d_i\rangle\}$ are quantized. The d-orbitals $\{|d_k^l\rangle\}$ quantized in this local frame can be given the symmetry classification σ, π_x, π_y, δ_{xy}, $\delta_{x^2-y^2}$ with respect to $\mathbf{Q}_l$, and these symmetry labels are used to identify the distinct bonding modes. When the local pseudosymmetry of cell l is effectively C_{2v} or higher, symmetry arguments suggest that the d-orbitals quantized with respect to $\mathbf{Q}_l$ as polar axis will diagonalize the potential $\hat{v}^l$ with expectation values

$$\left.\begin{aligned} &\langle d_{z^2}^l|\hat{v}^l|d_{z^2}^l\rangle = e_\sigma^l \\ &\langle d_{xz}^l|\hat{v}^l|d_{xz}^l\rangle = e_{\pi_x}^l;\quad \langle d_{yz}^l|\hat{v}^l|d_{yz}^l\rangle = e_{\pi_y}^l \\ &\langle d_{xy}^l|\hat{v}^l|d_{xy}^l\rangle = e_{\delta_{xy}}^l;\quad \langle d_{x^2-y^2}|\hat{v}^l|d_{x^2-y^2}\rangle = e_{\delta_{x^2-y^2}}^l. \end{aligned}\right\} \tag{84}$$

In such cases the unitary matrix $\mathbf{R}^l$ can be calculated purely from the geometry of the molecule as an orthogonal rotation matrix relating the global coordinate frame and the local coordinate frame for cell l based on $\mathbf{Q}_l$ as polar axis.

These observations have an important bearing on the practical implementation of the CLF as a *parametrization scheme.* If we had been given the explicit mathematical form for the potential $\hat{V}$ in equations (77) and (78) *any* decomposition into cells would be as valid as any other, and the unitary matrices $\{\mathbf{R}^l\}$ could then be calculated from (80) for any choice of cells; the 1 : 1 identification of cells with ligands is the natural, physical choice. However, when these equations are used parametrically, the matrices $\{R^l\}$ *must be assumed to be known* because we do not have $\hat{V}$ explicitly; in practice they are normally calculated as rotation matrices from the molecular structure as just outlined. At the same time, we should recognize the requirement that the rotation matrix $\mathbf{R}^l$ must also diagonalize the local cellular potential $\hat{v}^l$, as expressed by equation (80); some care must therefore be taken over the cellular decomposition of the potential $\hat{V}$, equation (78). Usually, there is a straightforward 1 : 1 identification between cells and ligands, as assumed in the original formulation of the AOM (Schäffer and Jørgensen 1958, 1965, Jørgensen *et al.* 1963, Schäffer 1968). Equally, however, the *theoretical consistency of the scheme may require there to be more cells than ligands in the molecular coordination sphere.* A well documented case of this type is exemplified by square-planar complexes for which, in addition to four cells associated with the four ligands in the molecular (xy-)plane, we must also take two further cells that are symmetrically disposed about the z-axis above and below the molecular plane and are *coordinatively void* (Smith 1977, Mackey *et al.* 1979, Woolley 1981, Gerloch 1984, Deeth and Gerloch 1984 a, b, 1985 a, b).

In summary then, the choice of cells in the CLF is determined by two requirements:

(*a*) the ligand-field potential should ideally be described by the expectation values alone (84), since it is obviously desirable to have as few parameters as possible;

(*b*) each cellular potential matrix in the d-orbital basis, $\mathbf{v}^l$, should be diagonalized by a unitary matrix $\mathbf{R}^l$ determined purely by the *structural parameters* of the complex.

There are physical circumstances where (*a*) and (*b*) cannot be achieved simultaneously, for example with chelating ligands, or ligands with donor atoms having lone pairs (Gerloch 1984, Deeth and Gerloch (1985 a, b). In such cases $\mathbf{R}^l$ is calculated from the molecular structure, and we admit off-diagonal elements to the matrix $\mathbf{e}^l$. The normal situation however is that each ligand l is described by the five diagonal matrix elements (at most) displayed in (84).

The parametrization of the ligand-field hamiltonian $\mathbf{H}_{\text{L.F.}}$, equation (64), is carried out with the aid of equation (83): a set of parameters $\{e_k^l\}$ is guessed, the associated matrix $\mathbf{V}$ is computed from (83), and this $\mathbf{V}$ forms the input for the construction of $\mathbf{V}_{\text{L.F.}}$ in equation (64) by vector coupling. The members of the parameter set $[P_\alpha]$ are varied until the resulting eigenvalues of $\mathbf{H}_{\text{L.F.}}$ give the closest fit to the energy levels deduced from the experimental data, cf. figures 1 and 2. One then has a best-fit value for the matrix $\mathbf{V}^{\text{exp}}$, and associated with it a set of best-fit parameters $\{e_k^l\}^{\text{exp}}$ (as well as best-fit parameters for interelectron repulsion and spin–orbit coupling). To be precise, we should note that all the experimental information is related to energy level *differences*, and so the diagonal elements of $\mathbf{V}$ are determined only to within some constant V_0 corresponding to a choice of energy zero,

$$(\mathbf{V})_{ij} = (\mathbf{V})_{ij}^{\text{exp}} + V_0\delta_{ij}; \tag{85}$$

apart from this ambiguity, which causes no difficulty, we shall assume that the best-fit matrix $\mathbf{V}^{\text{exp}}$ is unique, i.e. the equivalence class of matrices $[\mathbf{V}]$ that reproduce the experimental data can be expressed as above, equation (85). In practice, since the matrix $\mathbf{V}^{\text{exp}}$ is constructed with the aid of equation (83) the choice of energy zero is determined by the choice of parameters $\{e_k^l\}^{\text{exp}}$; we return to this point below (see equation (95)).

The promise of the CLF model is that the parameters $\{e_k^l\}$ can serve two purposes:

(i) to facilitate the reconstruction of the global ligand-field potential matrix $\mathbf{V}$, even when the complex has little or no point-group symmetry,

(ii) to provide information about the σ, π_x-,... bonding modes of the local metal-ion–ligand l interactions.

It is clear that there is much to commend the use of equation (83) for achieving (i); varying the $\{e_k^l\}^{\text{exp}}$ is a technically very convenient way of constructing the best-fit matrix $\mathbf{V}^{\text{exp}}$ because it brings useful information about the molecular structure to the parametrization in accordance with chemical intuitions about bonding, e.g. the pseudosymmetry argument leading to equation (84). Moreover, equation (83) tells us that any given set of $\{e_k^l\}$-parameters produces a unique matrix $\mathbf{V}$, so there is a direct correspondence between this chemical information and the parametrized Ligand-Field hamiltonian.

However, the *chemical interpretation* of the resulting set of parameters does require further discussion because another question about the relationship between $\mathbf{V}$ and the $\{e_k^l\}$-parameters arises from the foregoing: Given some hermitian matrix $\mathbf{V}$ (for example the best-fit $\mathbf{V}^{\text{exp}}$ for the complex), and the unitary structure matrices $\mathbf{R}^l$ for each cell l in the complex, one can ask whether the set of parameters $\{e_k^l\}$ used in the construction of $\mathbf{V}$ with the aid of equation (83) is unique, or are there actually many distinct sets of parameters $\{e_k^l\}$ that generate the same matrix $\mathbf{V}$? Analysis of equation (83) (Woolley 1981) suggests that, superficially at least, the $\{\mathbf{e}^l\}$ ought to be more or less arbitrary because we have apparently more unknowns than independent equations if we are given $\mathbf{V}$ and search for the $\{\mathbf{e}^l\}$. Such a conclusion, if valid, would be fatal for (ii) above. However, the position is not as bad as this since equation (83) must be supplemented by a variety of equations of constraint† imposed by the physics of the situation, and these are usually sufficient to guarantee that a *physically acceptable* set of $\{e_k^l\}$-parameters has a well defined relationship with the matrix $\mathbf{V}$. The reader is referred to full discussions of the matter (Woolley 1981, Gerloch 1984).

It is important to note that the constraints imposed on the $\{e_k^l\}^{\text{exp}}$-parameters imply *nothing* about the signs and magnitudes of the individual parameters not determined by symmetry, and so we expect the CLF parametrization to reflect faithfully electronic properties of the complex. This argument rests on general assumptions about the molecular structures and chemical species that we commonly deal with in ligand-field studies; there are bound to be cases where the arguments break down, and it is essential that the user of the CLF checks that these assumptions are physically reasonable in any given case.

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† A physically acceptable set of $\{e_k^l\}$-parameters must have definite relationships between its elements; these are normally sufficient to make the $\mathbf{V}\leftrightarrow\mathbf{e}^l$ relationship unique. For example, chemically equivalent ligands are expected to have identical $\{e_k^l\}$-parameters, and the local pseudo-symmetry of any one cell may impose relationships on the parameters for that cell. These statements do not rely on the presence of non-trivial point-group symmetry in the molecule as a whole.

4.4. *The chemical interpretation of the $\{e_k^l\}$-parameters*

The equation reviewed in section 4.3 take a particularly simple form in the special case of a complex, ML, containing a single ligand L, and this will be used to introduce the chemical bonding ideas. The summation over l in equations (78), (79) and (83) and the associated l superscript can be dropped and, assuming C_{2v} symmetry or higher for the molecule, the matrix **V** will be diagonal if we chose the ML bond-vector as the quantization axis for the d-orbitals. Comparison of equations (74), (79), (82) and (84) then shows that we may write

$$\text{LFO energy } E_k^* \equiv \text{CLF } e_k\text{-parameter,} \tag{86}$$

and for this case, equation (74) is also the theoretical expression for the $\{e_k\}$-parameters,

$$\underset{\text{ML complex}}{e_k = \varepsilon + \langle d_k|(\hat{\mathscr{H}}_{\mathrm{M}})_{\text{Non-sph}}|d_k\rangle} + \frac{|\langle d_k|(\hat{\mathscr{H}}_{\mathrm{M}})_{\text{Non-sph}}|\phi_{1k}\rangle|^2}{E_{\mathrm{M}k} - \bar{e}_{1k}} \quad k = \sigma, \pi_x, \dots . \tag{87}$$

A formal analysis suggests that $\langle d_{z^2}|(\hat{\mathscr{H}}_{\mathrm{M}})_{\text{Non-sph}}|d_{z^2}\rangle$ makes a positive contribution to e_σ, because $(\hat{\mathscr{H}}_{\mathrm{M}})_{\text{Non-sph}}$ is expected to be positive in the bond-region, while the analogous terms of π and δ symmetry are normally negligible in comparison (Woolley 1981). The discussion following (74) of the relative magnitudes of the three terms in E_k^* suggests that the *last* term in (87) is the one of interest; its numerator is positive because it is a matrix element squared, and therefore the *sign* of this term is governed by the energy denominator. Usually the energy, $\bar{e}_{1\sigma}$, of the σ-orbital $|\phi_{1\sigma}\rangle$ coupled to $|d_{z^2}\rangle$ is lower than that of $|d_{z^2}\rangle$ itself (i.e. $\bar{e}_{1\sigma} < \varepsilon$) so we expect both the second and third terms to give *positive* contributions to e_σ.

The perturbed d-orbital energy $E_{\mathrm{M}k}$ in (87) is expected to be close to the d-orbital energy, ε, and hence e_k is only significantly different from ε if the molecule is such that the chain orbital $|\phi_{1k}\rangle$ has an energy $\bar{e}_{1k}$, within a few eV (say $O(10^4)\,\mathrm{cm}^{-1}$ rather than $O(10^5)\,\mathrm{cm}^{-1}$) of ε. This is normally possible only if the ligand has valence orbitals having the symmetry of the d-orbital $|d_k\rangle$ and able to interact with metal ion *valence s- and/or p-orbitals*. The local pseudosymmetry of the metal–ligand donor-atom bond is useful here because it provides an approximate symmetry-based classification of the fragment orbitals that may contribute to a given $|\phi_{1k}\rangle$, and it also gives approximate selection rules for the resonance integrals $\langle d_k|(\hat{\mathscr{H}}_{\mathrm{M}})_{\text{Non-sph}}|\phi_{1k}\rangle$ since the molecular point-group symmetry is carried by $(\hat{\mathscr{H}}_{\mathrm{M}})_{\text{Non-sph}}$. If the local pseudosymmetry is the same as the point-group symmetry of ML, appropriate pseudosymmetry statements become exact. A useful way of thinking about the orbital $|\phi_{1k}\rangle$ is to picture it as a bond-orbital made up from a superposition of metal s and p-orbitals and suitable ligand orbitals with valence electron energies.

It will be seen from (87) that the theoretical $\{e_k\}$-parameters contain the d-orbital energy ε. Measured with respect to the conventional zero of energy corresponding to ionization, d-orbital energies are typically $\lesssim 10^5\,\mathrm{cm}^{-1}$; experimentally determined $\{e_k\}$-parameters are typically $\lesssim 5000\,\mathrm{cm}^{-1}$. There is nothing to worry about here, for the apparent discrepancy merely reflects a different (implicit) choice of zero of energy for the experimentally determined parameters; we set

$$\tilde{e}_k = e_k - e_\delta, \quad k = \sigma, \pi_x, \dots . \tag{88}$$

and identify the $\{\tilde{e}_k\}$ with the experimentally determined parameters $\{e_k\}^{\exp}$; the definition (88) eliminates the large, but uninteresting, d-orbital energy, ε, from the formalism. For the ML complex, the $\{\tilde{e}_k\}$ quantities are just the *spacings* between the ligand-field orbital energies $\{E_k^*\}$ and E_δ^*.

A 'large' value of an $\tilde{e}_k$-parameter is a few thousand wavenumbers which, by *chemical bonding standards*, is still a small energy; a 'large' $\tilde{e}$-parameter is *not* therefore indicative of substantial participation of the corresponding d-orbital, $|d_k\rangle$, in metal-ligand bonding. Rather, such a result tells us that the ligand in the complex has associated with it a chain orbital $|\phi_{1k}\rangle$ reflecting the bonding interactions between metal s and/or p-orbitals and appropriate ligand valence orbitals. On the other hand, a small or zero value for an $\tilde{e}_k$-parameter does indicate the lack of participation in metal–ligand bonding of such ligand valence orbitals. It cannot be emphasized too much that the discussion refers to the molecule as it is rather than to the putative donor/acceptor properties of the 'free' ligands. Synergic 'back-bonding' or other electronic processes will have taken place to meet as far as possible the requirements of the Electroneutrality Principle, and $|\phi_{1k}\rangle$ describes the environment of the metal ion in the complex in the final equilibrium structure of the crystal. *Thus the metal ion d-orbitals serve as a probe to monitor the significant chemical bonding interactions that have brought about formation of the complex.*

In the case of the general complex, ML_n ($n > 1$), the identity (86) no longer holds and the $\{e_k^l\}$-parameters must be identified through the cellular decomposition (79)–(82). Nevertheless, the $\{e_k^l\}$-parameters for a given cell l can be shown to have a *structure* similar to the $\{e_k\}$ for the ML case, with the difference that orbitals and potentials refer exclusively to just cell l. Equation (79) is valid for the particular d-orbital representation $\{|d_n\rangle\}$ in which $\mathbf{V}$ is diagonal, with eigenvalues E_n^*, so that we may always write

$$E_n^* = \sum_{l=1}^{N\text{ cells}} \langle d_n|\hat{v}^l|d_n\rangle = \sum_{l=1}^{N\text{ cells}} \sum_{k}^{5\text{ modes}} (\mathbf{R}^l)^\dagger_{nk}(\mathbf{R}^l)_{kn} e_k^l \tag{89}$$

where the $\mathbf{R}^l$ matrices relate the orbitals $\{|d_n\rangle\}$ to the d-orbitals in the local frame for cell l. The first two terms in (74) can be put in this form directly if we write

$$(\hat{\mathscr{H}}_M)_{\text{Non-sph}} = \sum_{l=1}^{N\text{ cells}} \hat{U}^l; \quad \varepsilon = \sum_{l=1}^{N\text{ cells}} (\varepsilon/N). \tag{90}$$

The cellular decomposition of the mean dynamic potential is more involved, and requires consideration of the energy factor $(E_{Mk} - \tilde{e}_{1k})^{-1}$ as a resolvent matrix element using a representation of the chain orbital $|\phi_{1k}\rangle$ as a superposition of localized bond-orbitals $\{|\chi_{l\alpha}\rangle\}$ associated with the individual cells (Woolley 1981, 1985, Gerloch and Woolley 1984). Each cell l is treated in a way that parallels the ML case and we find that we may write

$$e_k^l = \varepsilon/N + e_k^l(\text{static}) + e_k^l(\text{dynamic}) \tag{91}$$

where

$$e_k^l(\text{static}) = \langle d_k^l|\hat{U}^l|d_k^l\rangle \tag{92}$$

$$e_k^l(\text{dynamic}) = \sum_{\alpha} \frac{|\langle d_k^l|\hat{U}^l|\chi_{l\alpha}\rangle|^2}{E_{Mk} - \bar{\varepsilon}_{l\alpha}} \tag{93}$$

In these expressions, the $\{|d_k^l\rangle\}$ are the d-orbitals quantized in the local frame for cell l, equation (81), $\hat{U}^l$ is obtained from (88), and the $\{|\chi_{l\alpha}\rangle\}$ are localized bond-orbitals with mean energy $\bar{\varepsilon}_{l\alpha}$ associated with cell l. Once again we eliminate the d-orbital energy, ε, by setting†

$$\tilde{e}^l_k = e^l_k - e^l_\delta,\ k=\sigma, \pi_x, \dots \tag{94}$$

and identify the $\{\tilde{e}^l_k\}$ with the experimentally determined parameters $\{e^l_k\}^{\mathrm{exp}}$. The interpretation and use of equations (91)–(93) is completely analogous to that given above for the ML case, following equation (87).

The definition (94) implies that, for each cell l, one of the $\tilde{e}^l_\delta$-parameters is identically zero, and the other is negligible either because of the local pseudosymmetry or because of the weakness of δ-symmetry interactions; at the same time equations (91)–(93) show that the e^l_δ-parameters $\approx \varepsilon/N$. From equation (83) we then see that (88) and (94) correspond to writing

$$\begin{aligned}(\mathbf{V})_{ij} &= (\mathbf{V})^{\mathrm{exp}}_{ij} + \sum_{l=1}^{N\,\mathrm{cells}} (e^l_\delta)\delta_{ij}\\ &\sim (\mathbf{V})^{\mathrm{exp}}_{ij} + \varepsilon\delta_{ij}\end{aligned} \tag{95}$$

where $\mathbf{V}^{\mathrm{exp}}$ is constructed in the usual way from the $\{\tilde{e}^l_k\}$-parameters using (83), and the metal–ligand interaction in cell l is normally described by three parameters: $\tilde{e}^l_\sigma$, $\tilde{e}^{\,l}_{\pi_x}$, $\tilde{e}^{\,l}_{\pi_y}$.

We expect, and find in practice, substantial positive $\tilde{e}^l_\sigma$-parameters because coordinated ligands always carry suitable orbitals of local σ-symmetry; this is what we mean when we refer to the Lewis base (or σ-donor) behaviour of a ligand as far as its σ-interactions are concerned. The $\tilde{e}^l_\pi$-parameters may be equal by symmetry although we commonly need to distinguish between π-interactions parallel and perpendicular to some plane defined by the local molecular structure within a cell, for example a plane containing the metal ion and an aromatic ring system. The $\tilde{e}^l_\pi$-parameters vary in sign and magnitude from case to case, and therein lies much of the interest for chemistry afforded by the CLF parametrization of $\mathbf{V}$; both π-acceptor and π-donor behaviour ($\tilde{e}_\pi < 0$ and $\tilde{e}_\pi > 0$ respectively)‡ can be monitored through Ligand-Field Analysis.

There exists one class of complexes for which some large and negative (several thousands of wavenumbers) $\{e^l_\sigma\}^{\mathrm{exp}}$-parameters are found. These are planar coordinated species, and the cells associated with $\tilde{e}^l_\sigma < 0$ are those lying above and below the coordination plane, that is, the 'empty' or coordinationally void cells. Such empty cells are required because assigning the whole coordination volume to just the ligands is not consistent with the requirement (section 4.3) that the $\{\mathbf{R}^l\}$ matrices derived from the planar molecular structure diagonalize the $\{\mathbf{v}^l\}$ matrices of the ligands. There are no ligand orbitals with significant amplitude on the axis through the metal ion and perpendicular to the molecular plane, and the $\{|\chi_{l\alpha}\rangle\}$ orbitals for these two cells are mainly metal valence orbitals with energies *above* the d-orbital energy ε, hence the negative sign of the corresponding e_σ-parameter (Woolley 1981, Gerloch *et al.* 1981, Gerloch 1984, Gerloch and Woolley 1984, Deeth and Gerloch 1984 a, b, 1985 a, b). An example is discussed below.

Table 1 shows a set of typical $\{e^l_k\}^{\mathrm{exp}}$-parameters obtained from recent Ligand-Field Analyses of +II oxidation state metal complexes; they are determined to within a

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† In most practical applications, the local pseudosymmetry of the cell requires $e^{\,l}_{\delta_{xy}} = e^l_{\delta_{x^2-y^2}}$ and we do not distinguish between them.

‡ The donor/acceptor classification invoked here is a *convention*—an agreed definition determined by utility—and refers to metal–ligand interactions in the *finally formed complex*, rather than the free ligand.

Table 1. Typical values for 'best-fit' $\{e^l_k\}^{\mathrm{exp}}$-parameters (in cm^{-1}) for complexes of oxidation state +II metal ions of Group VIII. ∥ and ⊥ are with respect to the plane containing the metal ion and the ligand. The $\{e^l_k\}^{\mathrm{exp}}$ are to be identified with the theoretical quantities $\{\tilde{e}^l_k\}_l$ in equation (94).

Ligand	Typical $\{e^l_k\}^{\mathrm{exp}}$-parameters	Comments
NH_3	$e_\sigma \approx +5000$; $\lvert e_\pi \rvert \lesssim 50$	σ-donor only
Phosphines	$e_\sigma \approx +6000$; $e_\pi \approx -1500$	'strong' σ-donor and π-acceptor
pyridine	$e_\sigma \approx +4000$; $\lvert e_{\pi_\parallel} \rvert \lesssim 50$; $+50 \lesssim e_{\pi_\perp} \lesssim 150$	'weak' π-donor ⊥ to atomatic ring
quinoline	$e_\sigma \approx +4000$; $\lvert e_{\pi_\parallel} \rvert \lesssim 50$; $e_{\pi_\perp} \approx -500$	'moderate' π-acceptor
Cl^-, Br^-	$+3000 \lesssim e_\sigma \lesssim +4000$; $+500 \lesssim e_\pi \lesssim 800$	'moderate' π-donor

scatter of about ±10%. The relative magnitude and signs of these quantities accord well with accepted notions of the bonding modes of these ligators. A central feature of both the empirical record of analyses and the theoretical structure described here, is that the $\{e^l_k\}^{\mathrm{exp}}$-parameters refer to ligands (or coordination voids) in the *actual molecule;* as a result we ought to expect to find cases where the presence of particular ligands in a complex has discernible effect on the ligand-field parameters of *other* ligands—the very stuff of chemistry. Such is the case, and this means that 'parameter transferability'—the notion of using $\{e^l_k\}^{\mathrm{exp}}$-parameters obtained for a ligand in one complex in an analysis of another complex without modification—must be used with care.

One approach to parameter transferability which shows promise is based on the information contained in the trace, $\sum^{\mathrm{exp}}$, of the ligand-field matrix, $\mathbf{V}^{\mathrm{exp}}$. For fixed metal oxidation state, $\sum^{\mathrm{exp}}$ is approximately invariant for complexes that have related coordination. This conclusion has been demonstrated in recent Ligand-Field Analyses of a series of six chlorocuprates (Deeth and Gerloch *1985* a) with geometries approaching that of a tetragonally distorted octahedron (see figure 4), and confirmed for a group of isomorphous trigonal bipyramidal complexes (see figure 5) in which the ligand type is fixed and the metal ions, M, vary from Cr to Cu along the first transition-metal period (Deeth and Gerloch 1985 b).

In the chlorocuprates, there are four equatorial chlorine ligands (labelled a, b in figure 4) defining a near-D_{4h} geometry for the planar $CuCl_4^{2-}$ ion; the axial chlorines (labelled c in the figure) lie progressively further away from the Cu(II) ion as we move through the series (i)–(vi), which are distinguished by the accompanying cations. The last member, (vi), is a square-planar species and is expected to require parametrization of the coordination voids above and below the molecular plane (the final result of progressive tetragonal distortion). The dotted lines in figure 4 mark ligands that may act as bridges to other Cu(II) centres. The ligand-field is described by e_σ, $e_{\pi_\perp}$, $e_{\pi_\parallel}$ parameters for the equatorial chlorines ($e_{\pi_\perp} = e_{\pi_\parallel}$ except for (i) where $e_{\pi_\parallel} = 0$), and by e_σ only for the axial chlorines. Structural data, CLF parameters and $\sum^{\mathrm{exp}}$ values are reported for these species in table 2; the mean value of $\sum^{\mathrm{exp}} = 22\,650\,\mathrm{cm}^{-1}$ and its variation through the series is $\lesssim 10\%$, values that are well in line with those found earlier in a series of copper (II) amine complexes (Deeth and Gerloch 1984 a). The trends and behaviour of the parameters shown in table 2 are discussed in Deeth and Gerloch (1985 a); perhaps the most striking feature to note here is the steadily increasing *negative* values for $e_\sigma(\mathrm{ax})$ as the $R_{\mathrm{Cu-Cl}}(\mathrm{ax})$ distance increases, reaching a value of $-3200\,\mathrm{cm}^{-1}$ for the voids in the planar species (vi).

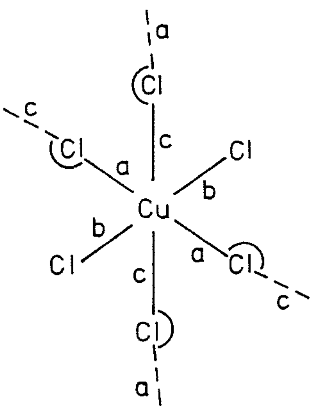

Figure 4. The coordination geometry in tetragonally distorted octahedral chlorocuprate complexes. Dotted lines indicate possible bridges to other Cu centres.

Table 2. Structural (Å) and best-fit ligand-field parameters (cm^{-1}) for a series of chlorocuprate complexes.

$\{e_k^l\}^{\mathrm{exp}}$ Cations	(i) Cs	(ii) NH_3Me	(iii) NH_3Et	(iv) NH_3n-Pr	(v) $Pt(NH_3)_4$	(vi)† nmph
e_σ(eq)	4500	4800	4737	4900	5100	5300
e_π(eq)	1100‡	550	455	600	1100	850
e_σ(ax)	375	−600	−828	−750	−2050	−3200
$\sum^{\mathrm{exp}}$	23150	22400	20930	22900	25100	21600
mean $R_{\mathrm{Cu-Cl(ax)}}$	2·78		2·98	3·04	3·26	—
mean $R_{\mathrm{Cu-Cl}}$(eq)	2·32		2·28	2·29	2·28	2·26

† nmph = $(C_6H_5(CH_2)_2NH_2CH_3^+)_2$.

‡ $e_{\pi\perp}$ value ($e_{\pi\parallel} = 0$).

$$\sum^{\mathrm{exp}} = \sum_{l=1}^{N\,\mathrm{cells}} (e_\sigma^l + e_{\pi\perp}^l + e_{\pi\parallel}^l).$$

Turning now to the second example, the high-spin complexes $[M(Me_6tren)Br]Br$: M = Cr, Fe, Co, Ni, Cu; Me_6tren = tris(dimethylaminoethyl)amine, are members of an extended isomorphous series of trigonal bipyramidal transition-metal compounds; the coordination about the metal ion M is shown in figure 5. The equatorial nitrogens are nearly coplanar with the central metal ion; the bromine and central nitrogen of the Me_6tren ligand are colinear with the metal ion and therefore the e_σ (axial) parameters can only be determined as an average for this pair of ligands. The ligand-field is described with the parameter set $e_\sigma(\overline{ax})$, e_π(Br), and $e_\sigma(N_{eq})$; the axial nitrogen has no π-bonding function. Structural data, best-fit ligand-field parameters and $\sum^{\mathrm{exp}}$ values for this series are reported in table 3. The mean value of $\sum^{\mathrm{exp}}$ is 23 280 cm^{-1} and again its variation is $\lesssim 10\%$ for the different metals; notice in particular that the value of $\sum^{\mathrm{exp}}$ for the Cu(II) complex here is close to that found in the chlorocuprates. Here the noticeable feature of the table is the near constancy of both the $\{e_k^l\}^{\mathrm{exp}}$-parameters and $\sum^{\mathrm{exp}}$ as the metal ion, and hence d^n-configuration, varies across the period (Deeth and Gerloch 1985 b).

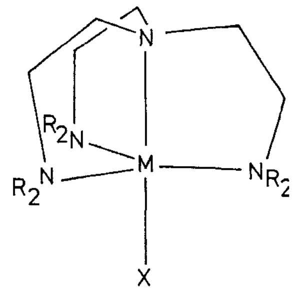

Figure 5. The coordination geometry in Me_6tren complexes: M = Cr, Fe, Co, Ni, Cu; R = Me.

Table 3. Structural (Å and degrees) and best-fit ligand-field parameters (cm^{-1}) for a series of [$M(Me_6tren)Br$] complexes.

	M				
	Cr	Fe	Co	Ni	Cu
M–N_{ax}	—	2·21	2·151	2·10	2·07
M–N_{eq}	—	2·15	2·080	2·13	2·14
M–Br	—	2·482	2·431	2·467	2·393
N_{eq}–M–N_{eq}	—	117·4	117·6	119·0	119·1
$e_\sigma(\overline{\mathrm{ax}})$	6000	4000	4000	5000	5800
$e_\sigma(N_{eq})$	3600	4000	4000	3900	3300
$e_\pi(\mathrm{Br})$	1000	1000	1000	1000	1000
$\sum^{exp}$	25200	22000	22000	23700	23500

These findings have been related to the theoretical formalism as follows (Woolley 1985). Using the unitarity of the $\mathbf{R}^l$ matrices with equation (83) we obtain

$$\sum \equiv \mathrm{Tr}(\mathbf{V}) = \sum_{l=1}^{N\,\mathrm{cells}} \sum_{k}^{5\,\mathrm{modes}} e_k^l \tag{96}$$

which may be compared with (76). The connection with the experimentally determined parameters is established using (94) and (96); we have

$$\sum = \sum_{l=1}^{N\,\mathrm{cells}} \sum_{k}^{5\,\mathrm{modes}} \bar{e}_k^l + 5 \sum_{l=1}^{N\,\mathrm{cells}} = \sum^{\mathrm{exp}} + 5 \sum_{l=1}^{N\,\mathrm{cells}} e_\delta^l, \tag{97}$$

and if we separate e_δ^l into the d-orbital energy, ε, and the correction to ε of δ-symmetry

$$e_\delta^l = \varepsilon/N + \Delta e_\delta^l \tag{98}$$

we obtain,

$$\sum^{\mathrm{exp}} \approx \sum\nolimits_1 \tag{99}$$

where $\sum_1$ is defined in (76), because the (Δe_δ^l) terms can be neglected in comparison with $\sum_1$ (Woolley 1985). The approximate constancy of the sum of $\{e_k^l\}^{\mathrm{exp}}$-parameters identified by Deeth and Gerloch (1984 a, 1985 a, b) therefore refers to $\sum_1$; this is in accordance with intuition for $\sum = \sum_0 + \sum_1$ is dominated by the d-orbital energy, ε, which is expected to alter markedly with variation in transition-metal ion.

The term $\sum_1$ was examined in section 4.2 (equation (76)) where we saw that it is essentially a sum over d-orbital–ligand resonance integrals squared and so must reflect changes in the radial parts of the d-orbitals. The main factors affecting these matrix elements are:

(*a*) the number, nature and bond-distances of the ligands about the metal ion,
(*b*) the oxidation state of the metal ion.

Tables 2 and 3 show that some variation in (*a*) is permissible without greatly affecting $\sum^{\mathrm{exp}}$. On the other hand, a change in oxidation state can be expected to have a considerable effect on the radial part of the d-orbitals, and the $\sum_1$ values for metals in different oxidation states are expected to be quite distinct. Preliminary results appear to bear out this expectation (Deeth and Gerloch 1985, personal communication). The finding that $\sum^{\mathrm{exp}}$ can be approximately invariant over a range of related compounds provides a basis for parameter transferability; one can discriminate between different parameter sets that reproduce the experimental data equally well by excluding those that give $\sum^{\mathrm{exp}}$ values out of line with the empirical trends exemplified in tables 2 and 3.

No comprehensive Ligand-Field Analyses are described here, for these are best reported in conjunction with a full discussion of the definiteness with which individual ligand-field parameters can be fixed using experimental data (seldom better than $\pm 10\%$). Furthermore, it is not unusual to find correlations between some members of the parameter set; these need to be identified and reported, and taken into account in the course of the interpretation of the parametrization that is achieved by the criterion of 'best-fit' to the experimental data. This has been standard practice in the recent literature of Ligand-Field Analysis (Gerloch 1984, Gerloch and Woolley 1984, Deeth and Gerloch 1984 a, b, 1985 a, b). It is hoped that the introduction to the theoretical basis and chemical applications of the Cellular Ligand-Field model given here will convey something of the flavour of the approach and its scope. Ligand-field theory in chemistry is alive and well!

5. Postlude: The electronic structure of materials

One of the principal ideas emphasized in this review is the need to go beyond a purely molecular theory and recognize ligand-field theory as a quantum mechanical model of a paramagnetic insulator. In the final analysis we cannot escape the truism that our experiments are performed on crystals (or macroscopic samples) rather than individual molecules; moreover the claim of modern quantum theory is that it is capable (in the form of a quantum field theory) of describing directly the electronic structure of materials. This final section is a short introduction to the qualitative ideas that have proved useful in this area of condensed-matter physics. It is hoped that it will provide a useful background to the main review.

One of the early successes of quantum theory was the Bloch–Wilson explanation of the fundamental distinction between metals and insulators (Mott 1974). The electronic structure of crystalline materials with idealized periodic lattices can be understood in terms of the wave properties of the electron. According to classical wave theory, standing waves in a periodic lattice are only possible for certain values of the wavevector $\mathbf{k}$, and so the electronic structure of such a solid should consist of bands of allowed energy levels separated by gaps where electron energy levels are forbidden. If the allowed energy bands are incompletely filled there should result a good electrical conductor, i.e. a metal, whereas if the electrons fill all the levels up to a forbidden energy range, the result is an insulator. Even though this picture of the electronic structure of the solid state is only partially valid, this account of the distinction between metals and insulators is one that is still widely taught.

Two examples demonstrate its weakness: copper sulphate pentahydrate is an exemplar of the ligand-field regime that we discussed in section 2.2.; as noted there, it has an incompletely filled valence d-band and yet is a good insulator. Even worse for the Bloch–Wilson viewpoint is the recognition that there should be *no* restrictions on the wavevectors of electron waves in *amorphous* materials which apparently ought to be metallic irrespective of their chemical constitution. The loss of long-range crystal order seems to be sufficient to remove the restrictions on the permissible wavevectors. Amorphous insulators are of course extremely common—a canonical example is ordinary window glass whose colourless transparency also points to an energy gap in excess of $\simeq 3$ eV, above its Fermi energy. From a traditional chemical point of view the resolution of the paradox is obvious. A silicate glass, although disordered, has a local structure of 2-electron covalent Si–O bonds which account for the valence electrons; from an 'old-fashioned' chemist's point of view the electrons should indeed be localized in the bonds so that saturated chemical bonds should imply an absence of free charge carriers. From this perspective the lack of crystalline order is irrelevant as far as the lack of electron mobility is concerned. It is only relatively recently that this heuristic chemical argument has been satisfactorily reconciled with electronic structure theory through the concept of electron *localization* (Mott 1974, Mott and Davis 1979, Elliott 1983, Kaveh and Mott 1985).

5.1. *Localization*

One of the key concepts in the quantum mechanical theory of materials is the idea of localization. Let $\langle r \rangle$ be the distance an electron moves, on average, from some atomic centre,[†] and let L measure the overall (linear) dimension of the electronic system. For small molecules, the domain of computational quantum chemistry, we have a limiting case where the relationship

$$\langle r \rangle \approx L \qquad \textit{small molecules}$$

is generally valid. In 'large' systems (macroscopic matter) we can have either

$$\langle r \rangle \approx L \qquad \textit{delocalized electrons} \Rightarrow \text{Metals}$$

or

$$\langle r \rangle \ll L \qquad \textit{localized electrons} \Rightarrow \text{Insulators}$$

depending on dynamical factors (the interactions) determined by the chemical composition of the material concerned, i.e. the atomic numbers $\{Z_i\}$ of the constituent nuclei and overall electroneutrality.

It may be helpful to digress for a moment to give some reassurance about the use of SCF one-electron models; almost any model of electronic structure that calculates accurately the effects of the *local atomic environment* of each atom in a molecule or solid, i.e. the coordination shell of the atom, can give a reasonable account of the *energetics* of the *ground electronic state*, because the energy is dominated by *short-range* interactions. So band theory or the SCF-MO model may still be useful even if $\langle r \rangle \ll L$; however, such calculations may be quite useless (qualitatively wrong) for properties *other* than the

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[†] For example, for a *localized* orbital $\chi \approx N \exp(-r/\lambda)$, we find $\langle r_\chi \rangle \approx O(\lambda)$.

energy, e.g. magnetism, conductivity, or spectroscopy. Thus, although the SCF-Hartree–Fock model has great difficulty with transition-metal complexes because of the d-electron correlations (Lüthi *et al.* 1984), density functional models have proved rather more successful (Jörg and Rösch 1985 and cited references).

5.2. *Coupling constants and the canonical types of electronic structure*

Modern electronic structure theory in condensed-matter physics gives us the following picture. There are *three* main types of interaction which we have to consider; we associate a characteristic energy or coupling constant with each. The three factors affect each other, and the actual electronic structure *and* associated crystal structure must in principle be determined *self-consistently*—a characteristic feature of a quantum field theory containing attractive interactions as well as repulsive forces. These three factors are:

(*a*) the *one-electron energy*, T—the concern of band theory and the SCF-MO model,
(*b*) the *interelectron repulsion energy*, U—responsible for electron correlation,
(*c*) the *vibronic interaction energy*, V—the coupling between electrons and nuclei.

I will describe each of them briefly.

(*a*) *The one-electron energy*, T

The one-electron hamiltonian, $\hat{h}_1$, describes the self-consistent behaviour of an electron in the presence of all the atoms in the system,

$$(\hat{h}_1 - e_n)\phi_n = 0.$$

In the absence of other interactions, the $\{e_n\}$ describe the electron energy levels and the band-orbitals $\{\phi_n\}$ are delocalized, $\langle r_\phi \rangle \approx L$. Electrons are delocalized by T unless other forces operate to confine them. The efficacy of T is largely determined by the magnitude of the *resonance integrals* connecting orbitals on different atoms in comparison with *other* energies in the system. Chemists have much experience in estimating such quantities.

(*b*) *The interelectron repulsion energy*, U

For *localized* orbitals $\{X, \langle r_X \rangle \ll L\}$, this energy can be thought of as a classical Coulomb interaction between charge distributions, including a self-interaction term (McWeeny and Sutcliffe 1976),

$$U \approx \sum_X \langle XX|g_{12}|XX\rangle + \sum_{X \neq Y} \langle XY|g_{12}|XY\rangle$$

but for materials, unlike small molecules, it is essential to write

$$g_{12} \approx \frac{1}{\varepsilon r_{12}}$$

where the effective dielectric constant, ε, must be determined self-consistently for any given system from some suitable many-body theory. The dielectric constant of a metal is large, corresponding to effective screening between the electrons (small U), whereas the dielectric constant for the electrons in an insulator is small, indicating poor screening and marked electron correlation. At a metal–insulator transition there is a *discontinuous* change in dielectric constant.

U favours *high-spin* arrangements, or ordered magnetic structures (cf. Hund's rules). U acts *against* T as far as delocalization is concerned because the loss of electron mobility throughout the material may be more than compensated for by confining the electrons to localized orbitals so as to keep them out of each other's way (Mott 1949).

(*c*) *The vibronic interaction energy, V*

This is the coupling energy between electrons and atomic vibrations. In adiabatic (Born–Oppenheimer) molecular theory it is discussed in terms of the effect of the 'pseudo-Jahn–Teller' interactions on the magnitude of the HOMO-LUMO energy gap. In 'large' systems the magnitude of V depends critically on the localization of the electrons concerned (Anderson 1972. 1975):

for $\langle r\rangle \approx L$, $V \lesssim$ typical vibrational quantum (phonon) energy, $\hbar\omega_D \approx 10^2\,\mathrm{cm}^{-1}$
for $\langle r\rangle \ll L$, $V \lesssim$ typical *electronic* excitation energy $E_{el} \approx$ a few eV. ($O(10^4\,\mathrm{cm}^{-1})$).

The important feature of V is that it is more nearly diagonal in a localized orbital basis, like U but unlike T. For localized orbitals $\{X\}$, V favours the pairing of electrons with antiparallel spins. It is involved in

(*a*) covalency (Lewis electron pairs)—bonding energy $\approx E_{el}$
(*b*) superconductivity in metals (Cooper pairs)—pair binding energy typically $O(10\,\mathrm{cm}^{-1}) < \hbar\omega_D$.

The signature of both (*a*) and (*b*) is their *diamagnetism*. Superconducting metals can be recognized as frustrated covalent insulators; the weak binding energy of Cooper pairs due to V is associated with an average separation of paired electrons of $O(10^3\,\text{Å})$. Cooper pairs form a boson gas; when the interaction between the electrons is greatly enhanced (remember V is attractive and in this case overcomes U) the 'gas' 'condenses' into an ordered electron pair structure that we recognize as a system of covalent bonds in an insulating material (Anderson 1974).

This must now be drawn together. There are three major limiting cases realized in practice, and these give rise to three main types of bonding:

(i)	$T > U, V$	'Metals'
(ii)	$U > V, T$	'Paramagnetic insulators'
(iii)	$V > T, U$	'Diamagnetic insulators'

The variation in bonding associated with these three coupling constants can be conveniently represented on a triangular (Roozeboom) plot, familiar in chemical thermodynamics from studies of ternary phase equilibria. Figure 6 shows such a plot with some representative materials marked.

This review has been concerned with materials located in figure 6 in the region where U is the important energy; the simple metals of Groups I to IV are located near the T vertex, while solid inert gases, the classical ionic solids (e.g. the alkali halides) and covalent networks are located near the V vertex. These examples illustrate the three main types of chemical bonding which are separated by phase boundaries. Crossing a boundary means a change in bond type and leads to:

(i) a large-scale reorganization of the electronic structure which is reflected in a drastic change in $\langle r\rangle$, and

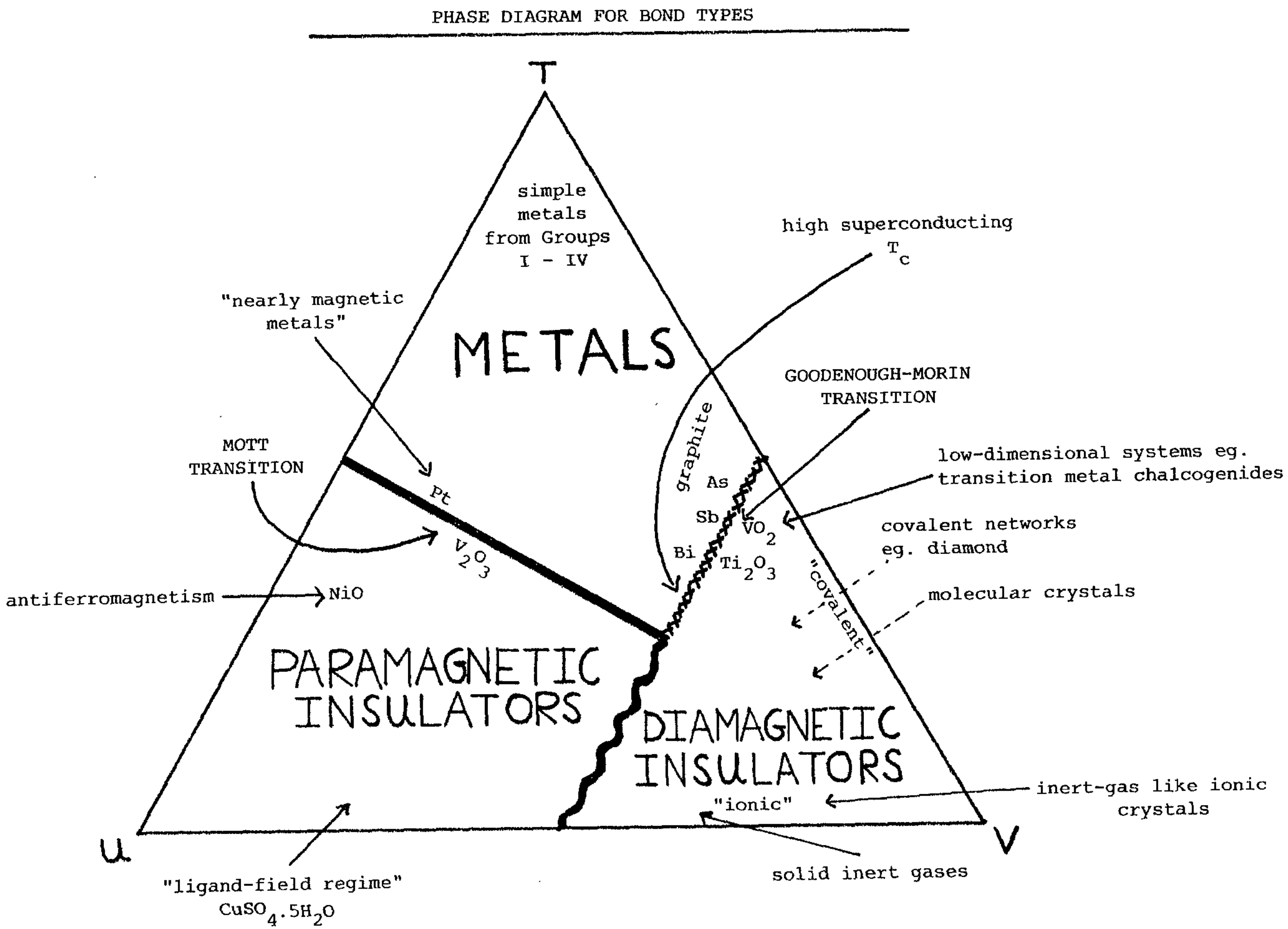

Figure 6. A Roozeboom plot showing the three canonical types of electronic structure separated by phase boundaries (see text for discussion of the diagram).

(ii) discontinuities or alterations in the thermodynamic state variables and transport coefficients (e.g. heat capacity, conductivity)—often a genuine phase transition (Gütlich 1981, Edwards and Sienko 1982).

Transitions across these boundaries are rather uncommon; almost all materials belong to one of the three canonical types of bonding, and no realistic experimental variation in pressure and/or temperature (and in mixed systems, mole fractions of components) can enforce a transition (Anderson 1974).

The reader will notice that there are two canonical types of insulator and hence two distinct types of metal–insulator transition. In some sense therefore it would seem that there are two classes of metals, although these are not obviously differentiated in the figure. This is indeed so. As we move away from the T vertex, the one-electron energy decreases while U and/or V are increasing. This means that we move either towards metals in which electrons are strongly interacting (U becoming dominant) or towards metals with enhanced vibronic interactions (V becoming important). Near the two boundaries that terminate metallic behaviour we do indeed find two distinct categories of metals:

(i) near the *paramagnetic insulator⇔metal* boundary we find metals characterized by strong *interelectron repulsion* interactions and pronounced *magnetism*—either the enhanced paramagnetism of 'nearly magnetic metals' such as platinum, or metals such as chromium and iron that exhibit magnetic ordering.
(ii) near the *diamagnetic insulator⇔metal* boundary interactions with the nuclei are important, and this is where we find the phenomenon of *superconductivity*.

Empirically it appears that magnetic ordering and superconductivity cannot be realized in the same material (Ashcroft and Mermin 1976) and this is reflected in figure 6 by the fact that superconducting and magnetically ordered materials are found in disjoint regions of the triangular plot.

Transitions across the diamagnetic insulator⇔paramagnetic insulator boundary are also of interest; an important class of materials associated with this boundary are transition metal complexes that undergo 'spin-crossover' transitions. A variety of iron (II) complexes that undergo structural phase transitions accompanied by changes of spin-state are now known (Gütlich 1981); these are reversible phase transitions induced by temperature variation.

One final point which must be emphasized is that figure 6 is schematic; the areas of the three regions must not be taken literally and it is speculative as to whether the 'triple-point' at the centre of the diagram is of physical significance. Nevertheless, the figure does offer a new and powerful classification of chemical bonding in materials that is not tied to the Periodic Table, and it affords a much more discriminating description than the conventional division between 'covalent', 'ionic' and 'metallic' bond types.

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