Answers – Chapter 24

[1a] Under inversion symmetry i, **r** becomes **-r** and **p** becomes **-p**, so that **r**×**p** remains unchanged. Consequently, the spin orientations of the spin sites **1** and **2** should be identical as shown in Fig. 2b.

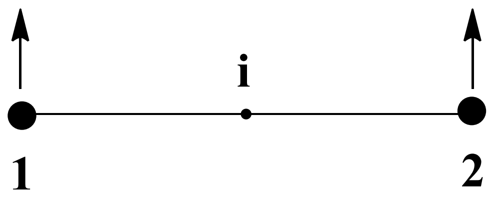


Fig. 2b

[1b] Under the mirror plane of symmetry m, **r** becomes **-r** but **p** remains unchanged, so that **r**×**p** becomes **-r**×**p** (Fig. 3b). Consequently, the spin orientations of the spin sites **1** and **2** should be opposite as shown in Fig. 3c.

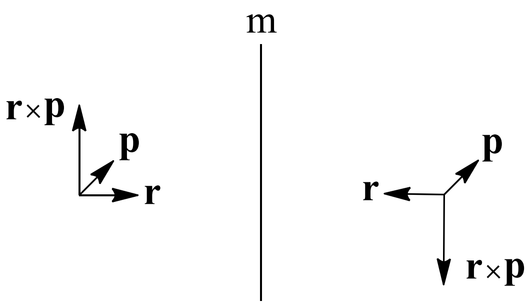


Fig. 3b

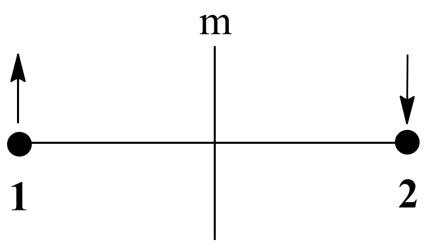


Fig. 3c

[1c] Under the mirror plane of symmetry m, both **r** and **p** remain unchanged, so that the **r**×**p** remains unchanged, as shown in Fig. 4a. Consequently, the orientations of the spins at sites **1** and **2** are the same as depicted in Fig. 4b.

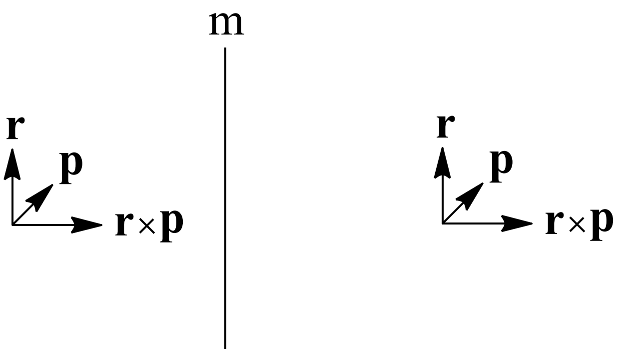


Fig. 4a

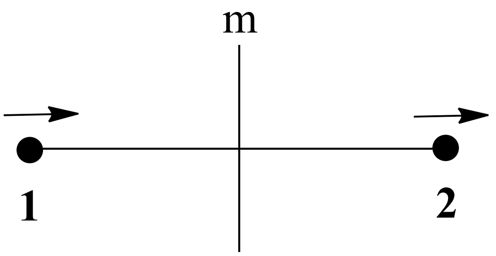


Fig. 4b

[2] We note that **p** = m**v** = m(d**r**/dt). Consequently, under time reversal t → -t, **p** becomes **-p** whereas **r** remains unchanged so that the **r**×**p** becomes **-r**×**p**. Thus, the spin orientation is reversed under time reversal. For example, under time reversal, α spin becomes β spin, and vice versa.

[3] Under magnetic field **H**, a spin angular momentum **S** interacts with the magnetic field to give the Zeeman energy given by E = $2\mu_B$**S**·**H**. Therefore, the two opposite spin orientations **S** = $|S, S_z\rangle$ and **-S** = $|S, -S_z\rangle$, which are degenerate in the absence of magnetic field, become different in energy.

[4] To answer this question, it is necessary to evaluate how the levels $|1,1\rangle, |1,0\rangle$, and $|1,-1\rangle$ interact under $\hat{H}_{zf}$. Thus, we first calculate the matrix elements $\langle i|\hat{H}_{zf}|j\rangle$, where i, j = $|1,1\rangle$, $|1,0\rangle$, $|1,-1\rangle$. Using the following relationship

$$\hat{S}_z|S,S_z\rangle = S_z|S,S_z\rangle$$
$$\hat{S}_+|S,S_z\rangle = \sqrt{S(S+1) - S_z(S_z+1)}\,|S,S_z+1\rangle$$
$$\hat{S}_-|S,S_z\rangle = \sqrt{S(S+1) - S_z(S_z-1)}\,|S,S_z-1\rangle$$

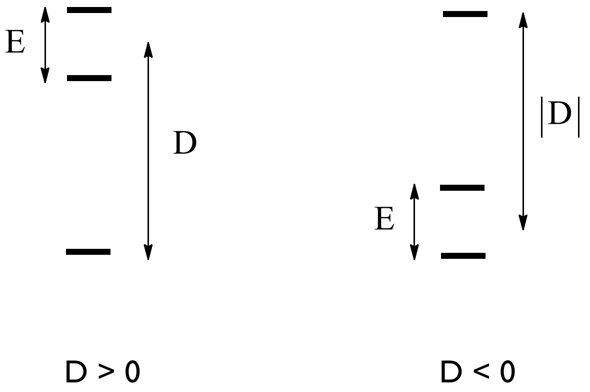
we obtain

$$\hat{H}_{zf}\left|1,1\right\rangle = \tfrac{1}{3}D\left|1,1\right\rangle + \tfrac{1}{2}E\left|1,-1\right\rangle$$
$$\hat{H}_{zf}\left|1,0\right\rangle = -\tfrac{2}{3}D$$
$$\hat{H}_{zf}\left|1,-1\right\rangle = \tfrac{1}{3}D\left|1,-1\right\rangle + \tfrac{1}{2}E\left|1,1\right\rangle$$

Consequently, the $\left\langle i\right|\hat{H}_{zf}\left|j\right\rangle$ matrix elements are given by

$$\left\langle 1,1\right|\hat{H}_{zf}\left|1,1\right\rangle = \left\langle 1,-1\right|\hat{H}_{zf}\left|1,-1\right\rangle = \tfrac{1}{3}D$$
$$\left\langle 1,0\right|\hat{H}_{zf}\left|1,0\right\rangle = -\tfrac{2}{3}D$$
$$\left\langle 1,1\right|\hat{H}_{zf}\left|1,-1\right\rangle = \left\langle 1,-1\right|\hat{H}_{zf}\left|1,1\right\rangle = \tfrac{1}{2}E$$
$$\text{All other } \left\langle i\right|\hat{H}_{zf}\left|j\right\rangle = 0$$

The above shows that the average energy of the $\left|1,1\right\rangle$ and $\left|1,-1\right\rangle$ levels is separated from the $\left|1,0\right\rangle$ level by D, and that the $\left|1,1\right\rangle$and $\left|1,-1\right\rangle$ levels interact leading to the energy split given by E. This is illustrated below for the cases of D > 0 and D < 0, respectively.



[5] We note that

$$\hat{H}_{zf}\left|1/2,1/2\right\rangle = 0$$
$$\hat{H}_{zf}\left|1/2,-1/2\right\rangle = 0$$

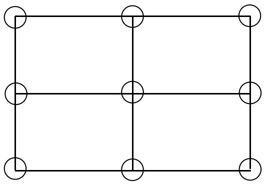
Therefore,

$$\left\langle 1/2,1/2\right|\hat{H}_{zf}\left|1/2,1/2\right\rangle = 0$$
$$\left\langle 1/2,-1/2\right|\hat{H}_{zf}\left|1/2,-1/2\right\rangle = 0$$
$$\left\langle 1/2,1/2\right|\hat{H}_{zf}\left|1/2,-1/2\right\rangle = 0$$

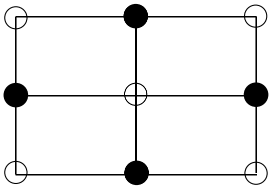
Namely, the $\alpha = \left|1/2,1/2\right\rangle$ and $\beta = \left|1/2,-1/2\right\rangle$ states do not interact under under $\hat{H}_{zf}$, and have the same energy. Namely, the two states remain degenerate under $\hat{H}_{zf}$, as dictated by the Kramer's degenerate theorem.

However, it is incorrect to infer from the result of this problem and that of Problem [4] that the spin-1/2 system has no magnetic anisotropy. The Kramer's degenerate theorem for a spin-1/2 system does not say anything about the preferred direction of the α and β spins. It simply dictates that the α and β spin states be degenerate no matter what their preferred spin orientation is.

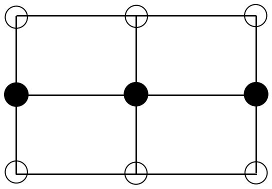
[6] Since there are three J parameters to evaluate, we may consider the following four ordered spin states, FM, AF1, AF2 and AF3, shown below.



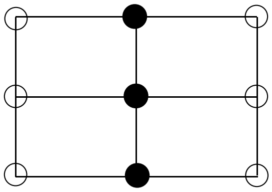
FM



AF1



AF2



AF3

The smallest unit cell common to all the four states has four spin sites (i.e., one rectangle consisting of four spin sites). Thus, we calculate the total spin exchange interaction energy for each state per four spin sites by using the spin Hamiltonian $\hat{H}_{spin} = -\sum_{i<j} J_{ij}\hat{S}_i \cdot \hat{S}_j$.

Since all spin sites have spin S, we have $J_{ij}\hat{S}_i \cdot \hat{S}_j = J_{ij}S^2$ if the two spins have a ferromagnetic arrangement, but $J_{ij}\hat{S}_i \cdot \hat{S}_j = -J_{ij}S^2$ the two spins have an antiferromagnetic arrangement. In counting the spin exchange interaction that each magnetic bond contributes to a unit cell, we note that each magnetic bond contained within a unit cell contributes all its spin exchange energy to a unit cell, but that between adjacent unit cells contributes only half its exchange energy. For example, the FM state has two J_1 bonds in a unit cell and four J_1 bonds between unit cells, leading to four J_1 bonds per unit cell containing four spin sites.

Consequently, the total spin exchange energies of the four states per four spin sites are given by

$$E_{FM} = (-4J_1 - 4J_2 - 8J_3)S^2$$
$$E_{AF1} = (+4J_1 + 4J_2 - 8J_3)S^2$$
$$E_{AF2} = (-4J_1 + 4J_2 + 8J_3)S^2$$
$$E_{AF3} = (+4J_1 - 4J_2 + 8J_3)S^2$$

Thus, once the energies of the FM, AF1, AF2 and AF3 states are determined by DFT calculations, one can do mapping analysis to determine the values of J_1, J_2 and J_3.

[7] Under $\hat{H}_{spin} = -J\hat{S}_1 \cdot \hat{S}_2$ (i.e., in the absence of the DM interaction), the energies of the singlet and triplet states (E_S and E_T, respectively) of the antiferromagnetic ($J < 0$) spin dimer are given by

$E_S = 3J/4$

$E_T = -J/4$.

Namely, the singlet state is lower in energy than the triplet state by $|J|$. The DM interaction makes the singlet state interact with the triplet state and hence acquire the triplet character. In most cases $\vec{D}$ is small in magnitude compared with J (i.e., $|D/J| \le 0.1$), we can treat the $\vec{D} \cdot (\hat{S}_1 \times \hat{S}_2)$ term as perturbation.

The $\vec{D} \cdot (\hat{S}_1 \times \hat{S}_2)$ term is written as

$$\vec{D} \cdot (\hat{S}_1 \times \hat{S}_2) = (\hat{i}D_x + \hat{j}D_y + \hat{k}D_z) \cdot \begin{vmatrix} \hat{i} & \hat{j} & \hat{k} \\ S_{1x} & S_{1y} & S_{1z} \\ S_{2x} & S_{2y} & S_{2z} \end{vmatrix}$$

Without loss of generality, we assume the DM vector $\vec{D}$ to be along the z-direction so that $D_x = D_y = 0$, and

$$\vec{D} \cdot (\hat{S}_1 \times \hat{S}_2) = D_z(\hat{S}_{1x}\hat{S}_{2y} - \hat{S}_{2x}\hat{S}_{1y}).$$

Using the definitions of the ladder operators $\hat{S}_+ = \hat{S}_x + i\hat{S}_y$ and $\hat{S}_- = \hat{S}_x - i\hat{S}_y$, the above expression is rewritten as

$$\vec{D} \cdot (\hat{S}_1 \times \hat{S}_2) = i\frac{D}{2}(\hat{S}_{1+}\hat{S}_{2-} - \hat{S}_{1-}\hat{S}_{2+}).$$

Consequently, we find

$$
\begin{aligned}
\vec{D}\cdot(\hat{S}_1\times\hat{S}_2)\left|\Phi_S\right\rangle &= i\frac{D}{2}(\hat{S}_{1+}\hat{S}_{2-}-\hat{S}_{1-}\hat{S}_{2+})\frac{1}{\sqrt{2}}\left(\left|\frac{1}{2},\frac{1}{2}\right\rangle_1\left|\frac{1}{2},-\frac{1}{2}\right\rangle_2-\left|\frac{1}{2},-\frac{1}{2}\right\rangle_1\left|\frac{1}{2},\frac{1}{2}\right\rangle_2\right)\\
&= -i\frac{D}{2}\frac{1}{\sqrt{2}}\left(\left|\frac{1}{2},\frac{1}{2}\right\rangle_1\left|\frac{1}{2},-\frac{1}{2}\right\rangle_2+\left|\frac{1}{2},-\frac{1}{2}\right\rangle_1\left|\frac{1}{2},\frac{1}{2}\right\rangle_2\right)\\
&= -i\frac{D}{2}\left|\Phi_{T1}\right\rangle
\end{aligned}
$$

so that

$$
\begin{aligned}
&\left\langle\Phi_{T1}\right|\vec{D}\cdot(\hat{S}_1\times\hat{S}_2)\left|\Phi_S\right\rangle = -i\frac{D}{2}\\
&\left\langle\Phi_{T2}\right|\vec{D}\cdot(\hat{S}_1\times\hat{S}_2)\left|\Phi_S\right\rangle = \left\langle\Phi_{T3}\right|\vec{D}\cdot(\hat{S}_1\times\hat{S}_2)\left|\Phi_S\right\rangle = 0
\end{aligned}
$$

This means that the singlet state Φ_S interacts with the triplet state Φ_{T1}, but not with the triplet states Φ_{T2} and Φ_{T3}.

Therefore, according to perturbation theory, the ground-state wave function Φ_G and energy E_G are given by

$$
\Phi_G = \left(1-\frac{1}{2}\tau^2\right)\Phi_S - i\tau\Phi_{T1}
$$

$$
E_G = \frac{3}{4}J + \frac{D_z^2}{4J}
$$

where the mixing coefficient t is given by $\tau = \frac{D_z}{2J}$. Thus, the ground state wave function Φ_G is is largely described by Φ_S but has a small amount of Φ_{T1} due to the DM interaction. The ground state energy E_G is lower than the singlet state energy E_S by $\frac{D_z^2}{4|J|}$.

[8] The $Cu(O_{eq})_4$ square planar units of $A_2Cu(PO_4)_2$ (A = Ba, Sr) are arranged as depicted below, where the $Cu(O_{eq})_4$ square planes are coplanar in each row along the b-direction but are not between adjacent rows (see Fig. 6c). Consequently,

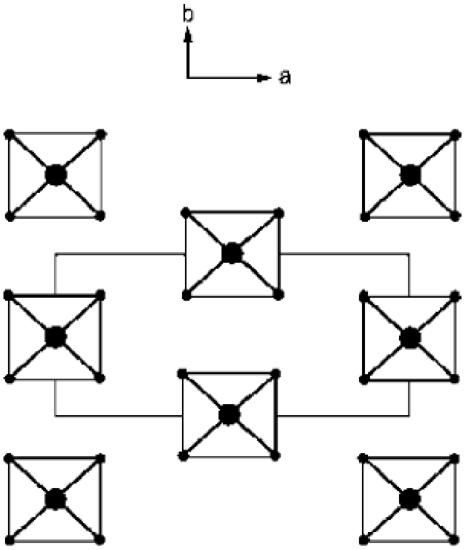


Fig. 6c

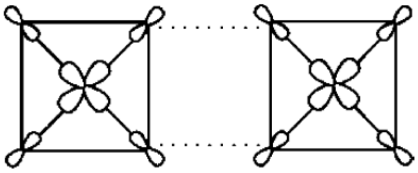


Fig. 6d

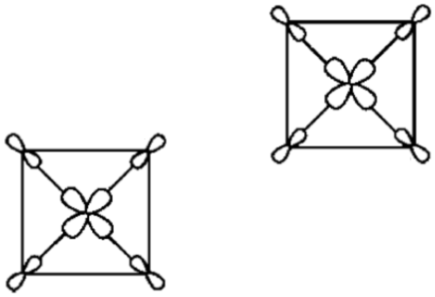


Fig. 6e

the x^2-y^2 magnetic orbitals of adjacent $Cu(O_{eq})_4$ square planes overlap well within each row along the b-direction (Fig. 6d), but overlap poorly between adjacent rows (Fig. 6e). Consequently, the Cu^{2+} ions of $A_2Cu(PO_4)_2$ (A = Ba, Sr) behave as Heisenberg 1D antiferromagnetic chains (Inorg. Chem. 2005, 44, 4359).

[9] As depicted below (Fig. 7b), there occur Cu-O…O-Cu spin exchange interactions between adjacent chains. These interactions, which are isolated from one another, are stronger than the Cu-O-Cu spin exchange within each chain. Consequently, the magnetic susceptibility behaves like an isolated antiferromagnetic dimer (Inorg. Chem. 2005, 44, 4359).

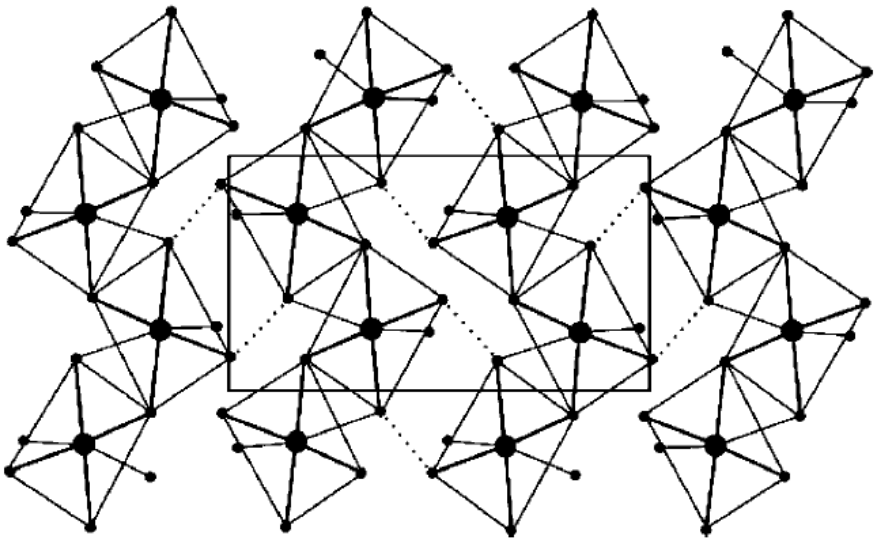


Fig. 7b

[10] As can be seen from Fig. 8b, the spin exchange interaction between adjacent Cu^{2+} ions in a Cu_4 tetrahedral unit will be very weak because their x^2-y^2 magnetic orbitals are nearly orthogonal to each other. However, between adjacent Cu_4 tetrahedral units along the (a+b)- and (-a+b)-directions, there occur Cu-X…X-Cu spin exchange interactions depicted in Fig. 8c. These interactions are isolated from one another so that $Cu_2Te_2O_5X_2$ (X = Cl, Br) behaves as an isolated Heisenberg antiferromagnetic dimer (Inorg. Chem. 2003, 42, 3898), so that it has a spin gap.

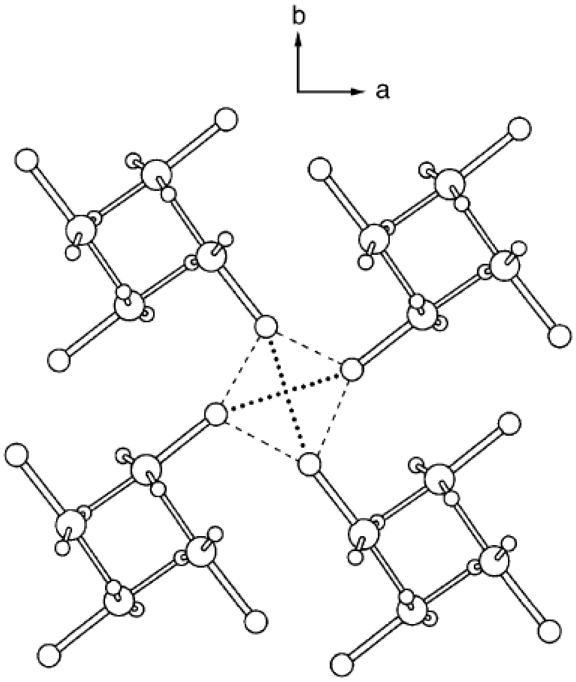


Fig. 8b

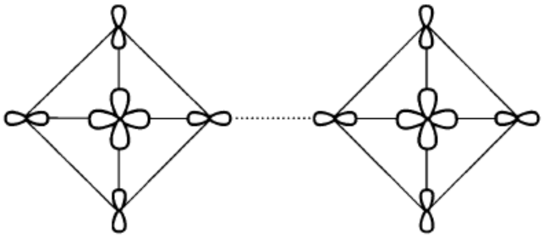


Fig 8c