Articles

Alternating Chains with Ferromagnetic and Antiferromagnetic Interactions. Theory and Magnetic Properties

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In this paper we focus on the thermodynamical properties of the $S = {}^1/_2$ Heisenberg chain with alternating antiferromagnetic and ferromagnetic exchange interactions, J_1 and J_2. In the first step, the magnetic and specific heat properties of this system have been calculated as function of $\alpha = J_2/|J_1|$ from a general numerical procedure based on closed spin chains of increasing length. A distinctive behavior characterized by a maximum in the χT vs T plot is predicted when the ferromagnetic interaction is the dominant one (i.e., for $\alpha > 1$). Conversely, antiferromagnetic-like behaviors are predicted when the antiferromagnetic interaction dominates (i.e., for $\alpha < 1$). With respect to the magnetic specific heat, two rounded maxima can be distinguished in the C_p/R vs T plot for sufficiently different exchange values and dominant ferromagnetic exchange, which have been associated with the two kinds of exchange interactions. The magnetic susceptibility results derived from the model have been conveniently fitted to rational unified expressions. These expressions were used to describe the magnetic behaviors of two copper(II) complexes exhibiting alternating chain structures: The compound Cu(TIM)$CuCl_4$ (TIM = 2,3,9,-10-tetramethylcyclo-1,4,8,11-tetraazatetradecane-1,3,8,10-tetraene), which shows dominant ferromagnetic exchange ($J_1/k = -7.5$ K; $\alpha = 3$), and the compound [Cu(bpym)$(OH)_2(NO_3)_2$]·$2H_2O$ (bpym = 2,2′ bipyrimidine), which exhibits dominant antiferromagnetic exchange ($J_1/k = -200$ K; $\alpha = 0.75$).

Introduction

One dimensional (1D) magnetic systems provide excellent examples on which the development of suitable theoretical models affords a better understanding of the exchange interactions in extended lattices. In the last two decades this area has been characterized by a close interaction between inorganic chemists and physicists.[1] More recently, the advent of organic/molecular-based magnets has enriched this field leading to a very productive interplay between organic and inorganic chemists.[2] As a result, new classes of molecular magnetic materials, often displaying low dimensional structures, have been discovered which require the development of new theoretical models in order to correlate crystal and molecular structures with magnetic properties. In this work we focus on systems containing simultaneously ferro- and antiferromagnetic exchange interactions. Several examples of compounds of this kind have been recently reported in both organic and inorganic chemistries although no theoretical model is available for analysis of the magnetic data. However, there are at least two reasons that justify the theoretical effort in this sense: (1) Often these systems have controversial ground spin states which depend on the relative magnitude and topology of the two exchange interactions.[3] (2) A detailed knowledge of the value of the two exchange parameters and the subsequent correlation with the structure is of particular importance in organic chemistry in the design and construction of new high-spin organic polymers.[4]

The simplest case showing alternating exchange interactions, J_1 and J_2, is that encountered in a linear chain of spins $S = {}^1/_2$. The restricted dimensionality of such a system permits a quantitative estimate of the magnetic properties as a function of J_1 and J_2. The case for a positive alternating parameter $\alpha = J_2/J_1$ (i.e. antiferromagnetic/antiferromagnetic (AF/AF) system) has been extensively studied in recent years[5,6] due to its similarity with one-dimensional materials that undergo a spin−Peierls transition.[7] Little theoretical work has been developed for $\alpha < 0$ (i.e. ferromagnetic/antiferromagnetic (F/AF) system). Preliminary magnetic results on several inorganic compounds showing exchange alternation were recently reported by Hatfield et al.[8] In this paper we focus on the thermodynamical properties of the alternating F/AF Heisenberg chain. From a numerical procedure based on closed spin chains of increasing length, the magnetic and specific heat properties of this system are

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(1) (a) *Extended Linear Chain Compounds*; Miller, J. S., Ed.; Plenum: New York, 1983; Vol. 3. (b) *Organic and Inorganic Low Dimensional Crystalline Materials*; Delhaes, P., Drillon, M., Eds.; NATO ASI Series 168; Plenum: New York, 1987.
(2) *Magnetic Molecular Materials*; Gatteschi, D., Kahn, O., Miller, J. S., Palacio, F., Eds.; NATO ASI Series 198; Plenum: New York, 1991.
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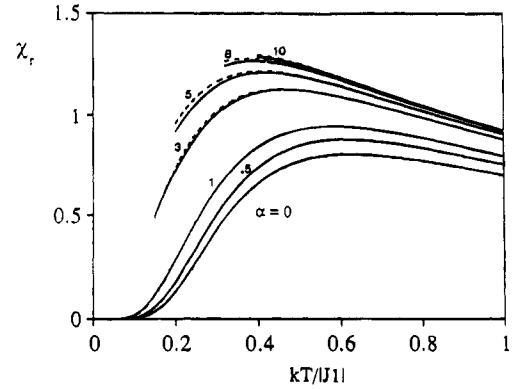

Figure 1. Thermal dependence of the reduced susceptibility of $N = 6$ (dotted line) and $N = 7$ (solid line) rings for different values of the alternating parameter α.

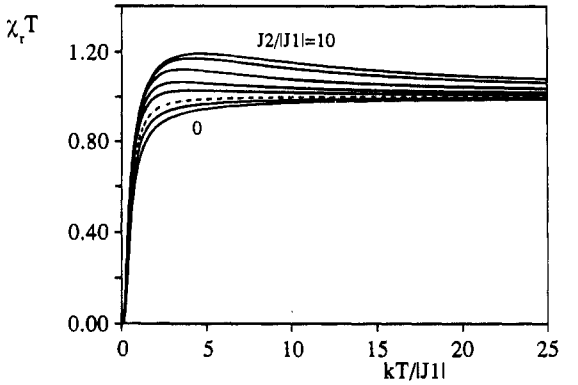

Figure 2. Thermal dependence of the reduced product χT of the N = 7 ring for different values of the alternating parameter α. The dashed curve corresponds to α = 1. Above and below this curve are situated the curves for α > 1 (2, 3, 5, 8, 10) and α < 1 (0, 0.5).

calculated and fitted (in the former case) to closed-form expressions. These are very convenient to fit the data of real compounds exhibiting alternating chain structures.

Model

We have developed a general computing program for solving the problem of a Heisenberg chain containing $2N$ identical spins with spin quantum number S. The model can take into account alternating nearest-neighbor interactions, J_1 and J_2, which can be anisotropic, and a next-nearest neighbor interaction, J_3, that can also be anisotropic. Further, a term considering the local anisotropy, D, can also be introduced.[9] The principal aim of the program is to compute numerically the parallel and perpendicular susceptibilities. Other thermodynamical properties such as the specific heat can be calculated at the same time. Closed chains are considered since then some additional symmetries in the final Hamiltonian, as for example spin space and geometrical symmetries, can be introduced. As shown before, these symmetries drastically reduce the size of the matrices to be diagonalized and the required computing time.[10,11] A more detailed description of the program is described in the Appendix.

In the present case the spin is $S = {}^1/_2$, J_3 is ruled out, and J_1 and J_2 are assumed to be isotropic and of different sign. J_1 is negative and corresponds to the antiferromagnetic coupling, while J_2 is positive and corresponds to the ferromagnetic one. The exchange hamiltonian can be written as

$$H = -\sum_{i=1}^{N-1} [J_1 \mathbf{S}_{2i} \cdot \mathbf{S}_{2i+1} + J_2 \mathbf{S}_{2i} \cdot \mathbf{S}_{2i-1}] \qquad (1)$$

The calculations are limited up to rings of 14 spins ($N = 7$) using a IBM 3090/2VF machine. Notice that previous calculations on alternating chains were limited to $N = 5$ in the AF/AF case,[6] and to $N = 6$ in the F/AF one.[8]

Magnetic Properties

All the magnetic curves are plotted in terms of reduced (nondimensional) quantities. The reduced temperature is defined as $T_r = kT/|J_1|$ and the reduced susceptibility as $\chi_r = \chi_M|J_1|/[N_A g^2 \mu_B{}^2/4]$. In this way the product $\chi_r T_r$ tends toward unity in the high temperature limit. In Figure 1 the thermal variations of the magnetic susceptibility for $N = 6$ and 7 are compared for different values of the alternating parameter α, defined as $J_2/|J_1|$. As may be seen, for the lower α values, the two curves are coincident in the reported temperature range (down to $T_r = 0.05$). Little differences in χ_r become to be observable in the low temperature range (below $T_r \approx 0.4$) for $\alpha \geq 3$ and increaseswhen α is increased. The two set of curves differ by less than 4% at $T_r = 0.15$, indicating that above this temperature the convergence is rather rapid, and the $N = 7$ ring should describe the behavior of the infinite chain in a satisfying manner, making it unnecessary to extrapolate the finite-ring results (probably the values for $N = 7$ differs from the true limiting curve by less than 1%) to the infinite limit.

With regard to the influence of the exchange alternation, the plot described above shows that when α increases, the maximum in χ increases and its position is shifted toward low temperatures. A more convenient plot is that of the product $\chi_r T_r$ vs T_r (Figure 2). This plot is particularly useful when the ferromagnetic exchange J_2 is the leading parameter ($\alpha > 1$). In such cases $\chi_r T_r$ exhibits a continuous increase as T is raised, followed by a rounded maximum which can be taken as the signature of an alternating F/AF chain with dominant ferromagnetic interactions; finally, $\chi_r T_r$ sharply decreases towards zero when approaching $T = 0$, in agreement with the nonmagnetic $S = 0$ ground-state of the chain. When antiferromagnetic interactions are the dominant ones ($\alpha < 1$), antiferromagnetic-like behavior is observed. This behavior exhibits little sensitivity to the ferromagnetic exchange value. This observation emphasizes that it will be very difficult to make clear the presence of ferromagnetic exchange interactions from the magnetic data.

In order to handle with ease the above numerical results for the analysis of experimental data, it is convenient to fit these theoretical susceptibility curves to a unified expression for χ_r as a function of T_r and of the alternation parameter α. Following a similar procedure to that reported by Hatfield et al.[6] for the alternating antiferromagnetic case, we found that the simplest rational expression which better reproduce the numerical results is

$$\chi_r = [AT_r^3 + BT_r^2 + CT_r + D]/[T_r^4 + ET_r^3 + FT_r^2 + GT_r + H] \qquad (2)$$

where $A-H$ are the fitting parameters. In view of the definition of χ_r, parameter A is equal to unity. For the rest of the parameters, a careful study of their dependence on α allows them to be fit to polynomial expressions of third degree in α:

$$X_i = x_0 + x_1\alpha + x_2\alpha^2 + x_3\alpha^3 \qquad (3)$$

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Table 1. Coefficients for the Polynomials Valid in the Range $0 \leq \alpha \leq 2$

	x_0	x_1	x_2	x_3
A	1	0	0	0
B	5	0	0	0
C	−1	0	0	0
D	0.05	0	0	0
E	5.2623	−0.33021	0	0
F	0.44976686	−0.99234827	−0.00881524	0.15481517
G	0.18948031	0.36766434	0.51001414	−0.2795751
H	0.28437797	−0.16749925	−0.18725364	0.09374817

Table 2. Coefficients for the Polynomials Valid in the Range $2 \leq \alpha \leq 8$

	x_0	x_1	x_2	x_3
A	1	0	0	0
B	5	0	0	0
C	18.49535656	−6.1326294	1.63540894	−0.114937
D	−1.476022	0.238098	−0.0394290	0.001851
E	5.3195744	−0.25251758	0	0
F	20.12902219	−7.98423527	1.827504022	−0.116829819
G	−2.696851543	2.7164805741	−0.310485224	0.008341925
H	5.1120826687	−2.478242688	0.457077363	−0.02686769

Two sets of polynomials have been obtained which are valid in two different ranges of α. The former one covers the range $0 \leq \alpha \leq 2$ (Table 1), while the second one is valid for $2 \leq \alpha \leq 8$ (Table 2). The agreement obtained from these two sets of parameters is excellent. In the overall temperature range[12] these two expressions reproduce the numerical results with an agreement criterion, defined as the square of the relative deviations, much better than 0.1%.

Using these expressions we have analyzed the magnetic behavior of two copper complexes exhibiting alternating chain structures. These illustrate the use of the model in two relevant situations for the exchange alternation, namely $\alpha > 1$ (dominant ferromagnetic exchange) and $\alpha < 1$ (dominant antiferromagnetic exchange).

The case with dominant ferromagnetic exchange is illustrated by the compound $Cu(TIM)CuCl_4$ (TIM = 2,3,9,10-tetramethyl-1,4,8,11-tetraaztetradecane-1,3,8,10-tetraenecyclo), recently described by Willett, et al.[13] The structure of this compound contains $Cu(TIM)^{2+}$ cations bridged by distorted tetrahedral anions $CuCl_4^{2-}$ to form alternating $[Cu(TIM)CuCl_4]_n$ chains. The magnetic properties exhibit the typical behavior of a F/AF chain with a maximum in the χT vs T plot around 20 K (Figure 3). The developed model results in an excellent fit to the data with the best-fit parameters being $J_1/k = -7.5$ K, $J_2/k = 22.5$ K ($\alpha = 3$), and $g = 2.1$.

Dominant antiferromagnetic exchange interactions have been found in the complex $[Cu(bpym)(OH)_2(NO_3)_2]\cdot 2H_2O$ (bpym = 2,2′-bipyrimidine) recently reported by Julve et al.[14] The structure consists of chains of Cu(II) alternatively bridged by bpym and two hydroxo groups. While the former bridge is able to transmit a very strong antiferromagnetic coupling, the bridging angles Cu−O−Cu (of ca. 96°) favor a relatively strong ferromagnetic exchange through the hydroxo groups. Accordingly, the magnetic behavior exhibits a rounded maximum in χ at about 120 K (Figure 4), which is clearly situated above that predicted for an antiferromagnetic dimer (dotted line). This behavior has been satisfactorily reproduced in the overall temperature range from the F/AF alternating model giving J_1/k = −200 K, $J_2/k = 150$ K ($\alpha = 0.75$), and $g = 2.02$. Notice that in this case the plot of χ vs T is preferable to that of χT vs T since the former is more sensitive to the exchange alternation as we can see from a comparison of Figures 1 and 2.

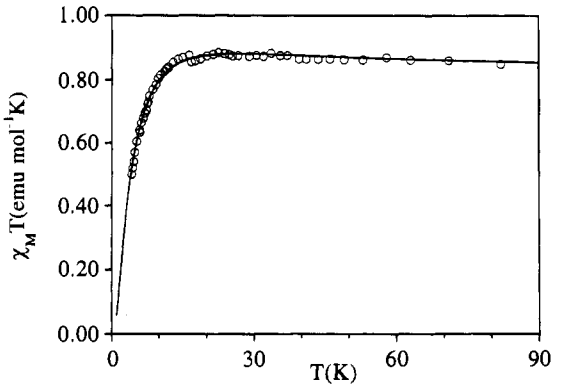

Figure 3. Magnetic behavior of the compound $Cu(TIM)CuCl_4$. The solid line corresponds to the best fit to the alternating chain model.

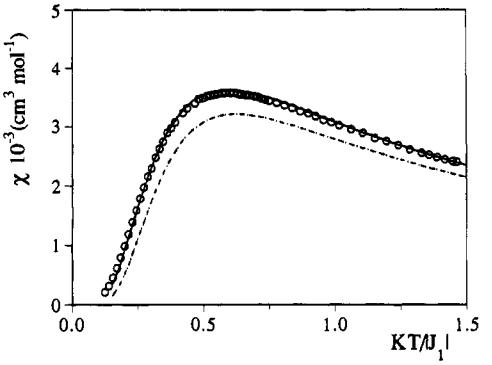

Figure 4. Magnetic behavior of the compound $[Cu(bpym)(OH)_2(NO_3)_2]\cdot 2H_2O$. The solid line corresponds to the best fit to the alternating chain model. The behavior of an antiferromagnetic dimer with $J/k = 150$ K is plotted as dashed line.

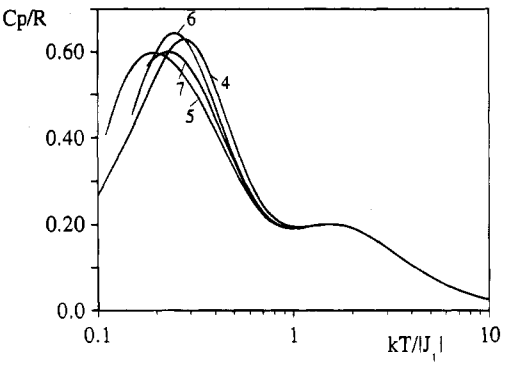

Figure 5. Magnetic specific heat (per spin pair of ions) of $[1/2 - 1/2]_N$ rings for $\alpha = 4$.

Specific Heat

Now consider the dependence of the magnetic specific heat on N (Figure 5). Unlike the magnetic susceptibility, the specific heat curves for finite N display a complicated and slower convergence, with successive curves crossing at low temperatures; this feature prevents extrapolation procedures in this region. Notice that the crossings are shifted to higher temperatures as α increases. Above these temperatures the limiting curve is very close to the curve for $N = 7$ and is apparently bracketed by the curves for odd N, which approach monotonically from below, and those for even N, which approach monotonically from above. Therefore, the calculated curves

(12) The minimum values of T_r above which expression 2 is valid are 0.09 for $\alpha < 2$, 0.15 for $2 \leq \alpha \leq 5$, and 0.20 for $\alpha > 5$.

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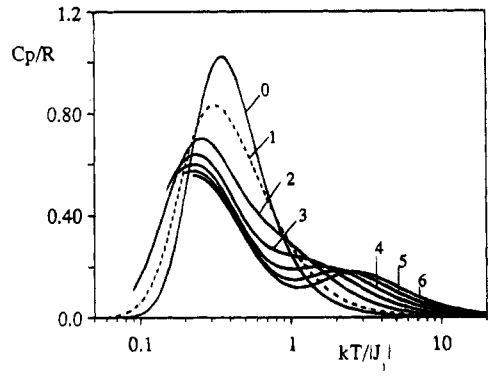


Figure 6. Magnetic specific heat of the $N = 7$ ring for different values of the alternating parameter α.

Table 3. Position of Both First and Second Maxima of Specific Heat Curves

	1st max		2nd max	
$J_2/\|J_1\|$	$kT_{max}/\|J_1\|$	$C_{p_{max}}/R$	$kT_{max}/\|J_1\|$	$C_{p_{max}}/R$
0	0.35112	1.02350		
1	0.31328	0.83680		
2	0.26649	0.71470		
3	0.2434	0.6681		
4	0.2425	0.5989	1.5515	0.20159
5	0.225	0.5740	2.110	0.18682
6	0.22	0.56	2.620	0.17988

for $N = 7$ should describe satisfactorily the limiting behavior only in this region.

The curves for $N = 7$ giving the thermal variation of the magnetic specific heat for different values of α are plotted in Figure 6. The most remarkable feature is the occurrence of two rounded maxima when the two exchange parameters are sufficiently different. Thus, the single maximum observed for the antiferromagnetic dimer limit ($\alpha = 0$) broadens, decreases in height and is shifted to lower temperatures as α is increased, and for $\alpha \geq 2$ a second feature becomes apparent as a shoulder, which progressively is resolved into a second maximum of lower height. The coordinates of these two maxima for different α values are summarized in Table 3. It is interesting to notice that the second maximum approaches to the specific heat curve of a ferromagnetic dimer as α is increased. Thus, as can be seen in Figure 7 the two curves are almost coincident for $\alpha >$ 10 in this region (their values differ by less than 3% around the maximum). Therefore, while the first maximum depends on the two exchange parameters, the second one is only dependent on the ferromagnetic exchange. On the other hand, larger variations in the specific heat curves are observed for small α values (see Table 3 and Figure 6). For example, the height of the maximum is reduced by ca. 20% when α is increased from 0 to 1, or from 1 to 2; furthermore, under these conditions its position is shifted by ca. 10%.

From the above discussion it may be concluded that for these 1D systems, specific heat measurements complement magnetic measurements. Thus, the presence of two maxima when the ferromagnetic exchange is large compared to the antiferromagnetic should provide an accurate determination of the two exchange parameters. In the other limit (ferromagnetic exchange lesser than or similar to the antiferromagnetic one), the fact that the specific heat is much more sensitive to the exchange alternation than the magnetic susceptibility makes the thermal measurements advantageous for providing information on ferromagnetic exchange. Notice, however, that the use of specific heat measurements to obtain magnetic information is limited by the lattice specific heat, since this contribution completely mask the magnetic contribution at temperatures

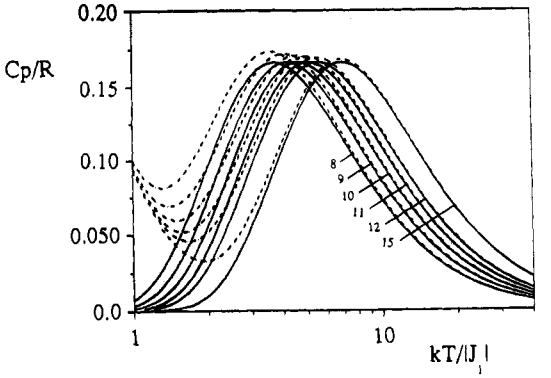
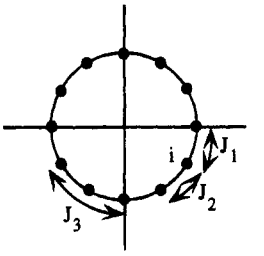


Figure 7. Magnetic specific heat of the $N = 7$ ring with dominant ferromagnetic exchange (dashed lines with α between 8 and 15). Thermal behaviors of a ferromagnetic dimer with J/k between 8 and 15 K are given in solid lines.

Scheme 1



above 10−15 K. In the present case this fact limits the specific heat study to systems with weak or intermediate exchange interactions ($|J_1| < 40-50$ K and $J_2 < 20-25$ K).

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Appendix: Description of the Computing Program

This program has been elaborated for solving the problem of a closed spin chain described by the following Hamiltonian:

$$H = -\sum_{i=1}^{N-1} [J_1^{\parallel} S_{2i}^z S_{2i+1}^z + J_1^{\perp}(S_{2i}^x S_{2i+1}^x + S_{2i}^y S_{2i+1}^y) + J_2^{\parallel} S_{2i}^z S_{2i-1}^z + J_2^{\perp}(S_{2i}^x S_{2i-1}^x + S_{2i}^y S_{2i-1}^y)] - \sum_{i=1}^{2N-2} [J_3^{\parallel} S_i^z S_{i+2}^z + J_3^{\perp}(S_i^x S_{i+2}^x + S_i^y S_{i+2}^y)] + \sum_{i=1}^{2N} [D(S_i^z)^2]$$

Here J_1 and J_2 are the two types of nearest neighbor interactions, and J_3 is the next nearest neighbor interaction (see Scheme 1).

The numerical treatment required for solving the above chain Hamiltonian is based on the Bonner−Fisher procedure. Since the method may require the extrapolation of the properties of a finite length system to an infinite one, it is equivalent to work with rings instead of working with open chains. From a mathematical point of view this has the advantage of introducing an elementary translation symmetry **T**, which, when applied repeatedly, conserves the ring. We assume that some further mirror operator **S** also conserves the ring. The general method involves five steps: (i) creating pertinent localized states; (ii) deducing symmetrized Bloch states; (iii) calculating the cor-

responding matrix Hamiltonian; (iv) solving for the eigenvalues; (v) calculating the thermal dependence of the thermodynamical properties.

We consider a $2N$ unit cell ring. Starting from the fully aligned spin state $|S\rangle$ (total spin S, total component M along the quantification axis S), it is possible to get the set of states with $M = S - 1$ by applying the total spin reduction operator $\mathbf{S}^-$. These states are gathered in subsets among which each one corresponds to one another through a combination of $\mathbf{T}^n$ ($n = 1$ to $2N$) and $\mathbf{S}^\epsilon$ ($\epsilon = 0, 1$) operations. Only one state $|S - 1, \alpha\rangle$ is retained from each subset. Applying $\mathbf{S}^-$ to the $|S - 1, \alpha\rangle$'s and operating a similar selection, we get the sets $|S - 2, \beta\rangle$, $|M, \gamma\rangle$, down to $M = 0$ or $^1/_2$ depending on whether S is integer of half integer. Now, for each M value, the transformations to symmetrized Bloch states can be written as

$$|M, \lambda, k, \epsilon, \eta\rangle = A^{M,\lambda}_{k,\epsilon,\eta} \sum_n f_\eta(kn) \hat{T}^n (1 + \epsilon \hat{S}) |M, \lambda\rangle$$

with $\epsilon = 0, 1$; $\eta = \pm 1$; $n = 1, 2, \ldots, 2N$; and

$$f_+(kn) = \cos(2k\pi(n/N)); f_-(kn) = \sin(2k\pi(n/N))$$

It appears from representation theory that the ring Hamiltonian has nonvanishing terms between the states: $|M, \lambda, k, \epsilon, \eta\rangle$ and $|M', \lambda', k', \epsilon', \eta'\rangle$ only for $M = M'$, $k = k'$, and $\epsilon\eta = \epsilon'\eta'$. This results in a considerable reduction in the size of the matrices to be diagonalized, and therefore it is possible to handle larger N values.