In the examples discussed in this paper we frequently have $\langle\langle \mathcal{H}'(\lambda)\rangle\rangle = \langle\langle \mathcal{H}'(\lambda)A\rangle\rangle = 0$. Under these circumstances the result to second order in $\mathcal{H}'$ is

$$\langle A\rangle \approx \langle A\rangle_0 + \int_0^\beta d\lambda \int_0^\lambda d\lambda' [\langle \mathcal{H}'(\lambda)\mathcal{H}'(\lambda')A\rangle_0 - \langle \mathcal{H}'(\lambda)\mathcal{H}'(\lambda')\rangle_0 \langle A\rangle_0] , \quad \text{(A8)}$$

where we have employed the standard notation for averages with respect to the unperturbed Hamiltonian:

$$\langle X\rangle_0 \equiv \mathrm{Tr}\,(e^{-\beta\mathcal{H}_0} X)/\mathrm{Tr}\, e^{-\beta\mathcal{H}_0} . \quad \text{(A9)}$$

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High-Spin Expansion for Heisenberg Spin Systems

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It is known that in a well-defined high-spin limit, the properties of systems of quantum spins approach those of a corresponding system of classical spins. In this paper we give a method for computing corrections to this limit. We give the first nontrivial corrections to the partition function and spin-spin correlation function for a linear chain of Heisenberg-coupled spins. We briefly discuss possible comparisons with experiment.

I. INTRODUCTION

Several materials have been found in recent years which behave magnetically like one-dimensional crystals.[1–10] These crystals consist of chains of strongly coupled spins with a much weaker interchain coupling. At low enough temperatures the weak interchain coupling produces a phase transition to a state with three-dimensional long-range order, but above this temperature these systems appear one-dimensional in character.

One such material is $(CH_3)_4NMnCl_3$ known as TMMC. There is experimental[4,7] evidence that TMMC behaves as a one-dimensional system down to 1 °K. This system appears to be an isotropic spin-$\frac{5}{2}$ Heisenberg antiferromagnet. Birgeneau *et al.*[7] have found that Fisher's[11] solution of the classical Heisenberg chain fits the measured staggered susceptibility of TMMC from $T = 1$ °K to $T = 40$ °K. This classical model was also used by Dingle *et al.*[4] to fit susceptibility data for TMMC.

It is surprising that a classical spin model can be used at low temperatures. One might expect quantum effects to be important when kT is smaller than the energy required to change the state of a single spin, that is, when $JS/kT > 1$, where J is the Heisenberg coupling constant and S is the magnitude of the spin. This parameter ranges between 1 and 50 for TMMC at temperatures between 40 and 1 °K.

In this paper we describe a calculation of the first nontrivial quantum correction to the classical Heisenberg model. The method we describe is a general one, suitable for high-spin systems, and lattices of any dimensionality. It appears to be a series expansion in the parameter $1/S(S+1)$, although we have not been able to prove this. It is in this property that our method is different from previous methods[12] which do not seem feasible for high spin systems.

The actual computation of corrections requires knowledge of the exact solution of the corresponding classical model and therefore can be carried out only for one-dimensional spin systems. Even in this case the calculation is so long that we cannot give the details here. We shall give the method and the results. The complete calculation can be found in the thesis of Harrigan[13] which is available upon request.

II. METHOD OF COMPUTING QUANTUM CORRECTIONS

We take the Heisenberg Hamiltonian in the form

$$\mathcal{H}=-\frac{1}{2}\sum_{ij}\sum_{\alpha=1}^{3}J_{ij}^{\alpha}S_i^{\alpha}S_j^{\alpha}-g\mu_B\sum_j\vec{\mathrm{H}}\cdot\vec{\mathrm{S}}_j, \tag{1}$$

where J_{ij}^{α} is the exchange coupling between S_i^{α} and S_j^{α}, the αth components of the spin operators on lattice sites i and j. g is the gyromagnetic ratio, μ_B the Bohr magneton and H an external magnetic field. The classical Heisenberg model is obtained by replacing the quantum spin operators $\vec{\mathrm{S}}_i$ by classical unit vectors $\vec{\mathrm{X}}_i$. The classical model is a high spin limit of the quantum model in the following sense. Millard and Leff[14] have shown, as suggested by Fisher,[11] that if one takes a limit in which S (the maximum projection of the quantum $\vec{\mathrm{S}}_i$) becomes large but holding $J_{ij}S^2$ and gS fixed, then the quantum and classical partition functions are related by $\lim_{S\to\infty}S^{-N}Z_Q=(2\pi)^{-N}Z_C$. This result suggests that we look for an expansion of Z_Q (or other quantities of interest) in which the first term is the classical Z_C and higher terms vanish something like $1/S^n$ at fixed $J_{ij}S^2$ and gS.

In order to accomplish this it is convenient to define spin states which are as "classical" as possible. The state $|\theta,\phi)$ is defined to be such that the spin "points" in the direction of the polar angles (θ,ϕ). More exactly, if $\vec{\mathrm{X}}$ is a unit vector in the direction (θ,ϕ), then the state $|\theta,\phi)$ is defined by

$$\vec{\mathrm{X}}\cdot\vec{\mathrm{S}}|\theta,\phi)=S|\theta,\phi). \tag{2}$$

It follows that the expectation value of the normalized spin operator, $\vec{\mathrm{t}}=\vec{\mathrm{S}}/S$, in the state $|\theta,\phi)$ is given by

$$(\theta,\phi|\vec{\mathrm{t}}|\theta,\phi)=\vec{\mathrm{X}}. \tag{3}$$

These states are used by Wigner[15] in his consideration of the classical limit of certain angular-momentum matrix elements. He has shown that the normalized states can be written

$$|\theta,\phi)=\sum_{\mu=-S}^{+S}D_{S,\mu}^{(S)}(\theta,\phi)|\mu), \tag{4}$$

where $|\mu)$ is an eigenstate of S_z corresponding to eigenvalue μ, and the $D^{(S)}$ are $2S+1$ dimensional representations of the rotation group. [The third Euler angle is not important for the (S,μ) elements of $D^{(S)}$.] Using Eq. (4) and either the group orthogonality relations or the explicit expressions[15] for the $D_{S,\mu}^{(S)}(\theta,\phi)$, it is easy to show the trace of any operator A can be written[16]

$$\begin{aligned}\mathrm{Tr}\,A&=\sum_{\mu=-S}^{+S}(\mu|A|\mu)\\&=\frac{2S+1}{4\pi}\int_0^{2\pi}d\phi\int_0^{\pi}\sin\theta\,d\theta\,(\theta,\phi|A|\theta,\phi).\end{aligned} \tag{5}$$

A property of the states $|\theta,\phi)$ which is important in this paper is that the dispersion of the normalized quantum spin operator $\vec{\mathrm{t}}$ in these states is small for large S, so that these states are nearly classical for large S. This is most easily seen for the state $|0,0)$ along the z axis. If $\Delta\vec{\mathrm{t}}=\vec{\mathrm{t}}-(0,0|\vec{\mathrm{t}}|0,0)=\vec{\mathrm{t}}-\vec{\mathrm{X}}$, then one easily finds $(0,0|(\Delta t^z)^2|0,0)=0$ and $(0,0|(\Delta t^x)^2|0,0)=(0,0|(\Delta t^y)^2|0,0)=1/2S$. For an arbitrary state $|\theta,\phi)$ the dispersion of $\vec{\mathrm{t}}$ depends on θ and ϕ, but the $1/S$ dependence remains. We can also consider higher order dispersion. We can argue, in general, that

$$\begin{aligned}(\theta,\phi|\Delta t^{\alpha_1}\cdots\Delta t^{\alpha_n}|\theta,\phi)&\sim S^{-n/2} \qquad n \text{ even}\\&\sim S^{-(n+1)/2}, \quad n \text{ odd}.\end{aligned} \tag{6}$$

We have explicitly computed all quantities of this form up to $n=6$. For our calculation of the first nontrivial quantum corrections we shall need them to $n=4$. These are given in the Appendix.

Now suppose we want to compute the large S behavior of trace $A(\vec{\mathrm{t}})$, where A is a function of the normalized spin $\vec{\mathrm{t}}$. Equations (3), (5), and (6) suggest that we write $\vec{\mathrm{t}}=\vec{\mathrm{X}}+\Delta\vec{\mathrm{t}}$ and attempt to expand A about $\vec{\mathrm{X}}$ in powers of $\Delta\vec{\mathrm{t}}$. From Eq. (5) the first term in the expansion will be just an integral of the classical function $A(\vec{\mathrm{X}})$. From Eq. (6) we would expect higher order terms in the expansion to vanish with increasing powers of $1/S$.

To apply this idea to systems of many spins we use direct products of single spin states. Let $|\Omega_i)=|\theta_i,\phi_i)$ define the state of the ith spin. Then we define a normalized N spin state $|\Omega)=|\Omega_1\cdots\Omega_N)=|\theta_1,\phi_1)\otimes|\theta_2,\phi_2)\otimes\cdots\otimes|\theta_N,\phi_N)$. Set $d\Omega=\prod_{i=1}^{N}\sin\theta_i\,d\theta_i\,d\phi_i$. Then Eq. (5) generalizes to

$$\mathrm{Tr}A(\vec{\mathrm{t}}_1,\ldots,\vec{\mathrm{t}}_N)=\left(\frac{2S+1}{4\pi}\right)^N\int(\Omega|A|\Omega)\,d\Omega. \tag{7}$$

If we put $\vec{\mathrm{S}}_i=S\vec{\mathrm{t}}_i=S(\vec{\mathrm{X}}_i+\Delta\vec{\mathrm{t}}_i)$ in the Hamiltonian (1), we can write

$$\mathcal{H}=\mathcal{H}_C+\mathcal{H}_1+\mathcal{H}_2, \tag{8a}$$

where

$$\mathcal{H}_C=-\frac{1}{2}\sum_{i,j}\sum_{a}(J^a_{ij}S^2)X^a_iX^a_j, \tag{8b}$$

$$\mathcal{H}_1=-\sum_{i,j}\sum_{a}(J^a_{ij}S^2X^a_i+gS\mu_BH^a)\Delta t^a_j, \tag{8c}$$

$$\mathcal{H}_2=-\frac{1}{2}\sum_{i,j}\sum_{a}(J^a_{ij}S^2)\Delta t^a_i\Delta t^a_j. \tag{8d}$$

$\mathcal{H}_C$ is the corresponding classical Hamiltonian. $\mathcal{H}_1$ and $\mathcal{H}_2$ are, respectively, linear and quadratic in the deviation $\Delta\vec{t}_i$ from the classical X_i.

We are interested in computing the partition function and the spin-spin correlation functions given by

$$Z=\mathrm{Tr}e^{-\beta\mathcal{H}}, \tag{9a}$$

$$\langle\vec{S}_i\cdot\vec{S}_{i+l}\rangle=Z^{-1}\mathrm{Tr}(e^{-\beta\mathcal{H}}\vec{S}_i\cdot\vec{S}_{i+l}). \tag{9b}$$

We will use the partition function to illustrate the method. Using Eqs. (7) and (8) we can write the partition function as

$$Z=\left(\frac{2S+1}{4\pi}\right)^N\int(\Omega|e^{-\beta(\mathcal{H}_C+\mathcal{H}_1+\mathcal{H}_2)}|\Omega)d\Omega.$$

Since $\mathcal{H}_C$ commutes with $\mathcal{H}_1$ and $\mathcal{H}_2$ we can expand the exponential operator in powers of $\mathcal{H}_1+\mathcal{H}_2$ to obtain

$$Z=\left(\frac{2S+1}{4\pi}\right)^N\sum_{n=0}^{\infty}\frac{(-\beta)^n}{n!}\int e^{-\beta\mathcal{H}_C}(\Omega|(\mathcal{H}_1+\mathcal{H}_2)^n|\Omega)d\Omega. \tag{10}$$

The zeroth-order term is the classical partition function and higher order terms generate corrections in powers of $1/S$. If we want to compute corrections up to order $1/S^2$ we should, in view of Eq. (6) and the fact that $\mathcal{H}_1$ is linear in Δt and $\mathcal{H}_2$ quadratic in Δt, keep terms in Eq. (10) where the sum of the subscripts is no greater than 4. That is, to order $1/S^2$ terms of the form $\mathcal{H}_1$, $\mathcal{H}_1^2$, $\mathcal{H}_1^3$, $\mathcal{H}_1^4$, $\mathcal{H}_1^2$, $\mathcal{H}_2\mathcal{H}_1,\ldots,\mathcal{H}_2^2$ will contribute. The diagonal matrix elements of these terms can be computed using Eq. (8) and the matrix elements listed in the Appendix. We must then integrate the result over all angles Ω. These angular integrals in Eq. (10) can be reduced to integrals over certain multiple-spin correlation functions of the corresponding classical model. Therefore, the corresponding classical model must be manageable if we are to do these calculations. For this reason, the results given from here on apply only to the isotropic nearest-neighbor chain in zero external field. For this system we have used the above method to compute, to order $1/S^2$, the quantum corrections to the free energy and the spin-spin correlation function. The $1/S$ corrections can be absorbed[11] into the classical result by replacing JS^2 by $JS(S+1)$. We have checked these calculations by comparing the high-temperature limit of this method with the high-spin limit of the Rushbrooke and Wood[17,18] high-temperature expansion.

III. RESULTS

If we set $K=JS(S+1)/kT$ and $L(K)=\coth K-1/K$ then our results can be written

$$\ln Z_Q=\frac{\ln(2S+1)^N}{(4\pi)^N}+\ln Z_C-\frac{(N-1)}{12S(S+1)}K^2\left(1+L(K)-\frac{3L(K)}{K}+L^2(K)\right) \tag{11}$$

and

$$\langle\vec{S}_i\cdot\vec{S}_{i+l}\rangle=S(S+1)\left\{L^1(K)+\frac{\delta_{10}K^2}{S(S+1)}\left[\left(\frac{1}{4K}-\frac{1}{12}\right)\frac{dL^l}{dk}-\frac{L^l}{6}\frac{dL}{dK}-\frac{lL^{l-1}}{6K}+\frac{lL^l}{4K^2}-\frac{L^{l+1}}{6K}-\frac{\delta_{l1}L^l}{6K}+(l-1)\left(\frac{-L^{l-2}(1-3L/K)^2}{3}\right.\right.\right.$$

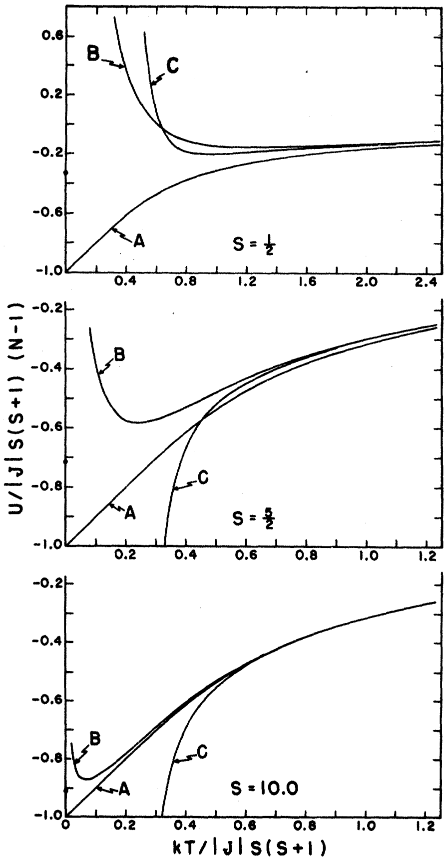

FIG. 1. Internal energy of a ferromagnet: (A) classical limit; (B) corrected classical (our result); (C) high-temperature series of Rushbrooke and Wood.

$$+\frac{L^{l-1}(1-3L/K)}{4}+\frac{L^{l+2}}{12}\Big)\Big]\Big\} . \quad (12)$$

The internal energy and the heat capacity can be found from Eq. (11) by the usual differentiations with respect to temperature. Susceptibilities and staggered susceptibilities can be found from Eq. (12) using the usual sum rules[11] relating susceptibilities and spin-spin correlation functions.

To show the character of our results we have included a number of graphs of internal energy and both staggered and normal susceptibility. On each graph three curves are shown, the classical result (A), our result (B), and the high-temperature series of Rushbrooke and Wood (C). In all of the graphs the three curves agree at high temperature as they should. The Rushbrooke-Wood[17] series is exact in $1/S$ and contains six terms in powers of $1/T$ for the susceptibility and five terms for the internal energy. We have truncated the series beyond these terms and numerically evaluated them for various T on the computer. Our results are to second order in $1/S$ but the T dependence is more complicated. In going from Eq. (9) to Eq. (10) we have made a high-temperature expansion of $e^{-\beta(\mathcal{H}_1+\mathcal{H}_2)} = e^{-\beta(\mathcal{H}-\mathcal{H}_C)}$ so we would expect our method to go bad at low enough temperatures. However, since we are expanding in the difference $\mathcal{H}-\mathcal{H}_C$ between the true and the classical Hamiltonian we might expect, for large S, our method to converge at lower temperatures than the usual high temperature expansions. One can see from the curves, at least for $S=\frac{5}{2}$, 10, that the two terms of our series appear more accurate at low temperatures than five terms in the Rushbrooke-Wood series. One can find, in many of the graphs (Figs. 1–4), ranges of temperature in which curves B and C are nearly identical but different from the classical curve A. Since B and C are obtained from quite different expansions we take this as a strong indication that B and C are accurately giving the quantum corrections to A in these temperature ranges. Another indication that the corrections are accurate in this region comes from taking the high-spin limit of the high-temperature-series curve C. In these temperature

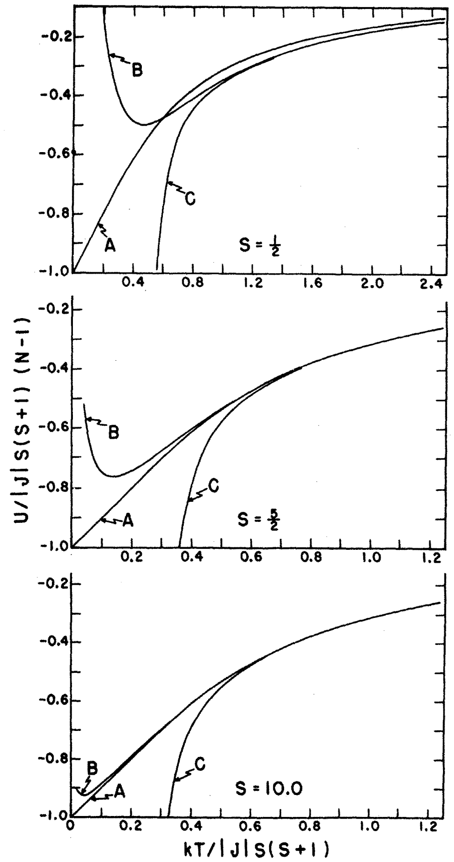

FIG. 2. Internal energy of an antiferromagnet: (A) classical limit; (B) corrected classical (our result); (C) high-temperature series of Rushbrooke and Wood.

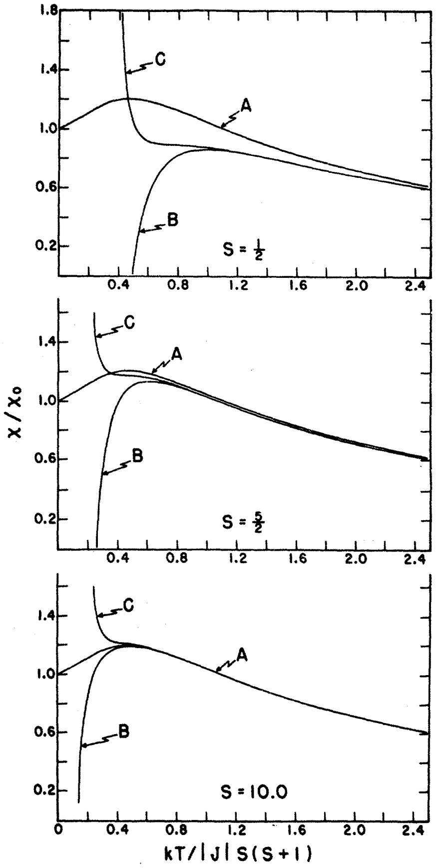

FIG. 3. Susceptibility of an antiferromagnet: (A) classical limit; (B) corrected classical (our result); (C) high-temperature series of Rushbrooke and Wood, $X_0=Ng^2 \times\mu_B^2 6|J|$.

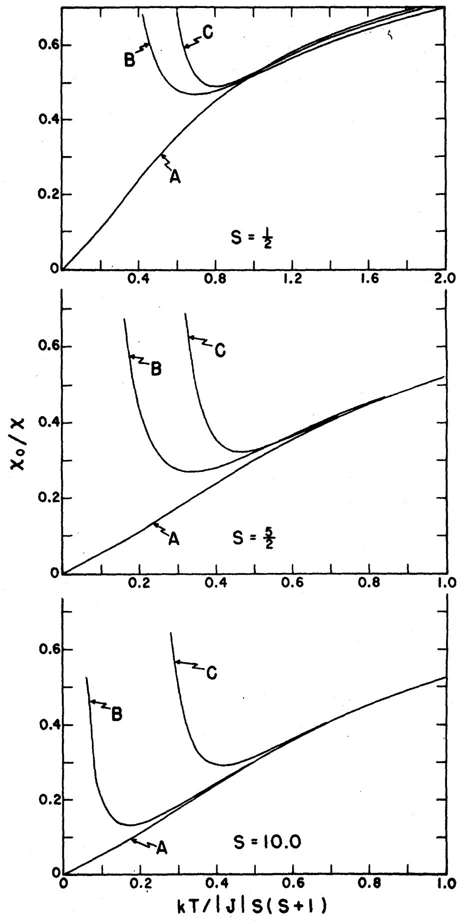

FIG. 4. Staggered susceptibility of an antiferromagnet: (A) classical limit; (B) corrected classical (our result); (C) high-temperature series of Rushbrooke and Wood, $X_0 = Ng^2\mu_B^2 S(S+1)/3kT$.

ranges this limit accurately reproduces the classical curve A, indicating that the high temperature series is converging.

On the graphs of internal energy we have plotted the exact ground-state energy, where known, as a point on the ordinate. The true internal energy curve must pass through this point with zero slope. One can see that curves B, neglecting the low temperature regions where they are obviously diverging, have a rather natural extrapolation to these ground-state energies.

The spin-$\frac{5}{2}$ staggered susceptibility curve is of interest with regard to the experimental data[7] on TMMC mentioned in the introduction. The temperature range of these experiments corresponds to a range of K^{-1} of $0.007 \le kT/S(S+1)|J| = K^{-1} \le 0.3$. It is clear that our correction cannot be trusted below $K^{-1} = 0.4$. However, the agreement of our curve with the Rushbrooke–Wood result in the region just above this suggests there is a significant correction to the classical curve. It is of course possible that the classical and quantum curves come together again at low temperatures. In any event, our calculations seem to indicate a quantum correction to the classical result becoming significant at about the temperature one would expect. This makes the agreement between very low temperature experiments and the classical model seem even more strange.

It is disappointing that our method will not reach the temperatures involved in the TMMC experiments. One might try to extend the temperature range of these calculation by computing higher-order terms in the series. The amount of labor involved seems large enough to make this unattractive. The S dependence of the terms in the high-temperature series expansion is always in powers of $S(S+1)$. This suggests that the next nontrivial correction in our method is of order $1/S^4$. It would be better to find a way to calculate the high spin quantum corrections which was valid at low temperatures, that is, which avoided the expansion involved in Eq. (10). The low-temperature problem, however, presents difficulties we have not yet overcome.

Our present calculation could better be compared with experiments at higher temperatures where one would expect the classical model to be nearly correct and where the prediction of our calculation might be accurate. There are a number of experiments which are natural candidates for such a comparison, and we are currently engaged in this.

APPENDIX

In this appendix we show how the matrix elements (6) are found and list them up to fourth order.

To compute quantities of the form $(\theta,\phi|\Delta t^{\alpha_1}\cdots\Delta t^{\alpha_n}|\theta,\phi)$, it is convenient to introduce a rotated set of coordinate axes (x', y', z') such that the z' axis is in the direction (θ,ϕ). Spin components in the two frames are related by the usual[15] orthogonal matrix $R_{\alpha\beta}$ according to

$$S^\alpha = \sum_\beta R_{\alpha\beta} S'^\beta. \tag{A1}$$

If we define $\Delta t^\alpha = 1/S[S^\alpha - (\theta,\phi|S^\alpha|\theta,\phi)]$ and $\Delta t'^\alpha = 1/S[S'^\alpha - (\theta,\phi|S'^\alpha|\theta,\phi)]$, then one can easily show from (A1) that

$$(\theta,\phi|\Delta t^{\alpha_1}\cdots\Delta t^{\alpha_n}|\theta,\phi)$$

$$= \sum_{\beta 1}\cdots\sum_{\beta n} R_{\alpha_1\beta_1}\cdots R_{\alpha_n\beta_n}(\theta,\phi|\Delta t'^{\beta_1}\cdots\Delta t'^{\beta_n}|\theta,\phi). \tag{A2}$$

In the primed frame (θ,ϕ) is a state of maximum projection along the z' axis so $(\theta,\phi|t'^z|\theta,\phi) = 1$, $(\theta,\phi|t'^x|\theta,\phi) = 0 = (\theta,\phi|t'^y|\theta,\phi)$. Hence

$$\Delta t'^x = t^x = S'^x/S, \quad \Delta t'^y = t^y = S'^y/S,$$

$$\Delta t'^z = t'^z - 1 = (S'^z - S)/S .$$

These relations simplify the computation of the matrix elements in the primed frame. Beyond this we just grind it out by expanding S'^x and S'^y in terms of raising and lowering operators and using their known properties. One must consider many special cases, find a formula fitting all of them, put these results in (A2), and do the sums. We give here the results of this procedure up to $n=4$. The detailed calculations are found in Ref. 13.

Let $\delta_{\alpha\beta}$ be the Kronecker δ and $\epsilon_{\alpha\beta\gamma}$ the usual completely antisymmetric tensor. Then

$$(\theta, \phi \,|\, \Delta t^\alpha \Delta t^\beta \,|\, \theta, \phi) = \frac{1}{2S}\,(\delta_{\alpha\beta} - X^\alpha X^\beta + i\epsilon_{\alpha\beta\gamma} X^\gamma), \quad \text{(A3)}$$

where $\vec{X}$ is a unit vector in the direction (θ, ϕ):

$$(\theta, \phi \,|\, \Delta t^\alpha \Delta t^\beta \Delta t^\gamma \,|\, \theta, \phi) = -(X^\beta/S)(\theta, \phi \,|\, \Delta S^\alpha \Delta S^\gamma \,|\, \theta, \phi), \quad \text{(A4)}$$

$$\begin{aligned}(\theta, \phi \,|\, \Delta t^\alpha \Delta t^\beta \Delta t^\gamma \Delta t^\nu \,|\, \theta, \phi) &= (\theta, \phi \,|\, \Delta t^\alpha \Delta t^\beta \,|\, \theta, \phi)(\theta, \phi \,|\, \Delta t^\gamma \Delta t^\nu \,|\, \theta, \phi)\\ &\quad + 2(\theta, \phi \,|\, \Delta t^\alpha \Delta t^\nu \,|\, \theta, \phi)(\theta, \phi \,|\, \Delta t^\beta \Delta t^\gamma \,|\, \theta, \phi)\\ &\quad + (1/S)[(X^\beta X^\gamma/S)(\theta, \phi \,|\, \Delta t^\alpha \Delta t^\nu \,|\, \theta, \phi)\\ &\quad - (\theta, \phi \,|\, \Delta t^\alpha \Delta t^\nu \,|\, \theta, \phi)(\theta, \phi \,|\, \Delta t^\beta \Delta t^\gamma \,|\, \theta, \phi)]. \quad \text{(A5)}\end{aligned}$$

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Conduction-Electron Contribution to Electric Field Gradients in Rare-Earth Metals

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The conduction-electron contribution to the electric field gradients in the heavy rare-earth metals has been calculated using a modified orthagonalized-plane-wave approach. Experimental results can be easily explained within the confines of the model and the amount of $5d$ character mixed into the conduction-electron wave function (characterized by a parameter ϵ_d) agrees well in both magnitude and sign with previous independent methods of determination. An attempt is made to correlate the magnitude of the $5d$ admixture with the d density of states in the conduction band.

INTRODUCTION

It is to be anticipated that the presence of conduction electrons in a metal may substantially modify the crystalline electric fields (CEF's) and electric field gradients (EFG's) from those which one might expect on the basis of insulator theory. One could envisage strong screening effects which would reduce the effective fields to below the point-charge values. However, experimental evidence shows that the point-charge fields may be enhanced and even changed in sign.[1-3] It is therefore clear that conduction electrons must play an important role in this respect. A growing experimental interest in the determination of CEF's and EFG's by susceptibility, neutron-scattering, and Mössbauer-