

Spin multipole moments as collective quantum phenomena

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Abstract. In this paper we investigate the occurrence of multipole moments of a collection of spins in a quantum magnetic system. To get insights into the behaviour of such systems we start by considering small spin clusters composed of dimers, trimers, as well as mixed spin systems with four spins. We focus our attention on the quantum multipole states, that gave rise to the widely discussed spin nematic and spin liquid phases. The magnetic properties of these systems are computed and the main differences between bosonic and fermionic multipolar states are discussed.

1. Introduction

For the past two decades quantum magnetic systems have attracted the attention of many condensed matter physicists and still are one of the main topics of interest (see e.g. [1–3] and references therein). The occurrence of exotic non-magnetic phases involving higher degree of symmetry, such as nematic phases, have been widely discussed, theoretically as well as experimentally [4–6]. On the experimental side the layered compound NiGa_2S_4 , the compounds LaNb_2O_7 and FeSe have been pointed as materials exhibiting such ordering. Spin-half frustrated ferromagnets on a square lattice [7, 8] and a triangular lattice [9] of ^3He thin films exhibit a bond-type spin nematic order. Other enticing possibilities are the different nematic orders of spin-one system on a square lattice [10, 11] and a triangular lattice [12, 13].

In this report we restrict our attention on the determination of multipole moments in quantum spin clusters with finite number of magnetic moments. We show, by means of quantum mechanical treatment, that at any level beyond the singlet, only the quadrupole state survive. For higher symmetries we have always local dipole components, which makes them observable by experimental means.

We consider spin- $\frac{1}{2}$, spin-1 and mixed dimers, spin- $\frac{1}{2}$ trimer and as a final example a mixed four spin cluster. We report the properties of such systems to get fundamental understanding of the quantum nature of this non-magnetic states before tackling more complex systems with direct application in condensed matter physics. We anticipate that for such systems we have non-zero multipole moments, even when the total spin quantum number is zero or half. Showing that unlike the single spin space, the Hilbert spaces of a spin clusters with the same spin quantum number possess additional symmetries.

The rest of the report is organized as follows: In Section 2 we present the basic notations and general definition to be used later. In Sections 3 and 4 we investigate the properties of clusters with identical of mixed spins. Section 5 presents a summary of our results.

2. General Statements

Below we denote the basis in a 2D vector space by $\{|c^+\rangle, |c^-\rangle\}$, the spherical basis in a 3D space by $\{|d^+\rangle, |d^0\rangle, |d^-\rangle\}$ and the Cartesian basis – $\{|d^x\rangle, |d^y\rangle, |d^z\rangle\}$, with $|d^x\rangle = \frac{1}{\sqrt{2}}(|d^+\rangle - |d^-\rangle)$, $|d^y\rangle =$



$\frac{1}{\sqrt{2}}(|d^+\rangle + |d^-\rangle)$, $|d^z\rangle = -i|d^0\rangle$. The matrices $\{\lambda^i\}_{i=1}^8$ and the $\{\gamma^i\}_{i=1}^{15}$ are the SU(3) and SU(4) generators [14], respectively. We denote the spin-half operator by $\hat{\sigma}$, the spin-one operator by $\hat{S}$ and by $\mathbb{1}_n$ the unitary operator acting in n dimensional Hilbert space. Also, i denotes the imaginary unity, s the spin quantum number and m the magnetic quantum number. We set $\hbar = 1$ and the magnetic easy axis is chosen to coincide with the z axis. For brevity we define the set $\mathbb{K} = \{x, y, z\}$.

For a preselected basis in Hilbert space of dimension $2s + 1$ an arbitrary spin can be uniquely determined via the following relations

$$[\hat{s}^\alpha, \hat{s}^\beta] = i\varepsilon_{\alpha\beta\gamma}\hat{s}^\gamma \quad \hat{s}^2|s, m\rangle = s(s+1)|s, m\rangle, \quad \hat{s}^z|s, m\rangle = m|s, m\rangle, \quad (1)$$

Beside the dipolar ordering described by dipole moments, quantum systems possess additional symmetries associated with different physical properties, such as quadrupole and octupole moments to name a few [15].

The multipole operators are uniquely determined in terms of the spin of the quantum system. Here we concentrate on bosonic systems.

For integer spins s , at any level beyond the singlet state, one can find a set of time reversal invariant non-magnetic states $|s, q^\alpha\rangle$ with eigenvalues

$$\hat{s}^2|s, q^\alpha\rangle = s(s+1)|s, q^\alpha\rangle, \quad \hat{s}^\alpha|s, q^\alpha\rangle = 0|s, q^\alpha\rangle. \quad (2)$$

This eigenvectors are entanglement states and therefore describe multipole moments as a collective quantum phenomena, which is an example demonstrating the physical richness of boson systems. Notice for arbitrary spin one works with SU(2s+1) groups. A clear example is the spin-one, where the extension of SU(2) to SU(3) naturally leads to the following representations $\hat{S} = (\lambda^7, -\lambda^5, \lambda^2)$ and $\hat{Q} = (-\lambda^3, \lambda^8, -\lambda^1, -\lambda^6, -\lambda^4)$. Note that in this case all time reversal invariant non-magnetic states are quadrupole states. For a single spin with $s > 1$, or spin clusters this is no longer true and as we shall see one non-magnetic state may refer to a different multipole moments. More details about spin-one quadrupole states and the related nematic order can be found in references [4, 13].

3. Dimers and trimers

3.1. Spin-half dimer

We discuss the most simple quantum system composed of a pair of half spins, with total spin $\hat{s} = \hat{\sigma}_1 + \hat{\sigma}_2$. It is interesting that a pair of half spin may couple to form a dipole, as well as a quadrupole and even an octupole. We have one magnetic parameter $m = \pm 1, 0$ and two non-magnetic parameters, the level

Table 1. The eigenvalues of triplet, multipole and singlet states.

$\hat{s}^2$	s	m	$\hat{s}^x$	$\hat{s}^y$	$\hat{s}^z$	Eigenstates	Label	$\hat{\sigma}_1 \cdot \hat{\sigma}_2$
2	1	± 1	—	—	—	$ c^\pm c^\pm\rangle$	$ T^\pm\rangle$	$\frac{1}{4}$
2	1	0	—	—	0	$\frac{1}{\sqrt{2}}(c^+ c^- + c^- c^+\rangle)$	$ T^0\rangle$	$\frac{1}{4}$
2	1	—	0	—	—	$\frac{i}{\sqrt{2}}(T^+\rangle - T^-\rangle)$	$ q^x\rangle$	$\frac{1}{4}$
2	1	—	—	0	—	$\frac{1}{\sqrt{2}}(T^+\rangle + T^-\rangle)$	$ q^y\rangle$	$\frac{1}{4}$
2	1	0	—	—	0	$-i T^0\rangle$	$ q^z\rangle$	$\frac{1}{4}$
0	0	0	0	0	0	$\frac{1}{\sqrt{2}}(c^+ c^- - c^- c^+\rangle)$	$ S\rangle$	$-\frac{3}{4}$

parameter $s = 1, 0$ and the eigenvalue of the operator $(\hat{\sigma}_1 \cdot \hat{\sigma}_2)$. We have two magnetic states, which are components of the symmetric triplet group $\{|T^\pm\rangle, |T^0\rangle\}$ and an antisymmetric singlet state $|S\rangle$. In table 1 one can find the various non-magnetic states of the system, where we adopt the notation $|q^\alpha\rangle$

instead of $|s, q^\alpha\rangle$. An arbitrary state function is then written as $|c\rangle = c^x|q^x\rangle + c^y|q^y\rangle + c^z|q^z\rangle + c^s|S\rangle$, with unit vector $\mathbf{c} \in \mathbb{C}^4$, $\mathbf{c} = (c^x, c^y, c^z, c^s)$. Clearly, any state with $\mathbf{c} \in \mathbb{R}^4$ is non-magnetic. Setting $\mathbf{c} = (-\frac{1}{\sqrt{2}}(\sin\phi + i\cos\theta\cos\phi), \frac{1}{\sqrt{2}}(\cos\phi - i\cos\theta\sin\phi), \frac{1}{\sqrt{2}}\sin\theta)$, we obtain the coherent states of the system, where the triplet level represent the spin-one spin

$$|c\rangle = \frac{1}{2}e^{-i\phi}(1 + \cos\theta)|T^+\rangle + \frac{1}{\sqrt{2}}\sin\theta|T^0\rangle + \frac{1}{2}e^{i\phi}(1 - \cos\theta)|T^-\rangle. \quad (3)$$

An illustration of possible collective spin states, describing an octopole, a quadrupole and a dipole moments, are shown in figure 1, where the director is represented by red line. The quadrupole and octopole components are written as $\hat{Q}^0 = \frac{1}{\sqrt{3}}(|q^x\rangle\langle q^x| + |q^y\rangle\langle q^y| - 2|q^z\rangle\langle q^z|)$ and $\hat{O}^0 = \frac{1}{\sqrt{6}}(|q^x\rangle\langle q^x| + |q^y\rangle\langle q^y| + |q^z\rangle\langle q^z| - 3|S\rangle\langle S|)$. Within the SU(4) group and the basis $\{|q^x\rangle, |q^y\rangle, |q^z\rangle, |S\rangle\}$ for the total spin operator we have $\hat{s} = (\gamma^7, -\gamma^5, \gamma^2)$ and for the quadrupolar operator $\hat{Q} = (-\gamma^3, \gamma^8, -\gamma^1, -\gamma^6, -\gamma^4)$. The SU(2) algebra and s are preserved and in addition we get $\hat{s}^\alpha|S\rangle = 0|S\rangle$, $\gamma^7|q^x\rangle = 0|q^x\rangle$, $\gamma^5|q^y\rangle = 0|q^y\rangle$, $\gamma^2|q^z\rangle = 0|q^z\rangle$. The remaining seven generators can be used to construct the octupolar operator, where $\hat{O}^0 = \gamma^{15}$ [14]. Therefore, unlike single spin-one this dimer is a good example for the existence of additional symmetries and it clearly reveals the quantum collective nature of the multipole moments.

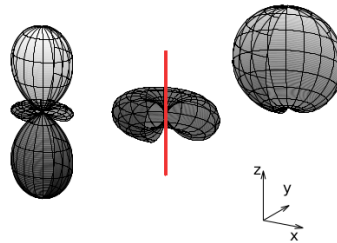


Figure 1. Representation of octopole moment on the left $|\langle\hat{O}^0\rangle| = \frac{1}{\sqrt{6}}(\sin^2(\theta) - 3\cos^2(\theta))$, quadrupole moment on the middle $|\langle\hat{Q}^0\rangle| = \frac{2}{\sqrt{3}}\sin^2(\theta)$ and on the right a fully polarized state(dipole moment) toward the z direction with $|\langle\hat{s}\rangle| = \frac{1}{4}(1 + \cos\theta)^2$. The director is illustrated as a red line.

3.2. Spin-one dimer

Naturally the spin-1 spin can form a quadrupole by itself. The quantum numbers for this system are $s = 2, 1, 0$ and $m = \pm 2, \pm 1, 0$. This system has a symmetry higher than octupole, such as hexadecapole and so on. When a pair of spin-1 are coupled to each other we have, [4, p. 337],

$$\hat{Q}_1 \cdot \hat{Q}_2 = 2\hat{P}_{12} - \hat{S}_1 \cdot \hat{S}_2 - \frac{2}{3}\mathbb{1}_9, \quad \hat{Q}_1 \cdot \hat{Q}_2 = 2(\hat{S}_1 \cdot \hat{S}_2)^2 + \hat{S}_1 \cdot \hat{S}_2 - \frac{8}{3}\mathbb{1}_9. \quad (4)$$

Together with the biquadratic form the permutation operator $\hat{P}_{12}$ defines a fundamental constrain between dipole-dipole and quadrupole-quadrupole correlations. Estimating the quantum properties of this pair we work with the magnetic parameter m , the level parameter s and the eigenvalues of the bilinear forms $\hat{S}_1 \cdot \hat{S}_2$ and $\hat{Q}_1 \cdot \hat{Q}_2$. The value $s = 2$ now defines the quintet level with some of the possible eigenstates presented in table 2.

We have six eigenstates associated to pure multipole moments, three symmetric and three anti-symmetric, see table 3. The other two superpositions stand for the symmetric multipole states $|2, q_1\rangle = \frac{1}{\sqrt{2}}(|d^x d^y\rangle + |d^y d^x\rangle)$ and $|2, q_2\rangle = \frac{1}{\sqrt{2}}(|d^y d^y\rangle - |d^x d^x\rangle)$, which preserves the spin quantum number, but are not eigenvectors of $\hat{s}^\alpha$ operators. We remark also that all eigenstates in table 3 are entanglement states and therefore the discussions of the nematic order is not feasible. Despite the property of spin-1 in developing a pure quadrupole, here by the quantum nature of the dimer, we cannot conclude whether a pure quadrupole in the spin-one subspace exists or not. In fact such an estimation can be done by using the variational approach. For instance, the state $|d^+ d^z\rangle$ corresponds to spin $\langle\hat{S}_1\rangle$ pointing along the z axis

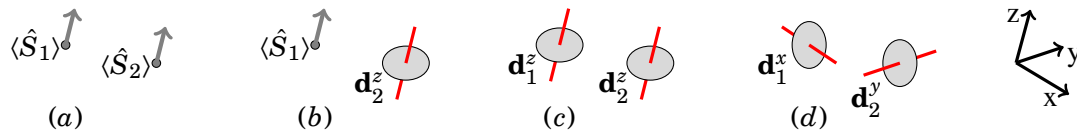
Table 2. The eigenvalues for quintet, triplet and singlet states are presented.

$\hat{s}^2$	s	m	Eigenstates	Label	$\hat{S}_1 \cdot \hat{S}_2$	$\hat{Q}_1 \cdot \hat{Q}_2$
6	2	± 2	$ d^\pm d^\pm\rangle$	$ \mathcal{Q}^{2\pm}\rangle$	1	$\frac{1}{3}$
6	2	± 1	$\frac{1}{\sqrt{2}}(d^\pm d^0\rangle + d^0 d^\pm\rangle)$	$ \mathcal{Q}^\pm\rangle$	1	$\frac{1}{3}$
6	2	0	$\frac{1}{\sqrt{6}}(d^+ d^- \rangle + d^- d^+ \rangle + 2 d^0 d^0 \rangle)$	$ \mathcal{Q}^0\rangle$	1	$\frac{1}{3}$
2	1	± 1	$\frac{1}{\sqrt{2}}(d^\pm d^0\rangle - d^0 d^\pm\rangle)$	$ T^\pm\rangle$	-1	$-\frac{5}{3}$
2	1	0	$\frac{1}{\sqrt{2}}(d^+ d^- \rangle - d^- d^+ \rangle)$	$ T^0\rangle$	-1	$-\frac{5}{3}$
0	0	0	$\frac{1}{\sqrt{3}}(d^+ d^- \rangle + d^- d^+ \rangle - d^0 d^0 \rangle)$	$ S\rangle$	-2	$\frac{10}{3}$

Table 3. The eigenvalues for all non-magnetic eigenstates. The three antisymmetric states are presented in third row.

$\hat{s}^2$	s	$\hat{s}^x$	$\hat{s}^y$	$\hat{s}^z$	Eigenstates	Label	$\hat{S}_1 \cdot \hat{S}_2$	$\hat{Q}_1 \cdot \hat{Q}_2$
6	2	0	-	-	$\frac{1}{\sqrt{2}}(d^y d^z\rangle + d^z d^y\rangle)$	$ 2, q^x\rangle$	1	$\frac{1}{3}$
6	2	-	0	-	$\frac{1}{\sqrt{2}}(d^x d^z\rangle + d^z d^x\rangle)$	$ 2, q^y\rangle$	1	$\frac{1}{3}$
6	2	-	-	0	$\frac{1}{\sqrt{6}}(d^x d^x\rangle + d^y d^y\rangle - 2 d^z d^z\rangle)$	$ 2, q^z\rangle$	1	$\frac{1}{3}$
2	1	0	-	-	$\frac{1}{\sqrt{2}}(d^y d^z\rangle - d^z d^y\rangle)$	$ 1, q^x\rangle$	-1	$-\frac{5}{3}$
2	1	-	0	-	$\frac{1}{\sqrt{2}}(d^x d^z\rangle - d^z d^x\rangle)$	$ 1, q^y\rangle$	-1	$-\frac{5}{3}$
2	1	-	-	0	$\frac{1}{\sqrt{2}}(d^x d^y\rangle - d^y d^x\rangle)$	$ 1, q^z\rangle$	-1	$-\frac{5}{3}$
0	0	0	0	0	$\frac{1}{\sqrt{2}}(d^x d^x\rangle + d^y d^y\rangle + d^z d^z\rangle)$	$ S\rangle$	-2	$\frac{10}{3}$

and quadrupole with a director parallel to z axis, where $\langle \hat{S}_1 \cdot \hat{S}_2 \rangle = 0$ and $\langle \hat{Q}_1 \cdot \hat{Q}_2 \rangle = -\frac{2}{3}$. Now changing only the orientation of the director, so that we have the state $|d^+ d^y\rangle$ with a director $\mathbf{d}_2^y$, it changes only the expectation value of the quadrupole interaction, or $\langle \hat{Q}_1 \cdot \hat{Q}_2 \rangle = \frac{1}{3}$. Furthermore, the state $|d^z d^x\rangle$ is a quadrupole state with orthogonal directors $\mathbf{d}_1^z$ and $\mathbf{d}_2^x$ and correlators $\langle \hat{S}_1 \cdot \hat{S}_2 \rangle = 0$ and $\langle \hat{Q}_1 \cdot \hat{Q}_2 \rangle = -\frac{2}{3}$, while the quadrupole state $|d^x d^x\rangle$ describe two quadrupoles with parallel directors oriented along the x axis with correlators $\langle \hat{S}_1 \cdot \hat{S}_2 \rangle = 0$ and $\langle \hat{Q}_1 \cdot \hat{Q}_2 \rangle = \frac{4}{3}$. On figure 2 we have introduce the geometrical interpretation of arbitrary chosen states for the sake of clarity. Although these states do not reveal the real quantum nature of the system, they might help in understanding the exchange mechanism.

**Figure 2.** Geometrical representation of (a) ferromagnetic order $|\mathcal{Q}^{2+}\rangle$; (b) mixed state $|d^+ d^z\rangle$; (c) ferroquadrupole order, with state function $|d^z d^z\rangle$; (d) anti-ferroquadrupole order, the corresponding state is $|d^x d^y\rangle$.

3.3. Mixed dimer

Fermions always possess a magnetic moment and therefore we can find non-magnetic states only by considering the average of the total spin. There are two types of non-magnetic states, those that preserve

the spin quantum number and those that do not. Using the eigenvectors of table 4 we can obtain six non-magnetic states, with the corresponding quantum number s . A good example is the superposition $\frac{1}{\sqrt{2}}(|Q^{3+}\rangle + |Q^{3-}\rangle)$ with $\langle \hat{s} \rangle = 0$ and $\langle \hat{\sigma}_1 \cdot \hat{S}_2 \rangle = \frac{3}{2}$. It is fascinating that even for $s = \frac{1}{2}$ the system exhibits multipole moments. The operator $\hat{Q} \neq 0$ and $\frac{1}{\sqrt{2}}(|D^+\rangle \pm |D^-\rangle)$ are the corresponding non-magnetic states. Moreover, the non-magnetic state $\frac{1}{\sqrt{2}}(|c^+ d^x\rangle + |c^- d^y\rangle)$ for which $\langle \hat{s} \rangle = 0$ and $\langle \hat{\sigma}_1 \cdot \hat{S}_2 \rangle = 0$ does not preserve the spin quantum number and therefore we cannot deduce that we have collective multipole. This state actually signals the formation of a quadrupole in boson space. Such case can be considered as a spin-half, but notice that we do not have a two level system. Another example is the function $|c^+ d^y\rangle$ with $\langle \hat{s} \rangle = \frac{1}{2}$ and $\langle \hat{\sigma}_1 \cdot \hat{S}_2 \rangle = 0$. The similar is the case (b) illustrated in figure 2. However, there exists four non-magnetic states that preserve s and should not be omitted $\frac{1}{\sqrt{2}}(|c^- d^z\rangle - i|c^+ d^y\rangle)$, $\frac{1}{\sqrt{2}}(|c^- d^y\rangle + i|c^+ d^z\rangle)$, $\frac{1}{\sqrt{2}}(|c^+ d^x\rangle + |c^- d^z\rangle)$ and $\frac{1}{\sqrt{2}}(|c^+ d^z\rangle - |c^- d^x\rangle)$. Note that this states are not time reversal invariant. Finally we end up with twelve non-magnetic states that preserve s .

Table 4. Eigenvalues of quartet (middle row) and doublet states are presented.

s^2	s	m	Eigenstates	Label	$\hat{\sigma}_1 \cdot \hat{S}_2$
$\frac{15}{4}$	$\frac{3}{2}$	$\pm \frac{3}{2}$	$ c^\pm d^\pm\rangle$	$ Q^{3\pm}\rangle$	$\frac{1}{2}$
$\frac{15}{4}$	$\frac{3}{2}$	$\pm \frac{1}{2}$	$\frac{1}{\sqrt{3}}(c^\mp d^\pm\rangle + \sqrt{2} c^\pm d^0\rangle)$	$ Q^\pm\rangle$	$\frac{1}{2}$
$\frac{3}{4}$	$\frac{1}{2}$	$\pm \frac{1}{2}$	$\frac{1}{\sqrt{3}}(\sqrt{2} c^\mp d^+\rangle - c^\pm d^0\rangle)$	$ D^\pm\rangle$	-1

3.4. Spin-half trimer

This system is analogous to the one discussed in the previous Section, where the total spin quantum number takes the values $s = \frac{1}{2}, \frac{3}{2}$.

In this case the doublet level consists of twelve eigenstates. We assume six of them as a general, which can be used to construct the remaining ones, see table 5. This is not unexpected, we have three couples and therefore three pairs of doublet states which are local singlet states. Clearly, for all α we have

Table 5. Quartet and doublet states of a three spin-half cluster together with the eigenvalues of all bilinear forms are presented.

s^2	s	m	Eigenstates	Label	$\hat{\sigma}_1 \cdot \hat{\sigma}_2$	$\hat{\sigma}_1 \cdot \hat{\sigma}_3$	$\hat{\sigma}_2 \cdot \hat{\sigma}_3$
$\frac{15}{4}$	$\frac{3}{2}$	$\pm \frac{3}{2}$	$ c^\pm c^\pm c^\pm\rangle$	$ Q^{3\pm}\rangle$	$\frac{1}{4}$	$\frac{1}{4}$	$\frac{1}{4}$
$\frac{15}{4}$	$\frac{3}{2}$	$\pm \frac{1}{2}$	$\frac{1}{\sqrt{3}}(c^- c^\pm c^+\rangle + c^+ c^\pm c^-\rangle + c^\pm c^\mp c^\pm\rangle)$	$ Q^\pm\rangle$	$\frac{1}{4}$	$\frac{1}{4}$	$\frac{1}{4}$
$\frac{3}{4}$	$\frac{1}{2}$	$\pm \frac{1}{2}$	$\frac{1}{\sqrt{2}}(c^+ c^- c^\pm\rangle - c^- c^+ c^\pm\rangle)$	$ D_{12}^\pm\rangle$	$-\frac{3}{4}$	$-$	$-$
$\frac{3}{4}$	$\frac{1}{2}$	$\pm \frac{1}{2}$	$\frac{1}{\sqrt{2}}(c^+ c^\pm c^-\rangle - c^- c^\pm c^+\rangle)$	$ D_{13}^\pm\rangle$	$-$	$-\frac{3}{4}$	$-$
$\frac{3}{4}$	$\frac{1}{2}$	$\pm \frac{1}{2}$	$\frac{1}{\sqrt{2}}(c^\pm c^+ c^-\rangle - c^\pm c^- c^+\rangle)$	$ D_{23}^\pm\rangle$	$-$	$-$	$-\frac{3}{4}$

$(\hat{\sigma}_i^\alpha + \hat{\sigma}_j^\alpha)|D_{ij}^\pm\rangle = 0$ and thus the eigenvalues $(\hat{\sigma}_1 \cdot \hat{\sigma}_3 + \hat{\sigma}_2 \cdot \hat{\sigma}_3)|D_{12}^\pm\rangle = 0|D_{12}^\pm\rangle$, $(\hat{\sigma}_1 \cdot \hat{\sigma}_2 + \hat{\sigma}_2 \cdot \hat{\sigma}_3)|D_{13}^\pm\rangle = 0|D_{13}^\pm\rangle$, as well as $(\hat{\sigma}_1 \cdot \hat{\sigma}_2 + \hat{\sigma}_1 \cdot \hat{\sigma}_3)|D_{23}^\pm\rangle = 0|D_{23}^\pm\rangle$. Furthermore $\frac{1}{\sqrt{2}}(|D_{12}^+\rangle + |D_{13}^+\rangle) = \frac{1}{\sqrt{6}}(|c^+ c^+ c^-\rangle + |c^+ c^- c^+\rangle - 2|c^- c^+ c^+\rangle)$, is an eigenstate of the operators $(\hat{\sigma}_2 \cdot \hat{\sigma}_3)$ and $(\hat{\sigma}_1 \cdot \hat{\sigma}_2 + \hat{\sigma}_1 \cdot \hat{\sigma}_3)$ with eigenvalue $\frac{1}{4}$ and -1 , respectively. The total magnetic quantum number is $m = \frac{1}{2}$ and the correlators take the values $\langle \hat{\sigma}_1 \cdot \hat{\sigma}_2 \rangle = -\frac{1}{2}$, $\langle \hat{\sigma}_1 \cdot \hat{\sigma}_3 \rangle = -\frac{1}{2}$ and $\langle \hat{\sigma}_2 \cdot \hat{\sigma}_3 \rangle = \frac{1}{4}$. On the other hand, the eigenstate with the same eigenvalue and $m = -\frac{1}{2}$ is $\frac{1}{\sqrt{2}}(|D_{12}^-\rangle + |D_{13}^-\rangle) = \frac{1}{\sqrt{6}}(|c^- c^- c^+\rangle + |c^- c^+ c^-\rangle - 2|c^+ c^- c^-\rangle)$. Therefore, the system has in

total sixteen non-magnetic states that preserve s . Moreover, there are eighteen mixed states. For instance, in order to describe the system in which the spins $\hat{\sigma}_1$ and $\hat{\sigma}_2$ pair into a quadrupole we can use either of the sixth states $|q^\alpha c^\pm\rangle$.

4. Mixed four spin cluster

We consider a four spin cluster, with alternating spin- $\frac{1}{2}$ and spin-1 spins. The maximum number of eigenstates per level is seven, forming the septet group $\{|\mathcal{S}^{3\pm}\rangle, |\mathcal{S}^{2\pm}\rangle, |\mathcal{S}^\pm\rangle, |\mathcal{S}^0\rangle\}$. We also have seven groups of quintet states $\{|\mathcal{Q}_i^{2\pm}\rangle, |\mathcal{Q}_i^\pm\rangle, |\mathcal{Q}_i^0\rangle\}_{i=1}^7$, seven groups of triplet states $\{|T_i^\pm\rangle, |T_i^0\rangle\}_{i=1}^7$ and one singlet state. Hence the cluster exhibits sixty four unique eigenstates. Among all the magnetic states we have fifteen non-magnetic states satisfying (2), that describe quantum collective multipoles. The other forty eight eigenvectors can be used to construct the remaining non-magnetic multipole states that preserve s , but only thirty are unique. For example, the eigenvectors $|1, q_1^x\rangle = \frac{1}{\sqrt{2}}(|T_1^+\rangle - |T_1^-\rangle)$, $|1, q_1^y\rangle = \frac{1}{\sqrt{2}}(|T_1^+\rangle + |T_1^-\rangle)$ and $|1, q_1^z\rangle = -i|T_1^0\rangle$ are non-magnetic states with zero eigenvalues. They also share the eigenvalues of the first triplet state shown in table 6. The representation of the components of the triplet $|T_1\rangle$ group

Table 6. Septet, quintet, triplet and singlet eigenstates and the corresponding eigenvalues for the bilinear forms (fourth and fifth column) together with $\hat{M}$, permutation operators and composition operators $(\hat{S}, \hat{M}) = (\hat{S}_2 \cdot \hat{S}_4 + \hat{M})$, $(\hat{\sigma}, \hat{M}) = (\hat{\sigma}_1 \cdot \hat{\sigma}_3 + \hat{M})$ and $(\hat{\sigma}, \hat{S}, \hat{M}) = (\hat{\sigma}_1 \cdot \hat{\sigma}_3 + \hat{S}_2 \cdot \hat{S}_4 + \hat{M})$.

	s^2	s	m	$\hat{\sigma}_1 \cdot \hat{\sigma}_3$	$\hat{S}_2 \cdot \hat{S}_4$	$\hat{M}$	$(\hat{S}, \hat{M})$	$(\hat{\sigma}, \hat{M})$	$(\hat{\sigma}, \hat{S}, \hat{M})$	$\hat{P}_{13}$	$\hat{P}_{24}$
$ \mathcal{S}^0\rangle$	12	3	0	$\frac{1}{4}$	1	2	3	$\frac{9}{4}$	$\frac{13}{4}$	1	1
$ \mathcal{Q}_1^0\rangle$	6	2	0	$-\frac{3}{4}$	1	0	1	$-\frac{3}{4}$	$\frac{1}{4}$	-1	1
$ \mathcal{Q}_2^{2+}\rangle$	6	2	2	-	-	-	-	-	$\frac{1}{4}$	-	1
$ T_1^0\rangle$	2	1	0	$\frac{1}{4}$	-2	0	-2	$\frac{1}{4}$	$-\frac{7}{4}$	1	1
$ T_2^0\rangle$	2	1	0	$-\frac{3}{4}$	-1	0	-1	$-\frac{3}{4}$	$-\frac{7}{4}$	-1	-1
$ T_3^+\rangle$	2	1	1	$\frac{1}{4}$	-	-	-2	-	$-\frac{7}{4}$	1	-
$ S\rangle$	0	0	0	$\frac{1}{4}$	-1	-2	-3	$-\frac{7}{4}$	$-\frac{11}{4}$	1	-1

is $|T_1^+\rangle = (|c^+d^+c^+d^-\rangle + |c^+d^-c^+d^+\rangle - |c^+d^0c^+d^0\rangle)$, $|T_1^-\rangle = (|c^-d^-c^-d^-\rangle + |c^-d^-c^-d^-\rangle - |c^-d^0c^-d^0\rangle)$ and $|T_1^0\rangle = \frac{1}{\sqrt{6}}(|c^+d^+c^-d^-\rangle + |c^+d^-c^-d^+\rangle + |c^-d^+c^+d^-\rangle + |c^-d^-c^+d^+\rangle - |c^+d^0c^-d^0\rangle - |c^-d^0c^+d^0\rangle)$. Also, we have $(\hat{\sigma}_1^\alpha + \hat{\sigma}_3^\alpha)|1, q_1^\alpha\rangle = 0|1, q_1^\alpha\rangle$ and $(\hat{S}_2^\alpha + \hat{S}_4^\alpha)|1, q_1^\alpha\rangle = 0|1, q_1^\alpha\rangle$. Therefore, we have two local multipoles. For example, the SU(3) spin-one subspace representation $|1, q_1^z\rangle = -\frac{i}{\sqrt{6}}\sum_\alpha(|c^+d^\alpha c^-d^\alpha\rangle + |c^-d^\alpha c^+d^\alpha\rangle)$, corresponding to a triplet paired spin-half spins forming a quadrupole and two spin-one spins associated to a local singlet state, see table 1 and equation (3). Further, the state $|\mathcal{Q}_1^0\rangle = \frac{1}{\sqrt{12}}(|c^+d^+c^-d^-\rangle - |c^+d^-c^-d^+\rangle - |c^-d^+c^+d^-\rangle - |c^-d^-c^+d^+\rangle + 2|c^+d^0c^-d^0\rangle - 2|c^-d^0c^+d^0\rangle)$, is also a time reversal invariant non-magnetic state. On one hand spin-one spins formed a local quadrupole, see table 2, on the other the two half spins define the local singlet, see table 1. Getting back again to table 2 we see that the non-magnetic state $|T_2^0\rangle = \frac{1}{\sqrt{4}}(|c^+d^+c^-d^-\rangle - |c^+d^-c^-d^+\rangle - |c^-d^+c^+d^-\rangle + |c^-d^-c^+d^+\rangle)$ corresponds to a similar case. The spin-1 spins formed a couple being in a $m = 0$ triplet and the spin-half paired in multipole described by a singlet. We further have $(\hat{\sigma}_1 \cdot \hat{S}_2 + \hat{\sigma}_1 \cdot \hat{S}_4)|T_2^0\rangle = 0|T_2^0\rangle$ and $(\hat{\sigma}_3 \cdot \hat{S}_2 + \hat{\sigma}_3 \cdot \hat{S}_4)|T_2^0\rangle = 0|T_2^0\rangle$. The singlet state of the cluster $|S\rangle = \frac{1}{\sqrt{12}}(|c^+d^+c^-d^-\rangle - |c^+d^-c^-d^+\rangle + |c^-d^+c^+d^-\rangle - |c^-d^-c^+d^+\rangle - \sqrt{2}|c^-d^+c^-d^0\rangle + \sqrt{2}|c^-d^0c^-d^+\rangle + \sqrt{2}|c^+d^-c^+d^0\rangle - \sqrt{2}|c^+d^0c^+d^-\rangle)$, refers to a two local triplet states, see table 6. Besides, for identical spins $i = 1, 3$ and $j = 2, 4$, either of the

bilinear forms $\hat{\sigma}_i \cdot \hat{S}_j |S\rangle \neq 0 |S\rangle$, while $(\hat{\sigma}_1 \cdot \hat{S}_2 + \hat{\sigma}_1 \cdot \hat{S}_4) |S\rangle = -1 |S\rangle$, $(\hat{\sigma}_3 \cdot \hat{S}_2 + \hat{\sigma}_3 \cdot \hat{S}_4) |S\rangle = -1 |S\rangle$ and $(\hat{S}_2^z + \hat{S}_4^z) |S\rangle \neq 0 |S\rangle$. Therefore, this is the only level on which all the spins are coupled, forming a multipole. It is also interesting to mention that some of the states which are not eigenstates of the operators $\hat{\sigma}_1 \cdot \hat{\sigma}_3$ and $\hat{S}_2 \cdot \hat{S}_4$ can be eigenstates of the permutation operators associated to these pairs. This particular property can be seen by presenting the vector $|\mathcal{Q}_2^{2+}\rangle = \frac{1}{\sqrt{13}}(2|c^+d^+c^-d^+\rangle - 4|c^-d^+c^+d^+\rangle + \frac{1}{\sqrt{2}}|c^+d^+c^+d^0\rangle + \frac{1}{\sqrt{2}}|c^+d^0c^+d^+\rangle)$, which is an eigenstate of $\hat{P}_{24}$, but not of $\hat{P}_{13}$. So concerning the relation (4), in some states we are not able to determine the correlation between quadrupoles. This is the case with the triplet $|T_3^+\rangle = \frac{1}{\sqrt{4}}(|c^-d^-c^-d^+\rangle - |c^+d^+c^+d^-\rangle + |c^+d^0c^+d^0\rangle - \frac{1}{\sqrt{2}}|c^+d^+c^-d^0\rangle - \frac{1}{\sqrt{2}}|c^-d^0c^+d^+\rangle)$. These entanglement states are a sign of frustration. For a chosen convenient microscopic model they may appear as a ground states describing a frustrated system, where neither of the known orders take place.

5. Summary

We have studied the quantum properties of some basic spin clusters revealing the fundamental essence of the spin coupling. An example of this collective phenomena is shown in figure 1 illustrating three different multipole moments. It is clear that by the treatment of quantum mechanic, in a spin system with half integer s only the dipole moments survived. In the boson systems, on the other hand, the existence of multipoles as a quantum occurrence naturally emerge.

It is really fascinating, but not unexpected, that we have non-zero multiple moments even when $s = 0, \frac{1}{2}$, showing that unlike the single spin space, a spin clusters with the same spin quantum number possess additional symmetries. The spin-half dimer is a bright example of this collective phenomena. A coupled fluctuations are shown in figure 1 illustrating three different multipole moments. The discussed different range of pairing (entangled spins) are a simple example of a valence bond. As we have seen, the formation of octupole includes partially developed local dipole moments. Therefore, this property may play an important role for the rearranging of the nearest valence bonds in spin liquids and for the experimental observation of multipolar order.

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