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Aufgabenblatt 13

13.1 Produktreduktion

Zeigen Sie, dass für C_{3v} gilt:

a. $A_2 \times E = E$;

b. $E \times E = A_1 + A_2 + E$.

13.2 Energieeigenwerte des Spindreiecks im Heisenbergmodell mittels irreduzibler Tensoroperatoren

Arbeiten Sie folgenden Auszug aus dem Buch von Boris Tsukerblatt durch und bestimmen Sie die Energieeigenwerte eines Spindreiecks im Heisenbergmodell mittels irreduzibler Tensoroperatoren.
Sie können ebenfalls den Artikel von Gatteschi und Pardi (Gazz. Chim. Ital. **123** (1993) 231) nutzen, allerdings ist dieser voller Tippfehler. Wer findet die meisten?

where the rank K of the tensor product obeys the vector rule: $K = \kappa_1 + \kappa_2$, $\kappa_1 + \kappa_2 - 1, \ldots, |\kappa_1 - \kappa_2|$.

The exchange Hamiltonian of a trimeric compound with Hamiltonian (13.26) can be written in tensor form as

$$\hat{H} = 2\sqrt{\tfrac{1}{3}}[J_{12}\{\hat{\mathbf{S}}^{(1)}(1)\otimes\hat{\mathbf{S}}^{(1)}(2)\}^{(0)} + J_{13}\{\mathbf{S}^{(1)}(1)\otimes\mathbf{S}^{(1)}(3)\}^{(0)} + J_{23}\{\hat{\mathbf{S}}^{(1)}(2)\otimes\hat{\mathbf{S}}^{(1)}(3)\}^{(0)}] \qquad (13.65)$$

where $\hat{\mathbf{S}}^{(1)}_{\mu}(i)$ $(i = 1, 2, 3)$ are the first rank irreducible tensors acting in the spin-spaces of individual ions. We have used the relations (arising from (13.63) and (13.64)) between the scalar product of vector operators $\mathbf{S}_i$ and the scalar convolution of first order irreducible tensors $\hat{\mathbf{S}}^{(1)}_{\mu}(i)$

$$\mathbf{s}_1\mathbf{s}_2 = -\sqrt{3}\left\{\hat{\mathbf{S}}^{(1)}(1)\otimes\hat{\mathbf{S}}^{(1)}(2)\right\}^{(0)}, \quad \text{etc.}$$

Calculations of the matrix elements of the Hamiltonian (13.65) (as well as the matrix elements of more general spin-coupling operators) can be performed by means of the so-called *recoupling procedure*.

Let us start with a dimeric system consisting of two ions i and j with spins s_i and s_j and consider the matrix elements of the two-particle tensor operator $\hat{\mathbf{Q}}^{\kappa_{ij}}_{\mu_{ij}}$ ("particles" in this context are the ions with the total spins s_i and s_j):

$$\hat{\mathbf{Q}}^{(\kappa_{ij})}_{\mu_{ij}} = \left\{\hat{\mathbf{S}}^{(\kappa_i)}(i)\otimes\hat{\mathbf{S}}^{(\kappa_j)}(j)\right\}^{(\kappa_{ij})}_{\mu_{ij}} = \sum_{\mu_i\mu_j}\hat{\mathbf{S}}^{(\kappa_i)}_{\mu_i}(i)\hat{\mathbf{S}}^{(\kappa_j)}_{\mu_j}(j)\langle\kappa_i\mu_i\kappa_j\mu_j|\kappa_{ij}\mu_{ij}\rangle \qquad (13.66)$$

In (13.66) $\hat{\mathbf{S}}^{(\kappa_i)}_{\mu_i}(i)$ and $\hat{\mathbf{S}}^{(\kappa_j)}_{\mu_j}(j)$ are the irreducible tensor operators acting in the spin spaces of ions i and j respectively. Matrix elements of these one-particle operators are expressed by means of the Wigner–Eckart theorem

$$\langle s_i m_i|\hat{\mathbf{S}}^{(\kappa_i)}_{\mu_i}|s_i m_i'\rangle = (-1)^{s_i - m_i}\langle s_i\|\hat{\mathbf{S}}^{(\kappa_i)}\|s_i\rangle\begin{pmatrix} s_i & \kappa_i & s_i \\ -m_i & \mu_i & m_i' \end{pmatrix}. \qquad (13.67)$$

The reduced matrix elements in (13.67) for $\kappa_i = 0, 1$ and 2 are:

$$\langle s\|\hat{\mathbf{S}}^{(0)}\|s\rangle = (2s+1)^{1/2},$$

$$\langle s\|\hat{\mathbf{S}}^{(1)}\|s\rangle = [s(s+1)(2s+1)]^{1/2},$$

$$\langle s\|\mathbf{S}^{(2)}\|s\rangle = (1/\sqrt{6}[2s(2s+3)(2s+2)(2s+1)(2s-1)]^{1/2}. \qquad (13.68)$$

While calculating the matrix elements of $\hat{\mathbf{Q}}^{(\kappa_{ij})}_{\mu_{ij}}$ let us use as the basis set wavefunctions of two interacting ions belonging to the full spins $S_{ij} = s_i + s_j$, $s_i + s_j - 1, \ldots |s_i - s_j|$ and to the projections m_{ij}:

$$|s_i s_j S_{ij} m_{ij}\rangle = \sum_{m_i, m_j}|s_i m_i\rangle|s_j m_j\rangle\langle s_i m_i s_j m_j|s_{ij} m_{ij}\rangle. \qquad (13.69)$$

Applying the Wigner–Eckart theorem (6.4) to the irreducible tensor $\hat{\mathbf{Q}}^{(\kappa_{ij})}_{\mu_{ij}}$ we obtain:

$$\langle s_i s_j S_{ij} m_{ij} | \hat{\mathbf{Q}}^{(\kappa_{ij})}_{\mu_{ij}} | s_i s_j S'_{ij} m'_{ij} \rangle = \frac{(-1)^{2\kappa_{ij}}}{(2s_{ij}+1)^{1/2}} \langle s_i s_j S_{ij} \| \hat{\mathbf{Q}}^{(\kappa_{ij})} \| s_i s_j S'_{ij} \rangle$$
$$\times \langle S_{ij} m_{ij} | S'_{ij} m'_{ij} \kappa_{ij} \mu_{ij} \rangle \equiv (-1)^{s_{ij}-m_{ij}} \langle s_i s_j S_{ij} \| \hat{\mathbf{Q}}^{(\kappa_{ij})} \| s_i s_j S'_{ij} \rangle \begin{pmatrix} s_{ij} & \kappa_{ij} & S'_{ij} \\ -m_{ij} & \mu_{ij} & m'_{ij} \end{pmatrix}. \tag{13.70}$$

The quantity $\langle s_i s_j S_{ij} \| \hat{\mathbf{Q}}^{(\kappa_{ij})} \| s_i s_j S'_{ij} \rangle$ is the so-called two-particle reduced matrix element. Using the Clebsch–Gordan expansion for $\hat{\mathbf{Q}}^{(\kappa_{ij})}_{\mu_{ij}}$ (13.66) and for basis sets (13.69) one can express the two-particle reduced matrix element in terms of the one-particle ones [2, 62]:

$$\langle s_i s_j S_{ij} \| \{\hat{\mathbf{S}}^{(\kappa_i)}(i) \otimes \hat{\mathbf{S}}^{(\kappa_j)}(j)\}^{(\kappa_{ij})} \| s_i s_j S'_{ij} \rangle = [(2S_{ij}+1)(2\kappa_{ij}+1)(2S'_{ij}+1)]^{1/2}$$
$$\times \begin{Bmatrix} \kappa_{ij} & S_{ij} & S'_{ij} \\ \kappa_i & S_i & S_i \\ \kappa_j & S_j & S_j \end{Bmatrix} \langle s_i \| \hat{\mathbf{S}}^{(\kappa_i)}(i) \| s_i \rangle \langle s_j \| \hat{\mathbf{S}}^{(\kappa_j)}(j) \| s_j \rangle. \tag{13.71}$$

In (13.71) $\{\vdots \ \vdots \ \vdots\}$ is the $9j$-symbol defined in Section 13.3.3 and $\langle s_i \| \hat{\mathbf{S}}^{(\kappa_i)}(i) \| s_i \rangle$ is the reduced matrix elements of the irreducible tensor operators $\hat{\mathbf{S}}^{(\kappa_i)}_{\mu}(i)$ (equation (13.68). *Equation* (13.71) *allows us to express a matrix element of the two-particle operator involving spin variables of two interacting subsystems in terms of one-particle matrix elements relating to each system* (*recoupling*). It should be stressed that in contrast to the illustrative example of Section 13.3.2 no wavefunctions in the explicit form have been used.

Now we can proceed to the consideration of a more complicated case of a trimeric system. The Hamiltonian (13.63) can be considered as a particular case of the generalized spin-Hamiltonian of the interaction of three ions with spins s_1, s_2, s_3:

$$\hat{H}^{(3)} = \sum_{\kappa} (2\kappa+1)^{1/2} \{c^{(\kappa)}$$
$$(\kappa_1 \kappa_2 \kappa_{12} \kappa_3) \otimes \{\{\hat{\mathbf{S}}^{(\kappa_1)}(1) \otimes \hat{\mathbf{S}}^{(\kappa_2)}(2)\}^{(\kappa_{12})} \otimes \hat{\mathbf{S}}^{(\kappa_3)}(3)\}^{(\kappa)}\}^{(0)}, \tag{13.72}$$

As earlier in (13.72), $\hat{\mathbf{S}}^{(\kappa_i)}(i)$ is the irreducible tensor of rank κ_i acting in the spin-space of i-th ion, $0 \le \kappa_i \le 2S_i, \kappa_{12} = \kappa_1 + \kappa_2, \kappa_1 + \kappa_2 - 1, \ldots, |\kappa_1 - \kappa_2|$, $c^{(\kappa)}(\ldots)$ are the numerical parameters. Hamiltonian (13.72) involves three-particle interactions and the original Hamiltonians (13.26) and (13.65) can be easily deduced from (13.72). Actually providing for example, $\kappa_1 = \kappa_2 = 1, \kappa_3 = 0, \kappa_{12} = 0$ and comparing (13.72) and (13.26) we obtain

$$c^{(0)}(1\,1\,0\,0)\{\hat{\mathbf{S}}^{(1)}(1) \otimes \hat{\mathbf{S}}^{(1)}(2)\}^{(0)} \equiv -2J_{12}\mathbf{s}_1\mathbf{s}_2, \tag{13.73}$$

so that

$$c^{(0)}(1\,1\,0\,0) = 2\sqrt{3}J_{12}.$$

Applying the recoupling procedure to the three particle operator

$$\hat{\mathbf{Q}}_{\mu}^{(\kappa)} = \{\{\hat{\mathbf{S}}^{(\kappa_1)}(1)\otimes\hat{\mathbf{S}}^{(\kappa_2)}(2)\}^{(\kappa_{12})}\otimes\hat{\mathbf{S}}^{(\kappa_3)}(3)\}_{\mu}^{(\kappa)}, \tag{13.74}$$

one can obtain the following result for the reduced matrix element in the basis set $|s_1s_2(S_{12})s_3SM\rangle$ of a trimeric cluster consisting of spins s_1, s_2, s_3:

$$\begin{aligned}
&\langle s_1s_2(S_{12})s_3S\|\hat{\mathbf{Q}}^{(\kappa)}\|s_1s_2(S'_{12})s_3S'\rangle \\
&= [(2S+1)(2S'+1)(2\kappa+1)(2S_{12}+1)(2S'_{12}+1)(2\kappa_{12}+1)]^{1/2} \\
&\quad\times \begin{Bmatrix} S_{12} & S'_{12} & \kappa_{12} \\ s_3 & s_3 & \kappa_3 \\ S & S' & \kappa \end{Bmatrix} \begin{Bmatrix} s_1 & s_1 & \kappa_1 \\ s_2 & s_2 & \kappa_2 \\ S_{12} & S'_{12} & \kappa_{12} \end{Bmatrix} \\
&\quad\times \langle s_1\|\hat{\mathbf{S}}^{(\kappa_1)}\|s_1\rangle\langle s_2\|\hat{\mathbf{S}}^{(\kappa_2)}\|s_2\rangle\langle s_3\|\hat{\mathbf{S}}^{(\kappa_3)}\|s_3\rangle.
\end{aligned} \tag{13.75}$$

In the case of isotropic Heisenberg exchange under consideration ($\kappa = 0$ and one of $\kappa_i = 0$ in (13.74)) the $9j$-symbols in (13.75) reduce to $6j$-symbols (Section 13.3.3). Using (13.75) one can easily obtain the following matrix elements of three operator terms of exchange Hamiltonian (13.26) [62, 87]:

$$\begin{aligned}
&\langle s_1s_2(S_{12})s_3SM|\mathbf{s}_1\mathbf{s}_2|s_1s_2(S'_{12})s_3S'M'\rangle \\
&\quad= \delta_{SS'}\delta_{MM'}\delta_{S_{12}S'_{12}}[S_{12}(S_{12}+1) - s_1(s_1+1) - s_2(s_2+1)]/2, \\
&\langle s_1s_2(S_{12})s_3SM|s_1s_3|\mathbf{s}_1\mathbf{s}_2(S'_{12})s_3S'M'\rangle \\
&\quad= \delta_{SS'}\delta_{MM'}(-1)^{s_1+s_2+s_3+S+1}[(2S_{12}+1)(2S'_{12}+1) \\
&\quad\times (2s_1+1)(s_1+1)s_1(2s_1+3)s_3(s_3+1)]^{1/2} \\
&\quad\times \begin{Bmatrix} S_{12} & S'_{12} & 1 \\ s_3 & s_3 & S \end{Bmatrix} \begin{Bmatrix} s_1 & s_1 & 1 \\ S'_{12} & S_{12} & s_2 \end{Bmatrix}, \\
&\langle s_1s_2(S_{12})s_3SM|\mathbf{s}_2\mathbf{s}_3|s_1s_2(S'_{12})s_3S'M\rangle \\
&\quad= \delta_{SS'}\delta_{MM'}(-1)^{S_{12}+S'_{12}+s_1+s_2+s_3+S+1}[(2S_{12}+1) \\
&\quad\times (2S'_{12}+1)s_1(s_1+1)(2s_1+1)s_3(s_3+1)(2s_3+1)]^{1/2} \\
&\quad\times \begin{Bmatrix} S_{12} & S'_{12} & 1 \\ s_3 & s_3 & S \end{Bmatrix} \begin{Bmatrix} S_{12} & S'_{12} & 1 \\ s_2 & s_2 & s_1 \end{Bmatrix}.
\end{aligned} \tag{13.76}$$

As pointed out in Section 13.3.1, isotropic exchange couples the states of the system with the same quantum numbers S and M in conformity with (13.76).