Chapter 3
Two (or More) Magnetic Centers

Abstract The description of the magnetic interactions is now extended to more than one magnetic center. First it is shown that the two-electron/two-orbital system can be approached from different viewpoints using (de-)localized, (non-)orthogonal orbitals. After this quantum chemical description of the magnetic interaction we discuss the more phenomenological approach based on spin operators. Starting with the standard Heisenberg Hamiltonian for isotropic bilinear interactions, the chapter discusses how biquadratic, anisotropic and four-center interactions can be accounted for within this spin formalism. Furthermore, it is shown how the microscopic electronic interaction parameters can be used to describe macroscopic properties by diagonalization of model Hamiltonians, Monte Carlo simulations and some other techniques.

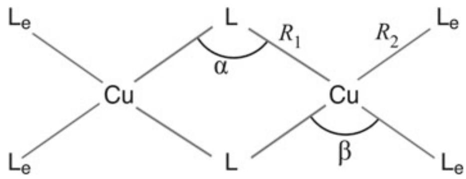
3.1 Localized Versus Delocalized Description of the Two-Electron/Two-Orbital Problem

The most simple magnetic systems have only two magnetic sites, each with spin $\frac{1}{2}$. Examples are doubly bridged binuclear Cu^{II} complexes. The energy splitting between the lowest singlet and triplet spin states in such complexes turns out to depend strongly on the geometry of the bridging Cu–L_2–Cu units (R_1, R_2, α, β, etc.) depicted in Fig. 3.1 and this magneto-structural correlation can be well explained by using simple quantum theoretical models that can be developed "*on the back of an envelope*". The basis for such models is provided in this section, they are further elaborated in Chap. 4. We consider a many-electron system, which, in addition to closed shells of electrons, has two *magnetic* electrons which are mainly localized on two magnetic sites A and B. We assume that the orbitals of the complex, i.e. its molecular orbitals (MOs), have been determined by a self-consistent field procedure.

Configuration Interaction using delocalized orbitals: We first consider the case where the two magnetic electrons are coupled to a spin triplet, $S = 1$. The simplest description of the $M_S = 1$ component of the lowest lying triplet state is one single Slater determinant

C. Graaf and R. Broer, *Magnetic Interactions in Molecules and Solids*,
Theoretical Chemistry and Computational Modelling,
DOI 10.1007/978-3-319-22951-5_3

Fig. 3.1 Schematic representation of a complex with a bridging CuL_2Cu unit and four external ligands L_e



$$\Phi^{12}(S, M_S) = \Phi^{12}(1, 1) = |\ldots\phi_1\phi_2| \tag{3.1}$$

where the MOs ϕ_1 and ϕ_2 are bonding and antibonding combinations of *atomic* orbitals localized at/around the magnetic centers A and B. In other words: ϕ_1 and ϕ_2 are *molecular* orbitals that are delocalized over the two magnetic centers. In the case of two Cu^{II} centers they will mainly be built from bonding and antibonding combinations of Cu-3*d* orbitals. The dots in the determinant denote the other electrons of the system, in doubly occupied MOs. In the following these closed shell, *inactive*, electrons will be omitted from the notation for the Slater determinants:

$$\Phi^{12}(1, 1) = |\phi_1\phi_2| \tag{3.2a}$$

The orbitals ϕ_1 and ϕ_2 are occupied with one electron and are often referred to as the magnetic orbitals. The Slater determinant shown in Eq. 3.2a has the correct spin symmetry for the $M_S = 1$ component of an $S = 1$ manifold, the corresponding wave function of the $M_S = -1$ component is given by

$$\Phi^{12}(1, -1) = |\overline{\phi}_1\overline{\phi}_2| \tag{3.2b}$$

and for the $M_S = 0$ component we need two Slater determinants:

$$\Phi^{12}(1, 0) = \left(|\phi_1\overline{\phi}_2| - |\phi_2\overline{\phi}_1|\right)/\sqrt{2} \tag{3.2c}$$

These three $S = 1$ wave functions belong to the electronic configuration $\ldots\phi_1^1\phi_2^1$, which in addition gives rise to a spin-singlet wave function,

$$\Phi^{12}(0, 0) = \left(|\phi_1\overline{\phi}_2| + |\phi_2\overline{\phi}_1|\right)/\sqrt{2} \tag{3.3}$$

In addition to the $\ldots\phi_1^1\phi_2^1$ electronic configuration, two more configurations can be defined using the two MOs ϕ_1 and ϕ_2. Both are of closed-shell character and can be written as $\ldots\phi_1^2$ and $\ldots\phi_2^2$. They give rise to two more Slater determinants

$$\Phi^{11}(0, 0) = |\phi_1\overline{\phi}_1| \tag{3.4}$$

and

$$\Phi^{22}(0, 0) = |\phi_2\overline{\phi}_2| \tag{3.5}$$

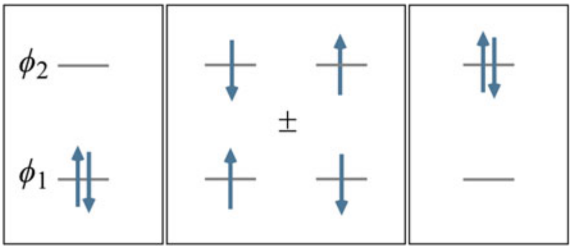


Fig. 3.2 Schematic representation of the four $M_S = 0$ CSFs that can be generated with two electrons in two orbitals

As we have seen in Eq. 3.2, the configuration $\ldots\phi_1^1\phi_2^1$ leads also to three $S = 1$ wave functions, with $M_S = 1, 0$ and -1. It is customary to call the simplest wave functions built from one electronic configuration that obey the spin (and spatial) symmetry requirements a Configuration State Function, CSF. Hence the approximate wave functions of Eqs. 3.2a–3.5 constitute the six CSFs that can be formed by distributing two electrons over the two MOs ϕ_1 and ϕ_2. Summarizing: the *two electrons in two orbitals* model, i.e. distributing two electrons over two orbitals in all possible ways yields three electronic configurations, which give rise to six CSFs. Three of them form the $M_S = 1, 0, -1$ components of an $S = 1$ state, the other three represent each a separate $S = 0$ CSF. Figure 3.2 represents the four $M_S = 0$ CSFs. From left to right, we have $\Psi^{11}(0, 0)$, $\Psi^{12}(0, 0)$ (*plus* combination), $\Psi^{12}(1, 0)$ (*minus* combination), and $\Psi^{22}(0, 0)$.

The relative energies of the four states can of course be computed by performing a complete active space configuration interaction (CASCI) calculation with the active orbitals being ϕ_1 and ϕ_2, but here we are going to analyze the relative energies by considering the physics of the system.

If the splitting between the bonding ϕ_1 and the antibonding ϕ_2 is large, the ground state is expected to be a spin singlet state, which is rather well described by $\Phi^{11}(0, 0)$. This is the situation that we would encounter, for example, if the ions A and B would be two Li atoms without any environment forming a Li_2 molecule, or, even simpler, two H atoms forming H_2. In these cases the stabilization of ϕ_1 is so large that the two electrons pair to occupy jointly this strongly bonding orbital. However, in magnetic systems the interaction between the magnetic ions A and B is quite weak. Moreover, in most complexes they are separated by *bridging* ligands. Then, the splitting between ϕ_1 and ϕ_2 is small and the three configurations $\ldots\phi_1^2$, $\ldots\phi_1^1\phi_2^1$ and $\ldots\phi_2^2$ are close in energy. The fact that we have three distinct low lying singlet CSFs suggests that we can use variation theory to generate improved descriptions of these three states, by forming linear combinations of $\Phi^{11}(0, 0)$, $\Phi^{12}(0, 0)$ and $\Phi^{22}(0, 0)$. On the contrary, in order to improve the description of the $S = 1$ state we would have to go beyond the *two electrons in two orbitals* model, but doing this only for the triplet and not for the singlet states would destroy the balance between them, preventing us from determining whether the ground state is magnetic ($S \neq 0$) or not ($S = 0$).

In many cases the A–B system is centrosymmetric, i.e. there is at least one symmetry operation that transforms A into B and *vice versa*. Then ϕ_1 and ϕ_2 belong to different irreducible symmetry representations, and consequently the wave functions corresponding to $\ldots\phi_1^1\phi_2^1$ belong also to a different representation compared to those of $\ldots\phi_1^2$ and $\ldots\phi_2^2$. As a result, in those cases there is no Hamiltonian matrix element of $\Phi^{11}(0,0)$ and $\Phi^{22}(0,0)$ with $\Phi^{12}(0,0)$:

$$\langle\Phi^{11}(0,0)|\hat{H}|\Phi^{12}(0,0)\rangle = \langle\Phi^{22}(0,0)|\hat{H}|\Phi^{12}(0,0)\rangle = 0 \tag{3.6}$$

Then, improved singlet variational wave functions can be formed by making linear combinations of only $\Phi^{11}(0,0)$ and $\Phi^{22}(0,0)$, whereas the singlet wave function corresponding to $\ldots\phi_1^1\phi_2^1$ cannot be improved within this *two electrons in two orbitals* scheme. In other magnetic systems there is no strict but only approximate symmetry, giving rise to non-zero but still quite small matrix elements $\langle\Phi^{11}(0,0)|\hat{H}|\Phi^{12}(0,0)\rangle$ and $\langle\Phi^{11}(0,0)|\hat{H}|\Phi^{12}(0,0)\rangle$. In the following we will assume symmetry, hence assume that these matrix elements are zero and turn our attention to the Hamiltonian matrix element $\langle\Phi^{11}(0,0)|\hat{H}|\Phi^{22}(0,0)\rangle$ that leads to an improved singlet wave function

$$\Psi(0,0) = c_1\Phi^{11}(0,0) + c_2\Phi^{22}(0,0) \tag{3.7}$$

where c_1 and c_2 are chosen to minimize the energy of $\Psi(0,0)$. Using the Slater–Condon rules we find for the Hamiltonian matrix element between the two closed shell determinants

$$\langle\Phi^{11}(0,0)|\hat{H}|\Phi^{22}(0,0)\rangle = \langle\phi_1(1)\phi_1(2)|\frac{1}{r_{12}}|\phi_2(1)\phi_2(2)\rangle \tag{3.8}$$

By rearranging the (real) functions in this integral, it becomes clear that the matrix element is equal to the exchange integral K_{12}

$$\langle\phi_1(1)\phi_1(2)|\frac{1}{r_{12}}|\phi_2(1)\phi_2(2)\rangle = \langle\phi_1(1)\phi_2(1)|\frac{1}{r_{12}}|\phi_2(2)\phi_1(2)\rangle = K_{12} \tag{3.9}$$

3.1 Demonstrate that $\langle\Phi^{11}(0,0)|\hat{H}|\Phi^{22}(0,0)\rangle = K_{12}$.

The exchange integral K_{12} does not vanish, not even in case of weakly interacting A and B centers. This becomes clear if we introduce the *localized orthogonal* orbitals ψ_a and ψ_b that can be constructed from the delocalized molecular orbitals ϕ_1 and ϕ_2:

$$\psi_a = \frac{1}{\sqrt{2}}(\phi_1 + \phi_2) \qquad \psi_b = \frac{1}{\sqrt{2}}(\phi_1 - \phi_2) \tag{3.10a}$$

If A and B are strongly coupled, ψ_a will be mainly localized on A, but with important *orthogonalization tails* on B and *vice versa*. Only if A and B are weakly coupled, ψ_a and ψ_b are nearly completely localized on A and B, respectively.

3.2 (a) Demonstrate that ψ_a and ψ_b are normalized and orthogonal (b) Consider the example where the delocalized orbitals ϕ_1 and ϕ_2 are bonding and antibonding combinations of atom centered basis functions χ_a and χ_b:

$$\phi_1 = \frac{\chi_a + \chi_b}{\sqrt{(2(1+S)}} \qquad \phi_2 = \frac{\chi_a - \chi_b}{\sqrt{(2(1-S)}}$$

with $S = \langle \chi_a | \chi_b \rangle$. Compute the coefficient of the orthogonalization tail of ψ_a on atom B, for $S = 0.2$ and for $S = 0.003$.

Using the inverse relations of Eq. 3.10a

$$\phi_1 = \frac{1}{\sqrt{2}}(\psi_a + \psi_b) \qquad \phi_2 = \frac{1}{\sqrt{2}}(\psi_a - \psi_b) \tag{3.10b}$$

the exchange integral K_{12} can be rewritten as a sum of Coulomb integrals

$$\begin{aligned} K_{12} &= \frac{1}{4}\langle(\psi_a + \psi_b)(\psi_a - \psi_b)|\hat{H}|(\psi_a - \psi_b)(\psi_a + \psi_b)\rangle \\ &= \frac{1}{4}\langle\psi_a\psi_a|\hat{H}|\psi_a\psi_a\rangle - 2\langle\psi_a\psi_b|\hat{H}|\psi_a\psi_b\rangle + \langle\psi_b\psi_b|\hat{H}|\psi_b\psi_b\rangle \\ &= \frac{1}{4}\big(J_{aa} - 2J_{ab} + J_{bb}\big) \end{aligned} \tag{3.11}$$

Only the term J_{ab} approaches zero for small coupling between A and B. The other terms are local Coulomb integrals which are both positive and both occur with a positive coefficient: these two terms do not cancel each other. Note, that since we have assumed centrosymmetry, $J_{aa} = J_{bb}$. Figure 3.3 shows the localized orthogonal orbitals ψ_a and ψ_b and the product of these as they appear in the Coulomb integrals of the expression of K_{12}. From this pictorial representation it is obvious that J_{ab}—with $\psi_a\psi_a \times \psi_b\psi_b$ in the numerator—is small for weak interaction between A and B, while J_{aa} and J_{bb} do not strongly depend on the distance between A and B.

Hence, there is significant interaction between the configurations $\ldots\phi_1^2$ and $\ldots\phi_2^2$. Note that the smaller J_{ab}, the larger is K_{12}, and therefore, in the case of weak coupling between A and B we need to use the two-configuration wave function of Eq. 3.7 instead of simply $\Phi^{11}(0,0)$. Clearly, the best two-configuration wave function is obtained by varying c_1/c_2 until the energy expectation value is minimal. Only in case of strong coupling between A and B (remember the case of Li_2 near equilibrium distance) J_{ab} may become so large that K_{12} and therewith c_2 becomes negligible so that the closed shell determinant $\Phi^{11}(0,0)$ is a reasonable *ansatz* for the lowest singlet wave function. For intermediate and small couplings the lowest $S = 0$ and $S = 1$ states are competing, i.e. close in energy. An approximate yet balanced treatment is obtained by describing the lowest $S = 0$ state using the expression of

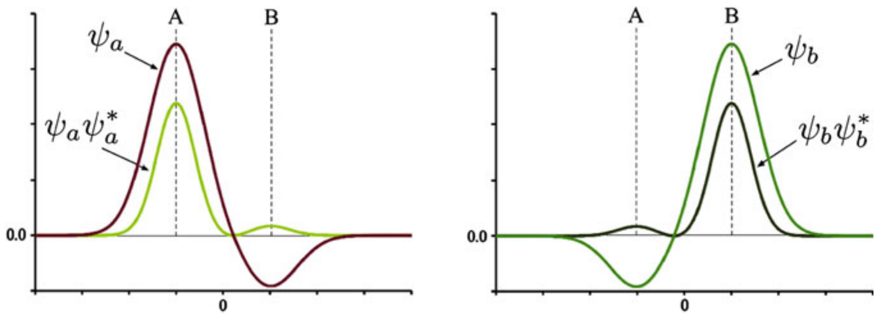


Fig. 3.3 Graphical representation of the localized orthogonal orbitals ψ_a (*left*) and ψ_b (*right*), and the respective products (charge densities) as they appear in the numerator of the Coulomb integrals

Eq. 3.7 and the $S = 1$ state using Eq. 3.2. Which state is the ground state, singlet or triplet, depends on the magnitudes of the two electron integrals J_{aa}, J_{ab} and K_{ab}.

Summarizing: A *Full CI* treatment of two electrons in two orbitals in a symmetric system leads to Eq. 3.7 for $S = 0$ and to Eq. 3.2 for $S = 1$. This approach forms a basis for the Hay–Thibeault–Hoffmann (HTH) model discussed in Chap. 4.

Valence Bond theory using localized orthogonal orbitals: For small couplings, i.e. nearly degenerate $S = 0$ and $S = 1$ states, Valence Bond (VB) theory provides a more intuitive starting point than the previous molecular orbital reasoning. For the $M_S = 0$ wave functions we make use of the local orthonormal orbitals ψ_a and ψ_b as defined in Eq. 3.10a and use them to construct two *neutral* determinants $|\psi_a\overline{\psi}_b|$ and $|\psi_b\overline{\psi}_a|$, where *neutral* does not mean that the centers A and B are uncharged, but maintain their oxidation state as in the ground configuration. Moreover, two *ionic* determinants are defined: $|\psi_a\overline{\psi}_a|$ and $|\psi_b\overline{\psi}_b|$. The simplest VB wave function for the lowest singlet state has the form

$$\Psi^{\mathrm{cov}}(0,0) = \frac{1}{\sqrt{2}}\left(|\psi_a\overline{\psi}_b| + |\psi_b\overline{\psi}_a|\right) \tag{3.12a}$$

which can also be written in terms of the symmetry-adapted, delocalized orbitals ϕ_1 and ϕ_2:

$$\Psi^{\mathrm{cov}}(0,0) = \frac{1}{\sqrt{2}}\left(|\phi_1\overline{\phi}_1| - |\phi_2\overline{\phi}_2|\right) \tag{3.12b}$$

The latter corresponds to a two-configuration CI wave function analogous to Eq. 3.7, be it with fixed coefficients $c_1 = -c_2 = 1/\sqrt{2}$. Note that it is tempting to characterize 3.12a as an open shell wave function, while the same wave function in 3.12b takes the form of a superposition of two closed shell determinants. The simplest VB representation for the $M_S = 0$ component of the lowest spin-triplet state is

$$\Psi^{\mathrm{cov}}(1,0) = \frac{1}{\sqrt{2}}\left(|\psi_a\overline{\psi}_b| - |\psi_b\overline{\psi}_a|\right) \tag{3.13a}$$

which in terms of ϕ_1 and ϕ_2 lead to $\Psi^{12}(1,0)$ of Eq. 3.2c. The other two $S = 1$ components are

$$\Psi^{\text{cov}}(1,1) = |\psi_a\psi_b| \tag{3.13b}$$

and

$$\Psi^{\text{cov}}(1,-1) = |\overline{\psi}_a\overline{\psi}_b| \tag{3.13c}$$

which written in terms of ϕ_1 and ϕ_2 yield the familiar Slater determinants $|\phi_1\phi_2|$ (Eq. 3.2a) and $|\overline{\phi}_1\overline{\phi}_2|$ (Eq. 3.2b).

3.3 Demonstrate the equivalence of the wave functions of Eqs. 3.12a and 3.12b, and those of Eqs. 3.2 and 3.13.

This simple Valence Bond *ansatz* with a common set of localized orthonormal orbitals for both states leads to a separation of the energy expectation values for singlet and triplet that reads

$$E_S^{\text{cov}} - E_T^{\text{cov}} = 2\langle\psi_a\psi_b|\frac{1}{r_{12}}|\psi_b\psi_a\rangle = 2K_{ab} \tag{3.14}$$

which is positive because the exchange integral

$$K_{ab} = \langle\psi_a(1)\psi_b(1)|\frac{1}{r_{12}}|\psi_a(2)\psi_b(2)\rangle \geqslant 0$$

3.4 Calculate the energy expectation values of the wave functions given in Eqs. 3.12a and 3.13a to demonstrate that $E_S^{\text{cov}} - E_T^{\text{cov}} = 2K_{ab}$.

$2K_{ab}$ is traditionally called the *direct* exchange. It favours high spin states. In this two electron case, treated with only covalent VB determinants, it favours $S = 1$ over $S = 0$. It is interesting to note that this positive energy difference between singlet and triplet spin states can be seen as a manifestation of Hund's rule for two electrons in two orbitals, be it in this case not for two degenerate orbitals on one site, but for two degenerate orbitals at two separate sites. In the single site case, i.e. for atoms, this Hund rule is almost always correct, however, in the two site case the sign of $E_S - E_T$ is often wrong. The simple covalent VB model using localized orthogonal orbitals is simply too crude.

The singlet VB wave function can be improved variationally by mixing in an ionic term

$$\Psi^{\text{ion}}(0,0) = \frac{1}{\sqrt{2}}\left(|\psi_a\overline{\psi}_a| + |\psi_b\overline{\psi}_b|\right) \tag{3.15}$$

leading to

$$\Psi(0,0) = C_{\text{cov}}\Psi^{\text{cov}}(0,0) + C_{\text{ion}}\Psi^{\text{ion}}(0,0) \tag{3.16}$$

which is the same as the CI wave function in Eq. 3.7, but now written in terms of the localized orthogonal orbitals ψ_a and ψ_b. Again, just as in the MO picture, there is no way to improve the $S = 1$ wave functions. A balanced VB treatment uses the wave functions of Eq. 3.16 for $S = 0$ and of Eq. 3.13 for $S = 1$, $M_S = 0$.

We can now draw the following conclusions:

- If we limit ourselves to using (apart from the doubly occupied orbitals) only two mutually orthogonal orbitals, either bonding and antibonding ϕ_a and ϕ_b, or localized ψ_a and ψ_b, then the best wave function for the lowest triplet state is the one given in Eq. 3.2 or, equivalently, 3.13a and the best wave function for the lowest singlet state is given in Eq. 3.7 or, equivalently, 3.16.
- It makes no difference whether we use MO theory and optimize the ratio c_1/c_2 in 3.7 or use VB theory and optimize the ratio $C_{\text{cov}}/C_{\text{ion}}$ in 3.16, both procedures lead to one and the same $S = 0$ wave function.
- For $\Psi(0,0)$ to become the ground state, the energy lowering due to mixing in of the ionic terms has to exceed the direct exchange $2K_{ab}$. This energy lowering is traditionally called the kinetic exchange. We will see in Chap. 4 that the kinetic exchange equals, to good approximation,[1] $4t_{ab}^2/(J_{aa} - J_{ab})$ with the *transfer* integral t_{ab} defined by $t_{ab} = \langle \psi_a \overline{\psi}_a | \hat{H} | \psi_a \overline{\psi}_b \rangle$.

Valence Bond theory using localized nonorthogonal orbitals: In the above we have used orthogonal localized orbitals ψ_a and ψ_b. What if we remove the orthogonality restriction? This nonorthogonal VB approach appeared for the first time in the work of Heitler and London [1]. It forms also the basis of the Kahn–Briat model discussed in the next chapter. We define normalized localized orbitals ϕ_a and ϕ_b with mutual overlap $S_{ab} = \langle \phi_a | \phi_b \rangle$. Then we write the covalent singlet wave function in terms of normalized Slater determinants that are now built from the nonorthogonal ϕ_a and ϕ_b:

$$\Psi(0,0) = \frac{1}{\sqrt{2 + 2S_{ab}^2}} \left(|\phi_a \overline{\phi}_b| + |\phi_b \overline{\phi}_a| \right) \tag{3.17}$$

Of course, we can formally express ϕ_a and ϕ_b in terms of our orthogonal localized orbitals ψ_a and ψ_b:

$$\begin{gathered} \phi_a = N(\psi_a + \nu\psi_b) \qquad \phi_b = N(\psi_b + \nu\psi_a) \\ \text{with} \quad N = \frac{1}{\sqrt{1+\nu^2}} \quad \text{and} \quad S_{ab} = \frac{2\nu}{1+\nu^2} \end{gathered} \tag{3.18}$$

Once we have optimized ν or, equivalently, S_{ab}, to obtain the lowest energy possible for the singlet wave function in Eq. 3.18 we have retrieved once more our familiar

[1] This expression is reasonable for $J_{aa} - J_{ab} \gg t_{ab}$, see Chap. 4.

singlet wave function shown earlier in Eqs. 3.7 and 3.16. Instead of introducing an extra variational freedom by adding ionic contributions with optimized weight, the extra freedom is now obtained by allowing the localized orbitals to be mutually nonorthogonal and optimizing their overlap. Not surprisingly, we get no additional improvement if we now include ionic terms, so this VB approach with nonorthogonal orbitals gives no improvement as compared to the VB approach with orthogonal orbitals and ionic terms, but the nonorthogonal VB approach does allow us to write the singlet wave function $\Psi(0, 0)$ in terms of a covalent contribution alone.

3.5 Show that the $S = 1$, $M_S = 0$ functions

$$\frac{1}{\sqrt{2+2S^2}}\left(|\phi_a\overline{\phi}_b| + |\phi_b\overline{\phi}_a|\right) \text{ and } \frac{1}{\sqrt{2}}\left(|\psi_a\overline{\psi}_b| + |\psi_b\overline{\psi}_a|\right)$$

are identical. Hint: rewrite the first wave function in terms of orthogonal orbitals using Eq. 3.18.

It is not difficult to show that in order to make the singlet state the ground state, the magnetic orbitals have to overlap considerably. However, atomic magnetic orbitals such as first row transition metal $3d$ orbitals are quite compact and their mutual overlap, especially in compounds where they are separated by bridging ions, is negligible. This suggests that in such systems only the direct exchange, would play a role, leading to *parallel* or *ferromagnetic* spin coupling. But in reality we have many systems whose nearest neighbour paramagnetic ions have *antiferromagnetic* spin coupling.

Already in 1934 Kramers attempted to explain the magnetic interaction in antiferromagnetic ionic solids, by noting that it is possible to have a two-center spin coupling that is mediated by the bridging non-magnetic atoms. He called this bridge-mediated spin coupling *superexchange*. In 1959 Anderson described the physical basis responsible for the generation of this superexchange: It is simply that spin-paired electrons can gain energy by spreading into nonorthogonal overlapping orbitals, whereas unpaired electrons cannot. The model of Anderson is easiest illustrated by considering again a centrosymmetric system of two magnetic ions A and B, for example Cu^{2+} ions, with (apart from electrons in double occupied orbitals) one unpaired electron in a $3d$-orbital, which are separated by a closed shell anion such as Cl^- or O^{2-} with (formally) three doubly occupied valence p orbitals. We denote the relevant atomic $3d$ functions χ_a and χ_b. It turns out that for structural and symmetry reasons commonly only one of the three valence p orbitals plays a role, so we consider only one bridging atomic function χ_h. We now allow the localized magnetic orbitals to have optimum admixture of the bridging ligand function:

$$\phi_a = c_a\chi_a + c_h\chi_h \qquad \phi_b = c_b\chi_b + c'_h\chi_h \tag{3.19}$$

as illustrated in Fig. 3.4.

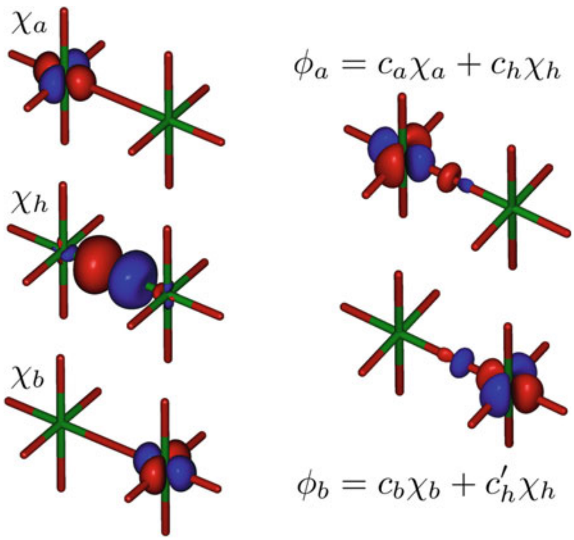


Fig. 3.4 In the *left column*: The localized magnetic orbitals (χ_a and χ_b) and the bridging atomic function (χ_h, which has small orthogonalization tails on the magnetic centers). On the *right*: Localized magnetic orbitals with optimally admixed ligand delocalization (ϕ_a and ϕ_b)

This gives the magnetic orbitals non-vanishing amplitudes also at the intermediate ligands and the exchange effects therefore need no longer be small. In quantum theoretical studies the name *Anderson model* is commonly associated with a CASSCF approach, in which the active electrons are the magnetic electrons, the active orbitals are predominantly the magnetic functions, but they are optimized in the SCF process. This guarantees that they contain the optimum amount of intermediate ligand character, so that the superexchange is accounted for.

3.2 Model Spin Hamiltonians for Isotropic Interactions

Under the assumption of a common spatial part of the wave function, the lowest energy levels of the two-electron/two-orbital problem discussed in the previous section can be described with a model Hamiltonian that only contains spin operators. Starting from a general expression of the interaction of two spatially separated spin moments S_1 and S_2 of arbitrary strength (not limiting ourselves to the $S = \frac{1}{2}$ case discussed before), the spin Hamiltonian can be written in terms of local spin operators $\hat{S}_1$ and $\hat{S}_2$

$$\hat{H} = \begin{pmatrix} \hat{S}_{x,1} & \hat{S}_{y,1} & \hat{S}_{z,1} \end{pmatrix} \begin{pmatrix} A_{xx} & A_{xy} & A_{xz} \\ A_{yx} & A_{yy} & A_{yz} \\ A_{zx} & A_{zy} & A_{zz} \end{pmatrix} \begin{pmatrix} \hat{S}_{x,2} \\ \hat{S}_{y,2} \\ \hat{S}_{z,2} \end{pmatrix} \quad (3.20)$$

This expression is greatly simplified by orienting the system along the magnetic axis frame making all non-diagonal elements of the A-tensor equal to zero.

$$\hat{H} = A_{xx}\hat{S}_{x,1}\hat{S}_{x,2} + A_{yy}\hat{S}_{y,1}\hat{S}_{y,2} + A_{zz}\hat{S}_{z,1}\hat{S}_{z,2} \tag{3.21}$$

It is common practice to divide the interaction in a part that does not depend on the spatial orientation of spin—the isotropic part, parametrized by the scalar J—and another part that models the anisotropy of the interaction parametrizing it with a diagonal tensor D.

$$\begin{aligned}\hat{H} = &-J\left(\hat{S}_{x,1}\hat{S}_{x,2} + \hat{S}_{y,1}\hat{S}_{y,2} + \hat{S}_{z,1}\hat{S}_{z,2}\right)\\ &+ D_{xx}\hat{S}_{x,1}\hat{S}_{x,2} + D_{yy}\hat{S}_{y,1}\hat{S}_{y,2} + D_{zz}\hat{S}_{z,1}\hat{S}_{z,2}\end{aligned} \tag{3.22}$$

The minus sign in front of J is by convention, but be aware that other definitions are often used in the literature. Negative J-values indicate antiferromagnetic coupling and positive values are characteristic of ferromagnetic interactions in the definition that we use here.

3.2.1 Heisenberg Hamiltonian

For the moment, we leave aside the anisotropic part of the interaction and concentrate on the isotropic part. The equation can then be written in the following from

$$\hat{H} = -J\hat{S}_1 \cdot \hat{S}_2 \tag{3.23}$$

which is known as the *Heisenberg* or *Heisenberg-Dirac-van Vleck* Hamiltonian. For systems with two magnetic sites, the eigenvalues of the Hamiltonian are easily derived by rewriting the product of local operators using the relation

$$\hat{S}^2 = (\hat{S}_1 + \hat{S}_2)^2 = \hat{S}_1^2 + \hat{S}_2^2 + 2\hat{S}_1 \cdot \hat{S}_2 \tag{3.24}$$

from this follows

$$\hat{S}_1 \cdot \hat{S}_2 = \frac{1}{2}(\hat{S}^2 - \hat{S}_1^2 - \hat{S}_2^2) \tag{3.25}$$

which leads to an alternative formulation of the Heisenberg Hamiltonian

$$\hat{H} = -\frac{1}{2}J(\hat{S}^2 - \hat{S}_1^2 - \hat{S}_2^2) \tag{3.26}$$

for which the eigenvalues can be written down directly

$$E(S) = -\frac{1}{2}J\big(S(S+1) - S_1(S_1+1) - S_2(S_2+1)\big) \tag{3.27}$$

3.6 Calculate the eigenvalues of the Heisenberg Hamiltonian of the spin eigenfunctions with maximum and minimum spin moment of a dimeric system with $S_1 = S_2$.

Since the reference point of energy can be chosen arbitrarily, the expression for the eigenvalues is usually simplified by adding a constant factor equal to $-\frac{1}{2}J\big(S_1(S_1+1) + S_2(S_2+1)\big)$, leading to

$$E(S) = -\frac{1}{2}JS(S+1) \tag{3.28}$$

From this it is easily derived that the difference between two subsequent eigenvalues is given by

$$E(S-1) - E(S) = JS \tag{3.29}$$

where S runs from $S_1 + S_2$ to $|S_1 - S_2|$. This regular Landé pattern gives the exact energy differences as long as the interaction with excited electronic configurations is negligible and is the basis for extracting magnetic coupling parameters from electronic structure calculations. The generalization of the Heisenberg Hamiltonian to multiple sites is straightforward

$$\hat{H} = \sum_{i>j} -J_{ij}\hat{S}_i\hat{S}_j \tag{3.30}$$

In systems with multiple magnetic sites, the number of energy differences between the different spin functions is not always enough to determine all the J-values. An obvious example is the three-center/three-electron case as depicted in Fig. 3.5. The Hamiltonian has three different J-values while the quartet and the two doublet states only define two energy differences. The effective Hamiltonian theory described in Chap. 1 is a more general approach to extract J-values, because it not only uses the energies but also information contained in the wave function. To illustrate the procedure we first treat a simple biradical model with two $S = \frac{1}{2}$ spins and after that focus on the three center problem.

The following results for the singlet and triplet states were obtained from an *ab initio* calculation on a dimer with two $S = \frac{1}{2}$ centers:

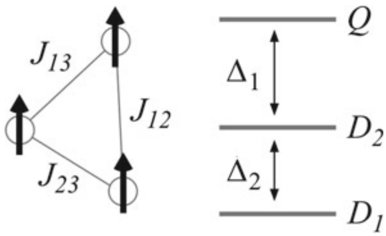


Fig. 3.5 Three center $S = 1/2$ system with a quartet (Q) and two doublets (D_1, D_2). The three J-values cannot be determined from the two energy differences

$$
\begin{aligned}
\Psi_S &= 0.6776|\phi_1\bar{\phi}_2| - 0.6776|\bar{\phi}_1\phi_2| + 0.1287|\phi_1\bar{\phi}_1| + 0.1287|\phi_2\bar{\phi}_2| + \dots \\
\Psi_T &= 0.7029|\phi_1\bar{\phi}_2| + 0.7029|\bar{\phi}_1\phi_2| + \dots \\
E_S &= -29.441750\ \mathrm{E_h} \\
E_T &= -29.438299\ \mathrm{E_h}
\end{aligned}
$$

Here, ϕ_1 and ϕ_2 are basis functions localized on site 1 and 2, respectively. The model space of the Heisenberg Hamiltonian is spanned by the $M_S = 0$ determinants $|\phi_1\bar{\phi}_2|$ and $|\bar{\phi}_1\phi_2|$ and the matrix representation of the Hamiltonian can be obtained by calculating the matrix elements $\langle\phi_1\bar{\phi}_2|\hat{H}|\phi_1\bar{\phi}_2\rangle$ and $\langle\phi_1\bar{\phi}_2|\hat{H}|\bar{\phi}_1\phi_2\rangle$. For this purpose, we first substitute the $\hat{S}_x$ and $\hat{S}_y$ operators by the ladder operators $\hat{S}^{\pm}$

$$\hat{H} = -J\left(\frac{1}{2}\left\{\hat{S}_1^+\hat{S}_2^- + \hat{S}_1^-\hat{S}_2^+\right\} + \hat{S}_{z,1}\hat{S}_{z,2}\right) \tag{3.31}$$

The action of the different operators on the model space determinants gives:

$$
\begin{aligned}
&\hat{S}_1^+\hat{S}_2^-|\phi_1\bar{\phi}_2| = 0 && \hat{S}_1^+\hat{S}_2^-|\bar{\phi}_1\phi_2| = |\phi_1\bar{\phi}_2| \\
&\hat{S}_1^-\hat{S}_2^+|\phi_1\bar{\phi}_2| = |\bar{\phi}_1\phi_2| && \hat{S}_1^-\hat{S}_2^+|\bar{\phi}_1\phi_2| = 0 \\
&\hat{S}_{z,1}\hat{S}_{z,2}|\phi_1\bar{\phi}_2| = -\frac{1}{4}|\phi_1\bar{\phi}_2| && \hat{S}_{z,1}\hat{S}_{z,2}|\bar{\phi}_1\phi_2| = -\frac{1}{4}|\bar{\phi}_1\phi_2|
\end{aligned}
\tag{3.32}
$$

and from this the matrix elements can directly be written down:

$$
\begin{aligned}
\langle\phi_1\bar{\phi}_2|\hat{H}|\phi_1\bar{\phi}_2\rangle &= -J\langle\phi_1\bar{\phi}_2|\left(0 + \frac{1}{2}|\bar{\phi}_1\phi_2\rangle - \frac{1}{4}|\phi_1\bar{\phi}_2\rangle\right) = \frac{1}{4}J \\
\langle\phi_1\bar{\phi}_2|\hat{H}|\bar{\phi}_1\phi_2\rangle &= -J\langle\phi_1\bar{\phi}_2|\left(0 + \frac{1}{2}|\phi_1\bar{\phi}_2\rangle + 0\right) = -\frac{1}{2}J
\end{aligned}
\tag{3.33}
$$

In matrix form:

$$
\begin{array}{c|cc}
 & |\phi_1\overline{\phi}_2\rangle & |\overline{\phi}_1\phi_2\rangle \\
\hline
\langle\phi_1\overline{\phi}_2| & \frac{1}{4}J & -\frac{1}{2}J \\
\langle\overline{\phi}_1\phi_2| & -\frac{1}{2}J & \frac{1}{4}J
\end{array}
\tag{3.34}
$$

The diagonalization of this matrix gives $E_1 = \frac{3}{4}J$ and $E_2 = -\frac{1}{4}J$ and the corresponding eigenvectors are $\Psi_1 = \frac{1}{\sqrt{2}}\left\{|\phi_1\bar{\phi}_2| - |\bar{\phi}_1\phi_2|\right\}$ and $\Psi_2 = \frac{1}{\sqrt{2}}\left\{|\phi_1\bar{\phi}_2| + |\bar{\phi}_1\phi_2|\right\}$. Note that the eigenfunctions of the Heisenberg Hamiltonian are multideterminantal functions; linear combinations of the basis determinants $|\phi_1\bar{\phi}_2|$ and $|\bar{\phi}_1\phi_2|$. In the next step, we build an effective Hamiltonian that connects the *ab initio* results with the model Hamiltonian. In the first place the wave functions are projected on the model space and orthonormalized:

$$\begin{aligned}
\text{Projections:}\quad & \widetilde{\Psi}_T = 0.7029|\phi_1\bar{\phi}_2| + 0.7029|\bar{\phi}_1\phi_2| \\
& \widetilde{\Psi}_S = 0.6776|\phi_1\bar{\phi}_2| - 0.6776|\bar{\phi}_1\phi_2| \\
\text{Norms:}\quad & \langle\widetilde{\Psi}_T|\widetilde{\Psi}_T\rangle = 0.7029^2 + 0.7029^2 = 0.9881 \\
& \langle\widetilde{\Psi}_S|\widetilde{\Psi}_S\rangle = 0.6776^2 + 0.6776^2 = 0.9183 \\
\text{Normalized projections:}\quad & \widetilde{\Psi}_T^N = 0.707107|\phi_1\bar{\phi}_2| + 0.707107|\bar{\phi}_1\phi_2| \\
& \widetilde{\Psi}_S^N = 0.707107|\phi_1\bar{\phi}_2| - 0.707107|\bar{\phi}_1\phi_2| \\
& \langle\widetilde{\Psi}_T^N|\widetilde{\Psi}_S^N\rangle = 0
\end{aligned}$$

In the next step, the effective Hamiltonian is constructed by substituting these normalized projections and the corresponding energies in the Bloch equation as discussed in Sect. 1.4.

$$\hat{H}^{eff} = \sum_i |\widetilde{\Psi}_i^N\rangle E_i \langle\widetilde{\Psi}_i^N| \tag{3.35}$$

The basis of the effective Hamiltonian is the same as for the Heisenberg Hamiltonian. The use of orthonormal projections ensures that the effective Hamiltonian is hermitian with $\langle\phi_1\bar{\phi}_2|\hat{H}^{eff}|\bar{\phi}_1\phi_2\rangle = \langle\bar{\phi}_1\phi_2|\hat{H}^{eff}|\phi_1\bar{\phi}_2\rangle$.

$$\begin{aligned}
\langle\phi_1\bar{\phi}_2|\hat{H}^{eff}|\phi_1\bar{\phi}_2\rangle &= \langle\phi_1\bar{\phi}_2|\left\{0.707107|\phi_1\bar{\phi}_2\rangle + 0.707107|\bar{\phi}_1\phi_2\rangle\right\}\cdot -29.438299 \\
&\quad \cdot\left\{0.707107\langle\phi_1\bar{\phi}_2| + 0.707107\langle\bar{\phi}_1\phi_2|\right\}|\phi_1\bar{\phi}_2\rangle \\
&\quad + \langle\phi_1\bar{\phi}_2|\left\{0.707107|\phi_1\bar{\phi}_2\rangle - 0.707107|\bar{\phi}_1\phi_2\rangle\right\}\cdot -29.441751 \\
&\quad \cdot\left\{0.707107\langle\phi_1\bar{\phi}_2| - 0.707107\langle\bar{\phi}_1\phi_2|\right\}|\phi_1\bar{\phi}_2\rangle \\
&= 0.707107^2\langle\phi_1\bar{\phi}_2|\phi_1\bar{\phi}_2\rangle\cdot -29.438299 + 0.707107^2\langle\phi_1\bar{\phi}_2|\phi_1\bar{\phi}_2\rangle\cdot \\
&\quad -29.441751 = 0.5\{-29.438299 - 29.441751\} = -29.440025\ \mathrm{E_h}
\end{aligned} \tag{3.36}$$

The other diagonal matrix element, $\langle\bar{\phi}_1\phi_2|\hat{H}^{eff}|\bar{\phi}_1\phi_2\rangle$, has the same numerical value. The off-diagonal matrix element is calculated by the same procedure:

$$\begin{aligned}
\langle\phi_1\bar{\phi}_2|\hat{H}^{eff}|\bar{\phi}_1\phi_2\rangle &= 0.707107\langle\phi_1\bar{\phi}_2|\phi_1\bar{\phi}_2\rangle\cdot -29.438299\cdot 0.707107\langle\bar{\phi}_1\phi_2|\bar{\phi}_1\phi_2\rangle \\
&\quad +0.707107\langle\phi_1\bar{\phi}_2|\phi_1\bar{\phi}_2\rangle\cdot -29.438299\cdot -0.707107\langle\bar{\phi}_1\phi_2|\bar{\phi}_1\phi_2\rangle \\
&= 0.5(-29.438299 + 29.441751) = 0.001726\ \mathrm{E_h}
\end{aligned} \tag{3.37}$$

Finally, the numerical effective Hamiltonian becomes:

$$\begin{array}{c|cc} & |\phi_1\overline{\phi}_2\rangle & |\overline{\phi}_1\phi_2\rangle \\ \hline \langle\phi_1\overline{\phi}_2| & -29.440025 & 0.001726 \\ \langle\overline{\phi}_1\phi_2| & 0.001726 & -29.440025 \end{array} \tag{3.38}$$

The two Hamiltonians (Eqs. 3.34 and 3.38) can only be compared when they have the same zero of energy. Therefore the diagonal matrix elements of the Heisenberg Hamiltonian are shifted by $-\frac{1}{4}J$ and those of the effective Hamiltonian by -29.440025 E_h. The comparison shows that there is a one-to-one correspondence between both matrices and that the magnetic coupling parameter is equal to -2×0.001726 $E_h = -757.6\,\text{cm}^{-1}$. In this simple case, the eigenfunctions of the Heisenberg Hamiltonian are the same as those of $\hat{S}^2$; Ψ_1 and Ψ_2 are directly the singlet and triplet functions, respectively. Hence J is also given by the difference of the singlet and triplet energies: $J = E_S - E_T = -29.441751 - -29.43830 = -0.003452$ $E_h = -757.6\ \text{cm}^{-1}$.

However, the extraction strategy based on effective Hamiltonians is generally applicable and in cases where the energies of the different spin states do not provide enough information to determine all the magnetic coupling parameters one necessarily has to rely on the effective Hamiltonian procedure. The three different magnetic coupling strengths J_{12}, J_{13} and J_{23} of the three center/three electron case of Fig. 3.5 cannot be extracted from the two energy differences defined by the quartet and the two doublets states. Instead an effective Hamiltonian has to be constructed from the *ab initio* wave functions and compared to the matrix representation of the Heisenberg Hamiltonian

$$\hat{H} = -J_{12}\hat{S}_1 \cdot \hat{S}_2 - J_{13}\hat{S}_1 \cdot \hat{S}_3 - J_{23}\hat{S}_2 \cdot \hat{S}_3 \tag{3.39}$$

$$\begin{array}{c|ccc} & |\overline{\phi}_1\phi_2\phi_3\rangle & |\phi_1\overline{\phi}_2\phi_3\rangle & |\phi_1\phi_2\overline{\phi}_3\rangle \\ \hline \langle\overline{\phi}_1\phi_2\phi_3| & \frac{1}{4}(J_{12}+J_{13}-J_{23}) & -\frac{1}{2}J_{12} & -\frac{1}{2}J_{13} \\ \langle\phi_1\overline{\phi}_2\phi_3| & -\frac{1}{2}J_{12} & \frac{1}{4}(J_{12}-J_{13}+J_{23}) & -\frac{1}{2}J_{23} \\ \langle\phi_1\phi_2\overline{\phi}_3| & -\frac{1}{2}J_{13} & -\frac{1}{2}J_{23} & \frac{1}{4}(-J_{12}+J_{13}+J_{23}) \end{array} \tag{3.40}$$

The quartet spin function $Q = |\alpha\alpha\alpha\rangle$ is an eigenfunction of the Heisenberg Hamiltonian of Eq. 3.39 with eigenvalue $-\frac{1}{4}(J_{12}+J_{13}+J_{23})$. However, the doublet functions D_1 and D_2 defined in Eq. 1.41 are not:

$$\begin{aligned} \hat{H}\big\{|\alpha\alpha\beta\rangle - |\beta\alpha\alpha\rangle\big\} = &-\frac{1}{4}(J_{12}-J_{23})\big(|\alpha\alpha\beta\rangle + |\beta\alpha\alpha\rangle\big) \\ &+ \frac{3}{4}J_{13}\big(|\alpha\alpha\beta\rangle - |\beta\alpha\alpha\rangle\big) + \frac{1}{2}(J_{12}-J_{23})|\alpha\beta\alpha\rangle \end{aligned} \tag{3.41}$$

$$\hat{H}\big\{2|\alpha\beta\alpha\rangle - |\alpha\alpha\beta\rangle - |\beta\alpha\alpha\rangle\big\} = \big(J_{12} + J_{23} - \frac{1}{2}J_{13}\big)|\alpha\beta\alpha\rangle$$
$$+ \big(\frac{1}{4}J_{12} - \frac{5}{4}J_{23} + \frac{1}{4}J_{13}\big)|\alpha\alpha\beta\rangle + \big(-\frac{5}{4}J_{12} + \frac{1}{4}J_{23} + \frac{1}{4}J_{13}\big)|\beta\alpha\alpha\rangle \tag{3.42}$$

In the special case of $J_{12} = J_{23} = J_1$; $J_{13} = J_2$, these two expression reduce to

$$\hat{H}D_1 = \frac{3}{4}J_2 D_1 \tag{3.43a}$$

$$\hat{H}D_2 = \big(J_1 - \frac{1}{4}J_2\big)D_2 \tag{3.43b}$$

and the two J-values can be directly extracted from the energy differences of the quartet and doublet states using the relations

$$J_1 = \frac{2}{3}\big(E(D_2) - E(Q)\big) \tag{3.44a}$$

$$J_2 = J_1 - \big(E(D_2) - E(D_1)\big) \tag{3.44b}$$

3.2.2 Ising Hamiltonian

The elimination of the anisotropic part in Eq. 3.22 leads to the Heisenberg Hamiltonian for isotropic magnetic interactions. The spins are considered as co-linear vectors whose principal quantization axis has no spatially preferred orientation. An even simpler model Hamiltonian can be obtained by putting A_{xx} and A_{yy} to zero in Eq. 3.21. Then, the spin reduces to a classical vector whose orientation in space is not defined and the resulting model Hamiltonian describes the isotropic coupling of two (anti-)parallel spins. Replacing A_{zz} by −J, the following expression is obtained

$$\hat{H} = -J\hat{S}_{z,1}\hat{S}_{z,2} \tag{3.45}$$

which is known as the Ising Hamiltonian. The big advantage of this simpler Hamiltonian is the fact that the eigenfunctions correspond to monodeterminantal functions, and therefore, this Hamiltonian can be used to determine the magnetic coupling strength from density functional theory (DFT) calculations and in extended systems treated in the periodic approximation. This is further discussed in the next chapters in Sects. 4.3.4 and 6.3. For now, we will restrict ourselves to some formal properties of the Ising Hamiltonian and a comparison with the Heisenberg Hamiltonian. To determine the magnetic coupling of the two-electron/two-orbital problem, two functions are needed describing parallel and anti-parallel coupling, $|\phi_1\phi_2|$ and $|\phi_1\bar{\phi}_2|$. By acting with the Ising Hamiltonian on these two function we get

$$-J\hat{S}_{z,1}\hat{S}_{z,2}|\phi_1\phi_2| = -\frac{1}{4}J|\phi_1\phi_2| \tag{3.46}$$

$$-J\hat{S}_{z,1}\hat{S}_{z,2}|\phi_1\bar{\phi}_2| = \frac{1}{4}J|\phi_1\bar{\phi}_2| \tag{3.47}$$

Assuming that the spatial part is identical in both functions (only spin degrees of freedom are taken into account for the moment), the energy difference between the two determinants gives an estimate of the magnetic coupling through $E_{LS} - E_{HS} = \frac{1}{2}J$. Here LS refers to the determinant with antiparallel alignment of the spins and HS to the parallel alignment. This expression is easily generalized to a pair of arbitrary spins

$$E_{LS} - E_{HS} = 2S_1S_2J \tag{3.48}$$

In any real case, the orbital part plays an important role and the influence of this on the extraction of the J-value from calculations will be discussed in the next chapter. The dimeric system $S_1 = S_2 = \frac{1}{2}$ only has HS and LS states, but for systems with higher spins there are several intermediate states. Remembering that the eigenfunctions of the Ising Hamiltonian are not necessarily spin eigenfunctions, we use a label to characterize the eigenfunctions that consists of the M_S-value of the two magnetic centers. Then the HS determinant is $|\pm\frac{1}{2}, \pm\frac{1}{2}\rangle$ and the LS state is represented as $|\pm\frac{1}{2}, \mp\frac{1}{2}\rangle$. For a system with two $S = 1$ spins, nine different determinants can be defined. The HS and LS states are separated by $2J$ as follows from the above equation, but in between these two, there is a set of five determinants with $M_S = 0$ functions on one or both magnetic centers with an expectation value equal to zero.

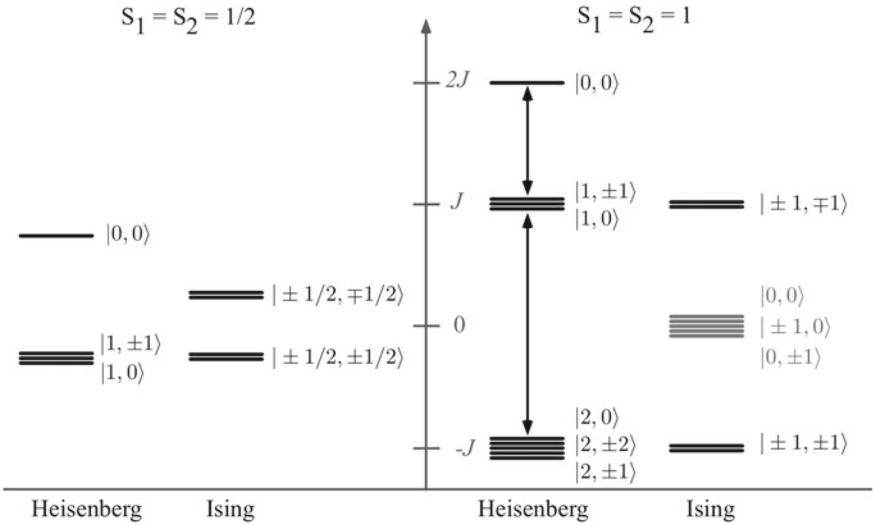


Fig. 3.6 Comparison of the Heisenberg and Ising eigenvalues for a dimeric system with $S_1 = S_2 = \frac{1}{2}$ (*left*) and 1 (*right*). The levels in *gray* are eigenfunctions of the Ising hamiltonian, but lie at much higher energy when the spatial part of the wave function is also considered

In the general case of $S_1 \neq S_2$, the gap between the lowest state and the group of degenerate first excited states of the Ising Hamiltonian is given by the value of the smallest spin. Figure 3.6 summarizes the energy levels of the Heisenberg and Ising Hamiltonians for the two systems.

3.2.3 Comparing the Heisenberg and Ising Hamiltonians

Table 3.1 compares some formal properties of the Ising and the Heisenberg Hamiltonian for symmetric dimeric systems with different spin moments. The spectral width W—defined as the difference between the lowest and highest eigenvalue—increases with the spin moment for both Hamiltonians. In absolute values the difference between Ising and Heisenberg grows larger, but it should be noted that the relative difference is significantly smaller for the system with $S = 5/2$ (16.7 %) than for the $S = 1/2$ case (50 %). For antiferromagnetic coupling (negative J), the first excited state of the Heisenberg Hamiltonian is always a threefold degenerate triplet state with a relative energy equal to J. In the Ising model, the gap depends linearly on the spin moment. For $S = 1/2$, the gap is smaller than in the Heisenberg model, but for the $S = 5/2$ system the separation of the ground state and the first excited state is much larger in the Ising model. In the case of ferromagnetic interaction, the spectrum of the Ising Hamiltonian is simply inverted, being symmetric around $E = 0$. This is not the case for the Heisenberg Hamiltonian. Except for the $S = 1/2$ system, the gap between ground and first excited state is larger, as is the degeneracy of the latter.

3.7 Complete the Table for atoms with six and seven unpaired electrons as can be found in the rare earth metal ions.

Before closing this section, a word of warning is needed concerning all the eigenstates of the Ising Hamiltonian between the ones with the highest and lowest energy.

Table 3.1 Spectral width (W), gap (Δ) and degeneracy of the first excited state of the Heisenberg and Ising Hamiltonian for a dimeric system with $S_1 = S_2 = 1/2 \ldots 5/2$ and $J = \pm 1$ K

Spin	Heisenberg					Ising		
	W	Δ		Degen.		W	Δ	Degen.
		AF	F	AF	F			
1/2	1	1	1	3	1	1/2	1/2	2
1	3	1	2	3	3	2	1	5
3/2	6	1	3	3	5	9/4	3/2	4
2	10	1	4	3	7	4	2	4
5/2	15	1	5	3	9	25/2	5/2	4

These eigenstates share the common feature that at least one of the local M_S values is not equal to $\pm M_S^{max}$. For example the Ising eigenstates in Fig. 3.6 with energy J have either on the left or the right (or both) centers an $\alpha\beta$ determinant. As soon as one adds the spatial part to the wave function, these determinants are raised in energy since they lack the stabilization by the exchange integral K present in the energy expression of the $|\alpha\alpha|$ and $|\beta\beta|$ determinants. Consequently, in any practical application focused on magnetic interactions one should only consider the eigenstates of the Ising Hamiltonian with $M_S = 0$ or M_S^{max}.

3.3 From Micro to Macro: The Bottom-Up Approach

In Sect. 2.3.2, we have shown how the temperature dependence of the magnetic susceptibility can be calculated based on the knowledge of the energy levels of the ion in a magnetic field. Substituting an analytical expression in the van Vleck equation, we derived the Curie law for paramagnetic systems without interaction between the magnetic centers. The same strategy can be followed for systems in which the interaction between the magnetic centers cannot be neglected, such as those discussed in this chapter so far. At difference with the derivation of Curie's law for isolated magnetic ions, we no longer can ignore the excited states and have to substitute $E^{(0)}$ by Eq. 3.28 in the van Vleck equation (Eq. 2.33). Using the same expression as before for $E^{(1)}$ we obtain

$$\chi = \frac{N_A \mu_B^2 g_e^2}{kT} \frac{\sum_{S=S_{min}}^{S_{max}} \sum_{M_S=-S}^{S} M_S^2 \exp(JS(S+1)/2kT)}{\sum_{S=S_{min}}^{S_{max}} \sum_{M_S=-S}^{S} \exp(JS(S+1)/2kT)} \tag{3.49}$$

which reduces to

$$\chi = \frac{N_A \mu_B^2 g_e^2}{3kT} \frac{\sum_{S=S_{min}}^{S_{max}} S(S+1)(2S+1) \exp(JS(S+1)/2kT)}{\sum_{S=S_{min}}^{S_{max}} (2S+1) \exp(JS(S+1)/2kT)} \tag{3.50}$$

by using Eq. 2.35. This so-called *Bleaney–Bowers* equation [2], which is normally used to fit experimental data to extract numerical values for J and g_e. The other way around is of course also possible; the equation can also be used to generate the $\chi(T)$ from an *ab initio* calculation of the microscopic parameters, J and sometimes g_e.

3.8 Confirm that the Bleaney–Bowers expression for a dimer with $S_1 = S_2 = \frac{1}{2}$ equals

$$\chi = \frac{2N_A\mu_B^2 g_e^2}{kT\big(3 + \exp(-J/kT)\big)}.$$

This is rather trivial as long as dimeric systems are concerned, because there is actually only one parameter in the analytical expression of χ and no new information is obtained by calculating $\chi(T)$ from the theoretical estimates of the J-value. The situation is different when polynuclear systems are considered. Most importantly, there are not many systems for which an exact expression of χ has been derived. In addition to the above stated expression for binuclear complexes, Boča derived expression for tri- and tetra-nuclear systems [3], which turn out to be rather lengthy. The situation is even more complicated for extended systems, which have (in principle) an infinite number of interacting magnetic centers.

In fact, the one-dimensional uniform Heisenberg chain is the only extended system for which an exact solution has been derived making use of the Bethe Ansatz [4]. Bonner and Fisher extended this $T = 0$ solution to finite temperatures by extrapolating the results obtained for small chains to chains of infinite length [5]. The Bonner-Fisher expression is still widely used to fit magnetic susceptibility data to determine the magnetic coupling strength in systems with a magnetic chain-like topology.

$$\chi(T) = \frac{N_A\mu_B^2 g_e^2}{kT}\,\frac{A + Bx + Cx^2}{1 + Dx + Ex^2 + Fx^3} \tag{3.51}$$

where the values of A–F are given in Appendix D and $x = |J|/2kT$. Similar strategies were used to derive expressions for $\chi(T)$ in magnetic chains in which the magnetic centers alternately interact through J_1 and J_2 [6]. Defining the Hamiltonian as

$$\hat{H} = -J\sum_{i=1}\big(\hat{S}_{2i}\cdot\hat{S}_{2i+1} + \alpha\hat{S}_{2i}\cdot\hat{S}_{2i-1}\big) \tag{3.52}$$

with the same quadratic/cubic equation as for the uniform Heisenberg chain for which A-F are also listed in the Appendix. Note that the Bonner-Fisher expression is only valid for $2kT/|J| > 0.5$ and hence the low-temperature data should not be included in the fitting procedure. Improvements upon the Bonner-Fisher expression for low temperatures have been published [7] and many more expressions for the magnetic susceptibility can be found in Ref. [8].

Magnetic susceptibility data in two-dimensional extended systems are often interpreted based on the work of Rushbrooke and Wood [9], who derived an expression for $\chi(T)$ valid for high temperatures. The discovery of the high T_c superconductors renewed the interest in the 2D Heisenberg lattices and the original work was extended to lower temperatures. A workable expression for a uniform lattice—characterized

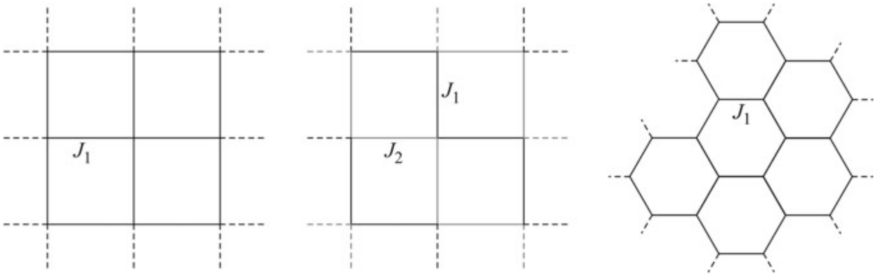


Fig. 3.7 Some examples of two-dimensional magnetic lattices for which analytical expressions have been derived to fit J from the temperature dependence of the magnetic susceptibility

by one single J, see Fig. 3.7 left—was given by Woodward and co-workers and reads

$$\chi(T) = \frac{N_A \mu_B^2 g_e^2}{kT} \sum_{n=1}^{5} \frac{a_n J/kT}{b_n J/kT} \tag{3.53}$$

More general expressions were derived by Curély for $S \neq 1/2$, for 2D lattices with different magnetic interaction paths (Fig. 3.7 middle) and to hexagonal (or honeycomb) lattices (Fig. 3.7 right) [10, 11].

When no analytical expression can be used to fit $\chi(T)$, the experimental data are interpreted by defining a magnetic model with the magnetic interactions that are considered *a priori* to be the most important ones. The corresponding Heisenberg Hamiltonian is then diagonalized and the resulting eigenvalues are substituted in the van Vleck equation. The J-values of the magnetic model are adjusted to give an optimal fit of the experimental data. However, one has to be aware that a multi-parameter fit can have several solutions of equal quality and that this way of deriving experimental J-values can be subject to uncertainties. Actually, this is where computations can be helpful to discern the important interactions from less important ones and determine the sign and order of magnitude of the interactions. This would in principle lead to a well-founded magnetic model that will lead to reliable J-values from the fitting procedure.

A closely related procedure allows theoreticians to take the full journey from microscopic to macroscopic in a three-step strategy [12]. In the first stage, one calculates as exhaustive as possible the interactions among the different magnetic centers. This should not be restricted to nearest neighbors and preferably also include three- or four-body interactions, see Sect. 3.4. Secondly, a magnetic model is defined by writing down the Heisenberg Hamiltonian with the most important interactions. When dealing with an extended system, periodic boundary conditions can be applied. This is best illustrated taking the 1D Heisenberg chain as example. As illustrated in Fig. 3.8, the first center in the chain not only interacts with center 2 on the right, but also with the last center in the chain. In this way, there is no open end in the chain, exactly as in an infinite 1D chain. The topology of the model is actually a ring, but this turns out

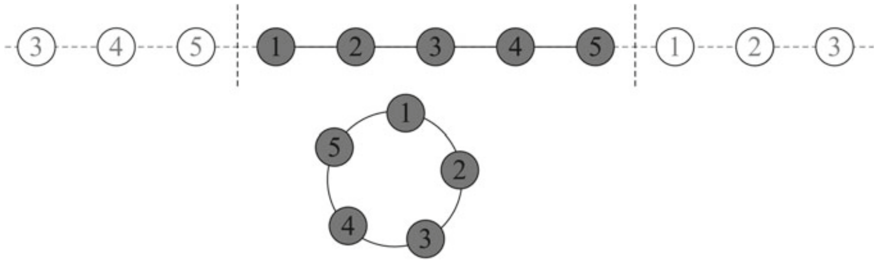


Fig. 3.8 Periodic boundaries in a one-dimensional chain. The central unit of five magnetic centers is repeated on the *left* and the *right* by introducing the interaction between center 1 and 5. The actual model is a closed ring of five centers

to be a very accurate representation of the 1D chain provided a large enough number of centers is considered. Finally, the Hamiltonian is diagonalized and the resulting eigenvalues are substituted in the van Vleck equation to obtain the magnetic susceptibility as function of the temperature from a rigorous *ab initio* treatment. The eigenvalues can of course also be used to derive any other macroscopic property such as the specific heat at constant magnetic field (C_B) by using the appropriate equation from standard statistical mechanics.

Inter- and intramolecular interactions: Generally speaking, transition metal based magnetic materials have large intramolecular interactions and weaker intermolecular interactions. Nevertheless, the control and understanding of the macroscopic properties depends critically on the knowledge of both types of interactions. Imagine a building block with two antiferromagnetically coupled spin moments as schematically depicted in the upper panel of Fig. 3.9. The interaction of the spin moments on the transition metals proceeds through the bridging ligand as will be profoundly analyzed in Chap. 5 and is also known as a through-bond interaction. Using transition metals with different spins ($S_1 \neq S_2$) causes that the unit has a net magnetic moment, despite the antiferromagnetic nature of the interaction. This is known as ferrimagnetism. The middle panel shows that a proper choice of the external ligands can link these building blocks into an *infinite* chain of antiferromagnetically coupled magnetic centers. Such entity is of course a very interesting object due to the net magnetic moment, however to take profit of this, one has to stick these chains together in a three-dimensional structure such that the chains are ferromagnetically coupled to each other as shown in the lower panel. This interchain coupling is typically much weaker as it does not involve magnetic centers that are connected by (covalent) bonds, and is usually referred to as through-space interaction. By carefully choosing the magnetic centers and the coordinating ligands, Kahn and co-workers were able to design and synthesize molecular-based magnets, initially with rather low critical temperatures for long-range order [13], but later many compounds have been reported with long-range order at much higher temperatures.

A different situation is encountered in most magnetic materials containing organic radicals. Typically, the building units are moieties with one unpaired electron, either

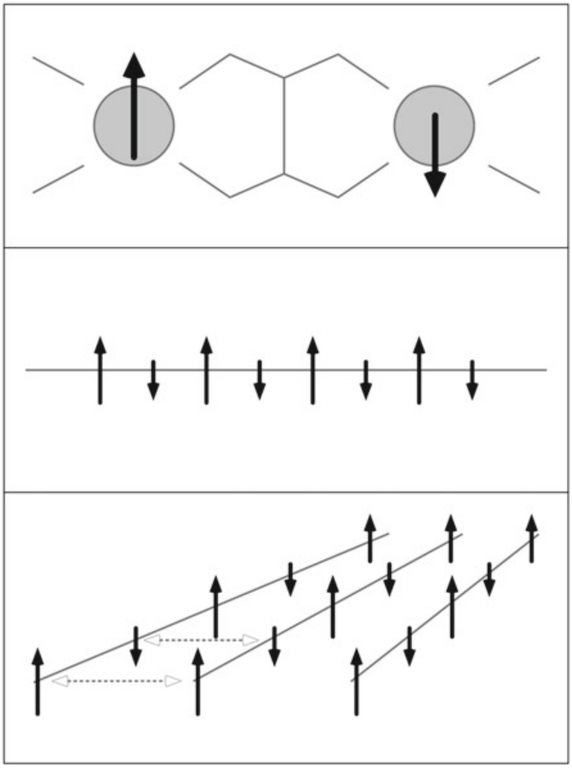


Fig. 3.9 *Upper* Antiferromagnetic coupling of two spins intermediated by a diamagnetic bridge (through-bond interactions). *Middle* After linking the units, a one-dimensional *ferrimagnetic* chain is obtained. *Lower* The 1D chains are linked together through weaker intramolecular (through-space) interactions, indicated by *dotted lines* (for simplicity only two dimensions are shown)

localized on a few atoms of the radical (N and O in nitroxides, central C in triarylmethyl, for example) or delocalized over a large part of the molecule (conjugated π-systems such as phenalenyl). The magnetic properties of these radical-based materials are determined by the through-space interactions between the units.

3.3.1 Monte Carlo Simulations, Renormalization Group Theory

There are powerful techniques to determine a few selected eigenvalues and eigenvectors of matrices of huge dimensions with millions or even billions of columns. This can be very efficiently exploited to calculate the electron correlation effects in the energy and wave function in electronic structure calculations where normally only the ground state and a few excited states are of interest. However, the accurate calculation of macroscopic properties such as the temperature dependence of the magnetic susceptibility cannot be done using only a few low lying eigenstates, but requires a much larger set. The eigenvalue spectrum of the Heisenberg Hamiltonian is very

Table 3.2 Dimension of the Heisenberg Hamiltonian for a system with N magnetic sites with $S = \frac{1}{2}$ and 1

S	$N = 2$	3	4	5	6	7	8	9	10	11	12
$\frac{1}{2}$	2	3	6	10	20	35	70	126	252	462	924
1	3	7	19	51	141	393	1107	3139	8953	25648	73764

dense and many levels are thermally occupied. Since selecting a balanced subset of states is nearly impossible, it is preferable to perform a full diagonalization of the Heisenberg Hamiltonian and include all states in the calculation of the macroscopic properties of the material under study.

However, the dimension g of the Heisenberg Hamiltonian grows rapidly with the number of magnetic sites N and the spin moment of these sites. For a model with all spin moments equal to $S = \frac{1}{2}$ the dimension is given by (Table 3.2)

$$
\begin{aligned}
g &= \frac{(2NS)!}{\big((NS)!\big)^2} \qquad \text{if } N \text{ is even} \\
g &= \frac{\big(2(NS+1/2)\big)!}{2\big((NS+1/2)!\big)^2} \qquad \text{if } N \text{ is odd}
\end{aligned}
\tag{3.54}
$$

and for lattices with $S = 1$ spin moments the dimension is given by

$$
g = 1 + \sum_{k=1}^{k<N/2} \binom{n}{2k}\binom{2k}{k} \tag{3.55}
$$

for higher spin moments the increase is even steeper. Brute force diagonalization techniques can handle models with up to 16 $S = \frac{1}{2}$ magnetic sites. Using more powerful techniques such as those based on the Lanczos algorithm can push the limit up to 40 centers, which for most practical applications seems to be large enough. However, for larger models and for larger spin moment, it can be useful to consider more approximate techniques to obtain information on the macroscopic properties from the electronic structure parameters in a bottom-up approach. A good example is the family of polynuclear complexes intensively investigated for the possibility of single molecule magnet behaviour. Complexes with 19 Fe^{III} ions can hardly be expected to be treated via a full diagonalization of the Heisenberg Hamiltonian, but still has been studied in a bottom-up approach [14]. Among the many different approaches to have access to macroscopic properties starting at the microscopic description but without going through the full diagonalization of the Heisenberg Hamiltonian we will shortly mention two techniques, namely the renormalization group (RG) theory and classical Monte Carlo simulations.

Renormalization Group theory: The partition function Q is the central quantity of statistical mechanics and many thermodynamic functions can be derived from it. The partition function of the one-dimensional Ising chain is

$$Q = \sum_{M_S=\frac{1}{2},-\frac{1}{2}} \exp[J(M_S(1)M_S(2) + M_S(2)M_S(3) + M_S(3)M_S(4) + \ldots)/k_BT] \tag{3.56}$$

with $K = J/2k_BT$ and $M_S = \frac{1}{2}\sigma$ ($\sigma = \pm 1$), this can be rewritten to

$$Q = \sum_{\sigma_i=\pm 1} e^{K(\sigma_1\sigma_2+\sigma_2\sigma_3)} e^{K(\sigma_3\sigma_4+\sigma_4\sigma_5)} \ldots \tag{3.57}$$

After summing over $\sigma_2 = \pm 1$, we arrive at

$$Q = \sum_{\substack{\sigma_i=\pm 1\\ i\neq 2}} [e^{K(\sigma_1+\sigma_3)} + e^{-K(\sigma_1+\sigma_3)}] e^{K(\sigma_3\sigma_4+\sigma_4\sigma_5)} \ldots \tag{3.58}$$

and when the summation is made over $\sigma_4, \sigma_6, \ldots$, the partition function becomes

$$Q = \sum_{\substack{\sigma_i=\pm 1\\ i=\text{ odd}}} \ldots [e^{K(\sigma_1+\sigma_3)} + e^{-K(\sigma_1+\sigma_3)}][e^{K(\sigma_3+\sigma_5)} + e^{-K(\sigma_3+\sigma_5)}] \ldots \tag{3.59}$$

If we can find a way to rewrite

$$[e^{K(\sigma_1+\sigma_3)} + e^{-K(\sigma_1+\sigma_3)}] \text{ as } f(K)e^{K'\sigma_1\sigma_3} \tag{3.60}$$

we can return to the original expression of the partition function but now with half the number of centers and replacing K, the interaction between magnetic centers by K', the effective interaction parameters between blocks containing two magnetic centers, as illustrated in Fig. 3.10. Substituting $\sigma_1 = \sigma_3 = \pm 1$ and $\sigma_1 = -\sigma_3 = \pm 1$, we obtain two equations from which $f(K)$ and K' can be determined

$$\left.\begin{array}{ll} \sigma_1 = \sigma_3 = \pm 1 & e^{2K} + e^{-2K} = fe^{K'} \\ \sigma_1 = -\sigma_3 = \pm 1 & 2 = fe^{K'} \end{array}\right\} \Rightarrow \begin{array}{l} K' = \frac{1}{2}\ln\, \cosh(2K) \\ f(K) = 2\cosh^{\frac{1}{2}}(2K) \end{array} \tag{3.61}$$

and

$$Q = \sum_{\substack{\sigma_i=\pm 1\\ i=\text{ odd}}} f(K)e^{K'\sigma_1\sigma_3} f(K)e^{K'\sigma_3\sigma_5} \ldots = f(K)^{N/2} \sum_{\substack{\sigma_i=\pm 1\\ i=\text{ odd}}} e^{K'\sigma_1\sigma_3} e^{K'\sigma_3\sigma_5} \ldots \tag{3.62}$$

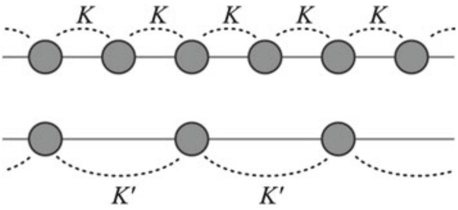


Fig. 3.10 Illustration of the renormalization procedure. In the *upper part* N particles are considered with an interaction K, while in the *lower part* the interaction K between sites is replaced by a larger-scale effective interaction K'

Hence, we have shown that the partition function of the whole system can be written in terms of properties that only depend on half the number of centers

$$Q(N, K) = f(K)^{N/2} Q(N/2, K') \tag{3.63}$$

and the recursive application of this formula connects the microscopic description with the thermodynamic large-scale properties. To elaborate the procedure a little more we use the relation of the free energy A and the partition function as given by statistical mechanics

$$\ln Q(N, K) = \frac{A}{-kT} = N\xi(K) \tag{3.64}$$

The free energy can be used to determine the specific heat and the temperature dependence of the specific heat can tell us something about the possible order-disorder phase transitions in magnetic systems. A is an extensive property and hence depends on the system size. It is here conveniently written as a product of the system size (N) and a system-size independent parameter ξ, which can be considered as the free energy per site.

$$\xi(K) = \frac{\ln Q}{N} = \frac{1}{2}\ln f(K) + \frac{1}{2}\xi(K') \tag{3.65}$$

where we have used $\ln x^a y = a \ln x + \ln y$ and $\ln Q(N/2, K') = (N/2)\xi(K')$, cf. Eq. 3.63. This brings us to the recursion relations to go from a description with N individual magnetic centers interacting through K to a description with ever increasing block size interacting through K'

$$\begin{aligned} K' &= \frac{1}{2} \ln\ \cosh(2K) \\ \xi(K') &= 2\xi(K) - \ln(2\cosh^{\frac{1}{2}}(2K)) \end{aligned} \tag{3.66}$$

The inverse relation can also be of use, especially in those cases where the property under study (here the free energy per site) is known in the thermodynamic limit, that is $K' \approx 0$

$$\begin{aligned} K &= \frac{1}{2}\cosh^{-1}(e^{2K'}) \\ \xi(k) &= \frac{1}{2}\ln 2 + \frac{1}{2}K' + \frac{1}{2}\xi(K') \end{aligned} \tag{3.67}$$

The one-dimensional Ising chain is not the most interesting magnetic system to study with renormalization theory, since it is known from the exact solution that there is no phase transition, the chain is disordered at any finite temperature. The two-dimensional Ising lattice does have an order/disorder phase transition, nicely reproduced with the renormalization procedure as discussed in Refs. [15, 16]. Such phase transition does not exist in a two-dimensional lattice described with the Heisenberg Hamiltonian. For this model, a non-zero interaction along the third dimension is needed to have an ordered (anti-)ferromagnetic system at finite temperature as stated by the Mermin-Wagner theorem.

Monte Carlo simulations: An alternative strategy to calculate thermodynamic properties is to explicitly follow the trajectory of a magnetic system by a computer simulation of the system. Along such trajectory, the system will adopt many conformations with different energy, magnetization and other microscopic observables. If the sampling of the conformational space is done correctly, a good estimate of the partition function can be made and with this all type of thermodynamic functions can be calculated.

There are basically two types of simulations to sample the conformational space. The first one is known as Molecular Dynamics and propagates a system in time by integrating the Newton's equations of motion. In its most rudimentary form the procedure can be described as follows. For a given set of atomic positions $r(t = t_0)$, one calculates the forces and from these the velocities $v(t_0)$, accelerations $a(t_0)$ and usually some higher derivatives. The atoms are then moved from $r(t_0)$ to $r(t_0 + \Delta t)$ by the formula $r(t_0 + \Delta t) = r(t_0) + v(t_0)\Delta t + (1/2)a(t_0)\Delta t^2 + \ldots$ and the time is updated from t_0 to $t_0 + \Delta t$. Then the cycle is repeated as long as one wants to follow the trajectory. The second method, the so-called Monte Carlo method, does not propagate the system in time but rather performs a *random* walk through the conformational space to calculate the partition function. Whereas numerical integration on a regular grid is much more efficient for low-dimensional functions, such approach is absolutely out of the question for extremely high dimensional functions, such as the partition function for any interesting N-particle system. In these cases a smart random walk is more effective and can be used to extract macroscopic properties as function of microscopic interactions.

To illustrate the procedure, we come back to the Ising model, but now focusing on the two-dimensional lattice with nearest neighbour interactions only. The sampling of the conformational space is usually done with the Metropolis algorithm, which starts by creating the initial spin conformation $\mathbb{S}_0$. This can be done in many ways, one of them is assigning a random spin direction $M_S = \pm\frac{1}{2}$ to each lattice point as shown in the left part of Fig. 3.11. After calculating the energy of this spin distribution, a trial step in conformational space is taken by inverting the spin at one of the lattice

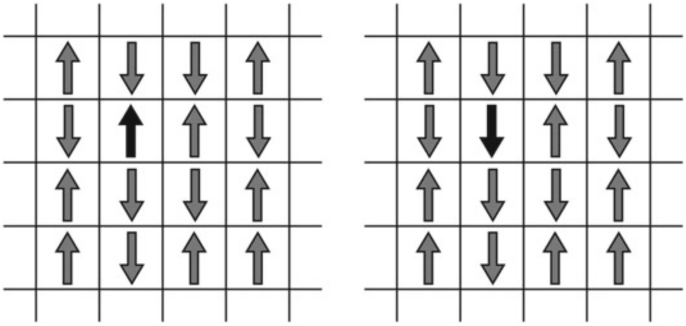
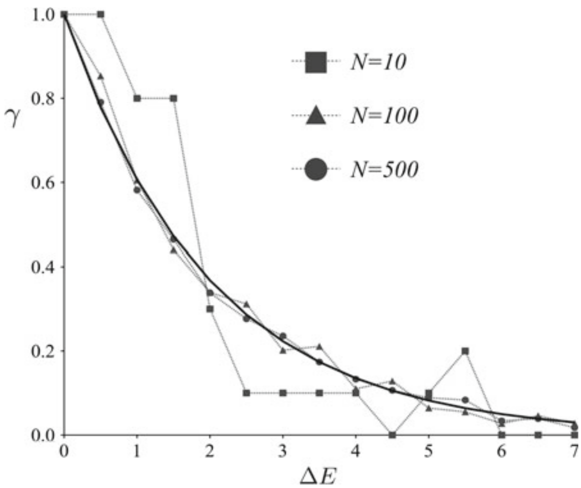


Fig. 3.11 *Left* Initial spin distribution $\mathbb{S}_0$ on a small part of the $N \times N$ spin lattice. *Right* Trial spin distribution $\mathbb{S}_t$ after inverting the M_S value of the *black* spin. Depending on the energy change, the new distribution can be accepted or rejected

sites to generate $\mathbb{S}_t$. The step is accepted when $\exp(-\Delta E/k_B T)$ is larger than a uniformly chosen random number between 0 and 1 and rejected otherwise (ΔE is the energy difference of $\mathbb{S}_t$ and $\mathbb{S}_0$). This means that trial spin distributions with lower energy are always accepted, while trial conformations with higher energies are accepted through an exponential weighting function. The closer the value of the exponential to 1 (that is, for small ΔE), the larger the chance for accepting the new conformation. Figure 3.12 shows how the ratio between accepted and rejected steps (γ) smoothly converges to an exponential function of the energy difference with an increasing number of steps in the conformational space.

In the trial distribution shown in the right panel of Fig. 3.11, the black spin was changed from $M_S = \frac{1}{2}$ to $-\frac{1}{2}$. The energy difference between $\mathbb{S}_t$ and $\mathbb{S}_0$ can easily be calculated by realizing that the only contributions to the energy difference arise

Fig. 3.12 Acceptance rate γ as function of the energy difference ΔE between the initial and trial spin conformation for three different simulation lengths N. The *black line* represents the weighting function $\exp(-0.5\Delta E)$



from the interaction involving the black spin. The differential part of the energy of $\mathbb{S}_0$ and $\mathbb{S}_t$ is

$$
\begin{aligned}
E'(\mathbb{S}_0) &= -J \cdot \frac{1}{2}\left(\frac{1}{2} - \frac{1}{2} - \frac{1}{2} - \frac{1}{2}\right) = \frac{1}{2}J \\
E'(\mathbb{S}_t) &= -J \cdot -\frac{1}{2}\left(\frac{1}{2} - \frac{1}{2} - \frac{1}{2} - \frac{1}{2}\right) = -\frac{1}{2}J
\end{aligned}
\tag{3.68}
$$

and from here the energy difference $\Delta E = -J$. When $J > 0$, that is for ferromagnetic interactions, the step is accepted because the energy of the system is lowered by the spin flip. Instead for antiferromagnetic interactions, $J < 0$, the energy difference is positive and the step will only be accepted when the $\exp(-\Delta E/k_B T)$ is larger than a random number between 0 and 1. Subsequently, the neighbouring spin is flipped and the accept/reject algorithm is repeated for all sites on the lattice. Then the total energy and magnetization (or other properties) are calculated and accumulated to determine the average properties after a certain amount of sweeps over the lattice.

In addition to the very basic application to the two-dimensional lattice with nearest neighbour interactions, this rather simple and intuitive approach to calculate thermodynamic properties can of course also be used to study magnetic systems with more complex magnetic structures. However, it fails badly when it comes to magnetic interactions between centers with spin moments different from $S = \frac{1}{2}$. In the basic form described above each lattice site can only adopt two states: *up* or *down*; α or β; positive or negative M_S. No distinction can be made between a lattice of magnetic sites with $S = \frac{1}{2}$ and any higher spin moment. For this purpose, the model Hamiltonian needs to be improved and a natural thing to do is to replace the Ising Hamiltonian with the Heisenberg Hamiltonian. An important drawback of using this more accurate model Hamiltonian is that the total energy of the lattice is no longer a simple sum of individual contributions as in the Ising case, and hence, the energy of a spin configuration cannot be calculated directly. Instead one can introduce two levels of accuracy in the Metropolis algorithm [17]. To decide on the acceptance of a spin flip the energy of a small cluster around the *active* lattice site is calculated with the Heisenberg Hamiltonian, while the rest of the lattice is considered as an Ising system. Keeping the cluster small enough, sweeping the lattice can be done rather efficiently in this half classic/half quantum treatment of the spin interactions. To study magnetic phenomena at low temperatures, one should definitely consider a full Quantum Monte Carlo approach [18].

3.4 Complex Interactions

The isotropic bilinear operator discussed so far is the most widely considered interaction in polynuclear magnetic systems since it accounts for an important part of the physics. However, it is not the whole story. In the very beginning of this chapter, we have set aside the spatial anisotropy in the interaction between two spin moments. Furthermore we have assumed that the interaction can be described with a simple vector product of linear operators and that more-than-two particle interactions are irrelevant. In this section, we will discuss refinements of the standard Hamiltonian and see how more complex interactions can be incorporated in the description of the magnetic couplings.

3.4.1 Biquadratic Exchange

The spin eigenfunctions for a binuclear complex with $S = 1$ magnetic centers are

$$\begin{aligned} Q &= \alpha\alpha\alpha\alpha \\ T &= \frac{1}{\sqrt{2}}(\alpha\alpha\beta\beta - \beta\beta\alpha\alpha) \\ S &= \frac{1}{2\sqrt{3}}\big(2(\alpha\alpha\beta\beta + \beta\beta\alpha\alpha) - \alpha\beta\alpha\beta - \alpha\beta\beta\alpha - \beta\alpha\alpha\beta - \beta\alpha\beta\alpha\big) \end{aligned} \tag{3.69}$$

which are also eigenfunctions of the Heisenberg Hamiltonian, with eigenvalues of $-J$, J and $2J$, respectively.

$$\hat{H}\Psi = -J\hat{S}_1 \cdot \hat{S}_2\Psi = -J\left[\frac{1}{2}(\hat{S}_1^+\hat{S}_2^- + \hat{S}_1^-\hat{S}_2^+) + \hat{S}_{z,1}\hat{S}_{z,2}\right]\Psi \tag{3.70}$$

with $\hat{S}_1 = \hat{s}(1) + \hat{s}(2)$ and $\hat{S}_2 = \hat{s}(3) + \hat{s}(4)$ (see Eq. 1.22), the eigenvalue of the quintet function arises from

$$\begin{aligned} \hat{H}Q = -J\Bigg[&\frac{1}{2}\left\{(\hat{s}^+(1) + \hat{s}^+(2))(\hat{s}^-(3) + \hat{s}^-(4)) + (\hat{s}^-(1) + \hat{s}^-(2))(\hat{s}^+(3) + \hat{s}^+(4))\right\} \\ &+(\hat{s}_z(1) + \hat{s}_z(2))(\hat{s}_z(3) + \hat{s}_z(4))\Bigg]\alpha(1)\alpha(2)\alpha(3)\alpha(4) \\ = -J\Bigg[&\frac{1}{2}\left\{(\hat{s}^+(1) + \hat{s}^+(2))\alpha\alpha\beta\beta + (\hat{s}^-(1) + \hat{s}^-(2)) \cdot 0\right\} \\ &+ (\hat{s}_z(1) + \hat{s}_z(2))\left(\frac{1}{2} + \frac{1}{2}\right)\alpha\alpha\alpha\alpha\Bigg] = -JQ \end{aligned} \tag{3.71}$$

The calculation of the eigenvalues of the triplet and singlet functions is slightly more involved but follows exactly the same mechanics and can be derived as a useful exercise.

3.9 Calculate the outcome of $(\hat{s}^+(1) + \hat{s}^+(2))(\hat{s}^-(3) + \hat{s}^-(4))$, $(\hat{s}^-(1) + \hat{s}^-(2))(\hat{s}^+(3) + \hat{s}^+(4))$ and $(\hat{s}_z(1) + \hat{s}_z(2))(\hat{s}_z(3) + \hat{s}_z(4))$ acting on $\alpha\alpha\beta\beta$, $\beta\beta\alpha\alpha$, $\alpha\beta\alpha\beta$, $\alpha\beta\beta\alpha$, $\beta\alpha\beta\alpha$ and $\beta\alpha\alpha\beta$. Use the results to verify the Heisenberg Hamiltonian eigenvalues of the singlet and triplet spin functions.

As long as magnetic anisotropy can be neglected, the regular spacing between the energy levels, the Landé pattern of Eq. 3.29 gives a very accurate representation of the experimental situation. However, sometimes deviations have been observed, which are usually ascribed to biquadratic interactions and subsequently incorporated in the model by adding an extra term to the Heisenberg Hamiltonian

$$\hat{H} = -J\hat{S}_1 \cdot \hat{S}_2 + \lambda(\hat{S}_1 \cdot \hat{S}_2)^2 \tag{3.72}$$

Before calculating the eigenvalues of this new spin Hamiltonian, the second term has to be worked out a little more

$$\begin{aligned}(\hat{S}_1 \cdot \hat{S}_2)^2 &= \left[\frac{1}{2}(\hat{S}_1^+\hat{S}_2^- + \hat{S}_1^-\hat{S}_2^+) + \hat{S}_{z,1}\hat{S}_{z,2}\right]\left[\frac{1}{2}(\hat{S}_1^+\hat{S}_2^- + \hat{S}_1^-\hat{S}_2^+) + \hat{S}_{z,1}\hat{S}_{z,2}\right] \\ &= \frac{1}{4}[\hat{S}_1^+\hat{S}_2^-\hat{S}_1^+\hat{S}_2^- + \hat{S}_1^+\hat{S}_2^-\hat{S}_1^-\hat{S}_2^+ + \hat{S}_1^-\hat{S}_2^+\hat{S}_1^+\hat{S}_2^- + \hat{S}_1^-\hat{S}_2^+\hat{S}_1^-\hat{S}_2^+] \\ &\quad + \frac{1}{2}[\hat{S}_1^+\hat{S}_2^-\hat{S}_{z,1}\hat{S}_{z,2} + \hat{S}_1^-\hat{S}_2^+\hat{S}_{z,1}\hat{S}_{z,2} + \hat{S}_{z,1}\hat{S}_{z,2}\hat{S}_1^+\hat{S}_2^- + \hat{S}_{z,1}\hat{S}_{z,2}\hat{S}_1^-\hat{S}_2^+] \\ &\quad + \hat{S}_{z,1}\hat{S}_{z,2}\hat{S}_{z,1}\hat{S}_{z,2}\end{aligned} \tag{3.73}$$

The different $\hat{S}_1$ and $\hat{S}_2$ operators are again replaced by the sum of the one-electron operators $\hat{s}(1)+\hat{s}(2)$ and $\hat{s}(3)+\hat{s}(4)$ and the effect of the nine operators on the seven different determinants can be evaluated. Using the results summarized in Table 3.3, the effect of the biquadratic exchange operator on the spin functions listed in Eq. 3.69 is easily established:

$$\lambda(\hat{S}_1\hat{S}_2)^2\alpha\alpha\alpha\alpha = \lambda\alpha\alpha\alpha\alpha = \lambda Q \tag{3.74a}$$

$$\begin{aligned}\lambda(\hat{S}_1\hat{S}_2)^2\frac{(\alpha\alpha\beta\beta - \beta\beta\alpha\alpha)}{\sqrt{2}} &= \frac{\lambda}{\sqrt{2}}\left[\frac{1}{4}(4\alpha\alpha\beta\beta + 4\beta\beta\alpha\alpha) - \frac{1}{2}\kappa + \alpha\alpha\beta\beta\right. \\ &\quad \left. - \frac{1}{4}(4\alpha\alpha\beta\beta + 4\beta\beta\alpha\alpha) + \frac{1}{2}\kappa - \beta\beta\alpha\alpha\right] = \frac{\lambda}{\sqrt{2}}(\alpha\alpha\beta\beta - \beta\beta\alpha\alpha) = \lambda T\end{aligned} \tag{3.74b}$$

Table 3.3 Effect of $(\hat{S}_1 \cdot \hat{S}_2)^2$ on the determinants that form the quintet, triplet and singlet spin functions of a binuclear system with $S = 1$

Operator	$\alpha\alpha\alpha\alpha$	$\alpha\alpha\beta\beta$	$\beta\beta\alpha\alpha$	$\alpha\beta\alpha\beta$	$\alpha\beta\beta\alpha$	$\beta\alpha\beta\alpha$	$\beta\alpha\alpha\beta$
$\hat{S}_1^+\hat{S}_2^-\hat{S}_1^+\hat{S}_2^-$	0	0	$4\alpha\alpha\beta\beta$	0	0	0	0
$\hat{S}_1^+\hat{S}_2^-\hat{S}_1^-\hat{S}_2^+$	0	$4\alpha\alpha\beta\beta$	0	κ	κ	κ	κ
$\hat{S}_1^-\hat{S}_2^+\hat{S}_1^+\hat{S}_2^-$	0	0	$4\beta\beta\alpha\alpha$	κ	κ	κ	κ
$\hat{S}_1^-\hat{S}_2^+\hat{S}_1^-\hat{S}_2^+$	0	$4\beta\beta\alpha\alpha$	0	0	0	0	0
$\hat{S}_1^+\hat{S}_2^-\hat{S}_{z,1}\hat{S}_{z,2}$	0	0	$-\kappa$	0	0	0	0
$\hat{S}_1^-\hat{S}_2^+\hat{S}_{z,1}\hat{S}_{z,2}$	0	$-\kappa$	0	0	0	0	0
$\hat{S}_{z,1}\hat{S}_{z,2}\hat{S}_1^+\hat{S}_2^-$	0	0	0	$-\alpha\alpha\beta\beta$	$-\alpha\alpha\beta\beta$	$-\alpha\alpha\beta\beta$	$-\alpha\alpha\beta\beta$
$\hat{S}_{z,1}\hat{S}_{z,2}\hat{S}_1^-\hat{S}_2^+$	0	0	0	$-\beta\beta\alpha\alpha$	$-\beta\beta\alpha\alpha$	$-\beta\beta\alpha\alpha$	$-\beta\beta\alpha\alpha$
$\hat{S}_{z,1}\hat{S}_{z,2}\hat{S}_{z,1}\hat{S}_{z,2}$	$\alpha\alpha\alpha\alpha$	$\alpha\alpha\beta\beta$	$\beta\beta\alpha\alpha$	0	0	0	0

$\kappa = \alpha\beta\alpha\beta + \alpha\beta\beta\alpha + \beta\alpha\beta\alpha + \beta\alpha\alpha\beta$

$$\begin{aligned}
&\lambda(\hat{S}_1\hat{S}_2)^2 \frac{1}{2\sqrt{3}}\big(2(\alpha\alpha\beta\beta + \beta\beta\alpha\alpha) - \alpha\beta\alpha\beta - \alpha\beta\beta\alpha - \beta\alpha\alpha\beta - \beta\alpha\beta\alpha\big) \\
&= \frac{\lambda}{2\sqrt{3}}\left[\frac{1}{4}(8\alpha\alpha\beta\beta + 8\beta\beta\alpha\alpha) - \frac{1}{2}2\kappa + 2\alpha\alpha\beta\beta + \frac{1}{4}(8\alpha\alpha\beta\beta + 8\beta\beta\alpha\alpha)\right. \\
&\qquad \left. - \frac{1}{2}2\kappa + 2\beta\beta\alpha\alpha - 4(\frac{1}{4}2\kappa - \frac{1}{2}\alpha\alpha\beta\beta - \frac{1}{2}\beta\beta\alpha\alpha)\right] \\
&= \frac{\lambda}{2\sqrt{3}}\big[8(\alpha\alpha\beta\beta + \beta\beta\alpha\alpha) + 4(-\alpha\beta\alpha\beta - \alpha\beta\beta\alpha - \beta\alpha\alpha\beta - \beta\alpha\beta\alpha)\big] = 4\lambda S
\end{aligned} \tag{3.74c}$$

and the eigenvalues of the Heisenberg Hamiltonian extended with a term for the biquadratic exchange are

$$\big(-J\hat{S}_1 \cdot \hat{S}_2 + \lambda(\hat{S}_1 \cdot \hat{S}_2)^2\big)Q = (-J + \lambda)Q \tag{3.75a}$$

$$\big(-J\hat{S}_1 \cdot \hat{S}_2 + \lambda(\hat{S}_1 \cdot \hat{S}_2)^2\big)T = (J + \lambda)T \tag{3.75b}$$

$$\big(-J\hat{S}_1 \cdot \hat{S}_2 + \lambda(\hat{S}_1 \cdot \hat{S}_2)^2\big)S = (2J + 4\lambda)S \tag{3.75c}$$

3.4.2 Four-Center Interactions

Magnetic interactions are not restricted to the exchange of the spin moments on two magnetic centers, but can be extended to the simultaneous interaction of three or four magnetic centers. These interactions are in general smaller than the two-body interactions but can not always be neglected. A clear example is given by the magnetic

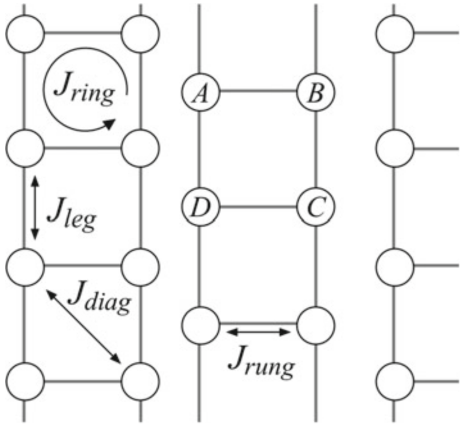


Fig. 3.13 Ladder-like structure formed by the Cu^{2+} ions in $SrCu_2O_3$. Oxygens on the *grey lines* between the copper ions are not shown. J_{leg}, J_{rung} and J_{diag} are the standard two-body interactions, J_{ring} is a four-body interaction that cyclically interchanges the four spins

interactions in the solid state compound $SrCu_2O_3$. This copper oxide has a layered structure, in which Cu_2O_3 layers are separated by Sr^{2+} ions. The Cu ions form a ladder-like structure as shown in Fig. 3.13 with oxygen ions between the magnetic centers. A straightforward fitting of the magnetic susceptibility with just the two-body interactions leads to the conclusion that the magnetic interaction along the legs is twice as large as the interactions along the rungs of the ladder. However, the local geometry does not support such a large difference; distances, angles, coordination are all very similar in both cases. Extending the model Hamiltonian used to fit experimental data with four-body interactions provides a more consistent picture: the interactions along leg and rung are similar and the four-body interaction is sizeable.

To get a hand on the four-body interactions, the four-center cluster ABCD shown in Fig. 3.13 is studied. The four magnetic centers, $A \dots D$, have one unpaired electron, and therefore, a magnetic moment of $S = 1/2$. The Hamiltonian of this system is a sum of the standard two-body interactions plus $\hat{P}_{1234}$, a four-body operator that cyclically permutes the four spin functions.

$$\hat{H} = \sum_{i<j} -J_{ij}\hat{S}_i \cdot \hat{S}_j + J_r \hat{P}_{1234} \tag{3.76}$$

To stay within a spin Hamiltonian formalism, the permutation operator has to be replaced by spin operators, which can be done in the following way [19]:

$$\hat{P}_{1234} = \kappa \left((\hat{S}_A \cdot \hat{S}_B)(\hat{S}_C \cdot \hat{S}_D) + (\hat{S}_A \cdot \hat{S}_D)(\hat{S}_B \cdot \hat{S}_C) - (\hat{S}_A \cdot \hat{S}_C)(\hat{S}_B \cdot \hat{S}_D) \right) \tag{3.77}$$

To check that this sum indeed cyclically permutes the spin functions, we compare the outcome of acting with $\hat{P}_{1234}$ and acting with the sum of bilinear operators on the wave function $\Psi = \alpha\beta\alpha\beta - \beta\alpha\beta\alpha$.

$$\hat{P}_{1234}(\alpha\beta\alpha\beta - \beta\alpha\beta\alpha) = \beta\alpha\beta\alpha - \alpha\beta\alpha\beta \tag{3.78}$$

Note that the wave function with only one of the terms is not an eigenfunction of the permutation operator $\hat{P}_{1234}$. To determine the result of the sum of four-spin operators, we will develop step-by-step the action of $(\hat{S}_A \cdot \hat{S}_D)(\hat{S}_B \cdot \hat{S}_C)$. The other two terms can be done by the reader as an exercise. In the first place, we need to establish the result of acting with $\hat{S}_i \cdot \hat{S}_j$ on the different two-electron determinants. By writing $\hat{S}$ as $\hat{S}_x + \hat{S}_y + \hat{S}_z$ and using Eq. 1.20a, the following relations are easily derived:

$$\begin{aligned}
\hat{S}_1 \cdot \hat{S}_2\alpha\alpha &= \frac{1}{4}\alpha\alpha & \qquad \hat{S}_1 \cdot \hat{S}_2\alpha\beta &= \frac{1}{2}\beta\alpha - \frac{1}{4}\alpha\beta \\
\hat{S}_1 \cdot \hat{S}_2\beta\beta &= \frac{1}{4}\beta\beta & \qquad \hat{S}_1 \cdot \hat{S}_2\beta\alpha &= \frac{1}{2}\alpha\beta - \frac{1}{4}\beta\alpha
\end{aligned} \tag{3.79}$$

Next, we use these results to determine how $\hat{S}_B \cdot \hat{S}_C$ and $\hat{S}_A \cdot \hat{S}_D$ act on $\alpha\beta\alpha\beta$

$$\begin{aligned}
\hat{S}_B \cdot \hat{S}_C\alpha(1)\beta(2)\alpha(3)\beta(4) &= \left[\hat{S}_B \cdot \hat{S}_C\beta(2)\alpha(3)\right]\alpha(1)\beta(4) \\
&= \left(\frac{1}{2}\alpha(2)\beta(3) - \frac{1}{4}\beta(2)\alpha(3)\right)\alpha(1)\beta(4) = \frac{1}{2}\alpha\alpha\beta\beta - \frac{1}{4}\alpha\beta\alpha\beta
\end{aligned} \tag{3.80}$$

with $\hat{S}_A \cdot \hat{S}_D\alpha\beta\alpha\beta = \frac{1}{2}\beta\beta\alpha\alpha - \frac{1}{4}\alpha\beta\alpha\beta$ and $\hat{S}_A \cdot \hat{S}_D\alpha\alpha\beta\beta = \frac{1}{2}\beta\alpha\beta\alpha - \frac{1}{4}\alpha\alpha\beta\beta$ the product $(\hat{S}_A \cdot \hat{S}_D)(\hat{S}_B \cdot \hat{S}_C)$ acting on $\alpha\beta\alpha\beta$ gives

$$\begin{aligned}
(\hat{S}_A \cdot \hat{S}_D)(\hat{S}_B \cdot \hat{S}_C)\alpha\beta\alpha\beta &= (\hat{S}_A \cdot \hat{S}_D)\left(\frac{1}{2}\alpha\alpha\beta\beta - \frac{1}{4}\alpha\beta\alpha\beta\right) \\
&= \frac{1}{4}\beta\alpha\beta\alpha - \frac{1}{8}\alpha\alpha\beta\beta - \frac{1}{8}\beta\beta\alpha\alpha + \frac{1}{16}\alpha\beta\alpha\beta
\end{aligned} \tag{3.81}$$

Repeating this for the other two products of bilinear operators and summing the results of acting on $\beta\alpha\beta\alpha$ as well, we obtain

$$\begin{aligned}
&\frac{1}{4}\beta\alpha\beta\alpha - \frac{1}{8}\alpha\beta\beta\alpha - \frac{1}{8}\beta\alpha\alpha\beta + \frac{1}{16}\alpha\beta\alpha\beta - \frac{1}{4}\alpha\beta\alpha\beta + \frac{1}{8}\beta\alpha\alpha\beta \\
&\quad + \frac{1}{8}\alpha\beta\beta\alpha - \frac{1}{16}\beta\alpha\beta\alpha + \frac{1}{4}\beta\alpha\beta\alpha - \frac{1}{8}\alpha\alpha\beta\beta - \frac{1}{8}\beta\beta\alpha\alpha + \frac{1}{16}\alpha\beta\alpha\beta \\
&\quad - \frac{1}{4}\alpha\beta\alpha\beta + \frac{1}{8}\beta\beta\alpha\alpha + \frac{1}{8}\alpha\alpha\beta\beta - \frac{1}{16}\beta\alpha\beta\alpha - \frac{1}{16}\alpha\beta\alpha\beta + \frac{1}{16}\beta\alpha\beta\alpha \\
&= \frac{7}{16}(\beta\alpha\beta\alpha - \alpha\beta\alpha\beta)
\end{aligned} \tag{3.82}$$

This shows that, except for a constant that can be absorbed in the interaction constant J_r, the action of the cyclic permutation operator is identical to the linear combina-

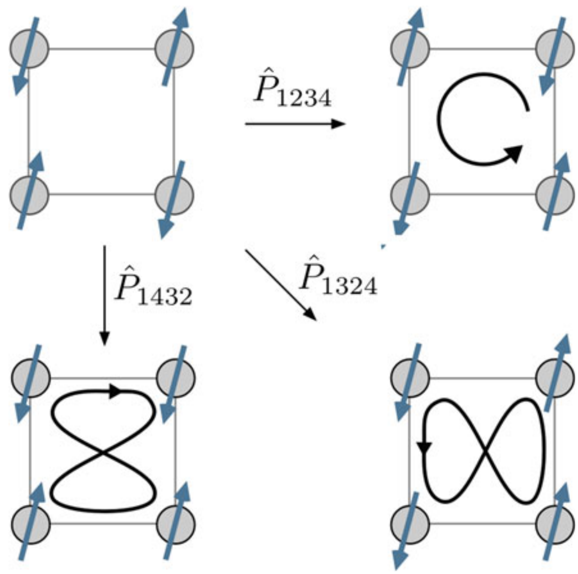


Fig. 3.14 The three different possibilities of the cyclic permutations of the spins on a *square* of *four* magnetic centers

tion of products of bilinear operators. Therefore, we define the Hamiltonian for the rectangle *ABCD* in Fig. 3.13 as

$$\hat{H} = -J_1(\hat{S}_A \cdot \hat{S}_B + \hat{S}_C \cdot \hat{S}_D) - J_2(\hat{S}_A \cdot \hat{S}_D + \hat{S}_B \cdot \hat{S}_C) - J_3(\hat{S}_A \cdot \hat{S}_C + \hat{S}_B \cdot \hat{S}_D) \\ + J_r\big[(\hat{S}_A \cdot \hat{S}_B)(\hat{S}_C \cdot \hat{S}_D) + (\hat{S}_A \cdot \hat{S}_D)(\hat{S}_B \cdot \hat{S}_C) - (\hat{S}_A \cdot \hat{S}_C)(\hat{S}_B \cdot \hat{S}_D)\big] \tag{3.83}$$

where the subscripts 1, 2, 3, and r stand for *leg, rung, diag* and *ring*, respectively. Before looking at the eigenvalues of this Hamiltonian, it should be mentioned that $\hat{P}_{1234}$ is not the only way to cyclically permute the four spin functions. Alternatively, one can apply the $\hat{P}_{1324}$ and $\hat{P}_{1423}$ operators to shift them around the rectangle as illustrated in Fig. 3.14. These possibilities are carefully worked out in Ref. [20], where the corresponding interaction parameters were shown to be so small that they will be neglected here for simplicity.

The four unpaired electrons on the rectangle occupy the magnetic orbitals a, b, c and d, respectively. They can be coupled to a quintet, three different triplets and two singlets. A common basis for these six states is given by the six $M_S = 0$ determinants $|a\bar{b}c\bar{d}|$, $|\bar{a}b\bar{c}d|$, $|ab\bar{c}\bar{d}|$, $|\bar{a}\bar{b}cd|$, $|a\bar{b}\bar{c}d|$ and $|\bar{a}bc\bar{d}|$. In the following, we will omit the spatial part and return to a spin-only notation, $|\alpha\beta\alpha\beta|$, $|\beta\alpha\beta\alpha|$, etc.

3.10 Couple the spins of the four centers in a sequential fashion in all possible ways to check the existence of one quintet, three different triplets and two singlets for a system with four $S = 1/2$ magnetic moments.

The matrix representation of $\hat{H}$ is

	$\vert\alpha\beta\alpha\beta\rangle$	$\vert\beta\alpha\beta\alpha\rangle$	$\vert\alpha\alpha\beta\beta\rangle$	$\vert\beta\beta\alpha\alpha\rangle$	$\vert\alpha\beta\beta\alpha\rangle$	$\vert\beta\alpha\alpha\beta\rangle$
$\langle\alpha\beta\alpha\beta\vert$	H_{11}					
$\langle\beta\alpha\beta\alpha\vert$	$-\frac{1}{2}J_r$	H_{22}				
$\langle\alpha\alpha\beta\beta\vert$	$-\frac{1}{2}J_1 + \frac{1}{8}J_r$	$-\frac{1}{2}J_1 + \frac{1}{8}J_r$	H_{33}			
$\langle\beta\beta\alpha\alpha\vert$	$-\frac{1}{2}J_1 + \frac{1}{8}J_r$	$-\frac{1}{2}J_1 + \frac{1}{8}J_r$	0	H_{44}		
$\langle\alpha\beta\beta\alpha\vert$	$-\frac{1}{2}J_2 + \frac{1}{8}J_r$	$-\frac{1}{2}J_2 + \frac{1}{8}J_r$	$-\frac{1}{2}J_3 + \frac{1}{8}J_r$	$-\frac{1}{2}J_3 + \frac{1}{8}J_r$	H_{55}	
$\langle\beta\alpha\alpha\beta\vert$	$-\frac{1}{2}J_2 + \frac{1}{8}J_r$	$-\frac{1}{2}J_2 + \frac{1}{8}J_r$	$-\frac{1}{2}J_3 + \frac{1}{8}J_r$	$-\frac{1}{2}J_3 + \frac{1}{8}J_r$	0	H_{66}

with

$$\begin{aligned} H_{11} = H_{22} &= \frac{1}{2}(J_1 + J_2 - J_3) + \frac{1}{16}J_r \\ H_{33} = H_{44} &= \frac{1}{2}(J_1 - J_2 + J_3) + \frac{1}{16}J_r \\ H_{55} = H_{66} &= \frac{1}{2}(-J_1 + J_2 + J_3) + \frac{1}{16}J_r \end{aligned} \tag{3.84}$$

The diagonalization of this matrix should in principle give the necessary relations to extract the bilinear exchange parameters and the strength of the four-center interaction. There are five energy differences and only four parameters to be determined. However, the resulting equations are rather awkward and it is easier to extract the parameters by constructing a numerical effective Hamiltonian with the extra advantage that the assumption of very small contribution from the other type of permutations can be checked. For a square complex with $J_1 = J_2 = J$, the equations for the energies of the spin states are significantly more simple, giving

$$E(Q) = 0 \tag{3.85}$$

$$E(T2) = E(T3) = J + J_3 \tag{3.86}$$

$$E(S2) = J + 2J_3 - \frac{1}{4}J_r \tag{3.87}$$

$$E(T1) = 2J - \frac{1}{2}J_r \tag{3.88}$$

$$E(S1) = 3J + \frac{3}{4}J_r \tag{3.89}$$

3.11 Extract the magnetic coupling parameters for a four-center Cu^{2+} complex with a square geometry. (i) Under the assumption of equal coupling along the edges of the square, zero coupling along the diagonal and no four-center interactions; (ii) with a non-negligible ring exchange ($J_1 = J_2$; $J_r \neq 0$ and $J_3 = 0$); (iii) considering the three different interactions. The following total energies for the spin states were calculated: E(Q) = −3953.38577312 E_h; E(T2) = E(T3) = −3953.39054141 E_h; E(S2) = −3953.39100763 E_h; E(T1) = −3953.39533075 E_h; E(S1) = −3953.39867933 E_h. Are the estimates of J the same in the first case when extracted from different ΔE's?

3.4.3 Anisotropic Exchange

In Sect. 3.2 we have introduced the general expression (Eq. 3.20) to describe the interaction between two spin moments on different magnetic centers. So far, only the isotropic interactions have been considered in this chapter; the total spin moment (and the single-ion spin) in itself has no preferred orientation in space, only the relative orientation—parallel or antiparallel—of the local spins has been looked at. This is of course only part of the story. Due to relativistic effects, in many systems the spin moment is anisotropic as seen in the previous chapter for mononuclear complexes. The magnetic anisotropy is in some compounds accompanied by ferroelectricity. These so-called *multiferroic* compounds, often perovskite transition metal oxides, have potential applications as switches, sensors or memory devices. Coming back to Eq. 3.20, we will separate isotropic and anisotropic interactions before orienting the molecule in such a way that the magnetic frame coincides with the cartesian axes frame. Then, the Hamiltonian becomes

$$\hat{H} = -J\hat{S}_1 \cdot \hat{S}_2 + \hat{S}_1 \overline{\overline{A}} \hat{S}_2 \tag{3.90}$$

As long as we are concerned with binuclear $S = 1/2$ complexes, no single-ion anisotropy has to be added and this Hamiltonian describes the lowest energy levels in the absence of an external magnetic field.

Symmetric anisotropy: The basis of this Hamiltonian can no longer be restricted to determinants with the same M_S value as was done for the isotropic interactions. The inclusion of magnetic anisotropy in the model causes the removal of the degeneracy of the different M_S levels and eventually mixing of the wave functions with different spin moment. Here, we have to consider four CSFs; the three components of the triplet plus the singlet. To facilitate the determination of the matrix elements of the model

Hamiltonian, it is common practice to consider the basis of *uncoupled* determinants and then transform to the basis of spin-adapted CSFs.

3.12 Perform the matrix multiplication of the anisotropic term in the model Hamiltonian.

The uncoupled basis is formed by the determinants $|\alpha\alpha|$, $|\alpha\beta|$, $|\beta\alpha|$ and $|\beta\beta|$. The result of acting with the isotropic part of Hamiltonian on these determinants can directly be written down with the help of Eqs. 3.79, but the anisotropic part requires a little more work. Based on the relations given in Eqs. 1.16a and 1.20a, the following is easily derived for the products of one-electron operators

- $\hat{S}_1\overline{\overline{A}}\hat{S}_2|\alpha\alpha|$

$$\begin{aligned}
A_{xx}\hat{S}_x\hat{S}_x\alpha\alpha &= \frac{1}{4}A_{xx}\beta\beta & A_{xy}\hat{S}_x\hat{S}_y\alpha\alpha &= -\frac{1}{4i}A_{xy}\beta\beta & A_{xz}\hat{S}_x\hat{S}_z\alpha\alpha &= \frac{1}{4}A_{xz}\beta\alpha\\
A_{yx}\hat{S}_y\hat{S}_x\alpha\alpha &= -\frac{1}{4i}A_{yx}\beta\beta & A_{yy}\hat{S}_y\hat{S}_y\alpha\alpha &= -\frac{1}{4}A_{yy}\beta\beta & A_{yz}\hat{S}_y\hat{S}_z\alpha\alpha &= -\frac{1}{4i}A_{yz}\beta\alpha\\
A_{zx}\hat{S}_z\hat{S}_x\alpha\alpha &= \frac{1}{4}A_{zx}\alpha\beta & A_{zy}\hat{S}_z\hat{S}_y\alpha\alpha &= -\frac{1}{4i}A_{zy}\alpha\beta & A_{zz}\hat{S}_z\hat{S}_z\alpha\alpha &= \frac{1}{4}A_{zz}\alpha\alpha
\end{aligned} \tag{3.91a}$$

- $\hat{S}_1\overline{\overline{A}}\hat{S}_2|\beta\beta|$

$$\begin{aligned}
A_{xx}\hat{S}_x\hat{S}_x\beta\beta &= \frac{1}{4}A_{xx}\alpha\alpha & A_{xy}\hat{S}_x\hat{S}_y\beta\beta &= \frac{1}{4i}A_{xy}\alpha\alpha & A_{xz}\hat{S}_x\hat{S}_z\beta\beta &= -\frac{1}{4}A_{xz}\alpha\beta\\
A_{yx}\hat{S}_y\hat{S}_x\beta\beta &= \frac{1}{4i}A_{yx}\alpha\alpha & A_{yy}\hat{S}_y\hat{S}_y\beta\beta &= -\frac{1}{4}A_{yy}\alpha\alpha & A_{yz}\hat{S}_y\hat{S}_z\beta\beta &= -\frac{1}{4i}A_{yz}\alpha\beta\\
A_{zx}\hat{S}_z\hat{S}_x\beta\beta &= -\frac{1}{4}A_{zx}\beta\alpha & A_{zy}\hat{S}_z\hat{S}_y\beta\beta &= -\frac{1}{4i}A_{zy}\beta\alpha & A_{zz}\hat{S}_z\hat{S}_z\beta\beta &= \frac{1}{4}A_{zz}\beta\beta
\end{aligned} \tag{3.91b}$$

- $\hat{S}_1\overline{\overline{A}}\hat{S}_2|\alpha\beta|$

$$\begin{aligned}
A_{xx}\hat{S}_x\hat{S}_x\alpha\beta &= \frac{1}{4}A_{xx}\beta\alpha & A_{xy}\hat{S}_x\hat{S}_y\alpha\beta &= \frac{1}{4i}A_{xy}\beta\alpha & A_{xz}\hat{S}_x\hat{S}_z\alpha\beta &= -\frac{1}{4}A_{xz}\beta\beta\\
A_{yx}\hat{S}_y\hat{S}_x\alpha\beta &= -\frac{1}{4i}A_{yx}\beta\alpha & A_{yy}\hat{S}_y\hat{S}_y\alpha\beta &= \frac{1}{4}A_{yy}\beta\alpha & A_{yz}\hat{S}_y\hat{S}_z\alpha\beta &= \frac{1}{4i}A_{yz}\beta\beta\\
A_{zx}\hat{S}_z\hat{S}_x\alpha\beta &= \frac{1}{4}A_{zx}\alpha\alpha & A_{zy}\hat{S}_z\hat{S}_y\alpha\beta &= \frac{1}{4i}A_{zy}\alpha\alpha & A_{zz}\hat{S}_z\hat{S}_z\alpha\beta &= -\frac{1}{4}A_{zz}\alpha\beta
\end{aligned} \tag{3.91c}$$

- $\hat{S}_1 \overline{\overline{A}} \hat{S}_2 |\beta\alpha|$

$$
\begin{array}{lll}
A_{xx}\hat{S}_x\hat{S}_x\beta\alpha = \frac{1}{4}A_{xx}\alpha\beta & A_{xy}\hat{S}_x\hat{S}_y\beta\alpha = -\frac{1}{4i}A_{xy}\alpha\beta & A_{xz}\hat{S}_x\hat{S}_z\beta\alpha = \frac{1}{4}A_{xz}\alpha\alpha \\
A_{yx}\hat{S}_y\hat{S}_x\beta\alpha = \frac{1}{4i}A_{yx}\alpha\beta & A_{yy}\hat{S}_y\hat{S}_y\beta\alpha = \frac{1}{4}A_{yy}\alpha\beta & A_{yz}\hat{S}_y\hat{S}_z\beta\alpha = \frac{1}{4i}A_{yz}\alpha\alpha \\
A_{zx}\hat{S}_z\hat{S}_x\beta\alpha = -\frac{1}{4}A_{zx}\beta\beta & A_{zy}\hat{S}_z\hat{S}_y\beta\alpha = \frac{1}{4i}A_{zy}\beta\beta & A_{zz}\hat{S}_z\hat{S}_z\beta\alpha = -\frac{1}{4}A_{zz}\beta\alpha
\end{array}
\tag{3.91d}
$$

Following common practice, we write the anisotropic interaction as the sum of symmetric

$$D_{ij} = D_{ji} = \frac{1}{2}(A_{ij} + A_{ji}) \tag{3.92a}$$

and antisymmetric contributions

$$d_{ij} = -d_{ji} = \frac{1}{2}(A_{ij} - A_{ji}) \tag{3.92b}$$

For the moment we neglect the antisymmetric interaction and write down the matrix representation of the Hamiltonian as sum of isotropic and symmetric anisotropic interactions.

	$\|\alpha\alpha\rangle$	$\|\alpha\beta\rangle$	$\|\beta\alpha\rangle$	$\|\beta\beta\rangle$
$\langle\alpha\alpha\|$	$-\frac{1}{4}(J + D_{zz})$	$\frac{1}{4}(D_{xz} - iD_{yz})$	$\frac{1}{4}(D_{xz} - iD_{yz})$	$\frac{1}{4}(D_{xx} - D_{yy} - 2iD_{xy})$
$\langle\alpha\beta\|$	$\frac{1}{4}(D_{xz} + iD_{yz})$	$\frac{1}{4}(J + D_{zz})$	$-\frac{1}{2}J + \frac{1}{4}(D_{xx} + D_{yy})$	$-\frac{1}{4}(D_{xz} - iD_{yz})$
$\langle\beta\alpha\|$	$\frac{1}{4}(D_{xz} + iD_{yz})$	$-\frac{1}{2}J + \frac{1}{4}(D_{xx} + D_{yy})$	$\frac{1}{4}(J + D_{zz})$	$-\frac{1}{4}(D_{xz} - iD_{yz})$
$\langle\beta\beta\|$	$\frac{1}{4}(D_{xx} - D_{yy} + 2iD_{xy})$	$-\frac{1}{4}(D_{xz} + iD_{yz})$	$-\frac{1}{4}(D_{xz} + iD_{yz})$	$-\frac{1}{4}(J + D_{zz})$

The next step is the transformation from the uncoupled basis to a basis in which the two spin moments are coupled, i.e. a basis of the singlet and the three components of the triplet.

	$\|T^+\rangle$	$\|T^0\rangle$	$\|T^-\rangle$	$\|S\rangle$
$\langle T^+\|$	$-\frac{1}{4}(J - D_{zz})$	$\frac{1}{2\sqrt{2}}(D_{xz} - iD_{yz})$	$\frac{1}{4}(D_{xx} - D_{yy} - 2iD_{yz})$	0
$\langle T^0\|$	$\frac{1}{2\sqrt{2}}(D_{xz} + iD_{yz})$	$-\frac{1}{4}(J + 2D_{zz})$	$-\frac{1}{2\sqrt{2}}(D_{xz} - iD_{yz})$	0
$\langle T^-\|$	$\frac{1}{4}(D_{xx} - D_{yy} + 2iD_{yz})$	$-\frac{1}{2\sqrt{2}}(D_{xz} + iD_{yz})$	$-\frac{1}{4}(J - D_{zz})$	0
$\langle S\|$	0	0	0	$\frac{3}{4}J$

where the diagonal elements are simplified by the notion that $\overline{\overline{D}}$ can be written as a traceless tensor, that is $D_{xx} + D_{yy} + D_{zz} = 0$. For example,

$$\begin{aligned}\langle\alpha\beta + \beta\alpha|\hat{H}|\alpha\beta + \beta\alpha\rangle = &-\frac{1}{4}(J + D_{zz}) + 2\big(\frac{1}{2}J + \frac{1}{4}(D_{xx} + D_{yy})\big)\\ &-\frac{1}{4}(J + D_{zz}) = \frac{1}{4}J - \frac{1}{4}D_{zz} + \frac{1}{4}D_{xx} + \frac{1}{4}D_{yy}\end{aligned} \tag{3.93}$$

which is simplified to $\frac{1}{4}(J - 2D_{zz})$ by subtracting $\frac{1}{4}(D_{xx} + D_{yy} + D_{zz})$, which equals zero.

3.13 (a) Show that transformation of the matrix representation in the uncoupled basis into the coupled basis can be done by applying the unitary transformation $\tilde{U}\hat{H}U$, where $\tilde{U}$ is the transpose of $U = \big(1,\ 0,\ 0,\ 0\ ;\ 0,\ 1/\sqrt{2},\ 0,\ 1/\sqrt{2}\ ;\ 0,\ 1/\sqrt{2},\ 0,\ -1/\sqrt{2}\ ;\ 0,\ 0,\ 1,\ 0\big)$ (b) Show that the Hamiltonian of Eq. 3.90 is hermitian. Assume a diagonal D-tensor and show that the triplet part of the matrix is related to the D-tensor of an $S = 1$ mononuclear complex (Eq. 2.21) by a factor of $\frac{1}{2}$. Hint: the trace of the two matrices can be adjusted to simplify the comparison.

The construction of a numerical effective Hamiltonian from accurate electronic structure calculations permits us to determine the complete D-tensor and therewith the orientation of the magnetic axes frame of the system with its easy axis or easy plane, depending on the relative energies of the different M_S components of the triplet. When the magnetic axes frame coincides with the cartesian axes frame, $\overline{\overline{D}}$ is diagonal and the energy levels of the triplet can be described with two parameters; the axial anisotropy D and the rhombic anisotropy E as defined in Eq. 2.16. Hence, the symmetric anisotropic interaction of the $S = 1/2$ spin moments, which by themselves are isotropic by definition, makes that the total spin moment of the system is no longer fully isotropic.

Anti-symmetric anisotropy: The second ingredient of the anisotropic interaction is the asymmetric part, also known as the Dzyaloshinskii–Moriya (DM) interaction. It is held responsible for the appearance of ferromagnetism in antiferromagnetically coupled Cu^{2+} systems. Whereas the isotropic and symmetric anisotropic interactions do not affect the collinearity of the two local magnetic axes frames, the anti-symmetric interaction makes that the principal axis of the local moments are no longer parallel. In a pictorial description of the effect, shown in Fig. 3.15, the cancellation of antiferromagnetically coupled spin moments is no longer complete and a (small) ferromagnetic moment appears.

A rigorous description of the anti-symmetric interaction is obtained by including the d_{ij} in the matrix elements among the four determinants that span the model space.

Fig. 3.15 Schematic representation of the net ferromagnetic interaction due to non-collinear antiferromagnetically coupled spin moments

As example we construct two matrix elements to illustrate the difference with the matrix elements when only the symmetric interaction is considered.

$$\langle\alpha\alpha|\hat{H}|\alpha\beta\rangle = \frac{1}{4}A_{zx} + \frac{1}{4i}A_{zy} = \frac{1}{4}\left(D_{xz} + d_{zx}\right) + \frac{1}{4i}\left(D_{yz} + d_{zy}\right)$$
$$= \frac{1}{4}\left(D_{xz} - d_{xz}\right) - \frac{1}{4}i\left(D_{yz} - d_{yz}\right) \tag{3.94a}$$

$$\langle\alpha\alpha|\hat{H}|\beta\alpha\rangle = \frac{1}{4}A_{xz} + \frac{1}{4i}A_{yz} = \frac{1}{4}\left(D_{xz} + d_{xz}\right) - \frac{1}{4}i\left(D_{yz} + d_{yz}\right) \tag{3.94b}$$

3.14 Use Eq. 3.92 to express A_{ij} and A_{ji} in terms of D_{ij} and d_{ij}.

The complete matrix representation of the Hamiltonian with isotropic and (anti-) symmetric anisotropic interactions in the uncoupled basis is directly obtained from the operations listed in Eq. 3.91 and using the definitions of D_{ij} in d_{ij} in Eq. 3.92

	$\|\alpha\alpha\rangle$	$\|\alpha\beta\rangle$	$\|\beta\alpha\rangle$	$\|\beta\beta\rangle$
$\langle\alpha\alpha\|$	$-\frac{1}{4}(J - D_{zz})$	$\frac{1}{4}\left(D_{xz} - d_{xz} - i(D_{yz} - d_{yz})\right)$	$\frac{1}{4}\left(D_{xz} + d_{xz} - i(D_{yz} + d_{yz})\right)$	$\frac{1}{4}\left(D_{xx} - D_{yy} - 2iD_{xy}\right)$
$\langle\alpha\beta\|$	$\frac{1}{4}\left(D_{xz} - d_{xz} + i(D_{yz} - d_{yz})\right)$	$\frac{1}{4}(J - D_{zz})$	$-\frac{1}{2}J + \frac{1}{4}\left(D_{xx} + D_{yy} + 2id_{xy}\right)$	$-\frac{1}{4}\left(D_{xz} + d_{xz} - i(D_{yz} + d_{yz})\right)$
$\langle\beta\alpha\|$	$\frac{1}{4}\left(D_{xz} + d_{xz} + i(D_{yz} + d_{yz})\right)$	$-\frac{1}{2}J + \frac{1}{4}\left(D_{xx} + D_{yy} - 2id_{xy}\right)$	$\frac{1}{4}(J - D_{zz})$	$-\frac{1}{4}\left(D_{xz} - d_{xz} - i(D_{yz} - d_{yz})\right)$
$\langle\beta\beta\|$	$\frac{1}{4}\left(D_{xx} - D_{yy} + 2iD_{xy}\right)$	$-\frac{1}{4}\left(D_{xz} + d_{xz} + i(D_{yz} + d_{yz})\right)$	$-\frac{1}{4}\left(D_{xz} - d_{xz} + i(D_{yz} - d_{yz})\right)$	$-\frac{1}{4}(J - D_{zz})$

and transformed to the coupled basis, the following Hamiltonian is obtained.

	$\lvert T^+\rangle$	$\lvert T^0\rangle$	$\lvert T^-\rangle$	$\lvert S\rangle$
$\langle T^+\rvert$	$-\frac{1}{4}(J - D_{zz})$	$\frac{1}{2\sqrt{2}}(D_{xz} - iD_{yz})$	$\frac{1}{4}(D_{xx} - D_{yy} + 2iD_{yz})$	$-\frac{1}{2\sqrt{2}}(d_{xz} - id_{yz})$
$\langle T^0\rvert$	$\frac{1}{2\sqrt{2}}(D_{xz} + iD_{yz})$	$-\frac{1}{4}(J - D_{xx} - D_{yy} + D_{zz})$	$-\frac{1}{2\sqrt{2}}(D_{xz} - iD_{yz})$	$-\frac{1}{2}id_{xy}$
$\langle T^-\rvert$	$\frac{1}{4}(D_{xx} - D_{yy} + 2iD_{yz})$	$-\frac{1}{2\sqrt{2}}(D_{xz} + iD_{yz})$	$-\frac{1}{4}(J - D_{zz})$	$-\frac{1}{2\sqrt{2}}(d_{xz} + id_{yz})$
$\langle S\rvert$	$-\frac{1}{2\sqrt{2}}(d_{xz} + id_{yz})$	$\frac{1}{2}id_{xy}$	$-\frac{1}{2\sqrt{2}}(d_{xz} - id_{yz})$	$\frac{3}{4}J - \frac{1}{4}(D_{xx} + D_{yy} + D_{zz})$

The triplet block and the diagonal elements are exactly the same as in the Hamiltonian that only considers the symmetric part of the anisotropic interaction. The anti-symmetric interaction introduces non-zero matrix elements for the coupling between singlet and triplet and causes a mixing between both spin states. The total spin quantum number is (at least formally) no longer a good quantum number. The number of parameters is now larger than the number of energy differences, even when the system is oriented in the coordinate frame that diagonalizes $\overline{\overline{D}}$. Therefore, a complete determination of the six parameters—J, D, E, d_{xy}, d_{xz} and d_{yz}—necessarily goes through the construction of a numerical effective Hamiltonian.

To close this section, we rewrite the Hamiltonian in the form that is most often used in the literature. The A-tensor in Eq. 3.90 is separated in a symmetric and anti-symmetric part.

$$\hat{H} = -J\hat{S}_1 \cdot \hat{S}_2 + \hat{S}_1\overline{\overline{D}}\hat{S}_2 + \hat{S}_1\overline{\overline{d}}\hat{S}_2 \tag{3.95}$$

where $\overline{\overline{D}}$ is diagonal if the orientation is chosen conveniently, and $\overline{\overline{d}}$ always has the following structure

$$\overline{\overline{d}} = \begin{pmatrix} 0 & d_{12} & -d_{13} \\ -d_{12} & 0 & d_{23} \\ d_{13} & -d_{23} & 0 \end{pmatrix} \tag{3.96}$$

This suggest that a shorter notation can be used by writing $\overline{\overline{d}}$ as a pseudovector $\mathbf{d} = (d_x, d_y, d_z)$ with $d_x = d_{23}$; $d_y = -d_{13}$ and $d_z = d_{12}$. The Hamiltonian then reads

$$\hat{H} = -J\hat{S}_1 \cdot \hat{S}_2 + \hat{S}_1\overline{\overline{D}}\hat{S}_2 + \mathbf{d}\hat{S}_1 \times \hat{S}_2 \tag{3.97}$$

Now, it also becomes clear that the DM interaction can only be non-zero when the local principal magnetic axis are not parallel. The situation becomes slightly more complicated when magnetic centers are considered with more than one unpaired electron. Then the single-ion anisotropy discussed in Chap. 2 has to be included in the model

$$\hat{H} = -J\hat{S}_1 \cdot \hat{S}_2 + \hat{S}_1\overline{\overline{D}}_1\hat{S}_1 + \hat{S}_2\overline{\overline{D}}_2\hat{S}_2 + \hat{S}_1\overline{\overline{D}}_{12}\hat{S}_2 + \mathbf{d}\hat{S}_1 \times \hat{S}_2 \tag{3.98}$$

and it has been shown that even biquadratic anisotropic interactions can play an important role in the description of the low-energy physics of the complex [21]. The corresponding operator is

$$\hat{\kappa} = (\hat{S}_1\hat{S}_1)\mathbf{D}_{aabb}(\hat{S}_2\hat{S}_2) \tag{3.99}$$

where $\mathbf{D}_{aabb}$ is tensor of rank 4 with 81 (3^4) parameters. However by choosing the proper magnetic axes frame this number is strongly reduced and when the system has a certain degree of symmetry one can eventually characterize the tensor with not more than nine parameters. Again one can resort to the numerical effective Hamiltonian to determine these parameters.

Problems

3.1 Overlap: Demonstrate that c_1/c_2 in Eq. 3.7 is equal to $1 - S_{ab}/1 + S_{ab}$, where $S_{ab} = \langle\phi_a|\phi_b\rangle$ and ϕ_a and ϕ_b are the orbitals of Eq. 3.17.

3.2 From delocalized to localized: Transform the following determinants and CSFs from a delocalized to a localized orbital basis. Determine the percentage of ionic and neutral character of the wave function. Are the wave functions eigenfunctions of $\hat{S}^2$?

a. $\Phi_1 = |g_1\overline{g}_1|$; $\Phi_2 = |g_1g_2|$; $\Phi_3 = |g_1\overline{u}_1|$
b. $\Psi_1 = (|g_1\overline{g}_1| + |u_1\overline{u}_1|)/\sqrt{2}$; $\Psi_2 = (|g_1\overline{g}_1| - |u_1\overline{u}_1|)/\sqrt{2}$
c. $\Phi_4 = |g_1u_1|$; $\Phi_5 = |g_1u_1v_1|$
d. $\Psi_3 = (2|g_1u_1\overline{v}_1| - |g_1\overline{u}_1v_1| - |\overline{g}_1u_1v_1|)/\sqrt{6}$

with $g_i = \frac{1}{\sqrt{2}}(a_i + b_i)$; $u_i = \frac{1}{\sqrt{2}}(a_i - b_i)$; $v_i = c_i$. a_i, b_i and c_i are orbitals localized on centers A, B and C, respectively.

3.3 Singlet and triplet eigenvalues: Calculate the eigenvalues of the Heisenberg Hamiltonian given in Eq. 3.31 of $\Phi(T) = |\alpha\alpha|$ and $\Phi(S) = (|\alpha\beta| - |\beta\alpha|)/\sqrt{2}$.

3.4 Extracting J-values for a three-center system: The following wave functions Ψ_k were obtained from an *ab initio* calculation on a system with three $S = 1/2$ magnetic centers. Each magnetic orbital ϕ_i is localized on center i and has the same spatial part in all five wave functions.

	Ψ_1	Ψ_2	Ψ_3	Ψ_4	Ψ_5
$\|\phi_1\phi_2\overline{\phi}_3\|$	−0.4426	−0.6583	0.5774	−0.1465	0.1135
$\|\phi_1\overline{\phi}_2\phi_3\|$	0.7706	−0.0661	0.5774	0.0367	−0.2476
$\|\overline{\phi}_1\phi_2\phi_3\|$	−0.3280	0.7243	0.5774	0.1098	0.1341
$\|\phi_1\overline{\phi}_1\phi_2\|$	0.0102	0.0234	0.0000	−0.0440	0.0017
$\|\phi_1\overline{\phi}_1\phi_3\|$	−0.0725	−0.0495	0.0000	0.1244	0.0341
$\|\phi_1\phi_2\overline{\phi}_2\|$	0.2243	−0.1120	0.0000	0.7653	−0.5685
$\|\phi_2\overline{\phi}_2\phi_3\|$	0.2017	0.1336	0.0000	−0.5805	−0.7636
$\|\phi_1\phi_3\overline{\phi}_3\|$	−0.0789	0.0407	0.0000	−0.1472	0.0147
$\|\phi_2\phi_3\overline{\phi}_3\|$	0.0076	0.0508	0.0000	0.0579	0.0127

The energies (in E_h) are $E_1 = -27.9611962$, $E_2 = -27.9601927$, $E_3 = -27.9596947$, $E_4 = -27.8326257$, $E_5 = -27.83169141$.

a. Determine the M_S quantum numbers of the determinants and identify Ψ_3 as a spin eigenfunction with $S = 3/2$.
b. Extract the J-values from the energies of the lowest three states under the assumption that $J_{12} = J_{23} \neq J_{13}$ (see Eq. 3.44).
c. Write down the determinants that span the model space of the Heisenberg Hamiltonian and determine the norm of the projections of Ψ_k on this model space.
d. Select the three roots with the largest norm and orthogonalize the projections $\widetilde{\Psi}_k$
e. Construct the 3×3 effective Hamiltonian and extract the different J-values by comparing with the matrix elements of the Heisenberg Hamiltonian given in Eq. 3.39.

3.5 Heisenberg twice. (a) Use the eigenvalues of Q, T and S for $\hat{H} = -J\hat{S}_1 \cdot \hat{S}_2$ to compute the eigenvalues of Q, T and S for the operator $\hat{S}_1 \cdot \hat{S}_2$. (b) From this, compute the eigenvalues of Q, T and S for the biquadratic operator $(\hat{S}_1 \cdot \hat{S}_2)^2$ and check the validity of Eq. 3.75.

3.6 Biquadratic interactions: Do the following total energies follow the regular spacing predicted by the Heisenberg Hamiltonian? $E_Q = -139.48992180\,E_h$, $E_T = -139.49305142\,E_h$ and $E_S = -139.49443101\,E_h$. Calculate J and λ (in meV) from the energy differences.

References

1. W. Heitler, F. London, Z. Phys. **44**, 455 (1927)
2. B. Bleaney, K.D. Bowers, Proc. R. Soc. Lond. Ser. A **214**, 451 (1952)
3. R. Boča, *Theoretical Foundations of Molecular Magnetism* (Elsevier, Amsterdam, 1999)
4. H. Bethe, Z. Phys. **71**, 205 (1931)
5. J.C. Bonner, M.E. Fisher, Phys. Rev. **135**(3A), A640 (1964)
6. J.W. Hall, W.E. Marsh, R.R. Weller, W.E. Hatfield, Inorg. Chem. **20**, 1033 (1981)
7. S. Eggert, I. Affleck, M. Takahashi, Phys. Rev. Lett. **73**(2), 332 (1994)
8. R. Georges, J.J. Borrás-Almenar, E. Coronado, J. Curély, M. Drillon, in *Magnetism: Molecules to Materials*, ed. by J.S. Miller, M. Drillon (Wiley-VCH, Weinheim, 2001), pp. 1–47, chap. 1

9. G.S. Rushbrooke, P.J. Wood, Mol. Phys. **1**, 257 (1958)
10. J. Curély, F. Lloret, M. Julve, Phys. Rev. B **58**, 11465 (1998)
11. J. Curély, J. Rouch, Physica B **254**, 298 (1998)
12. M. Deumal, M.J. Bearpark, J.J. Novoa, M.A. Robb, J. Phys. Chem. A **106**, 1299 (2002)
13. O. Kahn, Y. Pei, M. Verdaguer, J.P. Renard, J. Sletten, J. Am. Chem. Soc. **110**, 782 (1988)
14. E. Ruiz, A. Rodríguez-Fortea, J. Cano, S. Alvarez, J. Phys. Chem. Solids **65**, 799 (2004)
15. H.J. Maris, L.P. Kadanoff, Am. J. Phys. **46**, 652 (1978)
16. D. Chandler, *Introduction to Modern Statistical Mechanics* (Oxford University Press, Oxford, 1987)
17. J. Cano, R. Costa, S. Alvarez, E. Ruiz, J. Chem. Theory Comput. **3**, 782 (2007)
18. W. Schattke, R. Díez Muiño, *Quantum Monte Carlo Programming* (Wiley-VCH, Weinheim, 2013)
19. M. Roger, J.H. Hetherington, J.M. Delrieu, Rev. Mod. Phys. **55**, 1 (1983)
20. C.J. Calzado, C. de Graaf, E. Bordas, R. Caballol, J.P. Malrieu, Phys. Rev. B **67**, 132409 (2003)
21. R. Maurice, N. Guihéry, R. Bastardis, C. de Graaf, J. Chem. Theory Comput. **6**, 55 (2010)