

# Use of Green Functions in the Theory of Ferromagnetism. I. General Discussion of the Spin- $S$ Case

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The theory of ferromagnetism developed by Tyablikov for the case of spin- $\frac{1}{2}$  particles is extended to higher spin values. The chain of equations for the various Green functions is made finite by a decoupling which is completely analogous to the one used by Tyablikov and our results reduce to his for the case  $S=\frac{1}{2}$ . This decoupling procedure seems, however, to be better for larger  $S$  values. Explicit expressions are given for the magnetization for  $S=\frac{1}{2}, 1, \frac{3}{2}, 2, \frac{5}{2}$ , and 3 and those expressions are used to obtain series expansions at temperatures well below the Curie temperature, just below the Curie temperature, and well above the Curie temperature. The results obtained are compared with those of Dyson for the spin-wave region, with those of Lax obtained via the spherical model near the Curie point, and with those of the molecular-field theory at high temperatures. It is interesting to note that we obtain the same Curie temperatures as those following from the spherical model. The results obtained here seem to be reasonable. In the appendix we examine critically similar work by Izyumov and Yakovlev and by Kawasaki and Mori.

## 1. INTRODUCTION

TEMPERATURE-dependent Green functions have recently been applied to several solid-state problems, often with notable success. We may mention the work by Schwinger and co-workers<sup>1,2</sup> and by various Russian groups.<sup>3-18</sup> An extensive review of recent work has been given by Zubarev<sup>19</sup> (compare also the survey

paper by Alekseev<sup>20</sup>). Bogolyubov and Tyablikov<sup>3,4</sup> have applied this technique to the theory of a Heisenberg ferromagnet for the case where all spins have spin  $\frac{1}{2}$  (or rather  $\frac{1}{2}\hbar$ ). It turns out that in the simplest approximation one can obtain a formula for the magnetization which is valid over the whole temperature range and which is in reasonable agreement with known results; at low temperatures the result is in good agreement with spinwave results, near the Curie temperature with the molecular field theory, and at high temperatures with known expansions in inverse powers of the temperature.<sup>21</sup> The Curie temperature is obtained from requiring that on approaching this temperature from below the spontaneous magnetization vanishes, while the paramagnetic Curie temperature can be estimated from the high-temperature susceptibility expansion.

Izyumov and Yakovlev<sup>22</sup> attempted to extend the theory to the case of higher spin values. They assumed that on each lattice site a spin  $S$  can be constructed out of  $2S$  ferromagnetic electrons at that site, and that these electrons are in different orbital quantum states  $\lambda$ , so that they can add up to a total spin  $S$ . As one is now dealing with spin- $\frac{1}{2}$  particles, the same technique can be applied as to the spin- $\frac{1}{2}$  case. One can object to their treatment, since they introduce implicitly a constraint at each lattice site. This should have been done explicitly by incorporating the mutual interactions of the  $2S$  electrons and taking the limit where the interactions are so strong that only the parallel alignment is possible. The results following from their formulas can be compared with known results. This is done in Appendix A; the result of this comparison is that their theory appears to give reasonable results only in the case  $S=\frac{1}{2}$ —where it is identical with the Tyablikov theory, as is to be expected—or in the low-temperature region.

<sup>1</sup> P. C. Martin and J. Schwinger, *Phys. Rev.* **115**, 1342 (1959).

<sup>2</sup> G. Baym, *Ann. Phys.* **14**, 1 (1961).

<sup>3</sup> N. N. Bogolyubov and S. V. Tyablikov, *Doklady Akad. Nauk S.S.S.R.* **126**, 53 (1959) [translation: *Soviet Phys.—Doklady* **4**, 604 (1959)].

<sup>4</sup> S. V. Tyablikov, *Ukrain. Mat. Zhur.* **11**, 287 (1959).

<sup>5</sup> L. P. Gor'kov, *J. Exptl. Theoret. Phys. (U.S.S.R.)* **34**, 735 (1958) [translation: *Soviet Phys.—JETP* **7**, 505 (1958)].

<sup>6</sup> N. N. Bogolyubov, D. N. Zubarev, and Yu. A. Tserkovnikov, *Doklady Akad. Nauk S.S.S.R.* **117**, 788 (1957) [translation: *Soviet Phys.—Doklady* **2**, 535 (1957)].

<sup>7</sup> A. A. Abrikosov and L. P. Gor'kov, *J. Exptl. Theoret. Phys. (U.S.S.R.)* **35**, 1558 (1958) [translation: *Soviet Phys.—JETP* **8**, 1090 (1959)].

<sup>8</sup> A. A. Abrikosov, L. P. Gor'kov, and I. M. Khalatnikov, *J. Exptl. Theoret. Phys. (U.S.S.R.)* **35**, 265 (1958) [translation: *Soviet Phys.—JETP* **8**, 182 (1959)].

<sup>9</sup> N. N. Bogolyubov, D. N. Zubarev, and Yu. A. Tserkovnikov, *J. Exptl. Theoret. Phys. (U.S.S.R.)* **39**, 120 (1960) [translation: *Soviet Phys.—JETP* **12**, 88 (1961)].

<sup>10</sup> V. L. Bonch-Bruевич, *J. Exptl. Theoret. Phys. (U.S.S.R.)* **28**, 121 (1955); **30**, 342 (1956); **31**, 254 (1956) [translation: *Soviet Phys.—JETP* **1**, 168 (1955); **3**, 278 (1956); **4**, 196 (1957)].

<sup>11</sup> A. B. Migdal, *J. Exptl. Theoret. Phys. (U.S.S.R.)* **34**, 1438 (1958) [translation: *Soviet Phys.—JETP* **7**, 996 (1958)].

<sup>12</sup> A. A. Abrikosov, L. P. Gor'kov, and I. E. Dzyaloshinskii, *J. Exptl. Theoret. Phys. (U.S.S.R.)* **36**, 900 (1959) [translation: *Soviet Phys.—JETP* **9**, 636 (1959)].

<sup>13</sup> E. S. Fradkin, *J. Exptl. Theoret. Phys. (U.S.S.R.)* **36**, 1287 (1959) [translation: *Soviet Phys.—JETP* **9**, 912 (1959)].

<sup>14</sup> E. S. Fradkin, *Nuclear Phys.* **12**, 465 (1959).

<sup>15</sup> V. L. Bonch-Bruевич, *Doklady Akad. Nauk S.S.S.R.* **126**, 539 (1959); **129**, 529 (1959) [translation: *Soviet Phys.—Doklady* **4**, 596, 1275 (1959)]; *Fiz. Met. Metallov.* **6**, 590 (1958).

<sup>16</sup> V. L. Bonch-Bruевич and S. V. Tyablikov, *Green Function Methods in Statistical Mechanics* (Moscow, 1961); [English translation: North-Holland Publishing Company, Amsterdam, 1962].

<sup>17</sup> Sh. M. Kogan, *Doklady Akad. Nauk S.S.S.R.* **126**, 546 (1959) [translation: *Soviet Phys.—Doklady* **4**, 604 (1959)].

<sup>18</sup> I. P. Dzyub, *Doklady Akad. Nauk S.S.S.R.* **130**, 1241 (1960) [translation: *Soviet Phys.—Doklady* **5**, 125 (1959)].

<sup>19</sup> D. N. Zubarev, *Usp. Fiz. Nauk* **71**, 71 (1960) [translation: *Soviet Phys.—Uspekhi* **3**, 320 (1960)].

<sup>20</sup> A. I. Alekseev, *Usp. Fiz. Nauk* **73**, 41 (1961) [translation: *Soviet Phys.—Uspekhi* **4**, 23 (1961)].

<sup>21</sup> W. Opechowski, *Physica* **4**, 181 (1937).

<sup>22</sup> Yu. A. Izyumov and E. N. Yakovlev, *Fiz. Met. Metallov. Akad. Nauk S.S.S.R. Ural. Filial* **9**, 667 (1960).

Another attempt to extend the Tyablikov theory has recently been made by Kawasaki and Mori.<sup>23</sup> So far, this theory has only been given in outline for the case of  $S=1$ . We discuss it in Appendix B, but at this point we may mention that we feel that their way of decoupling is not a very good one, leading to errors of the relative order of magnitude  $T/T_C$  ( $T_C$ : Curie temperature). The validity of their results also seems to be restricted to the low-temperature region.

In the next section we shall, first of all, summarize those properties of the general spin operators and of the double-time temperature-dependent Green functions which we need in the following. In Sec. 3 we apply the Green function technique to a ferromagnetic system where on each lattice site there is a spin- $S$  particle which interacts with its nearest neighbors only. The interaction is assumed to be of the Heisenberg type. The equations of motion for the Fourier transform of the relevant Green functions are solved by a decoupling procedure similar to the one used by Bogolyubov and Tyablikov<sup>3</sup> for the spin- $\frac{1}{2}$  case. (When  $S=\frac{1}{2}$ , the decoupling is the same as theirs.) Once the decoupling has been performed, one can solve the equations and obtain an expression for the magnetization. This is done explicitly for  $S=\frac{1}{2}, 1, \frac{3}{2}, 2, \frac{5}{2}$ , and 3. In Sec. 4 we use the expressions obtained in this way to get series expansions for the magnetization and susceptibility at low temperatures, just below the Curie temperature, and at high temperatures. The low-temperature results are compared with Dyson's spin-wave results<sup>24</sup> in Sec. 5. The temperature region just below the Curie point is discussed in Sec. 6 and the results are compared with those for spherical model.<sup>25</sup> In Sec. 7 we discuss the high-temperature region and compare our results with those of the molecular field theory.<sup>26</sup>

## 2. PROPERTIES OF SPIN OPERATORS; EQUATIONS OF MOTION OF GREEN FUNCTIONS

We consider a lattice where on each lattice site,  $\mathbf{l}$ , there is a spin  $\mathbf{S}_l$ . If we write

$$S_l^\pm = S_l^x \pm iS_l^y, \quad (2.1)$$

the components of  $\mathbf{S}_l$  satisfy the basic commutation relations,

$$[S_l^+, S_l^-] = 2\hbar S_l^z \delta_{l,g}, \quad [S_l^\pm, S_l^z] = \mp \hbar S_l^\pm \delta_{l,g}. \quad (2.2)$$

For spin- $S$  spin vectors we have also the relation,

$$(\mathbf{S}_l \cdot \mathbf{S}_l) = (S_l^x)^2 + (S_l^y)^2 + (S_l^z)^2 \\ = \frac{1}{2}[S_l^+ S_l^- + S_l^- S_l^+] + (S_l^z)^2 = S(S+1)\hbar^2, \quad (2.3)$$

and from (2.2) and (2.3), it follows that

$$S_l^- S_l^+ = \hbar^2 S(S+1) - \hbar S_l^z - (S_l^z)^2. \quad (2.4)$$

A generalization of (1.4) is

$$(S_l^-)^n (S_l^+)^n = [S(S+1)\hbar^2 - n(n-1)\hbar^2 \\ - (2n-1)S_l^z \hbar - (S_l^z)^2] (S_l^-)^{n-1} (S_l^+)^{n-1}, \quad (2.5)$$

from which follows the relation,

$$(S_l^-)^n (S_l^+)^n = \prod_{p=1}^n [S(S+1)\hbar^2 - (n-p)(n-p+1)\hbar^2 \\ - (2n-2p+1)\hbar S_l^z - (S_l^z)^2]. \quad (2.6)$$

We shall also need the following operator equation:

$$\prod_{r=-S}^{+S} (S^z - r\hbar) = 0, \quad (2.7)$$

where  $r$  takes on integral or half-odd-integral values according to whether  $S$  is integral or half-odd-integral. We also need the following commutator relation:

$$[S_l^+, (S_l^-)^n (S_l^+)^{n-1}]_- \\ = [2n\hbar S_l^z + \hbar^2(n^2-n)] (S_l^-)^{n-1} (S_l^+)^{n-1} \\ = [2n\hbar S_l^z + \hbar^2(n^2-n)] \\ \times \prod_{p=1}^{n-1} [S(S+1)\hbar^2 - (n-p-1)(n-p)\hbar^2 \\ - (2n-2p-1)\hbar S_l^z - (S_l^z)^2]. \quad (2.8)$$

In the following, we shall use the double-time temperature-dependent Green functions. Their properties have been discussed at great length by Zubarev<sup>19</sup> to whom we refer for details.<sup>27</sup> Here, we shall only write down those relations which we need for our present discussion. If  $\langle\langle A; B \rangle\rangle$  denotes the Fourier transform of the Green function involving the operators  $A$  and  $B$ ,  $\langle\langle A; B \rangle\rangle$  will thus be a function of  $E$ , it satisfies the equation of motion,<sup>28</sup>

$$E\langle\langle A; B \rangle\rangle = (1/2\pi)\langle[A, B]_-\rangle + \langle\langle[A, H]_-; B\rangle\rangle, \quad (2.9)$$

where the double angular brackets  $\langle\langle \dots \rangle\rangle$  indicate Fourier transforms of the Green functions, and where the single angular brackets  $\langle \dots \rangle$  indicate averages over a canonical ensemble,

$$\langle F \rangle = \text{Tr} e^{-\beta H} F / \text{Tr} e^{-\beta H}, \quad (2.10)$$

with  $\beta = 1/k_B T$  ( $k_B$  = Boltzmann's constant;  $T$  = absolute temperature) and  $H$  the Hamiltonian of the system considered. From the analytical properties of the Green functions, it follows that the correlation function  $\langle B(t') A(t) \rangle$  can be obtained from the equation

$$\langle B(t') A(t) \rangle \\ = \lim_{\epsilon \rightarrow +0} i \int_{-\infty}^{+\infty} \frac{\langle\langle A; B \rangle\rangle_{E=\hbar\omega+i\epsilon} - \langle\langle A; B \rangle\rangle_{E=\hbar\omega-i\epsilon}}{e^{\beta\hbar\omega} - 1} \\ \times e^{-i\omega(t-t')} d\omega. \quad (2.11)$$

<sup>23</sup> K. Kawasaki and H. Mori, Progr. Theoret. Phys. (Kyoto) **25**, 1045 (1961).

<sup>24</sup> F. J. Dyson, Phys. Rev. **102**, 1230 (1956).

<sup>25</sup> M. Lax, Phys. Rev. **97**, 629 (1955).

<sup>26</sup> J. H. Van Vleck, J. Chem. Phys. **9**, 85 (1941).

<sup>27</sup> See also: W. E. Parry and R. E. Turner, Ann. Phys. **17**, 301 (1962).

<sup>28</sup> See Eqs. (2.17) and (3.106) of reference 19 or Eq. (7) of D. ter Haar, Kgl. Norske Videnskab. Selskab, Forh. Skrifter **34**, 77 (1961).

### 3. THE HEISENBERG FERROMAGNET

The Hamiltonian of our system is given by the equation

$$H = -(g\mu_B B/\hbar) \sum_{\mathbf{f}} S_{\mathbf{f}}^z - \sum_{\mathbf{f}, \mathbf{m}} I(\mathbf{f}-\mathbf{m}) (\mathbf{S}_{\mathbf{f}} \cdot \mathbf{S}_{\mathbf{m}}); \quad (3.1)$$

where  $B$  is the applied field which we assume to be along the  $+z$  direction,  $\mu_B$  is the Bohr magneton,  $g$  the Landé  $g$  factor,  $\mathbf{f}$  and  $\mathbf{m}$  number the lattice sites, and  $I(\mathbf{f}-\mathbf{m})$  is the exchange integral corresponding to the interaction between the spins on lattice sites  $\mathbf{f}$  and  $\mathbf{m}$ . For the sake of simplicity we assume

$$\begin{aligned} I(\mathbf{f}-\mathbf{m}) &= I, \quad \text{if } \mathbf{f} \text{ and } \mathbf{m} \text{ are nearest neighbors,} \\ I(\mathbf{f}-\mathbf{m}) &= 0, \quad \text{otherwise.} \end{aligned} \quad (3.2)$$

Later on we need the correlation functions

$$\langle [S_{\mathbf{f}}^-(t)]^n [S_{\mathbf{f}}^+(t)]^n \rangle$$

and we shall therefore study the Green's functions  $\langle\langle S_{\mathbf{g}}^+; (S_{\mathbf{f}}^-)^n (S_{\mathbf{f}}^+)^{n-1} \rangle\rangle$ , where  $n$  is a positive integer. The equation of motion of this Green's function is, according to (2.9),

$$\begin{aligned} E \langle\langle S_{\mathbf{g}}^+; (S_{\mathbf{f}}^-)^n (S_{\mathbf{f}}^+)^{n-1} \rangle\rangle &= (1/2\pi) \langle [S_{\mathbf{g}}^+, (S_{\mathbf{f}}^-)^n (S_{\mathbf{f}}^+)^{n-1}]_- \rangle \\ &\quad + \langle\langle [S_{\mathbf{g}}^+, H]_-; (S_{\mathbf{f}}^-)^n (S_{\mathbf{f}}^+)^{n-1} \rangle\rangle, \end{aligned} \quad (3.3)$$

and if we use (2.8) and the expression (3.1) for  $H$ , we get

$$\begin{aligned} E \langle\langle S_{\mathbf{g}}^+; (S_{\mathbf{f}}^-)^n (S_{\mathbf{f}}^+)^{n-1} \rangle\rangle &= \frac{\delta_{\mathbf{g}\mathbf{f}}}{2\pi} \langle [2n\hbar S_{\mathbf{f}}^z + \hbar^2(n^2-n)] \\ &\quad \times \prod_{p=1}^{n-1} [S(S+1)\hbar^2 - (n-p-1)(n-p)\hbar^2 \\ &\quad - (2n-2p-1)\hbar S_{\mathbf{f}}^z - (S_{\mathbf{f}}^z)^2] \rangle \\ &\quad + g\mu_B B \langle\langle S_{\mathbf{g}}^+; (S_{\mathbf{f}}^-)^n (S_{\mathbf{f}}^+)^{n-1} \rangle\rangle \\ &\quad - 2\hbar \sum_{\mathbf{f}} I(\mathbf{g}-\mathbf{f}) \langle\langle (S_{\mathbf{g}}^z S_{\mathbf{f}}^+ - S_{\mathbf{f}}^z S_{\mathbf{g}}^+); \\ &\quad (S_{\mathbf{f}}^-)^n (S_{\mathbf{f}}^+)^{n-1} \rangle\rangle. \end{aligned} \quad (3.4)$$

We note that (3.4) involves higher order Green's functions—a common feature in this technique—and

$$G_{\mathbf{k}}(E) = \frac{\langle [2n\hbar S^z + \hbar^2(n^2-n)] \prod_{p=1}^{n-1} [\hbar^2 S(S+1) - (n-p-1)(n-p)\hbar^2 - (2n-2p-1)S^z - (S^z)^2] \rangle}{2\pi(E - E_{\mathbf{k}}^{(S)})}, \quad (3.10)$$

where<sup>30</sup>

$$E_{\mathbf{k}}^{(S)} = g\mu_B B + 2\langle S^z \rangle \hbar [J(0) - J(\mathbf{k})]. \quad (3.11)$$

From (3.10), (2.11), and the identity

<sup>30</sup> Compare: R. Brout and H. Haken, *Bull. Am. Phys. Soc.* **5**, 148 (1960); F. Englert, *Phys. Rev. Letters* **5**, 102 (1960).

sooner or later we need to decouple the equations of motion. The philosophy and justification of the decoupling procedure is still far from being well understood<sup>29</sup>, but we shall introduce a decoupling which in the  $S=\frac{1}{2}$  case reduces to the one used by Bogolyubov and Tyablikov<sup>3</sup>:

$$\begin{aligned} \langle\langle S_{\mathbf{g}}^z S_{\mathbf{f}}^+; (S_{\mathbf{f}}^-)^n (S_{\mathbf{f}}^+)^{n-1} \rangle\rangle &= \langle S_{\mathbf{g}}^z \rangle \langle\langle S_{\mathbf{f}}^+; (S_{\mathbf{f}}^-)^n (S_{\mathbf{f}}^+)^{n-1} \rangle\rangle, \quad \mathbf{f} \neq \mathbf{g}. \end{aligned} \quad (3.5)$$

This assumes that we may neglect the correlations between  $S^+$  on one lattice site and  $S^z$  on another lattice site. If we introduce the decoupling (3.5) into (3.4), we are left only with Green's functions of the same structure as the one we are trying to find. We note, by the way, that because of the translational invariance of the lattice, all averages are independent of the lattice site index occurring within the  $\langle \dots \rangle$ . Also because of translational invariance we can Fourier transform our Green's functions with respect to the reciprocal lattice:

$$\begin{aligned} \langle\langle S_{\mathbf{g}}^+; (S_{\mathbf{f}}^-)^n (S_{\mathbf{f}}^+)^{n-1} \rangle\rangle &= (1/N) \sum_{\mathbf{k}} G_{\mathbf{k}}(E) e^{i(\mathbf{k} \cdot \mathbf{g} - \mathbf{l})}, \\ G_{\mathbf{k}}(E) &= (1/N) \sum_{\mathbf{g}} \sum_{\mathbf{l}} \langle\langle S_{\mathbf{g}}^+; (S_{\mathbf{f}}^-)^n (S_{\mathbf{f}}^+)^{n-1} \rangle\rangle \\ &\quad \times e^{-i(\mathbf{k} \cdot \mathbf{g} - \mathbf{l})}, \end{aligned} \quad (3.6)$$

where the first summation is over all wave vectors within the first Brillouin zone, and  $N$  is the total number of spins in the lattice.

As  $\delta_{\mathbf{g}\mathbf{l}}$  can be written as

$$\delta_{\mathbf{g}\mathbf{l}} = (1/N) \sum_{\mathbf{k}} e^{i(\mathbf{k} \cdot \mathbf{g} - \mathbf{l})}, \quad (3.7)$$

we get from (3.4), (3.5), and (3.6)

$$\begin{aligned} [E - g\mu_B B] G_{\mathbf{k}}(E) &= \frac{1}{2\pi} \langle [2n\hbar S^z + \hbar^2(n^2-n)] \\ &\quad \times \prod_{p=1}^{n-1} [\hbar^2 S(S+1) - (n-p-1)(n-p)\hbar^2 \\ &\quad - (2n-2p-1)\hbar S^z - (S^z)^2] \rangle \\ &\quad + 2\langle S^z \rangle \hbar [J(0) - J(\mathbf{k})] G_{\mathbf{k}}(E), \end{aligned} \quad (3.8)$$

where

$$J(\mathbf{k}) = \sum_{\mathbf{f}} I(\mathbf{g}-\mathbf{f}) e^{i(\mathbf{k} \cdot \mathbf{g} - \mathbf{f})}. \quad (3.9)$$

From (3.8) we get for  $G_{\mathbf{k}}(E)$  the equation

$$\begin{aligned} \lim_{\epsilon \rightarrow 0} \left[ \frac{1}{E - E_{\mathbf{k}}^{(S)} + i\epsilon} - \frac{1}{E - E_{\mathbf{k}}^{(S)} - i\epsilon} \right] &= -2\pi i \delta(E - E_{\mathbf{k}}^{(S)}), \end{aligned} \quad (3.12)$$

we get

<sup>29</sup> D. ter Haar, W. E. Parry, and R. E. Turner (unpublished).

$$\langle (S_1^-)^n (S_1^+)^n \rangle = \langle [2n\hbar S^z + \hbar^2(n^2 - n)] \times \prod_{p=1}^{n-1} [\hbar^2 S(S+1) - \hbar^2(n-p-1)(n-p) - (2n-2p-1)\hbar S^z - (S^z)^2] \Phi(S) \rangle, \quad (3.13)$$

where

$$\Phi(S) = (1/N) \sum_{\mathbf{k}} (e^{\beta E_{\mathbf{k}}(S)} - 1)^{-1}. \quad (3.14)$$

If we use (2.6), we get both on the left- and right-hand sides of (3.13) a sum of averages of powers of  $S^z$ . We can then write down  $2S$  independent, simultaneous linear equations in  $\langle S^z \rangle, \langle (S^z)^2 \rangle, \dots, \langle (S^z)^{2S} \rangle$ , by putting  $n$  in (3.13) equal to 1, 2,  $\dots$ ,  $2S$ , consecutively. The equations with  $n > 2S$  are not independent of the earlier ones, because of (2.7).

For  $S = \frac{1}{2}$  we get one equation

$$\langle S^- S^+ \rangle = \langle \frac{3}{4}\hbar^2 - \hbar S^z - (S^z)^2 \rangle = \langle 2\hbar S^z \rangle \Phi(\frac{1}{2}), \quad (3.15)$$

and from (2.7)

$$(S^z)^2 = \frac{1}{4}\hbar^2, \quad (3.16)$$

so that

$$\langle S^z \rangle_{S=\frac{1}{2}} = \frac{1}{2}\hbar / [1 + 2\Phi(\frac{1}{2})], \quad (3.17)$$

which is, of course, identical with Tyablikov's result.<sup>4</sup>

For  $S=1$  we have

$$\langle 2\hbar^2 - \hbar S^z - (S^z)^2 \rangle = 2\langle \hbar S^z \rangle \Phi(1), \quad (3.18)$$

$$\langle -6\hbar^3 S^z + \hbar^2 (S^z)^2 + 4\hbar (S^z)^3 + (S^z)^4 \rangle = \langle 4\hbar^4 + 6\hbar^3 S^z - 6\hbar^2 (S^z)^2 - 4\hbar (S^z)^3 \rangle \Phi(1), \quad (3.19)$$

$$(S^z)^3 - S^z \hbar^2 = 0, \quad (3.20)$$

from which it follows that

$$\langle S^z \rangle_{S=1} = \hbar \frac{1 + 2\Phi(1)}{1 + 3\Phi(1) + 3[\Phi(1)]^2}. \quad (3.21)$$

The results for higher values of  $S$  are obtained in a similar fashion, and we get

$$\langle S^z \rangle_{S=\frac{3}{2}} = \hbar \frac{\frac{3}{2} + 5\Phi(\frac{3}{2}) + 5[\Phi(\frac{3}{2})]^2}{[1 + \Phi(\frac{3}{2})]^4 - [\Phi(\frac{3}{2})]^4}, \quad (3.22)$$

$$\langle S^z \rangle_{S=2} = \hbar \frac{2 + 9\Phi(2) + 15[\Phi(2)]^2 + 10[\Phi(2)]^3}{[1 + \Phi(2)]^5 - [\Phi(2)]^5}, \quad (3.23)$$

$$\langle S^z \rangle_{S=\frac{5}{2}} = \hbar \frac{\frac{5}{2} + 14\Phi(\frac{5}{2}) + \frac{63}{2}[\Phi(\frac{5}{2})]^2 + 35[\Phi(\frac{5}{2})]^3 + \frac{35}{2}[\Phi(\frac{5}{2})]^4}{[1 + \Phi(\frac{5}{2})]^6 - [\Phi(\frac{5}{2})]^6}, \quad (3.24)$$

$$\langle S^z \rangle_{S=3} = \hbar \frac{3 + 20\Phi(3) + 56[\Phi(3)]^2 + 84[\Phi(3)]^3 + 70[\Phi(3)]^4 + 28[\Phi(3)]^5}{[1 + \Phi(3)]^7 - [\Phi(3)]^7}. \quad (3.25)$$

#### 4. SERIES EXPANSIONS FOR THE $\Phi(S)$

In this section we consider various series expansions of  $\Phi(S)$  which we shall use in subsequent sections to obtain expansions for the magnetization which can be compared with expansions obtained by other means. Let us first consider the low-temperature region for the case where  $B=0$ . We introduce a dimensionless reduced temperature  $\tau$  by the equation

$$\tau^{-1} = \beta J(0) \hbar^2. \quad (4.1)$$

We have then from (3.11) and (3.14)

$$\Phi(S) = \frac{1}{N} \sum_{\mathbf{k}} \left[ \exp \left( \frac{2\eta(\mathbf{k}) \langle S^z \rangle}{\hbar \tau} \right) - 1 \right]^{-1}, \quad (4.2)$$

where

$$\eta(\mathbf{k}) = 1 - J(\mathbf{k})/J(0). \quad (4.3)$$

We consider only crystals with cubic symmetry. For these lattices we can write for  $J(\mathbf{k})$ :

$$\begin{aligned} \text{simple cubic (sc), } J(\mathbf{k}) \\ = \frac{1}{3}J(0)[\cos(k_x a) + \cos(k_y a) + \cos(k_z a)], \end{aligned} \quad (4.4)$$

bcc,  $J(\mathbf{k})$

$$= J(0) \cos(\frac{1}{2}k_x a) \cos(\frac{1}{2}k_y a) \cos(\frac{1}{2}k_z a), \quad (4.5)$$

fcc,  $J(\mathbf{k})$

$$= \frac{1}{3}J(0)[\cos(\frac{1}{2}k_x a) \cos(\frac{1}{2}k_y a) + \cos(\frac{1}{2}k_y a) \times \cos(\frac{1}{2}k_z a) + \cos(\frac{1}{2}k_z a) \cos(\frac{1}{2}k_x a)], \quad (4.6)$$

where the nearest-neighbor distance is taken to be  $\mu a$  with  $\mu$  given by the equation

$$\mu^2 = 6/z, \quad (4.7)$$

with  $z$  the coordination number [sc:  $z=6$ ; bcc,  $z=8$ ; fcc,  $z=12$ ].

The sum in (4.2) is over the first Brillouin zone, but at low temperatures we may replace it by an integral over the whole of  $\mathbf{k}$  space and write

$$\begin{aligned} \Phi(S) = \frac{v}{(2\pi)^3} \int_0^{2\pi} d\psi \int_0^\pi \sin\theta d\theta \int_0^\infty k^2 dk \\ \times \sum_{r=1}^\infty \exp \left[ -\frac{2r\eta(k) \langle S^z \rangle}{\hbar \tau} \right], \end{aligned} \quad (4.8)$$

TABLE I. The simple cubic lattice.

$S$	$C_S$	$-D_S$	$\left(\frac{k_B T_C}{\hbar^2 I}\right)_{\text{ours}}$	$\left(\frac{k_B T_C}{\hbar^2 I}\right)_{\text{Brown and Luttinger}}$
$\frac{1}{2}$	1.978	1.078	1.978	1.93
1	2.119	1.262	5.276	5.36
$\frac{3}{2}$	2.128	1.278	9.892	10.63
2	2.099	1.253	15.83	17.46
$\frac{5}{2}$	2.063	1.222	23.08	25.81
3	2.029	1.063	31.65	35.74

where we have expanded the denominator in (4.2), and where  $\psi$  and  $\theta$  are polar angles, and  $v$  is the volume per site:

$$\text{sc}, v = a^3; \quad \text{bcc}, v = \frac{1}{2}a^3; \quad \text{fcc}, v = \frac{1}{4}a^3. \quad (4.9)$$

As only small values of  $k$  will appreciably contribute to  $\Phi(S)$  we expand  $\eta(\mathbf{k})$  in powers of  $k$  and on integrating we obtain a power series in ascending powers of  $\tau$  (our notation is similar to Dyson's<sup>24</sup>):

$$\Phi(S) = a_0 \left( \frac{3\hbar\tau}{4\pi\nu\langle S^z \rangle} \right)^{3/2} + a_1 \left( \frac{3\hbar\tau}{4\pi\nu\langle S^z \rangle} \right)^{5/2} + a_2 \left( \frac{3\hbar\tau}{4\pi\nu\langle S^z \rangle} \right)^{7/2} + \dots \quad (4.10)$$

where

$$a_0 = \zeta(3/2), \quad a_1 = \frac{3}{4}\pi\nu\zeta(5/2), \quad a_2 = \pi^2\omega\nu^2\zeta(7/2), \quad (4.11)$$

$$\text{sc}, \nu = 1; \quad \text{bcc}, \nu = \frac{3}{4}2^{2/3}; \quad \text{fcc}, \nu = 2^{1/3}, \quad (4.12)$$

$$\begin{aligned} \text{sc}, \omega = 33/32; \quad \text{bcc}, \omega = 281/288; \\ \text{fcc}, \omega = 15/16, \end{aligned} \quad (4.13)$$

and where  $\zeta(n)$  is the Riemann zeta function.

The next temperature range to be considered is that just below the Curie temperature, where  $\langle S^z \rangle / \hbar\tau$  tends to zero. If we rewrite (4.2) in the form

$$1 + 2\Phi(S) = (1/N) \sum_{\mathbf{k}} \coth[\eta(\mathbf{k})\langle S^z \rangle / \hbar\tau], \quad (4.14)$$

we get

$$1 + 2\Phi(S) = \frac{1}{N} \sum_{\mathbf{k}} \left[ \frac{\hbar\tau}{\eta(\mathbf{k})\langle S^z \rangle} + \frac{\eta(\mathbf{k})\langle S^z \rangle}{3\hbar\tau} - \frac{1}{45} \left( \frac{\eta(\mathbf{k})\langle S^z \rangle}{\hbar\tau} \right)^3 + \dots \right]. \quad (4.15)$$

We now must restrict our integration over  $\mathbf{k}$  to the first Brillouin zone. Using (4.4) to (4.6), we find

$$F(1) = 1, \quad F(2) = (z+1)/z, \quad F(3) = (z+3)/z, \quad (4.16)$$

where

$$F(n) = (1/N) \sum_{\mathbf{k}} [\eta(\mathbf{k})]^n. \quad (4.17)$$

The sums  $F(-1)$  are known<sup>31</sup> and we have

$$\begin{aligned} \text{sc}, F(-1) = 1.51638; \quad \text{bcc}, F(-1) = 1.39320; \\ \text{fcc}, F(-1) = 1.34466. \end{aligned} \quad (4.18)$$

Finally, we consider the high-temperature region, where we expand in terms of  $\tau^{-1}$ , or rather in terms of  $t_1$  given by the equation

$$t_1 = \tanh(\eta(\mathbf{k})\langle S^z \rangle / \hbar\tau). \quad (4.19)$$

We must now consider the case where  $B \neq 0$ , as otherwise  $\langle S^z \rangle = 0$ . Introducing a quantity  $t_0$  by the relation

$$t_0 = \tanh(\frac{1}{2}\beta g \mu_B B), \quad (4.20)$$

we can write the equation which is the analogy of (4.14) for the  $B \neq 0$  case in the form

$$\begin{aligned} 1 + 2\Phi(S) &= \frac{1}{N} \sum_{\mathbf{k}} \frac{1 + t_0 t_1}{t_0 + t_1} \\ &= \frac{1}{N} \sum_{\mathbf{k}} \frac{1}{t_0} \left[ 1 + (1 - t_0^2) \sum_{r=1}^{\infty} (-1)^r \left( \frac{t_1}{t_0} \right)^r \right]. \end{aligned} \quad (4.21)$$

Expanding the hyperbolic tangent  $t_1$  and using (4.16), we now get from (4.21)

$$[\Phi(S)]_{\tau \gg 1} = \frac{1}{2t_0} \left[ 1 - \frac{\langle S^z \rangle}{\hbar t_0 \tau} + \frac{z+1}{z} \left( \frac{\langle S^z \rangle}{\hbar t_0 \tau} \right)^2 + O\left(\frac{1}{\tau^3}\right) \right]. \quad (4.22)$$

## 5. THE LOW-TEMPERATURE REGION

From (4.10) we see that when  $\tau \ll 1$ ,  $\Phi(S)$  will be small, and we can thus expand (3.17), (3.21) to (3.25) in powers of  $\Phi(S)$  and thus, of  $\tau$ . We get

$$\langle S^z \rangle_{S=\frac{1}{2}} = \hbar \left\{ \frac{1}{2} - \Phi\left(\frac{1}{2}\right) + 2[\Phi\left(\frac{1}{2}\right)]^2 + O([\Phi\left(\frac{1}{2}\right)]^3) \right\}, \quad (5.1)$$

$$\langle S^z \rangle_{S \geq 1} = \hbar \{ S - \Phi(S) + O([\Phi(S)]^3) \}. \quad (5.2)$$

This leads to the following expansions in  $\tau$  for  $\langle S^z \rangle$ :

$$\begin{aligned} \langle S^z \rangle_{S=\frac{1}{2}} &= \hbar \left[ \frac{1}{2} - a_0 \left( \frac{3\tau}{2\pi\nu} \right)^{3/2} - a_1 \left( \frac{3\tau}{2\pi\nu} \right)^{5/2} \right. \\ &\quad \left. - a_2 \left( \frac{3\tau}{2\pi\nu} \right)^{7/2} - \dots - a_0^2 \left( \frac{3\tau}{2\pi\nu} \right)^3 \right. \\ &\quad \left. - 4a_0 a_1 \left( \frac{3\tau}{2\pi\nu} \right)^4 - \dots \right], \end{aligned} \quad (5.3)$$

$$\begin{aligned} \langle S^z \rangle_{S \geq 1} &= \hbar \left[ S - a_0 \left( \frac{3\tau}{4\pi\nu S} \right)^{3/2} - a_1 \left( \frac{3\tau}{4\pi\nu S} \right)^{5/2} \right. \\ &\quad \left. - a_2 \left( \frac{3\tau}{4\pi\nu S} \right)^{7/2} - \dots - \frac{3}{2S} a_0^2 \left( \frac{3\tau}{4\pi\nu S} \right)^3 \right. \\ &\quad \left. - \frac{4}{S} a_0 a_1 \left( \frac{3\tau}{4\pi\nu S} \right)^4 - \dots \right]. \end{aligned} \quad (5.4)$$

<sup>31</sup> G. N. Watson, Quart. J. Math. **10**, 266 (1939); M. Tikson, J. Research Natl. Bur. Standards **50**, 177 (1953).

These results should be compared with the ones obtained by Dyson.<sup>24,32</sup> It turns out that the terms proportional to  $\tau^0$ ,  $\tau^{3/2}$ ,  $\tau^{5/2}$ , and  $\tau^{7/2}$  are the same as those given by Dyson, but he does not have a term in  $\tau^3$  and the coefficient of his  $\tau^4$  term is different from ours. This difference can be traced back for  $S \geq 1$  to the fact that the  $E_k^{(S)}$  given by (3.11) are not the correct spin-wave energies. We shall return to this point in paper II of the present series of papers, but at this point only mention that (3.11) leads to an expression of the type [compare (5.3)]

$$E_k^{(S)} = \alpha + \beta \tau^{3/2} + \dots, \quad (5.5)$$

while the correct spin-wave energies should be of the form<sup>33</sup>

$$E_k^{(S)} = \alpha + \gamma \tau^{5/2} + \dots. \quad (5.6)$$

In the case  $S = \frac{1}{2}$  there is, apart from the  $\tau^3$  term arising from the wrong spin-wave energies, also a  $\tau^3$  contribution arising from the term  $2[\Phi(\frac{1}{2})]^2$  in (5.1). This term is due to the limitations of the decoupling procedure (3.5). We shall return to this point also in a later part of this series of papers.

## 6. TEMPERATURES JUST BELOW THE CURIE TEMPERATURE

Just below the Curie temperature  $\Phi(S)$  is large compared to unity [see (4.15)], and it is thus convenient to expand  $\langle S^z \rangle$  in inverse powers of  $\Phi(S)$ . We note first of all that it follows from (3.13) and (2.6) that the expansion of  $\langle S^z \rangle$  in inverse powers of  $\Phi$  starts as follows

$$\langle S^z \rangle = S(S+1)/3\Phi(S) + O([\Phi(S)]^{-2}), \quad (6.1)$$

and as  $[\Phi(S)]^{-1}$  is proportional to  $\langle S^z \rangle$ , the Curie temperature is that temperature for which

$$3\Phi(S)\langle S^z \rangle = S(S+1), \quad \langle S^z \rangle = 0, \quad (6.2)$$

or from (4.15) and (4.17)

$$T_C = \Theta_C / F(-1), \quad (6.3)$$

where the molecular-field Curie temperature  $\Theta_C$  satisfies the equation<sup>26,34</sup>

$$k_B \Theta_C = \frac{2}{3} S(S+1) J(0). \quad (6.4)$$

The Curie temperature of (6.3) is exactly the one obtained in the spherical model.<sup>25</sup>

One can now expand in powers of  $\tau_C - \tau$ , where  $\tau_C$  is given by the equation [compare (4.1)]

$$\tau_C = k_B T_C / J(0) \hbar^2. \quad (6.5)$$

Writing

$$\sigma = \langle S^z \rangle / \hbar S, \quad (6.6)$$

<sup>32</sup> See also, T. Oguchi, Phys. Rev. **117**, 117 (1960); F. Keffer and R. Loudon, J. Appl. Phys. **32**, 2S (1961).

<sup>33</sup> R. Brout and F. Englert, Bull. Am. Phys. Soc. **6**, 55 (1961); see also Paper II of this series of papers, R. A. Tahir-Kheli and D. ter Haar, Phys. Rev. **127**, 95 (1962).

<sup>34</sup> D. ter Haar and M. E. Lines, Phil. Trans. Roy. Soc. (London) **254**, 521 (1962).

TABLE II. The body-centered cubic lattice.

$S$	$C_S$	$-D_S$	$\left(\frac{k_B T_C}{\hbar^2 I}\right)_{\text{ours}}$	$\left(\frac{k_B T_C}{\hbar^2 I}\right)_{\text{Brown and Luttinger}}$
$\frac{1}{2}$	2.153	1.328	2.871	2.39
1	2.229	1.397	7.656	7.82
$\frac{3}{2}$	2.197	1.332	14.36	15.42
2	2.145	1.298	22.97	25.17
$\frac{5}{2}$	2.096	1.251	33.50	37.10
3	2.053	1.235	45.94	51.19

we find up to terms quadratic in  $\tau_C - \tau$

$$\sigma^2 = C_S(1 - \tau/\tau_C) + D_S(1 - \tau/\tau_C)^2, \quad (6.7)$$

where the coefficients  $C_S$  and  $D_S$  depend both on the value of  $S$  and on the crystal structure of the lattice. In Tables I, II, and III we have given the values of  $C_S$ ,  $D_S$ ,  $k_B T_C / I \hbar^2$  following from (6.3), (6.4), (3.9), and (3.2), and the value of  $k_B T_C / I \hbar^2$  which Brown and Luttinger<sup>35</sup> imply to be their best value, namely, the value obtained from the Kramers-Opechowski method<sup>21</sup> by finding the temperature where the inverse susceptibility vanishes. Table I refers to the simple cubic lattice, and Tables II and III to the body-centered and face-centered cubic lattices, respectively.

One notices from the data in these tables, first of all, that the values of  $C_S$  and  $D_S$  are nearly independent of both  $S$  and the crystal structure. Secondly, one notices that apart from the case  $S = \frac{1}{2}$ , our Curie temperatures lie below those of Brown and Luttinger. The true Curie temperatures may well lie somewhere between our and their values except in the  $S = \frac{1}{2}$  case, where our theory seems to be rather less reliable than for higher  $S$ -values.

## 7. THE HIGH-TEMPERATURE REGION

At temperatures above the Curie temperature we must consider the case where there is a nonvanishing magnetic field present. We shall derive an expression for the susceptibility in zero field. We derived in Sec. 4 a series expansion in inverse powers of  $\tau$  for  $\Phi(S)$  and we can use this expansion to find  $\langle S^z \rangle$  and thus the susceptibility  $\chi$  per atom. We note from (4.21) and (4.20) that in the limit as  $B \rightarrow 0$  and  $\beta \rightarrow 0$ ,  $\Phi(S) \gg 1$  so that we can use an expansion similar to the one used

TABLE III. The face-centered cubic lattice.

$S$	$C_S$	$-D_S$	$\left(\frac{k_B T_C}{\hbar^2 I}\right)_{\text{ours}}$	$\left(\frac{k_B T_C}{\hbar^2 I}\right)_{\text{Brown and Luttinger}}$
$\frac{1}{2}$	2.231	1.508	4.462	4.24
1	2.275	1.476	11.90	12.74
$\frac{3}{2}$	2.225	1.392	22.31	24.67
2	2.164	1.320	35.70	40.00
$\frac{5}{2}$	2.109	1.265	52.06	58.74
3	2.062	1.298	71.39	80.89

<sup>35</sup> H. A. Brown and J. M. Luttinger, Phys. Rev. **100**, 685 (1955).

in the preceding section. Up to terms of order  $T^{-3}$ , we find

$$\chi = \frac{g^2 \mu_B^2 S(S+1)}{3k_B T} \left[ 1 + \frac{\Theta_C}{T} + \frac{z-1}{z} \left( \frac{\Theta_C}{T} \right)^2 + O\left(\frac{1}{\tau^3}\right) \right]. \quad (7.1)$$

We note that apart from the factor  $(z-1)/z$  in the third term within the square brackets, (7.1) up to terms of order  $T^{-3}$  is identical with the molecular-field result, the Curie-Weiss law,<sup>26</sup>

$$\chi_{\text{mol.f.}} = \frac{g^2 \mu_B^2 S(S+1)}{3k_B (T - \Theta_C)}. \quad (7.2)$$

The result (7.1) is also nearly the same as the exact result given by Brown and Luttinger.<sup>35</sup>

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#### APPENDIX

##### A. The Theory of Izyumov and Yakovlev

In the introduction we have referred to recent work by Izyumov and Yakovlev<sup>22</sup> who also extended Tyablikov's theory to the case of  $S > \frac{1}{2}$ , and we voiced misapprehensions about their basic assumptions. In this appendix we shall show how their basic equations lead to results which, in the case  $S > \frac{1}{2}$ , are rather poor.

Their Eq. (26) for  $\langle S^z \rangle$  can be written in our notation as follows

$$\frac{\hbar S - S^z}{S^z} = \frac{\Phi(S)}{S} + \frac{2S-1}{S} [\exp(g\beta\mu_B B + 2\beta\langle S^z \rangle \hbar J(0)) - 1]^{-1}. \quad (A1)$$

At temperatures well below the Curie temperature (A1) reduces for the case  $B=0$  to

$$\langle S^z \rangle = \hbar \{ S - \Phi(S) + S^{-1} [\Phi(S)]^2 + O([\Phi(S)]^3) \}, \quad (A2)$$

which must be compared with (5.1) and (5.2). Their result is reasonably satisfactory in this temperature range, as can be seen from a comparison with Dyson's results. We must note that (A2) is identical with (5.1) for  $S = \frac{1}{2}$ : Izyumov and Yakovlev's results reduce to those of Tyablikov, and thus also to ours for the case  $S = \frac{1}{2}$ .

At temperatures just below the Curie temperature (A1) reduces for  $B=0$  to

$$\frac{\langle S^z \rangle^2}{3\hbar^2 S \tau} = 1 - \frac{\tau}{2S^2} [F(-1) + (2S-1)] + \frac{\langle S^z \rangle^4}{90S^2 \hbar^4 \tau^3} \left( \frac{3}{z} + 2S \right), \quad (A3)$$

which leads to a Curie temperature given by the relation

$$\frac{k_B T_C}{I \hbar^2} = \frac{2S^2 z}{F(-1) + (2S-1)}, \quad (A4)$$

which differs from (6.3) by a factor  $(S+1)[F(-1) + (2S-1)]/3SF(-1)$  which is equal to 1.1 for  $S=1$  and a simple cubic lattice, and equal to 2.1 for  $S=3$  and a face-centered cubic lattice. As our estimates for  $T_C$  are likely to be too low, their result is clearly worse than ours.

The worst results are, however, obtained at high temperatures. We now consider the case where  $B \neq 0$ , and must expand the last term on the right-hand side of (A1) as well as  $\Phi(S)$ . The result for the susceptibility turns out to be

$$\chi = \frac{Sg^2 \mu_B^2}{2k_B T} \left[ 1 + \frac{S}{\tau} + (2S - \frac{1}{2}) \frac{S}{2\tau^2} + \dots \right], \quad (A5)$$

which does not even give the correct expression as  $T \rightarrow \infty$ , except for the  $S = \frac{1}{2}$  case. As was to be expected, their approximation breaks completely down at high temperatures.

##### B. The Theory of Kawasaki and Mori

In a recent paper Kawasaki and Mori<sup>23</sup> have very briefly reported on an extension of Tyablikov's method to the case  $S=1$ . They state that they have also studied higher spin-values, but it is not immediately clear from their paper how this can be done. They seem to neglect the difference between  $\langle S_{\mathbf{m}}^+ S_{\mathbf{g}}^- S_{\mathbf{g}}^z \rangle$  and  $\langle S_{\mathbf{m}}^+ S_{\mathbf{g}}^z S_{\mathbf{g}}^- \rangle$ , where  $\mathbf{m}$  and  $\mathbf{g}$  are neighboring lattice sites. From (2.2) it follows that they neglect terms of the order of  $\langle S_{\mathbf{m}}^+ S_{\mathbf{g}}^- \rangle$  which at low temperatures are of the order  $S - \langle S^z \rangle^2$  or  $\tau^{3/2}$ . We should thus again expect their result to be reasonable in the spin-wave region. At temperatures just below  $T_C$  one can again estimate the order of magnitude of  $\langle S_{\mathbf{m}}^+ S_{\mathbf{g}}^- \rangle$  and we find a term of order  $\tau/\tau_C$  which is not small in that temperature region. Finally, in the high temperature region we have used their Eq. (23) to evaluate the susceptibility and we find

$$\chi = \frac{2g^2 \mu_B^2}{3k_B T} \left[ 1 + \frac{16}{27\tau} + O(1/\tau^2) \right], \quad (B1)$$

while the correct expression for  $S=1$  is

$$\chi = \frac{2g^2 \mu_B^2}{3k_B T} \left[ 1 + \frac{4}{3\tau} + O(1/\tau^2) \right]. \quad (B2)$$

We believe that the reason for their relatively poor results lies in their decoupling procedure.