

## Chapter 2

# One Magnetic Center

**Abstract** This chapter discusses some of the magnetic phenomena that can be observed in systems with a single paramagnetic center. After shortly reviewing the basics of the magnetic moments of a free atom, we analyze the effect of spin-orbit coupling and an external magnetic field on the  $M_S$  levels of the ground state of larger systems. In a step-by-step procedure, we will first derive the model Hamiltonian to describe the magnetic anisotropy without external field, the so-called *zero-field splitting*. Secondly, the role of the external field is explored and a relation is established with the magnetic susceptibility, a macroscopic quantity. The chapter is closed by discussing the model Hamiltonian that combines the zero-field splitting and the anisotropy of the  $g$ -tensor to complete the description of the splitting of the  $M_S$  levels in systems with one, anisotropic, magnetic center.

### 2.1 Atomic Magnetic Moments

The two main sources for the magnetic moment of a free atom or molecule are the electronic spin moment and the angular momentum. The motion of electrons relative to the nucleus in atoms with filled shells and in closed shell molecules leads to zero spin moment and zero angular momentum. Therefore, such atoms and molecules can only have an induced magnetic moment when placed in an external magnetic field.

The simplest system with an intrinsic non-zero magnetic moment is an isolated one-electron atom or ion, treating both particles as point charges and neglecting the possible nuclear spin. The motion of the electron around the charged nucleus induces a microscopic current that produces a microscopic magnetic field. This leads to a so-called orbital magnetic moment which is proportional to the angular momentum of the electron. Taking  $z$  as our quantization axis, its  $z$ -component equals

$$m_z = -\mu_B m_l \quad (2.1)$$

where  $m_l$  is the magnetic quantum number of the electron:  $m_l = -l, -l+1 \dots l-1, l$ . The quantity  $\mu_B = eh/4\pi m_e$  (1/2 in atomic units) is the elementary unit of magnetic moment, called the Bohr magneton. Its value is  $9.27 \times 10^{-24} \text{ JT}^{-1}$ .

There is another contribution to the total magnetic moment of the electron in a hydrogenic atom, this is due to the electron spin. From a *classical* viewpoint, this contribution (the spin magnetic moment) is due to the rotation of the charged electron around its axis. Its magnitude is given by

$$m_{sz} = -g_e \mu_B m_s \quad (2.2)$$

with  $m_s = \frac{1}{2}, -\frac{1}{2}$ . The factor  $g_e$  turns out to be equal to 2.002319314. This value is slightly different from the value of 2 that might at first sight be expected from the analogy with the orbital magnetic moment, showing that this classical approach may be misleading. The difference with the value of 2 can be accounted for by the theory of quantum electron dynamics. The spin-orbit interaction is a relativistic effect, which appears in a natural way if we use Dirac's instead of Schrödinger's equation of motion. We can also describe it in an approximate sense by adding to the non-relativistic one-electron Hamiltonian a term that is proportional to the inner product of the vector operators  $\hat{l}$  and  $\hat{s}$

$$\hat{H}_{so} = \xi(r) \hat{l} \cdot \hat{s} \quad (2.3)$$

The average of  $\xi(r)$  over  $r$  is written  $hc\zeta$  and  $\zeta$  is called the spin-orbit constant. The spin-orbit constant of a hydrogenic atom turns out to be strongly dependent on  $Z$  and on the quantum numbers  $n$  and  $l$  of the electronic wave function

$$\zeta_{n,l} = \frac{\alpha^2 RZ^4}{n^3 l (l + \frac{1}{2}) (l + 1)} \quad (2.4)$$

where  $\alpha$  is the fine-structure constant ( $\sim 1/137$ ) and  $R$  is the Rydberg constant. The non-relativistic one-electron Hamiltonian commutes with  $\hat{l}^2$ ,  $\hat{s}^2$  and (taking  $z$  as the quantization axes) with  $\hat{l}_z$  and  $\hat{s}_z$ . Clearly, when we add  $\hat{H}_{so}$  to the Hamiltonian, the Hamiltonian no longer commutes with these four operators and  $l$ ,  $s$ ,  $m_l$  and  $m_s$  are no longer "good" quantum numbers. The only remaining quantum numbers are  $j$  (with values  $l + \frac{1}{2}$  and  $l - \frac{1}{2}$ ) and  $m_j = m_l + m_s$  (with values  $j, j - 1, \dots - j$ ).

**2.1** Calculate  $\zeta_{n,l}$  for the hydrogenic atoms H- $2p^1$ , Ca $^{19+}$ - $3p^1$ , Ca $^{19+}$ - $3d^1$ , U $^{91+}$ - $2p^1$ , U $^{91+}$ - $6d^1$  and U $^{91+}$ - $5f^1$ .

## 2.2 The Eigenstates of Many-Electron Atoms

In many-electron atoms we have an analogous situation, be it that the electron-electron interactions have to be included from the very beginning. We focus first on free many-electron atoms or ions, i.e. atoms or ions in a zero or uniform external

field, for the time being neglecting any spin-orbit coupling. The total orbital angular momentum operators  $\hat{L}^2$ ,  $\hat{L}_z$  and the total spin angular momentum operators  $\hat{S}^2$  and  $\hat{S}_z$  commute with the Hamilton operator  $\hat{H}$  where each electron moves in a field of spherical symmetry due to the nucleus and the field due to the other electrons. Therefore, the eigenfunctions of  $\hat{H}$  are in general also eigenfunctions of the other four operators. Only in the case of degenerate eigenstates of  $\hat{H}$  one may choose (or find) eigenfunctions that are not simultaneously eigenfunctions of the other four operators. In that case, however, the eigenfunctions of  $\hat{H}$  may always be rotated within the degenerate set to become also eigenfunctions of the other operators.

This implies that these eigenfunctions of  $\hat{H}$  can be labelled using the quantum numbers  $S$ ,  $M_S$ ,  $L$  and  $M_L$ . The energy eigenvalues only depend on the eigenvalues of  $\hat{L}^2$  and  $\hat{S}^2$ , and not on  $M_S$  and  $M_L$ . Therefore, the degenerate set of eigenfunctions of the free-atom Hamiltonian corresponding to one eigenvalue of  $\hat{L}^2$  and  $\hat{S}^2$  can be labelled by their values for  $L$  and  $S$ . It has become customary to use as labels not the spin moment  $S$  and orbital moment  $L$  but rather the spin multiplicity  $2S + 1$  and  $L$ , in the notation  $^{2S+1}L$ , where a *spectroscopic notation*  $S, P, D, F, G, \dots$  is used for  $L = 0, 1, 2, 3, 4, \dots$ . The degenerate set of  $(2S + 1) \times (2L + 1)$  eigenfunctions of  $^{2S+1}L$  is commonly called an *LS term*. Examples of free atom (ion) *LS terms* are  $^1S, ^2P, ^4F, \dots$

Since there is a one-to-one correspondence of the different  $L$  eigenvalues with the irreducible representations (IR) of the spherical symmetry group  $SO(3)$ , the labels of the *LS terms* are simultaneously symmetry labels. Note that the angular momentum operators  $\hat{L}_x, \hat{L}_y, \hat{L}_z$  transform as the rotation operators  $\hat{R}_x, \hat{R}_y, \hat{R}_z$ , i.e. as  $P$  [1]. The behavior of atoms and ions, free and in compounds, depends for a large part on the ground term and the lowest excited terms. The symmetry of these lowest *LS terms* and the ordering of their energies can in general be well deduced using a simple one configuration model.

So far we have not considered any relativistic effects for the atoms. In particular, spin appears in the wave function but not in the non-relativistic Hamiltonian. Traditionally, spin is introduced *ad hoc* to explain the splitting of a beam of silver atoms into two parts in the famous experiment of Stern and Gerlach in 1922. A similar splitting was observed for a beam of hydrogen atoms in a later experiment. The splitting indicates the presence of an angular momentum, but it cannot be an orbital angular momentum since both atoms have an  $L = 0$  ground state. Therefore, the spin property introduced to explain the splitting is considered to reflect an intrinsic angular momentum  $s$ , which for electrons must be  $1/2$ , and hence it is concluded that each electron has an additional quantum number  $s = 1/2$ , with a  $z$ -component  $s_z$  of either  $+1/2$  or  $-1/2$ . The individual spin angular moments of the electrons in an atom can be coupled together to give a total spin angular momentum  $S$ , analogous to the coupling of the individual orbital angular moments  $l$  to a total angular momentum  $L$ . Since there is no spin operator in the Hamiltonian, there is also no coupling between spin and orbital angular momentum.

The relativistic Hamilton operator for an electron can be derived, using the correspondence principle, from its relativistic classical Hamiltonian and this leads to the one-electron Dirac equation, which does contain spin operators. From the one-electron Dirac equation it seems trivial to define a many-electron relativistic equation, but the generalization to more electrons is less straightforward than in the non-relativistic case, because the electron-electron interaction is not unambiguously defined. The non-relativistic Coulomb interaction is often used as a reasonable first approximation. The relativistic treatment of atoms and molecules based on the many-electron Dirac equation leads to so-called *four-component* methods. The name stems from the fact that the electronic wave functions consist of four instead of two components. When the couplings between spin and orbital angular momentum are comparable to the electron-electron interactions this is the preferred way to explain the electronic structure of the lowest states.

In most cases, however, the relativistic effects are rather weak and may be separated into spin-orbit coupling effects and scalar effects. The latter lead to compression and/or expansion of electron shells and can rather accurately be treated by modifying the one-electron part of the non-relativistic many-electron Hamiltonian. With this *scalar-relativistic* Hamiltonian the (modified) energies and wave functions are computed and subsequently an effective spin-orbit part  $\hat{H}^{SO}$  is added to the Hamiltonian. The effects of the spin-orbit term on the energies and wave functions are commonly estimated using second-order perturbation theory. More information for the interested reader can be found in excellent textbooks on relativistic quantum chemistry [2, 3].

The standard way to include relativistic angular momentum couplings in the notation of eigenvalues and eigenfunctions of the thus obtained energies and wave functions is the so-called Russell–Saunders coupling scheme. It is adequate if the spin-orbit coupling is considered to be weak compared to the electron-electron interactions. For a free atom or ion the Russell–Saunders scheme implies that the one-electron moments  $l$  and  $s$  are first coupled to a many-electron angular momentum  $L$  and spin moment  $S$ , which are subsequently coupled to a total angular momentum  $J$ . Due to the spin-orbit coupling the wave functions are no longer eigenfunctions of the  $\hat{L}$  and  $\hat{S}$  operators ( $L$  and  $S$  are no longer “good quantum numbers”) but only of the  $\hat{J}$  operator and the degeneracy of the states belonging to one LS term is partly removed. Only the states corresponding to a particular  $J$  eigenvalue are degenerate, but nevertheless the states of one LS term are close in energy. Such a set of nearly-degenerate states originating from one LS term is called a Russell–Saunders (RS) term and commonly denoted by a Russell–Saunders term symbol  $^{2S+1}L_J$ . For example, the lowest energy RS term of an atom with a single valence  $p$ -electron is  $^2P_{1/2}$ , with the RS term  $^2P_{3/2}$  having a slightly higher energy. The  $^2P_{1/2}$  term is two-fold degenerate ( $M_J = 1/2, -1/2$ ) while the  $^2P_{3/2}$  term is four-fold degenerate ( $M_J = 3/2, 1/2, -1/2, -3/2$ ).

**2.2** Give the Russell–Saunders term symbol for the ground state of an atom with three electrons in the  $2p$  orbitals.

In cases where the spin-orbit coupling is strong compared to the electron-electron interactions it is more reasonable to account for the spin-orbit coupling by using the so-called  $j$ - $j$  coupling scheme. Here the orbital moment  $l$  and the spin  $s$  of each electron are coupled to give an individual angular moment for each electron. The individual  $j$  for each electron are then coupled to give a total angular moment  $J$ . Modern relativistic many-electron quantum mechanical computational treatments are able to treat the entire range of angular moment couplings, from negligible to dominant spin-orbit coupling. The results can be expressed in either terms of Russell–Saunders states or in  $j$ - $j$  coupled states, whatever representation gives better insight. For core-excited states where the core spin-orbit coupling is much larger than the valence spin-orbit coupling, a mixed notation is sometimes used, in which the open core shell is  $j$ - $j$  coupled and the open valence shell is Russell–Saunders coupled.

The many-electron states of an atom in a crystal field or a molecule can obviously not be labelled by the IRs of  $SO(3)$ , since the Hamilton operator, the angular momentum operator and therefore also the many-electron wave functions transform according to the IRs of a less symmetric point group. The lower symmetry may also remove the degeneracies of the LS terms. For example, the  ${}^2P$  ground term of a boron atom becomes  ${}^2T_{1u}$  in an octahedral crystal field so that the three fold degeneracy is retained, but splits into two LS terms of  ${}^2E$  and  ${}^2A_1$  symmetry when the crystal field symmetry is lowered to  $C_{3v}$ .

**Orbital moment quenching:** The eigenfunctions of the angular momentum operator  $\hat{l}^2$  are the spherical harmonics, characterized by the quantum numbers  $l$  and  $m$ .

$$\hat{l}^2 Y_{l,m} = l(l+1)Y_{l,m} \quad (2.5)$$

where  $\hbar$  is put to 1. On the other hand, these functions cannot be eigenfunctions simultaneously of the three components  $\hat{l}_{x,y,z}$ , because these operators do not commute. Choosing  $z$  to be the quantization axis gives

$$\begin{aligned} \hat{l}_z Y_{l,m} &= mY_{l,m} \\ \hat{l}_x Y_{l,m} &= \frac{1}{2}\sqrt{(l-m)(l+m+1)}Y_{l,m+1} + \frac{1}{2}\sqrt{(l-m+1)(l+m)}Y_{l,m-1} \\ \hat{l}_y Y_{l,m} &= \frac{1}{2i}\sqrt{(l-m)(l+m+1)}Y_{l,m+1} - \frac{1}{2i}\sqrt{(l-m+1)(l+m)}Y_{l,m-1} \end{aligned} \quad (2.6)$$

In general the spherical harmonics  $Y_{l,m}$  are complex functions, but linear combination can be made such that the eigenfunctions of  $\hat{l}^2$  become real. For example for the spherical harmonics with  $l = 1$  of a  $p^1$  electronic configuration:

$$p_x = \frac{1}{\sqrt{2}} [-Y_{1,1} + Y_{1,-1}] \quad p_y = \frac{+i}{\sqrt{2}} [Y_{1,1} + Y_{1,-1}] \quad p_z = Y_{1,0} \quad (2.7)$$

The first two functions are no longer eigenfunctions of  $\hat{l}_z$ , because linear combinations are made of functions with different  $m$  quantum number. The action of the  $\hat{l}_{x,y,z}$  on these functions is worked out for one case and then summarized in Eq. 2.9.

$$\hat{l}_z p_x = \frac{1}{\sqrt{2}} \hat{l}_z [-Y_{1,1} + Y_{1,-1}] = \frac{1}{\sqrt{2}} [-Y_{1,1} - Y_{1,-1}] = i p_y \quad (2.8)$$

$\psi$	$\hat{l}_x \psi\rangle$	$\hat{l}_y \psi\rangle$	$\hat{l}_z \psi\rangle$	
$p_x$	0	$-i p_z$	$i p_y$	(2.9)
$p_y$	$i p_z$	0	$-i p_x$	
$p_z$	$-i p_y$	$i p_x$	0	

The matrix elements of  $\hat{l} = \hat{l}_x + \hat{l}_y + \hat{l}_z$  in the basis of the  $p_{x,y,z}$  functions are easily obtained

$\langle \hat{l} \rangle$	$p_x$	$p_y$	$p_z$	
$p_x$	0	$-i$	$i$	(2.10)
$p_y$	$i$	0	$-i$	
$p_z$	$-i$	$i$	0	

and the subsequent diagonalization results in two non-zero expectation values of  $\langle \hat{l} \rangle$ . In analogy to the spin operators the  $N$ -electron angular momentum operators  $\hat{L}$  are obtained by summing over the corresponding one-electron operators. The  $N$ -electron eigenfunctions are products of the one-electron spherical harmonics  $Y_{l,m}$ . Notice that the orbital moment of the  $p^5$  electron configuration can be treated as if it were a one-electron system because of the hole-electron analogy.

**2.3** Confirm that  $\langle p_x | \hat{l}_z | p_y \rangle = -\langle p_y | \hat{l}_z | p_x \rangle = -i$ .

The situation changes drastically when an external potential removes the degeneracy of the three functions. This can be caused by the crystal field exerted by the ions in an extended lattice for solid state compounds or by the ligands in the coordination sphere of an ion in a coordination complex. Although magnetic phenomena are more common for systems with incomplete  $d$ -shells, we will continue with our example concerning the  $p^1$  configuration for simplicity. Imagine an external potential that makes, for example, the state with one electron in the  $p_x$  orbital lowest in energy and places the other two orbitals at slightly higher energy. Then, the orbital angular momentum of the ground state is defined from the matrix element  $\langle p_x | \hat{l} | p_x \rangle$  only, which is zero as can be seen in the matrix 2.10. In many physics textbooks, this effect is

called *orbital angular momentum quenching*. On the other hand, if the external potential destabilizes  $p_x$  with respect to  $p_{y,z}$ , the orbital angular momentum of the  $p^1$  electronic configuration is defined by the lower-right  $2 \times 2$  sub-block of matrix 2.10 and results in non-zero expectation values. Now, the orbital angular momentum is not quenched.

The general condition for non-zero orbital angular momentum for a given Russell-Saunders term  $^{2S+1}\Gamma$  is that the direct product  $\Gamma \times \Gamma$  contains irreducible representations of the orbital moment operators  $\hat{L}_{x,y,z}$ . Since these operators have identical transformation properties as the rotation operator  $\hat{R}_{x,y,z}$  (which is usually listed in the character tables of the symmetry point groups), it is easier to work with the rotation operator. For example, the ground state of the  $d^1$  electronic configuration in an octahedral surrounding is  $^2T_{2g}$ . The rotation operator transforms as  $T_{1g}$  in the  $O_h$  point group. Since the direct product  $T_{2g} \times T_{2g} = A_{1g} + E_g + T_{1g} + T_{2g}$  contains the irreducible representation of the rotation operator, one expects a non-zero orbital angular momentum for this system. Note, however, that the  $d^1$  electronic configuration is Jahn-Teller active and the geometry spontaneously distorts to a lower symmetry group accompanied by a (partial) *quenching* of the orbital angular momentum.

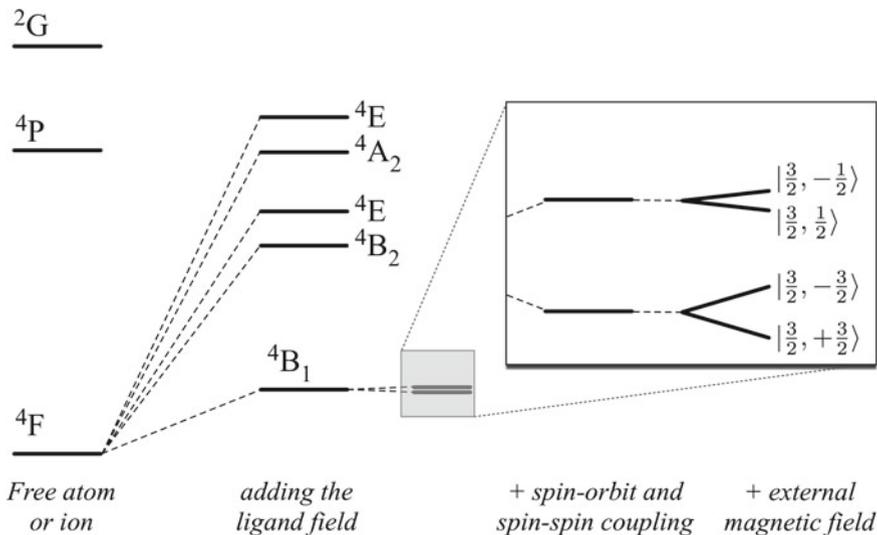
**2.4** Predict the (non-)existence of a net orbital angular momentum for the high-spin  $d^2$  electronic configuration in complexes with tetrahedral, octahedral and  $C_{2v}$  symmetry.

## 2.3 Further Removal of the Degeneracy of the $N$ -electron States

The first two columns of Fig. 2.1 show how the free atom levels of a  $d^7$  configuration are split by a distorted tetrahedral ligand-field. In this example, the states are labeled by the IR's of the  $D_{2d}$  subgroup of  $T_d$  and the  $^4F$  (with a degeneracy of  $(2S + 1) \times (2L + 1) = 4 \times 7 = 28$ ) is split in five energy levels. Based on the discussion in the previous section, one only expects a non-zero orbital moment for the  $^4E$  states. The inset of the figure zooms in on the levels of the  $^4B_1$  state and shows how the degeneracy is removed under the influence of spin-orbit coupling and when the system is placed in an external magnetic field. In the following two subsections we will discuss these two effects.

### 2.3.1 Zero Field Splitting

In  $3d$  transition metal complexes, the splitting of the Russell-Saunders terms due to spin-orbit coupling is in general more important than the one caused by the external magnetic field typically used in EPR experiments. Therefore, the description of the



**Fig. 2.1** Removal of the degeneracy of the energy levels of the  $d^7$  manifold (first column) in a distorted tetrahedral ligand-field (second column), under the influence of spin-orbit coupling (first column of the inset) and in an external magnetic field (inset, second column). Only the lower states are shown in the figure. The labelling in the first two columns is  $^{2S+1}\Gamma$ , where  $\Gamma$  is the irreducible representation of the many-electron wave function. The labelling in the inset is  $|J, M_J\rangle$

energy levels in these systems starts in general by addressing the zero field situation. In the absence of an external field and assuming a quenched orbital angular momentum, the effect of spin-orbit coupling on the levels of the ground state can be qualitatively analysed with second-order perturbation theory. The perturbation operator takes the following form

$$\hat{V} = \zeta \hat{L} \cdot \hat{S} \quad (2.11)$$

with  $\zeta$  a tabulated atomic spin-orbit parameter, determined either by calculation or extracted from experimental data. For those cases that the orbital angular momentum of the ground state is zero, it is convenient to derive a model Hamiltonian to describe the sub-levels of the ground state that only depends on the spin variables. Therefore, we write the unperturbed vectors as the product of the  $|L, M_L\rangle$  spatial and  $|S, M_S\rangle$  spin parts. The spatial part of the ground state is represented with  $|0\rangle$ , and  $|\kappa\rangle$  denotes the spatial part of the excited states. The spin-only Hamiltonian that describes the zero-field splitting (no external magnetic field) of the levels is derived as the sum of first and second-order corrections. In first-order perturbation theory the energy correction equals

$$\langle 0|V|0\rangle = \langle S, M_S|\zeta \hat{S}|S, M_S\rangle \langle 0|\hat{L}|0\rangle \quad (2.12)$$

Independent of the value of  $S$  or  $M_S$ , this product is strictly zero since we assumed that the ground state has no orbital angular momentum. This is often referred to in the

literature as the absence of a first-order angular moment. At second-order perturbation theory, the correction becomes slightly more involved

$$\begin{aligned} \sum_{\kappa \neq 0} \frac{\langle 0 | \hat{V} | \kappa \rangle \langle \kappa | \hat{V} | 0 \rangle}{E_0 - E_\kappa} &= \langle S, M_S | \zeta \hat{S} \sum_{\kappa \neq 0} \frac{\langle 0 | \hat{L} | \kappa \rangle \langle \kappa | \hat{L} | 0 \rangle}{E_0 - E_\kappa} \zeta \hat{S} | S, M_S \rangle \\ &= \langle S, M_S | \hat{S} \overline{\overline{D}} \hat{S} | S, M_S \rangle \end{aligned} \quad (2.13)$$

where the operator now only contains spin operators and the spin-anisotropy tensor  $\overline{\overline{D}}$  contains all the information about the spatial anisotropy of the system

$$\overline{\overline{D}} = \zeta^2 \sum_{\kappa \neq 0} \frac{\langle 0 | \hat{L} | \kappa \rangle \langle \kappa | \hat{L} | 0 \rangle}{E_0 - E_\kappa} \quad (2.14)$$

In the most general case, the  $D$ -tensor has nine non-zero elements but one can always find an orientation in space such that the tensor becomes diagonal (as will be shown below in a numerical example) and only three parameters remain. Furthermore, the tensor may be written in a traceless form (sum of the diagonal elements equal to zero) and then the spin Hamiltonian takes the following form with only two parameters

$$\hat{H}_{ZFS} = D \left( \hat{S}_z^2 - \frac{1}{3} \hat{S}^2 \right) + E (\hat{S}_x^2 - \hat{S}_y^2) \quad (2.15)$$

where  $D$  and  $E$  are defined as the axial and rhombic anisotropy parameter, respectively.

$$D = D_{zz} - \frac{1}{2}(D_{xx} + D_{yy}) \quad E = \frac{1}{2}(D_{xx} - D_{yy}) \quad (2.16)$$

with  $|D| \geq 3E \geq 0$ .

**2.5** Write out the  $\hat{S} \overline{\overline{D}} \hat{S}$  operator. The only non-zero elements of the  $D$ -tensor are  $D_{xx}$ ,  $D_{yy}$ , and  $D_{zz}$  on the diagonal. Determine the trace of the tensor and construct a traceless tensor  $\overline{\overline{\Delta}}$ . Write out the product  $\hat{S} \overline{\overline{\Delta}} \hat{S}$  and check that the outcome coincides with Eq. 2.15.

The next step is to calculate the matrix elements of this zero-field splitting Hamiltonian with the  $|S, M_S\rangle$  spin-functions of the ground state. The diagonalization of the resulting matrix gives the energies of the sub-levels under the influence of the spin-orbit coupling with the sub-levels of higher lying electronic states. The matrix elements for the different  $d^n$  configurations are well-documented in textbooks and articles and can be found in Appendix C. To illustrate the procedure we will derive the  $\langle 1, 1 | \hat{H}_{ZFS} | 1, 1 \rangle$  matrix element. To determine the effect of  $\hat{H}_{ZFS}$  on  $|1, 1\rangle$  we need to know how  $\hat{S}_{x,y,z}^2$  act on this function. Whereas  $|S, M_S\rangle$  are eigenfunctions of

$\hat{S}_z^2$ , the effect of  $\hat{S}_{x,y}^2$  is most easily determined via the ladder operators  $S^\pm$ . From the definitions  $\hat{S}_x = \frac{1}{2}(\hat{S}^+ + \hat{S}^-)$  and  $\hat{S}_y = -\frac{1}{2i}(\hat{S}^+ - \hat{S}^-)$  one arrives at

$$\begin{aligned}\hat{S}_x^2 &= \frac{1}{4} \left( \hat{S}^+ \hat{S}^+ + \hat{S}^- \hat{S}^- + \hat{S}^+ \hat{S}^- + \hat{S}^- \hat{S}^+ \right) \\ \hat{S}_y^2 &= -\frac{1}{4} \left( \hat{S}^+ \hat{S}^+ + \hat{S}^- \hat{S}^- - \hat{S}^+ \hat{S}^- - \hat{S}^- \hat{S}^+ \right)\end{aligned}\quad (2.17)$$

Using Eq. 1.23, it is easily seen that the first and the last term give zero when applied on  $|1, 1\rangle$  and that the other terms result in

$$\hat{S}^- \hat{S}^- |1, 1\rangle = 2|1, -1\rangle \quad \hat{S}^+ \hat{S}^- |1, 1\rangle = 2|1, 1\rangle \quad (2.18)$$

which defines the action of  $\hat{S}^2$  and  $\hat{S}_{x,y,z}^2$  on  $|1, 1\rangle$  as follows

$$\begin{aligned}\hat{S}^2 |1, 1\rangle &= S(S+1)|1, 1\rangle = 2|1, 1\rangle & \hat{S}_z^2 |1, 1\rangle &= |1, 1\rangle \\ \hat{S}_x^2 |1, 1\rangle &= \frac{1}{2}|1, -1\rangle + \frac{1}{2}|1, 1\rangle & \hat{S}_y^2 |1, 1\rangle &= -\frac{1}{2}|1, -1\rangle + \frac{1}{2}|1, 1\rangle\end{aligned}\quad (2.19)$$

Using the definition of Eq. 2.15 the matrix element becomes

$$\langle 1, 1 | \hat{H}_{ZFS} | 1, 1 \rangle = D \left( 1 - \frac{1}{3} \cdot 2 \right) + \frac{1}{2}E - \frac{1}{2}E = \frac{1}{3}D \quad (2.20)$$

The other matrix elements can be calculated following the same procedure and the final matrix representation of  $\hat{H}_{ZFS}$  is

	$ 1, 1\rangle$	$ 1, 0\rangle$	$ 1, -1\rangle$	
$\langle 1, 1 $	$\frac{1}{3}D$	$0$	$E$	(2.21)
$\langle 1, 0 $	$0$	$-\frac{2}{3}D$	$0$	
$\langle 1, -1 $	$E$	$0$	$\frac{1}{3}D$	

The eigenvalues are  $E_1 = -\frac{2}{3}D$ ;  $E_{2,3} = \frac{1}{3}D \pm E$  and the corresponding eigenvectors  $\Phi_1 = |1, 0\rangle$ ;  $\Phi_{2,3} = (|1, 1\rangle \pm |1, -1\rangle)/\sqrt{2}$ , which shows that the spin-orbit coupling between the  $|S, M_S\rangle$  levels of the ground state with those of the excited states removes the degeneracy in the ground state spin manifold in the absence of an external field.  $D$  and  $E$  are related to the energy differences by

$$D = \frac{1}{2}(E_2 + E_3) - E_1 \quad E = \frac{1}{2}(E_2 - E_3) \quad (2.22)$$

In systems with an even number of electrons and both  $D$  and  $E$  different from zero, the zero-field splitting completely removes the degeneracy of the ground state manifold. On the contrary, the levels in systems with an odd number of electrons remain doubly degenerate at zero-field, often referred to as Kramers doublets. For systems with integer spin moment, the wave function of the lowest level is dominated by the  $M_S = 0$  determinant when  $D$  is positive. This means that the projection of the spin moment on the magnetic  $z$ -axis is (practically) zero, while the projection on the  $x$ - $y$  plane is maximal; the system has *easy plane* magnetism. When  $D$  is negative, the largest contributions to the lowest level arise from the determinants with  $M_S = \pm M_{Smax}$ , and hence, maximal projection of the spin moment on the  $z$  axis. This is known as *easy-axis* magnetism. The same applies for half-integer spin moment systems.

**2.6** Demonstrate that the degeneracy of the  $M_S = \pm 1/2$  sub-levels of the  $S = 1/2$  manifold cannot be removed without an external magnetic field. Hint: Calculate the  $\langle 1/2, \pm 1/2 | \hat{H}_{ZFS} | 1/2, \pm 1/2 \rangle$  matrix elements.

### 2.3.2 Splitting in an External Magnetic Field

The last column in Fig. 2.1 shows how an external magnetic field  $\mathbf{H}$  affects the energies of the  $M_S$  sublevels of the electronic manifolds of a paramagnetic material. This effect is described by the Zeeman Hamiltonian

$$\hat{H}_{ZE} = \mu_B \mathbf{H} \cdot (\hat{L} + g_e \hat{S}) \quad (2.23)$$

When spin-orbit coupling is neglected and the ground state has no orbital moment, the expression reduces to its isotropic spin-only form

$$\hat{H}_{ZE} = \mu_B g_e \mathbf{H} \cdot \hat{S} \quad (2.24)$$

Defining the field direction as the  $z$ -axis, the Hamiltonian reduces to  $\mu_B g_e H \hat{S}_z$  and the energies of the  $M_S$  sublevels vary linearly with the field strength as

$$E_n = M_S \mu_B g_e H \quad (2.25)$$

Typical examples of such paramagnetic systems are organic radicals where spin-orbit coupling plays a minor role, but Eq. 2.25 can also be used to describe the evolution of the energy of the  $M_S$  sublevels of the ground state in  $3d$  transition metal complexes when the zero-field splitting is absent ( $S = 1/2$ ) or significantly larger than the effect of the external field and the spin-orbit interaction with excited states is small. This splitting of the energy levels with the external field is not only at the very origin

of electron paramagnetic resonance [4] techniques, but also manifests itself in the magnetic susceptibility of paramagnetic materials.

When a material is placed in a magnetic field, the sample becomes magnetized and the magnetization  $M$  is related to the field strength  $H$  by

$$\frac{\partial M}{\partial H} = \chi \quad (2.26)$$

The magnetic susceptibility  $\chi$  is material dependent. It is a tensor, although the sample can be oriented with respect to the external field such that it becomes diagonal. In most cases,  $\chi$  can be written as the sum of a diamagnetic ( $\chi^D$ ) and a paramagnetic contribution ( $\chi^P$ ). The latter contribution is temperature dependent and normally dominates in systems with unpaired electrons, i.e. in paramagnetic materials. The diamagnetic contribution does not depend on the temperature and can be estimated rather accurately from tabulated data for atoms and groups of atoms present in the material or by empirical formula [5]. Therefore, it is commonly assumed that the magnetic susceptibility data have been corrected for this contribution and one only has to analyze the paramagnetic part. For weak magnetic fields (and not too low temperatures),  $\chi$  is independent of  $H$  and the magnetization can be related to the field as

$$M = \chi H \quad (2.27)$$

The link with the variation of the microscopic energy levels is given by statistical mechanics through the Boltzmann distribution

$$M = -\frac{\partial E}{\partial H} = N_A \frac{\sum_n \frac{-\partial E_n}{\partial H} e^{-E_n/kT}}{\sum_n e^{-E_n/kT}} \quad (2.28)$$

where  $T$  is the temperature,  $N_A$  Avogadro's number and  $k$  represents Boltzmann's constant. This expression can be significantly simplified by two assumptions originally proposed by van Vleck. In the first place, it is assumed that the energy of a given sublevel can be approximated by a Taylor series in the magnetic field strength

$$E_n = E_n^{(0)} + E_n^{(1)}H + E_n^{(2)}H^2 + \dots \quad -\frac{\partial E_n}{\partial H} = -E_n^{(1)} - 2E_n^{(2)}H + \dots \quad (2.29)$$

The substitution of this expansion in the exponent of Eq. 2.28 leads to the second simplification when the series are limited to the first two terms

$$e^{-E_n/kT} = e^{(-E_n^{(0)} - E_n^{(1)}H)/kT} = e^{E_n^{(0)}/kT} e^{E_n^{(1)}H/kT} \approx e^{-E_n^{(0)}/kT} \left( 1 - \frac{E_n^{(1)}H}{kT} \right) \quad (2.30)$$

Applying these two simplifications transforms Eq. 2.28 to

$$M = \frac{N_A \sum_n (E_n^{(1)} - 2E_n^{(2)}H)(1 - E_n^{(1)}H/kT)e^{-E_n^{(0)}/kT}}{\sum_n (1 - E_n^{(1)}H/kT)e^{-E_n^{(0)}/kT}} \quad (2.31)$$

If we limit ourselves to materials without spontaneous macroscopic magnetization, that is  $M = 0$  at zero field, it is easily shown by substituting  $H = 0$  that  $\sum_n E_n^{(1)} e^{-E_n^{(0)}/kT} = 0$  and we arrive at

$$M = \frac{N_A H \sum_n (E_n^{(1)2}/kT - 2E_n^{(2)})e^{-E_n^{(0)}/kT}}{\sum_n e^{-E_n^{(0)}/kT}} \quad (2.32)$$

Realizing that in the present case of negligible spin-orbit coupling the energies vary linearly with the field, the  $E^{(2)}$ -term can be neglected and the van Vleck equation for the magnetic susceptibility emerges from Eq. 2.27

$$\chi = \frac{N_A \sum_n E_n^{(1)2} e^{-E_n^{(0)}/kT}}{kT \sum_n e^{-E_n^{(0)}/kT}} \quad (2.33)$$

Under the assumption that the excited states are sufficiently far away from the ground state that their effect can be neglected,  $E^{(0)}$  can be taken as reference point and put to zero. Then, Eqs. 2.25 and 2.29 can be used to obtain an analytical expression of  $E_n^{(1)}$ . The substitution of  $E^{(0)} = 0$  and  $E^{(1)} = \mu_B g_e M_S$  leads to

$$\chi = \frac{N_A (\mu_B g_e)^2 \sum_{M_S=-S}^S M_S^2}{kT (2S+1)} \quad (2.34)$$

The summation over  $M_S^2$  can be simplified using

$$\sum_{M_S=-S}^S M_S^2 = \frac{S(S+1)(2S+1)}{3} \quad (2.35)$$

and the final expression emerges

$$\chi = \frac{N_A (\mu_B g_e)^2}{3kT} S(S+1) \quad (2.36)$$

This expression shows that the magnetic susceptibility is inversely proportional to the temperature and is known as the Curie law:

$$\chi = \frac{C}{T} \quad (2.37)$$

where  $C$  is a constant that only depends on the spin quantum number of the ground state.

**2.7** (a) Show that the denominator in Eq. 2.33 is equal to  $2S + 1$  when  $E^{(0)} = 0$  and verify the expression for the summation over  $M_S$  of  $M_S^2$  for singlet, triplet and quintet states. (b) Many researchers in the field of molecular magnetism use the cgsemu (centimeter-gram-second electromagnetic units) system instead of the standard units defined by the international systems of units SI. In this alternative unit system, the value of  $N_A \mu_B^2 / 3k$  is equal to 0.12505 (nearly 1/8). Calculate  $C$  for the  $S$ -values that can be found for the TM ions and the lanthanides.

Virtually always deviations to the Curie law are observed at low enough temperatures, because the magnetic centers in any real system are never truly isolated but interact with their environment. Moreover, spin-orbit coupling can also introduce extra interactions not covered by the Curie law. The interactions with other magnetic centers will be addressed in more detail in Chap. 3, but we describe here a mean-field approach to include their effect. In this rather crude approximation, each magnetic center experiences an internal field due to the average interaction with the other centers in addition to the uniform external field. This internal field depends on the average magnetization ( $M$ ) of the material and is known as the Weiss field

$$\mathbf{H} = \mathbf{H}_{ext} + H_{int} = \mathbf{H}_{ext} + \lambda M \quad (2.38)$$

Combining this expression with the Eqs. 2.27 and 2.37 and assuming that  $H$  is aligned along  $z$ , one obtains

$$\chi = \frac{M}{H} = \frac{M}{H_{ext} + \lambda M} = \frac{C}{T} \quad (2.39)$$

Then, with  $H_{ext} = M((T - C\lambda)/C)$ , the measured susceptibility  $\chi_{ext}$  can be written as

$$\chi_{ext} = \frac{M}{H_{ext}} = \frac{C}{T - \lambda C} \quad (2.40)$$

known as the Curie-Weiss law.  $\lambda C$  is the Weiss constant and often written as  $\Theta$ . Positive values of  $\Theta$  are indicative of ferromagnetic interactions and a material with dominating antiferromagnetic interactions will show a negative  $\Theta$ .

A more specific expression of  $\Theta$  can be derived by extending the spin Hamiltonian of Eq. 2.24 with the Weiss field.

$$\hat{H} = \mu_B \mathbf{H} \cdot (\hat{L} + g_e \hat{S}_z) - nJ \langle S_z \rangle \hat{S}_z \quad (2.41)$$

where  $n$  is the number of magnetic centers interacting with the center under consideration,  $J$  parametrizes the strength of the interactions and  $\langle S_z \rangle$  is the average  $S_z$  value given by the Boltzmann distribution

$$\langle S_z \rangle = \frac{\sum_{M_S=-S}^S M_S e^{-E(S, M_S)}}{\sum_{M_S=-S}^S e^{-E(S, M_S)}} \quad (2.42)$$

Taking the external field along the  $z$ -axis, the eigenvalues of this mean-field Hamiltonian are

$$E_n = M_S \mu_B g_e H - nJ \langle S_z \rangle M_S \quad (2.43)$$

After expanding the exponents in Eq. 2.42 in a Taylor series and only maintaining the first two terms, the energy eigenvalues are inserted to arrive at

$$\begin{aligned} \langle S_z \rangle &= \frac{\sum_{M_S=-S}^S M_S (1 - M_S (\mu_B g_e H - nJ \langle S_z \rangle) / kT)}{\sum_{M_S=-S}^S (1 - M_S (\mu_B g_e H - nJ \langle S_z \rangle) / kT)} \\ &= \frac{-(S(S+1)(2S+1)/3)(\mu_B g_e H - nJ \langle S_z \rangle) / kT}{2S+1} \end{aligned} \quad (2.44)$$

using the simplification of the sum over  $M_S^2$  used before (Eq. 2.35). This equation requires some rewriting but finally the average  $S_z$  value reduces to

$$\langle S_z \rangle = -\frac{S(S+1)\mu_B g_e H}{3kT - nJS(S+1)} \quad (2.45)$$

which can be used to express the magnetization and the magnetic susceptibility

$$M = N_A \mu_B g_e \langle S_z \rangle \quad (2.46)$$

$$\chi = \frac{M}{H} = N_A \mu_B^2 g_e^2 \frac{S(S+1)}{3kT - nJS(S+1)} = \frac{C}{T - \Theta} \quad (2.47)$$

to obtain the Curie–Weiss law with an explicit expression for  $\Theta = nJS(S+1)/3k$ .

## 2.8 Derive Eq. 2.45 from Eq. 2.44.

**Anisotropy of the  $g$ -tensor:** Before combining the effect of the zero-field splitting and the external magnetic field, we have to establish how spin-orbit coupling affects the Zeeman effect. This is most easily done for a system with  $S = \frac{1}{2}$  and a quenched orbital moment. As an example, we will consider one unpaired electron. The  $g$ -factor in the Zeeman Hamiltonian of Eq. 2.24 is now replaced by a tensor

$$\hat{H}_{ZE} = \mu_B \bar{\mathbf{g}} \mathbf{H} \cdot \hat{S} \quad (2.48)$$

$\bar{\mathbf{g}}$  can be transformed to a diagonal form when the coordinate axis frames of the field and the  $g$ -tensor coincide. The axis frame that diagonalizes the  $g$ -tensor is not necessarily the same as the frame that diagonalizes the  $D$ -tensor introduced in the previous section, although this is often assumed to be the case. Furthermore, it should be noted that, strictly speaking  $S$  is not a good quantum number anymore when spin-orbit coupling is considered. Therefore, the spin operator in Eq. 2.48 is often replaced by an effective spin operator  $\tilde{S}$  with the same formal properties.

To evaluate the effect of spin-orbit coupling we will start writing down the first-order corrected wave functions of the  $M_S = \pm \frac{1}{2}$  sublevels, then calculate the matrix elements of the Zeeman Hamiltonian (Eq. 2.23) and compare these to the matrix elements of the (effective) spin-only Zeeman Hamiltonian given in Eq. 2.48 to find analytical expressions for the diagonal elements of  $\bar{\mathbf{g}}$ . With  $\zeta \hat{L} \cdot \hat{S}$  as perturbation operator, the wave functions that describe the lowest two levels become

$$\psi^{(1)} = \psi^{(0)} + \zeta \sum_{i \neq 0} \frac{\langle \psi_i^{(0)} | \hat{L} \cdot \hat{S} | \psi_0^{(0)} \rangle}{E_0 - E_i} \psi_i^{(0)} \quad (2.49)$$

where  $\psi_i^{(0)}$  represent the different  $M_S$  components of excited states. The spin part of the wave function is not written explicitly and can either be  $\alpha$  or  $\beta$ . Replacing  $\hat{L} \cdot \hat{S}$  by  $\hat{L}_z \hat{S}_z + \frac{1}{2}(\hat{L}^+ \hat{S}^- + \hat{L}^- \hat{S}^+)$  the expressions for the two wave functions can easily be derived

$$\begin{aligned} \psi^{(1)} &= \psi_0^{(0)} + \frac{1}{2}\zeta \sum_{i \neq 0} \frac{\langle \psi_i^{(0)} | \hat{L}_z | \psi_0^{(0)} \rangle}{E_0 - E_i} \psi_i^{(0)} + \frac{1}{2}\zeta \sum_{i \neq 0} \frac{\langle \psi_i^{(0)} | \hat{L}^+ | \psi_0^{(0)} \rangle}{E_0 - E_i} \bar{\psi}_i^{(0)} \\ \bar{\psi}^{(1)} &= \bar{\psi}_0^{(0)} - \frac{1}{2}\zeta \sum_{i \neq 0} \frac{\langle \psi_i^{(0)} | \hat{L}_z | \psi_0^{(0)} \rangle}{E_0 - E_i} \bar{\psi}_i^{(0)} + \frac{1}{2}\zeta \sum_{i \neq 0} \frac{\langle \psi_i^{(0)} | \hat{L}^- | \psi_0^{(0)} \rangle}{E_0 - E_i} \psi_i^{(0)} \end{aligned} \quad (2.50)$$

and show that the first-order corrected wave functions are no longer spin eigenfunctions, but rather a mixture of  $\alpha$  and  $\beta$  contributions.

**2.9** Show that the  $\hat{L} \cdot \hat{S}$  matrix elements of  $\psi_0^{(0)}$  and an excited state  $\psi_i^{(0)}$  are equal to  $\frac{1}{2}\langle\psi_i^{(0)}|\hat{L}_z|\psi_0^{(0)}\rangle$  when the spin part of  $\psi_0^{(0)}$  and  $\psi_i^{(0)}$  is identical and equal to  $\frac{1}{2}\langle\psi_i^{(0)}|\hat{L}^+|\psi_0^{(0)}\rangle$  when  $\psi_0^{(0)}$  has  $\alpha$ - and  $\psi_i^{(0)}$  has  $\beta$ -spin.

For a magnetic field along the  $z$ -axis (the quantization axis of the system),  $\mathbf{H}$  can be replaced by a scalar and the two expressions of the Zeeman Hamiltonian (Eqs. 2.23 and 2.48) reduce to  $\mu_B H(\hat{L}_z + g_e \hat{S}_z)$  and  $\mu_B H g_{zz} \hat{S}_z$ . The corresponding matrix elements are

$$\mu_B H g_{zz} \langle \psi^{(1)} | \hat{S}_z | \psi^{(1)} \rangle = \frac{1}{2} \mu_B H g_{zz} = \mu_B B \langle \psi^{(1)} | \hat{L}_z + g_e \hat{S}_z | \psi^{(1)} \rangle \quad (2.51)$$

$$\mu_B H g_{zz} \langle \bar{\psi}^{(1)} | \hat{S}_z | \bar{\psi}^{(1)} \rangle = -\frac{1}{2} \mu_B H g_{zz} = \mu_B B \langle \bar{\psi}^{(1)} | \hat{L}_z + g_e \hat{S}_z | \bar{\psi}^{(1)} \rangle \quad (2.52)$$

The off-diagonal elements are zero in both Hamiltonians due to the spin-orthogonality. Now an expression for  $g_{zz}$  emerges from either equation as

$$g_{zz} = 2 \left[ g_e \langle \psi^{(1)} | \hat{S}_z | \psi^{(1)} \rangle + \langle \psi^{(1)} | \hat{L}_z | \psi^{(1)} \rangle \right] = g_e + 2 \langle \psi^{(1)} | \hat{L}_z | \psi^{(1)} \rangle \quad (2.53)$$

The last term can be specified by substitution of the definitions given in Eq. 2.50

$$\begin{aligned} \langle \psi^{(1)} | \hat{L}_z | \psi^{(1)} \rangle &= \langle \psi^{(0)} | \hat{L}_z | \psi^{(0)} \rangle + \frac{1}{2} \zeta \sum_{i \neq 0} \frac{\langle \psi_i^{(0)} | \hat{L}_z | \psi_0^{(0)} \rangle \langle \psi_0^{(0)} | \hat{L}_z | \psi_i^{(0)} \rangle}{E_0 - E_i} \\ &+ \frac{1}{2} \zeta \sum_{i \neq 0} \frac{\langle \psi_i^{(0)} | \hat{L}_x + i \hat{L}_y | \psi_0^{(0)} \rangle \langle \psi_0^{(0)} | \hat{L}_z | \bar{\psi}_i^{(0)} \rangle}{E_0 - E_i} + \frac{1}{4} \zeta^2 \dots \\ &+ \langle \psi^{(0)} | \hat{L}_z | \psi^{(0)} \rangle + \frac{1}{2} \zeta \sum_{i \neq 0} \frac{\langle \psi_i^{(0)} | \hat{L}_z | \psi_0^{(0)} \rangle \langle \psi_0^{(0)} | \hat{L}_z | \psi_i^{(0)} \rangle}{E_0 - E_i} \\ &+ \frac{1}{2} \zeta \sum_{i \neq 0} \frac{\langle \psi_i^{(0)} | \hat{L}_x - i \hat{L}_y | \psi_0^{(0)} \rangle \langle \psi_0^{(0)} | \hat{L}_z | \bar{\psi}_i^{(0)} \rangle}{E_0 - E_i} + \frac{1}{4} \zeta^2 \dots \end{aligned} \quad (2.54)$$

Here,  $\hat{L}^\pm$  is replaced by the expression in terms of  $\hat{L}_{x,y}$  and the minus sign in front of  $i \hat{L}_y$  in the seventh term on the right arises from the fact that the complex conjugated function  $\Psi_1^{\dagger(1)}$  was written. Moreover, the third and seventh terms are zero because of the spin-orthogonality. The terms that are quadratic in  $\zeta$  are neglected. This somewhat awkward expression can be further simplified by taking into account that the zeroth-order wave function of the ground state has no orbital moment,  $\langle \psi^{(0)} | \hat{L}_z | \psi^{(0)} \rangle = 0$ .

Hence, we can write

$$g_{zz} = g_e + 2\zeta \sum_{i \neq 0} \frac{\langle \psi_i^{(0)} | \hat{L}_z | \psi_0^{(0)} \rangle \langle \psi_0^{(0)} | \hat{L}_z | \psi_i^{(0)} \rangle}{E_0 - E_i} \quad (2.55)$$

Next, we consider the case for a field along  $x$ , from which  $g_{xx}$  can be determined. The Hamiltonians can be written as  $\mu_B H(\hat{L}_x + g_e \hat{S}_x)$  and  $\mu_B H g_{xx} \hat{S}_x$  in this case and the matrix elements with  $\psi^{(1)}$  and  $\bar{\psi}^{(1)}$  are

$$\mu_B H g_{xx} \langle \psi^{(1)} | \hat{S}_x | \psi^{(1)} \rangle = \frac{1}{2} \mu_B H g_{xx} \langle \psi^{(1)} | \hat{S}^+ + \hat{S}^- | \psi^{(1)} \rangle = 0 \quad (2.56)$$

$$\begin{aligned} \mu_B H g_{xx} \langle \psi^{(1)} | \hat{S}_x | \bar{\psi}^{(1)} \rangle &= \frac{1}{2} \mu_B H g_{xx} \langle \psi^{(1)} | \hat{S}^+ + \hat{S}^- | \bar{\psi}^{(1)} \rangle = \frac{1}{2} \mu_B H g_{xx} \\ &= \mu_B H \langle \psi^{(1)} | \hat{L}_x + g_e \hat{S}_x | \bar{\psi}^{(1)} \rangle \end{aligned} \quad (2.57)$$

and analogous for the other two matrix elements. Working out the expression for the off-diagonal matrix element gives

$$g_{xx} = 2 \langle \psi^{(1)} | \hat{L}_x | \bar{\psi}^{(1)} \rangle + 2g_e \langle \psi^{(1)} | \hat{S}_x | \bar{\psi}^{(1)} \rangle = g_e + 2 \langle \psi^{(1)} | \hat{L}_x | \bar{\psi}^{(1)} \rangle \quad (2.58)$$

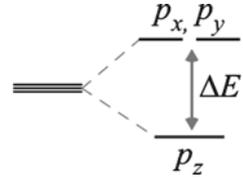
and one obtains the explicit equation for  $g_{xx}$  by substituting the definition of the first-order wave functions given in Eq. 2.50. Taking into account only the non-zero terms that are at most linear in  $\zeta$ , we arrive at

$$\begin{aligned} g_{xx} &= g_e + 2 \left( \frac{1}{2} \zeta \sum_{i \neq 0} \frac{\langle \psi_i^{(0)} | \hat{L}_x - i \hat{L}_y | \psi_0^{(0)} \rangle \langle \psi_0^{(0)} | \hat{L}_x | \psi_i^{(0)} \rangle}{E_0 - E_i} \right. \\ &\quad \left. + \frac{1}{2} \zeta \sum_{i \neq 0} \frac{\langle \psi_i^{(0)} | \hat{L}_x + i \hat{L}_y | \psi_0^{(0)} \rangle \langle \psi_0^{(0)} | \hat{L}_x | \psi_i^{(0)} \rangle}{E_0 - E_i} \right) \\ &= g_e + 2\zeta \sum_{i \neq 0} \frac{\langle \psi_i^{(0)} | \hat{L}_x | \psi_0^{(0)} \rangle \langle \psi_0^{(0)} | \hat{L}_x | \psi_i^{(0)} \rangle}{E_0 - E_i} \end{aligned} \quad (2.59)$$

The expression for  $g_{yy}$  is obtained by replacing  $\hat{L}_x$  with  $\hat{L}_y$ . Even the off-diagonal elements of the  $g$ -tensor, in case of a non-aligned sample, can be calculated with analogous equations combining the proper angular momentum operators.

The procedure is best illustrated with a simple example. For this purpose, we fall back on the  $p^1$  model system used before in the discussion of the orbital moment quenching. The external potential stabilizes the  $p_z$  orbital with respect to the degenerate  $p_x$  and  $p_y$  orbitals by an amount of  $\Delta E$  as shown in Fig. 2.2. Using the explicit notation for spatial and spin part, the zeroth-order wave functions are

**Fig. 2.2** stabilization of the  $p_z$  orbital by  $\Delta E$  with respect to the degenerate  $p_x$  and  $p_y$  orbitals due to an external potential



$$\psi_0^{(0)} = p_z\alpha = p_0\alpha \quad \bar{\psi}_0^{(0)} = p_z\beta = p_0\beta \quad (2.60)$$

$$\psi_i^{(0)} = \{p_x\alpha, p_x\beta, p_y\alpha, p_y\beta\} = \{p_+\alpha, p_+\beta, p_-\alpha, p_-\beta\} \quad (2.61)$$

Now we apply Eq. 2.50 to obtain the expression of the first-order corrected wave functions for the lowest two levels

$$\begin{aligned} \psi_0^{(1)} &= p_0\alpha + \frac{1}{2}\zeta \left[ \frac{\langle p_+|\hat{L}_z|p_0\rangle}{\Delta E} p_+\alpha + \frac{\langle p_-|\hat{L}_z|p_0\rangle}{\Delta E} p_-\alpha \right] \\ &+ \frac{1}{2}\zeta \left[ \frac{\langle p_+|\hat{L}_+|p_0\rangle}{\Delta E} p_+\beta + \frac{\langle p_-|\hat{L}_+|p_0\rangle}{\Delta E} p_-\beta \right] = p_0\alpha + \frac{1}{2}\sqrt{2}\zeta p_+\beta \end{aligned} \quad (2.62)$$

$$\begin{aligned} \bar{\psi}_0^{(1)} &= p_0\beta - \frac{1}{2}\zeta \left[ \frac{\langle p_+|\hat{L}_z|p_0\rangle}{\Delta E} p_+\beta + \frac{\langle p_-|\hat{L}_z|p_0\rangle}{\Delta E} p_-\beta \right] \\ &+ \frac{1}{2}\zeta \left[ \frac{\langle p_+|\hat{L}_-|p_0\rangle}{\Delta E} p_+\alpha + \frac{\langle p_-|\hat{L}_-|p_0\rangle}{\Delta E} p_-\alpha \right] = p_0\beta + \frac{1}{2}\sqrt{2}\zeta p_-\alpha \end{aligned} \quad (2.63)$$

The values of  $g_{zz}$  and  $g_{xx} = g_{yy}$  are determined from Eqs. 2.55 and 2.59 and lead to

$$g_{zz} = g_e + 2\zeta \left[ \frac{\langle p_+|\hat{L}_z|p_0\rangle\langle p_0|\hat{L}_z|p_+\rangle}{\Delta E} + \frac{\langle p_-|\hat{L}_z|p_0\rangle\langle p_0|\hat{L}_z|p_-\rangle}{\Delta E} \right] = g_e \quad (2.64)$$

$$\begin{aligned} g_{xx} &= g_e + 2\zeta \left[ \frac{\langle p_+|\hat{L}_x|p_0\rangle\langle p_0|\hat{L}_x|p_+\rangle}{\Delta E} + \frac{\langle p_-|\hat{L}_x|p_0\rangle\langle p_0|\hat{L}_x|p_-\rangle}{\Delta E} \right] \\ &= g_e + 2\zeta \left[ \frac{\frac{1}{2}\sqrt{2} \cdot \frac{1}{2}\sqrt{2}}{\Delta E} + \frac{\frac{1}{2}\sqrt{2} \cdot \frac{1}{2}\sqrt{2}}{\Delta E} \right] = g_e + \frac{2\zeta}{\Delta E} \end{aligned} \quad (2.65)$$

**2.10** Demonstrate that the matrix element  $\langle p_- | \hat{L}_x | p_0 \rangle$  and all other matrix elements in Eq. 2.65 are equal to  $\frac{1}{2}\sqrt{2}$ . Hint: substitute  $\hat{L}_x$  by  $(\hat{L}^+ + \hat{L}^-)/2$

### 2.3.3 Combining ZFS and the External Magnetic Field

The separate descriptions of the zero-field splitting and the effect of an external magnetic field on the atomic sublevels can now be combined into a unified description using the following spin Hamiltonian

$$\hat{H} = \mu_B \bar{\bar{g}} \cdot \mathbf{H} \hat{S} + \hat{S} \cdot \bar{\bar{D}} \cdot \hat{S} \quad (2.66)$$

In the coordinate frame that diagonalizes  $\bar{\bar{g}}$  and  $\bar{\bar{D}}$ , which is assumed to be the same for both, the spin Hamiltonian simplifies to

$$\hat{H} = \mu_B (g_x H_x \hat{S}_x + g_y H_y \hat{S}_y + g_z H_z \hat{S}_z) + D \left( \hat{S}_z^2 - \frac{1}{3} \hat{S}^2 \right) + E (\hat{S}_x^2 - \hat{S}_y^2) \quad (2.67)$$

In the first place we write down the explicit matrix representation of this Hamiltonian when the external field is aligned along the  $z$ -axis and assuming that the complex only presents axial anisotropy, that is  $E = 0$ . This means that both  $H_x$  and  $H_y$  are zero.

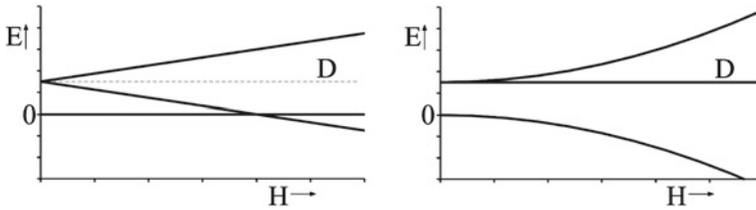
	$ 1, 1\rangle$	$ 1, 0\rangle$	$ 1, -1\rangle$	
$\langle 1, 1 $	$\frac{1}{3}D + \mu_B g_z H$	0	0	(2.68)
$\langle 1, 0 $	0	$-\frac{2}{3}D$	0	
$\langle 1, -1 $	0	0	$\frac{1}{3}D - \mu_B g_z H$	

After shifting the diagonal by  $\frac{2}{3}D$  to let the zero of energy coincide with the energy of the  $|1, 0\rangle$  state, the resulting energies are

$$E_1 = 0; \quad E_{23} = D \pm \mu_B g_z H_z \quad (2.69)$$

The energies of the  $|1, \pm 1\rangle$  states evolve linearly with  $H$  as shown on the left in Fig. 2.3.

The situation is slightly more complicated when the magnetic field is applied perpendicular to the principal magnetic axis. We will work out the matrix element between  $|1, 1\rangle$  and  $|1, 0\rangle$  and then give the full Hamiltonian for the field along the  $x$ -axis. The part of the Hamiltonian that accounts for the zero-field splitting does



**Fig. 2.3** Energies of the three components of a triplet state in an external field along the  $z$ -axis (*left*) and perpendicular to it (*right*)

not change, and hence, we can concentrate on the Zeeman interaction. The action of  $\hat{S}_x$  on  $|1, 0\rangle$  is easiest obtained by using the expression of  $\hat{S}_x$  in terms of the ladder operators  $\hat{S}^+$  and  $\hat{S}^-$ .

$$\begin{aligned} \langle 1, 1 | \mu_B g_x H_x \frac{1}{2} (\hat{S}^+ + \hat{S}^-) | 1, 0 \rangle \\ = \mu_B g_x H_x \frac{1}{2} \left( \langle 1, 1 | \sqrt{2} | 1, 1 \rangle + \langle 1, 1 | \sqrt{2} | 1, -1 \rangle \right) = \frac{\mu_B g_x H_x}{\sqrt{2}} \end{aligned} \quad (2.70)$$

The other off-diagonal elements are the same except the interaction between  $|1, 1\rangle$  and  $|1, -1\rangle$ , which is zero. The full Hamiltonian takes this form

	$ 1, 1\rangle$	$ 1, 0\rangle$	$ 1, -1\rangle$	
$\langle 1, 1  $	$\frac{1}{3}D$	$\frac{1}{\sqrt{2}}\mu_B g_x H_x$	$0$	(2.71)
$\langle 1, 0  $	$\frac{1}{\sqrt{2}}\mu_B g_x H_x$	$-\frac{2}{3}D$	$\frac{1}{\sqrt{2}}\mu_B g_x H_x$	
$\langle 1, -1  $	$0$	$\frac{1}{\sqrt{2}}\mu_B g_x H_x$	$\frac{1}{3}D$	

After shifting the diagonal by  $\frac{2}{3}D$ , the energy eigenvalues can be determined as

$$E_1 = D; \quad E_{2,3} = \frac{1}{2} \left( D \pm \sqrt{D^2 + 4\mu_B^2 g_x^2 H_x^2} \right) \quad (2.72)$$

**2.11** Confirm that the only effect of uniformly shifting the diagonal elements is the same shift of the energy eigenvalues.

The expressions for  $E_{2,3}$  can be simplified by the Taylor expansion  $\sqrt{p+q} = \sqrt{p} + \frac{1}{2}q/\sqrt{p} + \dots$ . Assuming that  $D^2$  is (much) larger than  $4\mu_B^2 g_x^2 H_x^2$ , the expansion

can be restricted to the first two terms only and the energies become

$$E_2 = D + \mu_B^2 g_x^2 H_x^2 / D; \quad E_3 = -\mu_B^2 g_x^2 H_x^2 / D \quad (2.73)$$

The evolution of the energies with increasing  $H_x$  is no longer linear and is depicted in the right part of Fig. 2.3. Applying the external field perpendicular to the  $z$ -axis implies of course not automatically that the field is oriented along the  $x$ -axis. It is therefore necessary to confront the above result to what is obtained when the field is applied along the  $y$ -axis. The Hamiltonian has the same general shape but the off-diagonal elements are slightly different now.

	$ 1, 1\rangle$	$ 1, 0\rangle$	$ 1, -1\rangle$	
$\langle 1, 1 $	$\frac{1}{3}D$	$-\frac{i}{\sqrt{2}}\mu_B g_y H_y$	$0$	(2.74)
$\langle 1, 0 $	$\frac{i}{\sqrt{2}}\mu_B g_y H_y$	$-\frac{2}{3}D$	$-\frac{i}{\sqrt{2}}\mu_B g_y H_y$	
$\langle 1, -1 $	$0$	$\frac{i}{\sqrt{2}}\mu_B g_y H_y$	$\frac{1}{3}D$	

However, this has no consequences for the eigenvalues of the matrix. Diagonalization of the (shifted) matrix gives exactly the same energies as derived from the Hamiltonian with the field along the  $x$ -axis as long as the system has no rhombic anisotropy;  $g_x = g_y = g_\perp$  and  $E = 0$ . In the general case of axial and rhombic anisotropy, no analytical expressions for the energies can be derived and one commonly resorts to numerical approaches [6].

## Problems

**2.1 Extracting  $D$  and  $E$  for a  $\text{Ni}^{\text{II}}$  complex.** The triplet ground state  $T_0$  of a  $\text{Ni}^{\text{II}}$  complex has three  $M_S$  sublevels, which are degenerate in the absence of an external magnetic field and neglecting spin-orbit coupling. However, the interaction with the  $M_S$  sublevels of excited states ( $T_1$ ,  $T_2$ ,  $S_1$ , etc.) through the spin-orbit operator removes the degeneracy. Since the molecule is oriented in an arbitrary axes frame, the cartesian  $z$ -axis does not coincide with the magnetic  $z$ -axis and the wave functions of the three sublevels are complex functions, mixtures of the  $M_S = 0, \pm 1$  components.

- a. Construct the matrix representation of the  $\hat{S} \cdot \overline{\overline{D}} \cdot \hat{S}$  spin Hamiltonian for an arbitrary axes frame, i.e.,  $\overline{\overline{D}}$  is not diagonal:

$$\hat{H} = (\hat{S}_x \hat{S}_y \hat{S}_z) \begin{pmatrix} D_{xx} & D_{xy} & D_{xz} \\ D_{yx} & D_{yy} & D_{yz} \\ D_{zx} & D_{zy} & D_{zz} \end{pmatrix} \begin{pmatrix} \hat{S}_x \\ \hat{S}_y \\ \hat{S}_z \end{pmatrix}$$

Use  $|S, M_S\rangle = \{|1, 1\rangle, |1, 0\rangle, |1, -1\rangle\}$  as basis.

- b. The *ab initio* wave functions of the three states with the largest projection on the model space are

$$\psi_1 = (0.686 - 0.024i)|1, -1\rangle + (-0.175 + 0.009i)|1, 0\rangle + (-0.685 + 0.046i)|1, 1\rangle$$

$$\psi_2 = (-0.664 + 0.197i)|1, -1\rangle + (0.036 + 0.123i)|1, 0\rangle + (-0.667 + 0.187i)|1, 1\rangle$$

$$\psi_3 = (0.110 - 0.108i)|1, -1\rangle + (0.957 - 0.147i)|1, 0\rangle + (-0.137 - 0.070i)|1, 1\rangle$$

Calculate the overlap matrix of  $\tilde{\Psi}_i$ , the projections of  $\Psi$  on the model space.

- c. The orthonormalized projections are given by

	$ 1, -1\rangle$	$ 1, 0\rangle$	$ 1, 1\rangle$
$\tilde{\Psi}'_1$	0.695504 - 0.023842i	-0.177003 + 0.008987i	-0.694343 + 0.046723i
$\tilde{\Psi}'_2$	-0.672287 + 0.199091i	0.035909 + 0.124483i	-0.675035 + 0.189566i
$\tilde{\Psi}'_3$	+0.110493 - 0.109038i	0.964328 - 0.147901i	-0.138092 - 0.070912i

$E_1 = 0.00$ ;  $E_2 = 11.54 \text{ cm}^{-1}$ ;  $E_3 = 37.55 \text{ cm}^{-1}$ . Construct the effective Hamiltonian and check the consistency of the model Hamiltonian by comparing the numerical matrix elements of the effective Hamiltonian with the symbolic matrix elements of the model Hamiltonian.

- d. Diagonalize the  $D$ -tensor, determine the axial ( $D$ ) and rhombic ( $E$ ) anisotropy parameters from Eq. 2.16 and compare the values with those obtained by extracting  $D$  and  $E$  from the energies differences (Eq. 2.22).

**2.2 Extracting  $D$  and  $E$  for a  $\text{Co}^{\text{II}}$  complex.** The ground state of a slightly distorted tetrahedral  $\text{Co}^{\text{II}}$  complex has quartet spin multiplicity. The fitting of the magnetic susceptibility shows that the complex has a rather large magnetic anisotropy, but it remains unclear whether the complex has an easy plane ( $D > 0$ ) or an easy axis ( $D < 0$ ) of magnetization.

1. Draw a level diagram showing the removal of the degeneracy of the  $M_S$  sublevels of the quartet state under the influence of (i) spin-orbit coupling and (ii) spin-orbit coupling and a small external magnetic field along the  $z$ -axis.
2. Can the anisotropy parameters  $D$  and  $E$  be determined from the energy differences at zero field? And the sign of  $D$ ?
3. Construct the matrix representation of  $\hat{S} \cdot \overline{\overline{D}} \cdot \hat{S}$  in an arbitrary frame in the  $\{| \frac{3}{2}, \frac{3}{2} \rangle, | \frac{3}{2}, \frac{1}{2} \rangle, | \frac{3}{2}, -\frac{1}{2} \rangle, | \frac{3}{2}, -\frac{3}{2} \rangle\}$  basis.
4. Use the following data to construct the numerical effective Hamiltonian and extract  $D$  and  $E$ . Decide if this complex has easy-axis or easy-plane magnetism.

	$E(\text{cm}^{-1})$	$ \frac{3}{2}, -\frac{3}{2}\rangle$	$ \frac{3}{2}, -\frac{1}{2}\rangle$	$ \frac{3}{2}, \frac{1}{2}\rangle$	$ \frac{3}{2}, \frac{3}{2}\rangle$
$\tilde{\Psi}'_1$	0.00	0.007808 + 0.008516i	0.058561 + -0.068873i	-0.207583 + -0.246313i	-0.709453 + 0.620169i
$\tilde{\Psi}'_2$	0.00	0.942302 + 0.000087i	0.005791 + 0.322067i	-0.089417 + -0.013321i	0.000274 + -0.011550i
$\tilde{\Psi}'_3$	32.47	0.090185 + -0.002021i	-0.000628 + 0.012098i	0.934946 + 0.117457i	-0.034599 + 0.320311i
$\tilde{\Psi}'_4$	32.47	0.255568 + -0.196167i	-0.586647 + -0.737404i	0.010006 + -0.006830i	-0.045185 + -0.078075i

**2.3 Anisotropic g values.** EPR measurement on a  $\text{Ti}^{\text{III}}$  complex reveals a relatively large axial magnetic anisotropy by the application of a small magnetic external field.

1. What is the electronic configuration of the  $\text{Ti}^{\text{III}}$  ion? Assuming that the ligands have a closed-shell configuration, can the complex display a splitting of the  $M_S$  levels of the ground state at zero field?
2. Use Eqs. 2.55 and 2.59 to calculate the deviations of  $g_x$  and  $g_z$  from the free-electron value  $g_e$  based on the following computational results.

	$E(\text{cm}^{-1})$	$ \hbar\bar{h}\phi_a\rangle$	$ \hbar\bar{h}\phi_b\rangle$	$ \hbar\bar{h}\phi_c\rangle$	$ \hbar\bar{h}\phi_d\rangle$	$ \hbar\bar{h}\phi_e\rangle$
$\tilde{\Psi}'_1$	0	0.6441	-0.7504	0.0179	0.1444	0.0304
$\tilde{\Psi}'_2$	1005	-0.7562	-0.6105	0.1406	0.1875	-0.0215
$\tilde{\Psi}'_3$	6662	-0.0772	-0.1649	-0.1597	-0.6456	0.7243
$\tilde{\Psi}'_4$	11060	0.0293	-0.1168	0.4849	-0.6864	-0.5284
$\tilde{\Psi}'_5$	13358	0.0805	0.1528	0.8481	0.2368	0.4414

	$\phi_a$	$\phi_b$	$\phi_c$	$\phi_d$	$\phi_e$
$3d_{z^2}$	-0.0593	-0.1176	-0.6905	-0.0964	-0.7046
$3d_{x^2-y^2}$	0.1174	-0.3047	0.6775	-0.295	-0.5841
$3d_{xy}$	0.3816	0.182	0.1216	0.8439	-0.2986
$3d_{yz}$	0.8647	0.2572	-0.1397	-0.4	0.0825
$3d_{xz}$	-0.2916	0.8897	0.1583	-0.1724	-0.2576

Although the normalized projections  $\tilde{\Psi}'_i$  are not strictly orthogonal, the deviation is small enough to be neglected.  $\zeta_{\text{Ti}} = 123 \text{ cm}^{-1}$ . Matrix elements of  $\hat{l}$  can be found in Appendix A.

3. Are the calculated  $g$ -values in line with the observed anisotropy? What is the effect of increasing/decreasing the gap between the ground state and the first excited state on  $g_z$  and  $g_x$ .

**2.4 Barrier for spin reversal:** Given a system with a total spin moment of  $S = 5$  and easy-axis anisotropy, calculate the energies of the different  $M_S$  components of the ground state wave function.

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