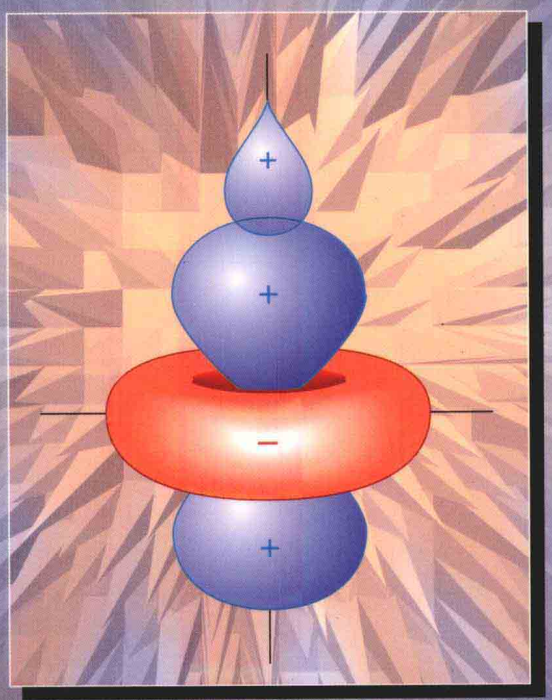
Metal–Ligand Bonding



Rob Janes
and
Elaine Moore

The Open University

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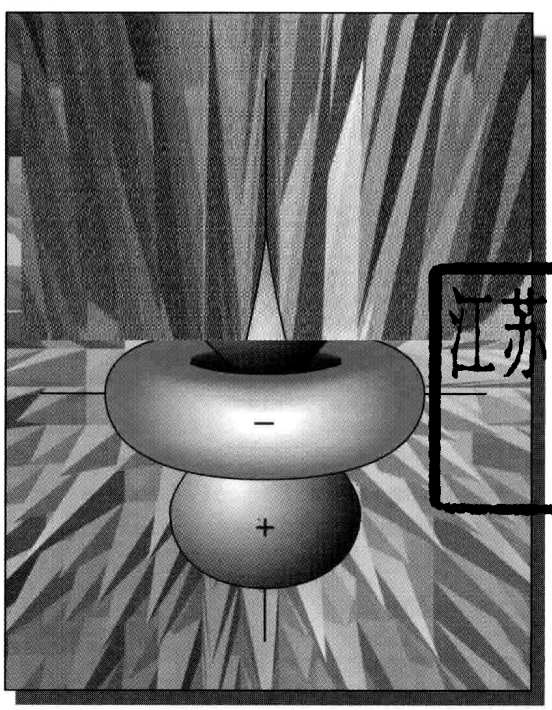

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PREFACE

This book aims to provide an accessible description of the theory of transition metal–ligand bonding, written in a detailed, yet non-mathematical manner. The way bonding models can be used to rationalise many of the chemical and physical properties of complexes is emphasised throughout. The text begins with a brief consideration of the electronic configuration of d electrons on metal ions and the anatomy of a complex, leading to a discussion of the delightfully simple yet extremely powerful crystal-field model. Using this model, we then describe the use of magnetic measurements to distinguish complexes with different electronic configurations and geometries. With basic symmetry concepts as a foundation, this is followed by a treatment of molecular orbital theory applied to transition-metal complexes, using a pictorial approach. Emphasis is placed on the relationship between crystal field and molecular orbital theories throughout. Both d–d and charge-transfer spectra are used to link theory to observation. Even though this text is centred on theoretical models, we have endeavoured to emphasise the practical relevance of the material by the inclusion of relevant experimental data and observations from everyday life.

Full colour energy-level diagrams and orbitals are used throughout. Included in the text are learning outcomes for each section, embedded questions (with answers), and revision exercise questions emphasising connections between different areas of the text. A basic knowledge of atomic and molecular orbitals as applied to main group elements is assumed.

Many people helped with the production of this book. We should like to thank Margaret Careford for word processing, Pam Owen for turning our rough sketches into handsome illustrations, Mike Levers for his high-quality photographs, Ian Nuttall for his thorough editing, Jane Sheppard for cover design and layout, our colleagues Dr Charlie Harding and Yvonne Ashmore, Dr Chris Jones of BNFL for helpful comments, and the RSC for their faith in agreeing to co-publish this text.

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Elaine Moore

CONTENTS

1 INTRODUCTION

The attribute of transition-metal ions on which this book focuses is their possession of partially occupied **d orbitals**. Across the fourth row of the Periodic Table, an electron enters the 4s sub-shell at potassium, and a second fills it at calcium. Then, from scandium to zinc, the 3d sub-shell is progressively filled. For the neutral atoms, the energies of the 3d and 4s orbitals are very close, and it is the *exchange energy stabilisation* † associated with half-filled and filled shells that gives rise to configuration irregularities at chromium and copper, respectively. This is shown in Table 1.1, where [Ar] represents the argon core electrons.

When transition-metal atoms form cations, the 4s electrons are lost first. On ionisation, the 3d orbitals are significantly more stabilised (that is, drop to lower energy) than the 4s would be. This stems from the fact that the 3d electrons are not shielded from the nucleus as well as the 4s electrons. Therefore, the +2 and +3 ions have electronic configurations of $[Ar]3d^n$ (or $1s^22s^22p^63s^23p^63d^n$). The electronic configurations of the +2 and +3 ions, which we shall refer to frequently, are shown in Table 1.2.

Table 1.1 Electronic configurations of the free atoms of the first transition series and zinc

Element	Configuration
Sc	$[Ar]3d^14s^2$
Ti	$[Ar]3d^24s^2$
V	$[Ar]3d^34s^2$
Cr	$[Ar]3d^54s^1$
Mn	$[Ar]3d^54s^2$
Fe	$[Ar]3d^64s^2$
Co	$[Ar]3d^74s^2$
Ni	$[Ar]3d^84s^2$
Cu	$[Ar]3d^{10}4s^1$
Zn	$[Ar]3d^{10}4s^2$

Table 1.2 Electronic configurations of the dipositive ions and tripositive ions of the first transition series, zinc and gallium

Configuration	M^{2+}	M^{3+}
$[Ar]3d^1$	[a] Sc^{2+}	Ti^{3+}
$[Ar]3d^2$	Ti^{2+}	V^{3+}
$[Ar]3d^3$	V^{2+}	Cr^{3+}
$[Ar]3d^4$	Cr^{2+}	Mn^{3+}
$[Ar]3d^5$	Mn^{2+}	Fe^{3+}
$[Ar]3d^6$	Fe^{2+}	Co^{3+}
$[Ar]3d^7$	Co^{2+}	Ni^{3+}
$[Ar]3d^8$	Ni^{2+}	Cu^{3+}
$[Ar]3d^9$	Cu^{2+}	—
$[Ar]3d^{10}$	Zn^{2+}	Ga^{3+}

a Compounds of scandium(II) are very rare.

One of the characteristic features of the chemistry of the transition elements is the formation of a vast number of complexes such as $[Ti(H_2O)_6]^{3+}$, $Ni(CO)_4$ and $[CoCl(NH_3)_4(H_2O)]^{2+}$. These are molecules that consist of a central metal atom or ion, to which is bonded a number of molecules or ions by coordinate-covalent bonds. We refer to the latter as **ligands**, and the number of electron pairs donated to the metal is its **coordination number**.

What is the coordination number of the metal in the following complexes?
(a) $[Ti(H_2O)_6]^{3+}$; (b) $Ni(CO)_4$; (c) $[CoCl(NH_3)_4(H_2O)]^{2+}$.

(a) 6; (b) 4; (c) 6.

† This is the energy term that is responsible for the 'special stability' of filled and half-filled shells.

Possibly the most striking property of transition-metal complexes is the wide range of colours they exhibit. This tells us that part of the visible region of the electromagnetic spectrum is being absorbed by the molecule. But what energy changes are actually occurring at the molecular level? There are also intriguing variations in the magnetic behaviour of transition-metal complexes. For example, although they both contain central Fe^{2+} ions, $[Fe(H_2O)_6]^{2+}$ is *paramagnetic* (it is attracted into a magnetic field), but $[Fe(CN)_6]^{4-}$ is *diamagnetic* (it is weakly repelled by a magnetic field). In this book, we shall look at some bonding theories to help us explain these, and other, observations.

Our starting point is crystal-field theory (Section 2). This is a delightfully simple approach, which, provides us with a remarkable insight into the chemical and physical properties of complexes of d-block metals. However, there are cases where this model is inadequate, and where molecular orbital theory is more appropriate. In developing a theory of bonding in transition-metal complexes, our starting point is a consideration of the properties of the d orbitals on the metal ion.

1.1 What do d orbitals look like?

There are five d orbitals, which, with reference to a set of mutually perpendicular axes, may be represented by their **boundary surfaces**, the contours inside which a d electron is found 95 per cent of the time. The orbitals shown in Figure 1.1 are strictly those for an electron in a hydrogen atom, but those for electrons in

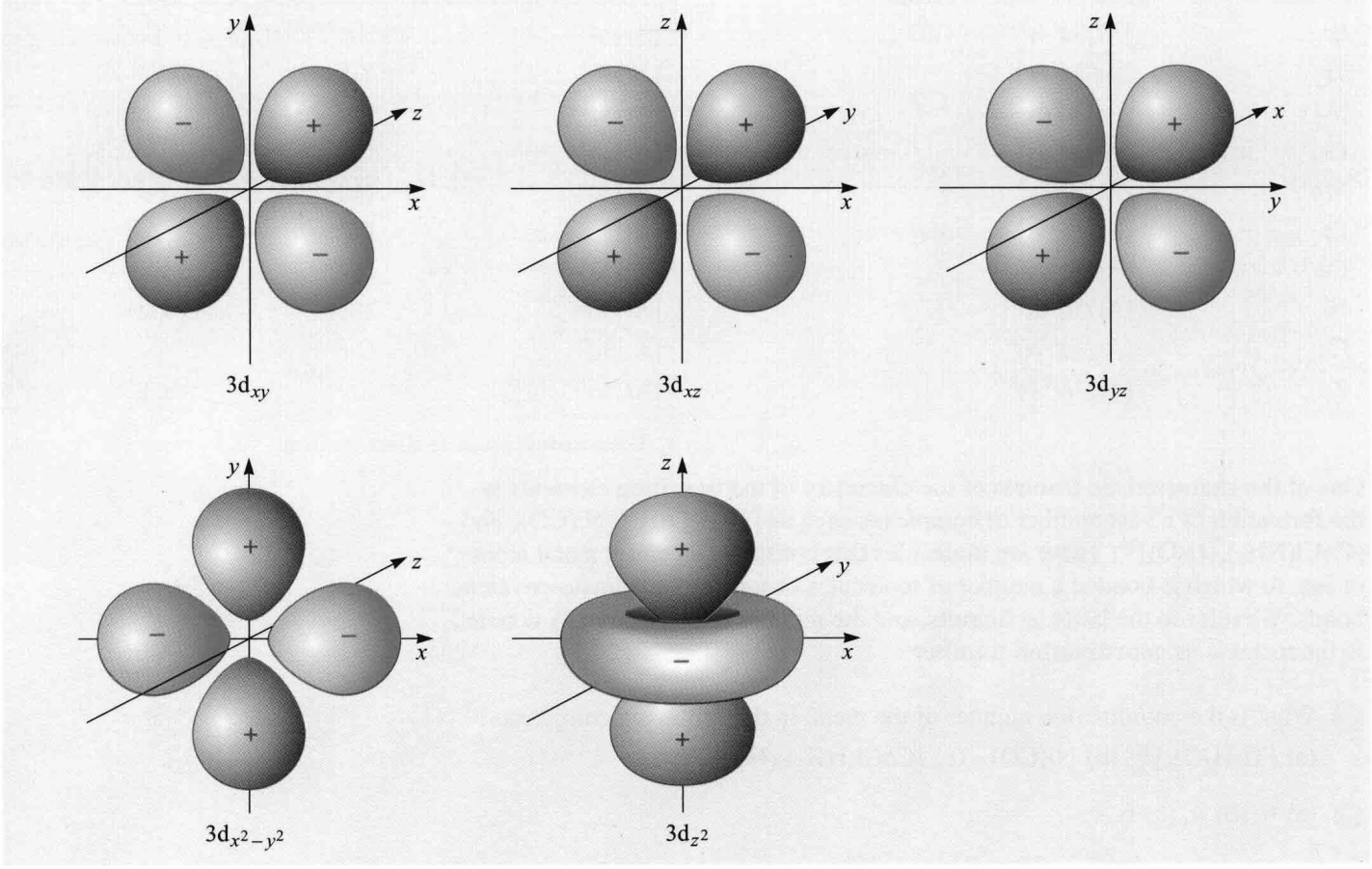
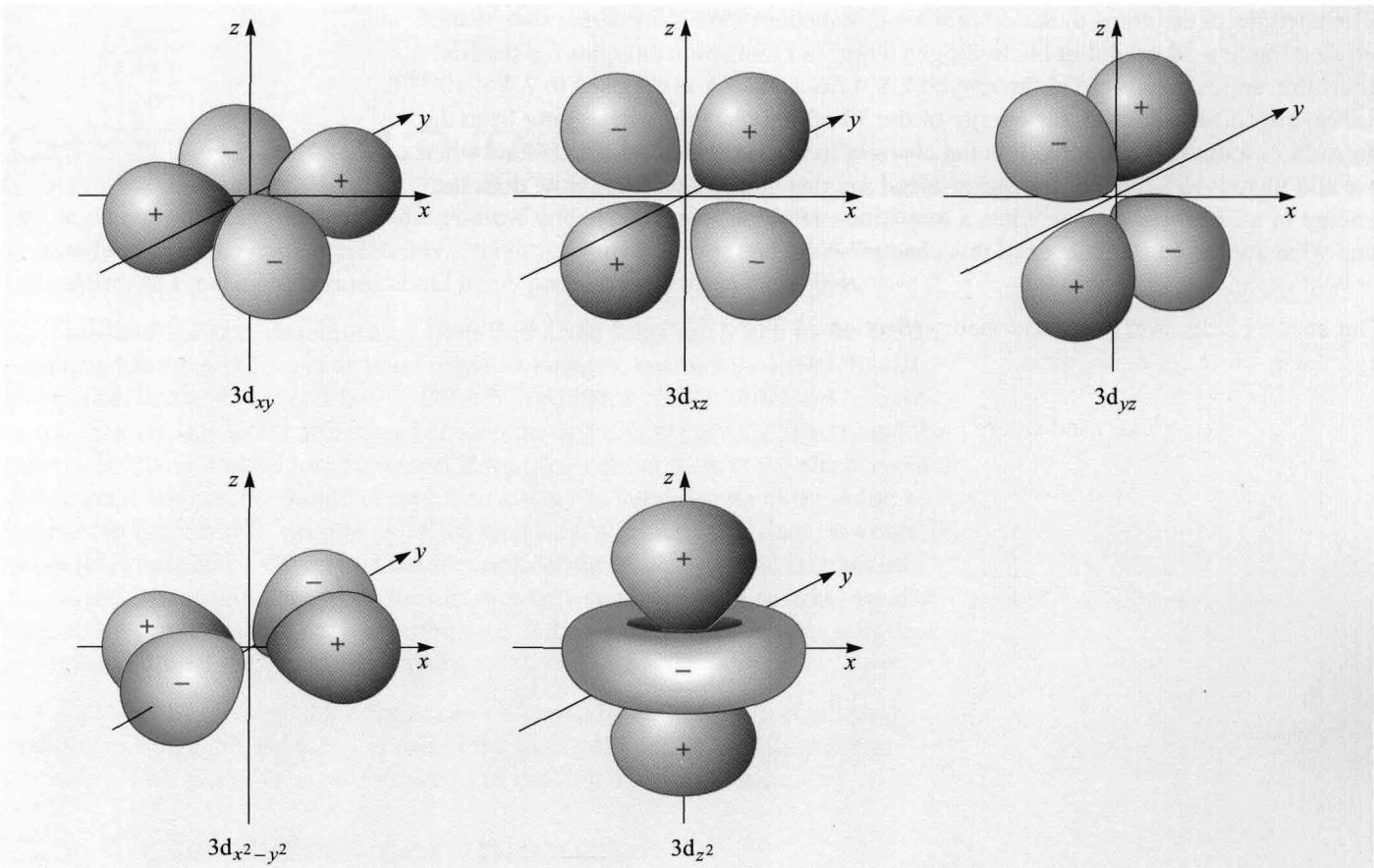


Figure 1.1 The shapes and orientation of the 3d orbitals. Note that in each case the orbital is viewed from the front, so the coordinate axes vary from orbital to orbital.

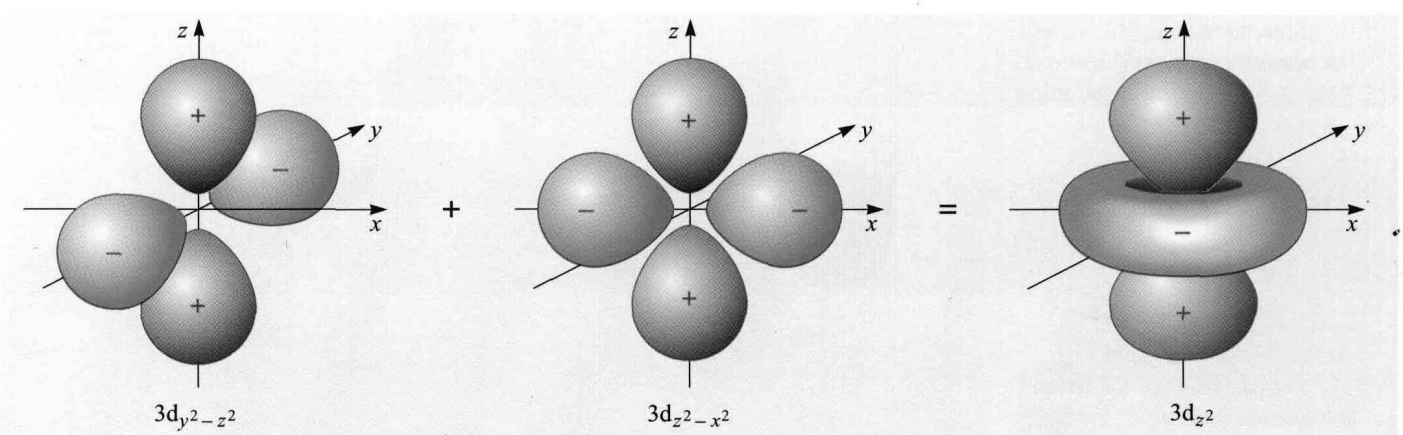


transition-metal ions will have the same shape. In Figure 1.2, the 3d orbitals are all presented from the same perspective, such that the xz plane is always the plane of the paper.

Figure 1.2 The shapes and orientation of the 3d orbitals, all shown with respect to the xz plane.

Four of these orbitals have the same shape but are orientated in different directions: the $3d_{xy}$, $3d_{yz}$ and $3d_{xz}$ orbitals have their lobes between the relevant coordinate axes, whereas the $3d_{x^2-y^2}$ orbital has its lobes along the x and y axes. The fifth, $3d_{z^2}$, looks different, but is, in fact, a combination of two orbitals $3d_{y^2-z^2}$ and $3d_{z^2-x^2}$, which are shaped like the other four (Figure 1.3).

Figure 1.3 The components of $3d_{z^2}$: the $3d_{y^2-z^2}$ and $3d_{z^2-x^2}$ orbitals.



The energies of electrons in the 3d orbitals in transition metals are larger than that of an electron in a 3d orbital in the hydrogen atom. (3d ionisation energies for the first transition series metals are in the range $12.8–17.6 \times 10^{-19}$ J as opposed to 2.4×10^{-19} J for hydrogen.) In addition, the energy of the 3d orbital changes when going from the free ion or atom to a complex. It is the changes in the energies of the d orbitals when we add ligands to a 'naked' transition-metal ion that concern us here. How does the energy of a 3d orbital change when a transition-metal ion is surrounded by ligands, and what are the consequences of this change?

2 CRYSTAL-FIELD THEORY

We begin our consideration of bonding in transition-metal complexes by looking at crystal-field theory, which is relatively straightforward to apply, and allows us to rationalise, and make predictions about many properties of these molecules.

Crystal-field theory, developed by Hans Bethe and John Van Vleck in the 1930s, assumes that ligands behave as point negative charges, and that the metal–ligand interaction occurs on several levels. Overall, a complex will be stabilised relative to the free ion, due to the attraction between the negatively charged ligands and the positively charged metal ion. However, if we take a closer look at the electrons in the metal-ion d orbitals, we would expect *their* energy to increase due to repulsion by the ligands. In other words, the energy of the metal-ion d orbitals will rise. However, this is not the whole story. Given that we are considering an electrostatic interaction, whose magnitude will depend on the distance between the charge centres, we also need to look at how close the d electrons are to the ligands. This, in turn, will depend on which d orbital the electron occupies.

We shall start by looking at the application of crystal-field theory to octahedral complexes, since this geometry is one of the most common in transition-metal chemistry. Our emphasis is on complexes of the first transition series.

2.1 Octahedral complexes

We begin by assuming that the ligand negative charges are concentrated at six points representing six octahedrally arranged ligands, two on the x-axis, two on the y-axis and two on the z-axis (Figure 2.1). For a free ion, the d orbitals are energetically equivalent. We already know that the energies of all the d orbitals will increase, but the key question is: *are* **all** *the 3d orbitals equally affected by this charge?*

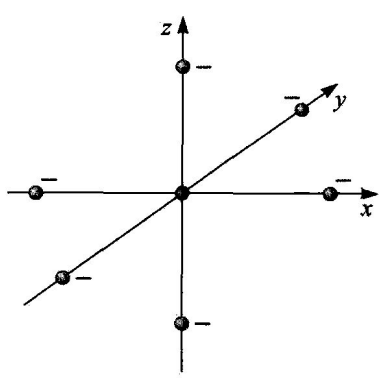


Figure 2.1 Six octahedrally disposed ligands represented as point negative charges.

To answer this question, let us look at the two d orbitals that are orientated in the xy-plane. Figure 2.2 shows the $3d_{xy}$ and $3d_{x^2-y^2}$ orbitals in the xy-plane, and the point charges on the x- and y-axes. By taking this bird's-eye view down the z-axis, you can see that whereas the $3d_{x^2-y^2}$ lobes are concentrated towards the point charges, those of the $3d_{xy}$ orbital lie between the charges.

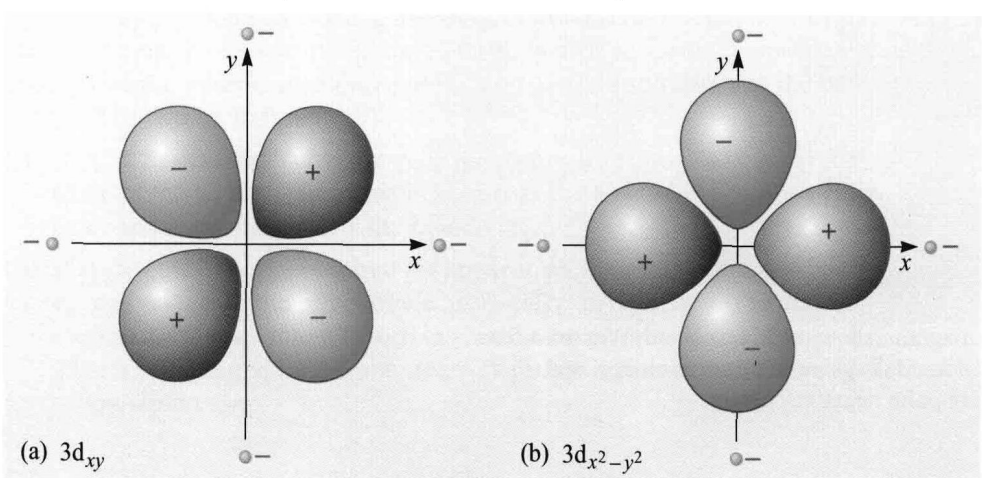


Figure 2.2 (a) $3d_{xy}$ and (b) $3d_{x^2-y^2}$ orbitals surrounded by point negative charges.

How do you think this will affect the energy of the two orbitals?

An electron in a $3d_{x^2-y^2}$ orbital comes closer to the point charges on average than does an electron in a $3d_{xy}$ orbital. Thus, the $3d_{x^2-y^2}$ electron will be repelled more by the ligands, and hence the $3d_{x^2-y^2}$ orbital will be higher in energy than the $3d_{xy}$ orbital.

Similarly, if you look at the *xz*-plane, you will find that an electron in $3d_{z^2}$ will experience a greater repulsion than one in the $3d_{xz}$ orbital, and if you considered the *yz*-plane, you would find that an electron in $3d_{z^2}$ would be repelled more than one in the $3d_{yz}$ orbital.

To summarise: for a set of octahedrally arranged charges (an octahedral crystal field), the energy of the orbitals aligned along the axes ($3d_{x^2-y^2}$ and $3d_{z^2}$) will be higher than those of the $3d_{xy}$, $3d_{xz}$ and $3d_{yz}$ orbitals, which are aligned between the axes (that is, further away from the ligands). This is represented in the form of an energy-level diagram in Figure 2.3. There are several points to note about this diagram. In both Figure 2.3a and b, the five d orbitals all have the same energy (they are referred to as being **degenerate**), and (b) simply represents the average energy of the orbitals in the complex, known as the **barycentre.** This level would correspond to a hypothetical situation in which the metal ion was surrounded by a sphere of negative charge. The splitting of the orbitals is shown in Figure 2.3c; they are 'balanced' about the barycentre. Furthermore, in an octahedral complex, the $3d_{xy}$, $3d_{xz}$ and $3d_{yz}$ orbitals are energetically equivalent, as are the $3d_{z^2}$ and $3d_{x^2-y^2}$ orbitals. The symbol Δ_o (pronounced delta 'oh' for octahedral) denotes the energy separation between the two sets of orbitals, and is referred to as the **crystal-field splitting energy**. The $3d_{xy}$, $3d_{xz}$ and $3d_{yz}$ orbitals have an energy $\frac{2}{5}\Delta_o$ less than the average energy of the orbitals, and the $3d_{z^2}$ and $3d_{x^2-y^2}$ orbitals are raised $\frac{3}{5}\Delta_o$ higher than the average.

Note that the levels in Figure 2.3 are labelled t_{2g} and e_g. These are symmetry labels for a complex (or molecule) belonging to the symmetry point group of an octahedron, $\mathbf{O_h}$.

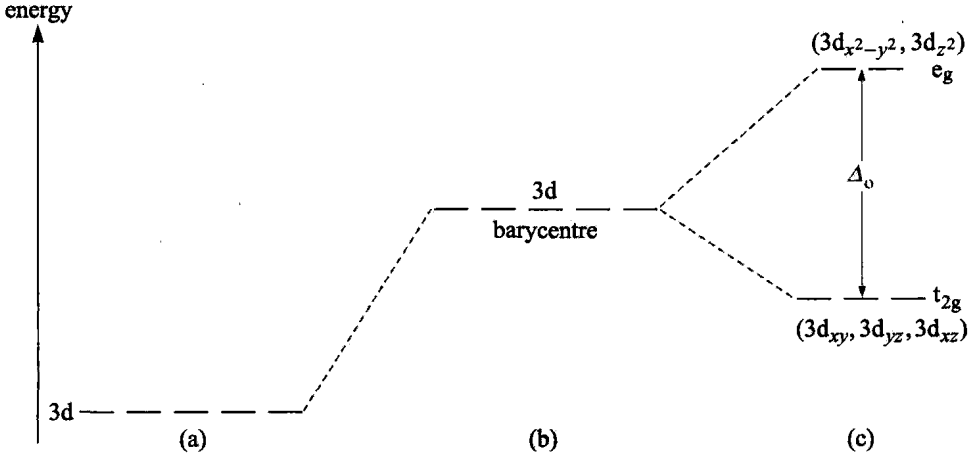


Figure 2.3 Partial orbital energy-level diagram (showing 3d levels only) for (a) a free transition-metal ion, (b) a transition-metal ion in a sphere of negative charge, and (c) a transition-metal ion in an octahedron of six point negative charges.

We shall consider these symbols in more detail in Section 10 in the context of molecular orbital theory, but for the present you need only consider them as labels:

- t denotes a triply degenerate orbital.
- e denotes a doubly degenerate orbital.

Later you will meet the symmetry labels 'a' and 'b', which are singly degenerate levels. The symbols 'g' and 'u' refer to the behaviour of an orbital under the operation of inversion (p. 57). They are only used for complexes that possess a centre of symmetry.

So we now have an energy-level diagram. But how can it be used to explain the properties of transition-metal complexes? The following steps will get us started:

(i) determine the oxidation state of the metal ion in the complex;

(ii) calculate the corresponding number of d electrons;

(iii) establish how these electrons occupy the energy-level diagram (bearing in mind that each energy level can hold a maximum of two electrons).

Firstly, let's consider a complex of titanium in its +3 oxidation state, where there is one d electron (Ti^{3+}, $3d^1$). This will enter the t_{2g} level (Figure 2.4a). It does not matter whether we place the electron in the d_{xy}, d_{yz} or d_{xz} orbital because they are degenerate. For complexes containing metal ions of configuration d^2 (Ti^{2+} and V^{3+}) or d^3 (V^{2+} and Cr^{3+}), the electrons enter the t_{2g} level, but they occupy separate orbitals with parallel spins (Figure 2.4b and c).

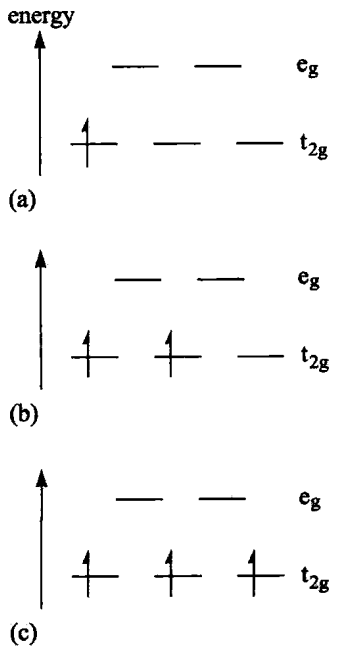


Figure 2.4 Occupation of 3d orbitals for (a) d^1; (b) d^2; (c) d^3 ions.

The energy of an orbital is determined by the attraction of the nuclei in the complex for an electron in that orbital. Generally, when assigning electrons to orbitals, we ignore any interaction between the electrons. However, in this case, we need to consider the repulsion of the negatively charged electrons in more detail. Two electrons in one orbital will repel each other more than two electrons in different orbitals because, on average, they will be closer together. In addition, electrons with paired spins repel each other more than those with parallel spins. Consequently, electron repulsion is minimised if the electrons are in different orbitals with parallel spins. The energy required to force two electrons into the same orbital is the **pairing energy**, ***P***.

The pairing energy becomes important when we reach the $3d^4$ situation, as we are now faced with two choices. The fourth electron could either enter the t_{2g} level and pair with an existing electron, or, it could avoid paying the price of the pairing energy by occupying the e_g level. Which of these possibilities occurs depends on the relative magnitude of the crystal-field splitting and the pairing energy. The two options are:

(i) If $\Delta_o < P$, the fourth electron goes into the e_g level, with a spin parallel to those of the t_{2g} electrons. This is known as the **weak-field** or **high-spin** case, and is represented by the notation $t_{2g}^3e_g^1$.

(ii) If $\Delta_o > P$, the energy required for an electron to occupy the upper level, e_g, will outweigh the effect of electron–electron repulsion. The fourth electron then goes into a t_{2g} orbital, where it has to be spin paired. This is represented by the notation $t_{2g}^4e_g^0$, and is known as the **strong-field** or **low-spin** case.

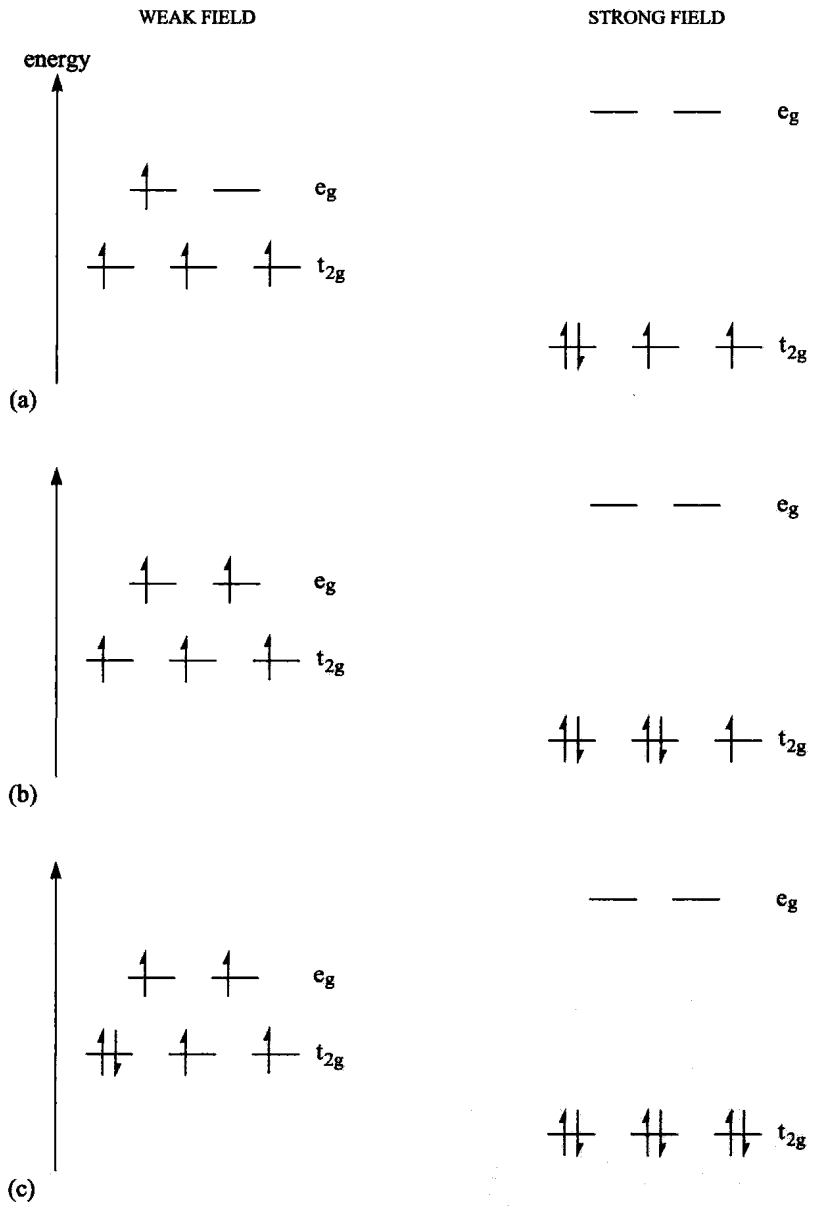


Figure 2.5 Occupation of 3d orbitals for (a) d^4, (b) d^5 and (c) d^6 complexes in weak and strong octahedral crystal fields.

These two possibilities are considered in Figure 2.5, which also includes high- and low-spin arrangements for d^5 and d^6.

- Sketch orbital energy-level diagrams similar to Figure 2.5 showing the weak-field and strong-field configurations for a d^7 complex.
- See Figure 2.6.

- Would we expect to see high-spin and low-spin complexes for d^8 and d^9 complexes in an octahedral crystal field?
- No; there is only one possible arrangement of electrons in both cases, the size of Δ_o makes no difference to the occupation of the levels, d^8: $t_{2g}^6e_g^2$ and d^9: $t_{2g}^6e_g^3$ (see Figure 2.7)

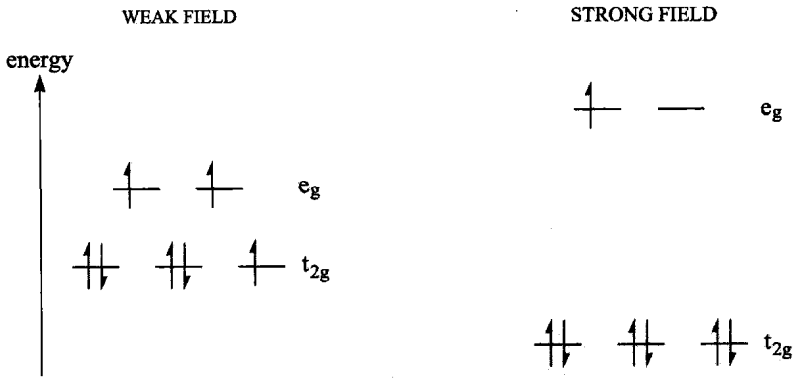


Figure 2.6 Occupation of 3d orbitals for a d^7 complex in weak and strong octahedral crystal fields.

You will notice that the different arrangements of electrons in the t_{2g} and e_g orbitals for d^4–d^7 ions can result in configurations where the d electrons are completely paired, or contain one or more unpaired electrons; that is, complexes containing these ions can be either diamagnetic or paramagnetic. The magnetic properties of transition-metal complexes are considered in more detail in Section 6, and at this stage we simply note the existence of these two possibilities.

We shall now use these d-electron configurations to explain the variations in an important property of transition-metal ions.

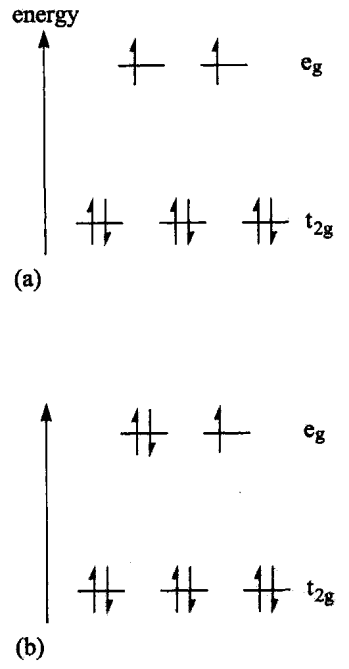


Figure 2.7 Occupation of 3d orbitals for (a) d^8 and (b) d^9 complexes in both weak and strong octahedral crystal fields. Note that Δ_o is bigger for strong-field ligands.

2.2 Ionic radii

A plot of the ionic radii of the dipositive ions for the first transition series shows an overall decrease with increasing atomic number, but with a double-bowl shaped profile. This is shown in Figure 2.8. As the nuclear charge increases, electrons enter the same sub-shell (3d); that is, the electrons are roughly the same distance from the nucleus. Electrons in the same shell do not screen the positive charge of the nucleus from each other very effectively. Hence the net nuclear charge experienced by the electrons increases as the atomic number increases. This increased charge causes the electrons to move closer to the nucleus, and hence the ionic radii of the first-row transition elements exhibit an overall decrease across the series.

If there were a spherical distribution of electric charge over the ions, we would expect a regular decrease in ionic radii (shown by the light green line in Figure 2.8), but clearly this is not the case. In fact, taking into account the regular distribution of

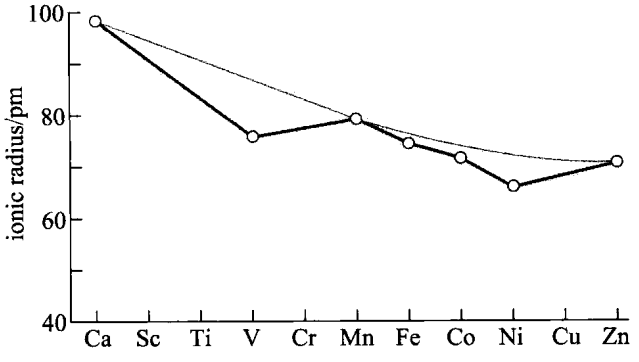


Figure 2.8 Ionic radii of the divalent ions of calcium and the first-row transition metals in the difluorides.

the d orbitals, this situation would only be achieved for d^0, d^5 (high spin) and d^{10}. Here crystal-field theory can help us. The radii in Figure 2.8 were obtained by measuring metal–fluorine distances in metal difluorides, and the crystal structures of these compounds are such that each metal ion is surrounded by an octahedron of fluoride ions. Hence, to a first approximation we are still dealing with octahedral complexes, so our d-orbital energy-level diagram derived in Section 2.1 (Figure 2.3) will apply.

Let us start with TiF_2, which is actually unknown, but we can still use Figure 2.8 to estimate and discuss its notional *internuclear distance*. The Ti^{2+} ion has two 3d electrons, and in an octahedral crystal field they will occupy t_{2g} orbitals with parallel spins. The electrons on the transition metal screen the fluoride ions (which we are regarding as point negative charges) from the charge of the metal nucleus. As the electrons are dividing their time between orbitals that are concentrated between the ligands, we would expect this screening to be less efficient than if the electrons were in e_g orbitals. Since the fluoride ions are screened less than we would expect if the crystal field were spherical, they move closer to the metal nucleus, hence shortening the metal–fluorine distance. Thus, from crystal-field theory, we expect Ti^{2+} to have a smaller ionic radius than if it were a spherical ion.

- What variation from the spherical ion depiction does crystal-field theory predict for V^{2+} in VF_2?
- V^{2+} would have three electrons in the t_{2g} level. So, like Ti^{2+}, V^{2+} will have a smaller ionic radius than would be expected for a spherical ion; in fact, it has the largest deviation from the spherical ion prediction of all the elements in the first transition series.

For Cr^{2+}, there are four d electrons, so we need to consider the possibility of high- and low-spin configurations. However, as we shall see later, fluoride ions are very weak-field ligands, so the complex will be high spin; that is, the fourth electron goes into the e_g level.

The Cr^{2+} ion will therefore have a smaller radius† than expected, but the deviation is less than for V^{2+} because we now have electron density in a d orbital pointing directly at the ligands and therefore screening the nuclear charge more efficiently.

- Use crystal-field theory to explain why the ionic radius for Mn^{2+} is that expected for a spherical ion.
- Mn^{2+} is a d^5 ion, and in the fluoride has three electrons in t_{2g} and two in e_g. Thus, all five d orbitals are equally occupied, and the Mn^{2+} ion is spherical.

Going on to Fe^{2+}, Co^{2+} and Ni^{2+}, the t_{2g} level is gradually filled, and, like Ti^{2+} and V^{2+}, these ions are smaller than expected. Cu^{2+} has its ninth electron in the e_g level, but this level is still not full, and therefore the radius is also less than expected for a spherical ion. Zn^{2+} is on the light green line because it has a filled 3d sub-shell and therefore is a spherical ion.

Crystal-field theory thus helps us understand the double-bowl variation of ionic radii across the first transition series. In the next Section, we shall see how it can be used to explain the variation of other properties.

† The plot in Figure 2.8 does not include points for Cr and Cu. The reason for this is that chromium(II) fluoride and copper(II) fluoride have distorted octahedral structures. Why this is so will become apparent in Section 4.

QUESTION 2.1

The cyanide ion, CN^-, gives rise to strong-field complexes. Suppose the ionic radii of the first transition series M^{2+} ions were taken not from fluorides but from cyanides, $M(CN)_2$, in which M^{2+} is octahedrally coordinated by six CN^- ligands. Describe how you would expect the plot of ionic radii to differ from Figure 2.8, and why. Sketch the curve you would predict from crystal-field theory for the ionic radii of the first transition series metal ions in cyanides, $M(CN)_2$.

QUESTION 2.2

Sketch the predicted variation across the first-row transition-metal series of the ionic radius of M^{2+} in the oxide MO. (O^{2-} is a weak-field ligand, so the ions will have high spin.)

2.3 Crystal-field stabilisation energy

We now turn our attention to the variation of the *lattice energy* of the chlorides MCl_2, where M is a metal of the first transition series. These are plotted in Figure 2.9, which also has a double-bowl shape. This is not surprising as lattice energy depends on ionic radius, which, as you will recall from Figure 2.8, exhibits a similar variation. Again, we can account for this variation with reference to crystal-field theory.

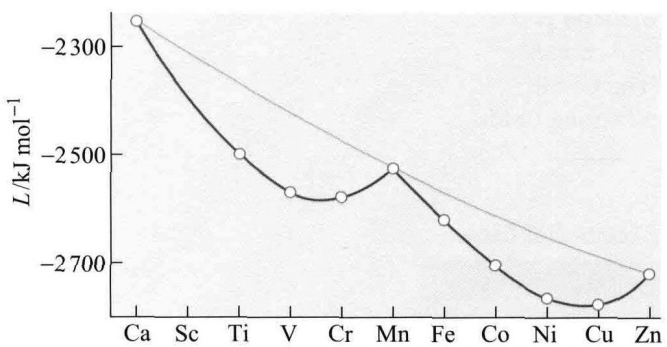


Figure 2.9 Lattice energies, L, of the dichlorides of calcium and the first-row transition metals.

In the dichlorides, the metal ions are in octahedral sites, and for $TiCl_2$, the ion Ti^{2+} has two d electrons, which will enter the t_{2g} orbitals with parallel spins. In Section 2.1 we noted that transition-element electrons in octahedral complexes enter a t_{2g} orbital with an energy $\frac{2}{5}\Delta_o$ less than the barycentre, but those in an e_g orbital are increased in energy by $\frac{3}{5}\Delta_o$. The orbital energy for Ti^{2+} in $TiCl_2$ is thus $2 \times \frac{2}{5}\Delta_o$ or $\frac{4}{5}\Delta_o$ below what we would expect for the ion if it were in a (hypothetical) spherical crystal field. This decrease in energy on going from the spherical situation to an octahedral crystal field is called the **crystal-field stabilisation energy, CFSE** †.

What is the CFSE for V^{2+} in an octahedral site?

V^{2+} has three 3d electrons, and so these will all go into the t_{2g} orbitals with parallel spins. The CFSE for V^{2+} is thus $(3 \times \frac{2}{5})\Delta_o = \frac{6}{5}\Delta_o$.

Returning to our consideration of lattice energies, it is clear that the value for VCl_2 in Figure 2.9 is further below the curve for an ion in a spherical environment than that for $TiCl_2$, due to the additional contribution from the CFSE. However, it is important to realise that the magnitude of the CFSE is small (about 10%) compared

† Make sure you do not confuse this term with 'crystal-field splitting energy'.