Kambe's Method for an isolated bowtie.

The Hamiltonian for the bow tie topology shown in Fig. 15 has Hamiltonian given by

$$\hat{\mathbf{H}} = -2J[\hat{\mathbf{S}}_1 \cdot \hat{\mathbf{S}}_2 + \hat{\mathbf{S}}_1 \cdot \hat{\mathbf{S}}_3 + \hat{\mathbf{S}}_1 \cdot \hat{\mathbf{S}}_4 + \hat{\mathbf{S}}_1 \cdot \hat{\mathbf{S}}_5] - 2J'[\hat{\mathbf{S}}_2 \cdot \hat{\mathbf{S}}_3 + \hat{\mathbf{S}}_4 \cdot \hat{\mathbf{S}}_5]$$

Define the following spin operators:

$$\hat{\mathbf{S}}_A = \hat{\mathbf{S}}_2 + \hat{\mathbf{S}}_3$$

$$\hat{\mathbf{S}}_B = \hat{\mathbf{S}}_4 + \hat{\mathbf{S}}_5$$

Taking the square of these terms gives:

$$\hat{\mathbf{S}}_A^2 = \hat{\mathbf{S}}_2^2 + \hat{\mathbf{S}}_3^2 + 2\hat{\mathbf{S}}_2 \cdot \hat{\mathbf{S}}_3$$

Therefore

$$2\hat{\mathbf{S}}_2 \cdot \hat{\mathbf{S}}_3 = \hat{\mathbf{S}}_A^2 - \hat{\mathbf{S}}_2^2 - \hat{\mathbf{S}}_3^2$$

Similarly

$$\hat{\mathbf{S}}_B^2 = \hat{\mathbf{S}}_4^2 + \hat{\mathbf{S}}_5^2 + 2\hat{\mathbf{S}}_4 \cdot \hat{\mathbf{S}}_5$$

gives

$$2\hat{\mathbf{S}}_4 \cdot \hat{\mathbf{S}}_5 = \hat{\mathbf{S}}_B^2 - \hat{\mathbf{S}}_4^2 - \hat{\mathbf{S}}_5^2$$

Now define the following spin operator

$$\hat{\mathbf{S}}_C = \hat{\mathbf{S}}_A + \hat{\mathbf{S}}_B$$

Expanding as above gives

$$\hat{\mathbf{S}}_C^2 = \hat{\mathbf{S}}_A^2 + \hat{\mathbf{S}}_B^2 + 2\hat{\mathbf{S}}_A \cdot \hat{\mathbf{S}}_B$$

Consequently

$$\hat{\mathbf{S}}_C^2 - \hat{\mathbf{S}}_A^2 - \hat{\mathbf{S}}_B^2 = 2(\hat{\mathbf{S}}_2 + \hat{\mathbf{S}}_3) \cdot (\hat{\mathbf{S}}_4 + \hat{\mathbf{S}}_5)$$

$$\hat{\mathbf{S}}_C^2 - \hat{\mathbf{S}}_A^2 - \hat{\mathbf{S}}_B^2 = 2[\hat{\mathbf{S}}_2 \cdot \hat{\mathbf{S}}_4 + \hat{\mathbf{S}}_3 \cdot \hat{\mathbf{S}}_4 + \hat{\mathbf{S}}_2 \cdot \hat{\mathbf{S}}_5 + \hat{\mathbf{S}}_3 \cdot \hat{\mathbf{S}}_5]$$

The terms in square brackets in the final equation are not required. They refer to the interaction between the corner atoms. If they were included, we would be treating the topology as a centred tetrahedron, this would have Hamiltonian:

$$\hat{\mathbf{H}} = -2J[\hat{\mathbf{S}}_1 \cdot \hat{\mathbf{S}}_2 + \hat{\mathbf{S}}_1 \cdot \hat{\mathbf{S}}_3 + \hat{\mathbf{S}}_1 \cdot \hat{\mathbf{S}}_4 + \hat{\mathbf{S}}_1 \cdot \hat{\mathbf{S}}_5] - 2J'[\hat{\mathbf{S}}_2 \cdot \hat{\mathbf{S}}_3 + \hat{\mathbf{S}}_4 \cdot \hat{\mathbf{S}}_5] - 2J''[\hat{\mathbf{S}}_2 \cdot \hat{\mathbf{S}}_4 + \hat{\mathbf{S}}_3 \cdot \hat{\mathbf{S}}_4 + \hat{\mathbf{S}}_2 \cdot \hat{\mathbf{S}}_5 + \hat{\mathbf{S}}_3 \cdot \hat{\mathbf{S}}_5]$$

The J'' refers to the long range cross terms.

Next we need to introduce the central atom. We proceed as before by first defining the spin operator

$$\hat{\mathbf{S}}_T = \hat{\mathbf{S}}_C + \hat{\mathbf{S}}_1$$

Then taking its square

$$\hat{\mathbf{S}}_T^2 = \hat{\mathbf{S}}_1^2 + \hat{\mathbf{S}}_C^2 + 2\hat{\mathbf{S}}_1 \cdot \hat{\mathbf{S}}_C$$

Thus

$$2\hat{\mathbf{S}}_1 \cdot [\hat{\mathbf{S}}_2 + \hat{\mathbf{S}}_3 + \hat{\mathbf{S}}_4 + \hat{\mathbf{S}}_5] = \hat{\mathbf{S}}_T^2 - \hat{\mathbf{S}}_1^2 - \hat{\mathbf{S}}_C^2$$

$$2[\hat{\mathbf{S}}_1 \cdot \hat{\mathbf{S}}_2 + \hat{\mathbf{S}}_1 \cdot \hat{\mathbf{S}}_3 + \hat{\mathbf{S}}_1 \cdot \hat{\mathbf{S}}_4 + \hat{\mathbf{S}}_1 \cdot \hat{\mathbf{S}}_5] = \hat{\mathbf{S}}_T^2 - \hat{\mathbf{S}}_1^2 - \hat{\mathbf{S}}_C^2$$

Substituting these results into the Hamiltonian for the centred tetrahedron gives

$$\hat{\mathbf{H}} = -2J[\hat{\mathbf{S}}_T^2 - \hat{\mathbf{S}}_1^2 - \hat{\mathbf{S}}_C^2] - J'[\hat{\mathbf{S}}_A^2 - \hat{\mathbf{S}}_2^2 - \hat{\mathbf{S}}_3^2] - J'[\hat{\mathbf{S}}_B^2 - \hat{\mathbf{S}}_4^2 - \hat{\mathbf{S}}_5^2] - 2J''[\hat{\mathbf{S}}_C^2 - \hat{\mathbf{S}}_A^2 - \hat{\mathbf{S}}_B^2]$$

The corresponding energies to this are then given by the expression:

$$E = -J[S_T(S_T+1) - S_C(S_C+1) - S_1(S_1+1)] - J'[S_A(S_A+1) + S_B(S_B+1) - S_2(S_2+1) - S_3(S_3+1) - S_4(S_4+1) - S_5(S_5+1)] - J''[S_C(S_C+1) - S_A(S_A+1) - S_B(S_B+1)]$$

The following simplifications are then made:

$S_1 = S_2 = S_3 = S_4 = S_5 = S$

And $J'' = 0$

Then

$$E = -J[S_T(S_T+1) - S_C(S_C+1) - S(S+1)] - J'[S_A(S_A+1) + S_B(S_B+1) - 4S(S+1)]$$

All of the possible spin state configurations and energies were calculated these are shown in the table (see ‘bowtie energies’ for energy levels for the isosceles bowtie model).

These were then substituted into the Van Vleck Equation

$$\chi = \frac{N_A \mu_B^2 g^2}{3k_B T} \frac{\sum_{S_T} S_T(S_T+1)(2S_T+1)\exp(-E(S_{T,}S_A, S_B, S_C, S)/k_B T)}{\sum_{S_T} (2S_T+1)\exp(-E(S_{T,}S_A, S_B, S_C, S)/k_B T)}$$