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Thermodynamics of interacting many-level systems from random-phase-approximation Green's functions*

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Standard-basis-operator (SBO) Green's function equations of motion are developed in the random-phase approximation (RPA) for a general Hamiltonian characterizing interacting systems having discrete energy levels. It is shown that the RPA equations have the same algebraic structure as the chain-diagram equations in the perturbation theory of SBO Green's functions. The earlier problems of redundancy and failure to satisfy the monotopic restrictions in the calculation of autocorrelation functions are resolved. Ratios of RPA autocorrelation functions can always be determined from commutator equations from which thermal average energy-level occupation probabilities P_β associated with state $|\beta\rangle$ are obtained. Using the properties of the SBO, a very simple derivation of an explicit formula for P_β is given for an important class of Hamiltonians, which includes the Hubbard s-band model and the Heisenberg ferromagnet. This derivation completely avoids the use of complicated methods such as the moment generator used to solve equations coupling average moments of the spin operator $\hat{S}_Z$ in ferromagnetic and antiferromagnetic systems.

I. INTRODUCTION

The equation-of-motion method using double-time temperature-dependent Green's functions[1,2] has received widespread use in various approximations to predict the thermodynamics of condensed-matter systems. A linearization scheme often used to decouple the Green's-function equations is the random-phase approximation (RPA). The RPA is the simplest approximation yielding interaction dispersed excitation energies, and it has been used with notable success in describing over a large temperature range the thermal-average properties of interacting systems.

In magnetic insulators with simple single-ion energy-level structure, early RPA Green's-function calculations appeared to yield a unique set of equations which determine the autocorrelation functions, in particular the thermal-average moments of the Z component of the single-ion spin operator.[3,4] Applying the RPA to more-complicated systems, for example, the Heisenberg ferromagnet with uniaxial single-ion anisotropy, which has received a great deal of theoretical attention for spin 1,[5–8] it became apparent that the RPA may lead to inconsistencies. The exact nature of the inconsistencies is most clearly manifested in the operator formalism originally introduced in the atomic representation by Hubbard to calculate the excitation spectra of various approximations to his tight-binding Hamiltonian.[9] These operators were later reintroduced and developed by Haley and Erdös as the standard-basis-operator (SBO) method in the Green's-function equation-of-motion technque[7] (referred to as I). In I it is shown that single-ion terms can always be treated exactly in any decoupling scheme when using Green's functions of SBO, thus solving one of the earlier problems of decoupling the interaction terms in a manner consistent with the approximate treatment of single-ion terms. This problem was first solved for the spin-1 anisotropic ferromagnet by Murao and Matsubara[6] using components of the quadrupole-moment operator; but in contrast to the SBO method their approach is not readily extended to complicated systems with many levels. Applying the SBO formalism in the RPA to the troublesome spin-1 anisotropic ferromagnet, Haley and Erdös found that, as in the Murao-Matsubara approach, the SBO Green's-function equations generate an overcomplete, or redundant, set of equations for the corresponding autocorrelation functions. It was demonstrated in I that even when the anisotropy was set to zero the redundancy prevails, and leads to nonunique values for $\langle\hat{S}_Z\rangle$. Furthermore, the RPA autocorrelation function equations for the spin-1 problem appeared to violate certain multiplication values of the SBO, referred to as "monotopic restrictions."

Diagrammatic techniques have been developed by B. Westwański[10] and by Yang and Wang[11] using temperature-dependent Green's functions of SBO. The latter authors applied their method to the spin-1 Heisenberg ferromagnet with single-ion anisotropy and showed that by carefully collecting all diagrams to first order in their perturbation parameter, the reciprocal interaction volume, that the monotopic restrictions were not violated to that order.[12] However, they did not solve the redundancy problem, but selected a certain coupled subset of equations to determine the autocorrelation functions. [This point is discussed in Sec. III following Eq. (3.20).]

Standard basis operators provide the most detailed and fundamental matrix representation for Hamiltonians modelling systems with discrete energy levels. Since all Hamiltonians expressed in terms of SBO have identical algebraic structure, and since the SBO form a closed set under one simple multiplication rule, these operators are particularly useful in formulating model-independent approximation schemes for interacting systems. In fact the nature of the SBO is such that it yields maximum information with minimum effort.

In view of the recent use of SBO Green's functions in the RPA for describing the excitations and the thermodynamics of transition metals,[13–15] and actinide compounds,[16,17] analysis of the general RPA equations using SBO formalism seems appropriate. In this paper, a systematic procedure for determining solutions of the RPA equations consistent with the monotopic restrictions is presented.

II. HAMILTONIAN AND SBO GREEN'S FUNCTIONS

The properties of standard basis operators have been given in detail in Hubbard IV[9] and in Haley and Erdö (I). In this section I cite for convenience some of these properties and develop a generalization of the RPA equations appearing in I for the double-time temperature-dependent Green's functions formed from SBO. The SBO are defined by

$$\hat{L}^{l}_{\alpha\alpha'} = |l\alpha\rangle\langle l\alpha'| \ , \tag{2.1}$$

where the complete set of functions $\{|l\alpha\rangle\}$ for $l = 1, \ldots, N$ and $\alpha = 1, \ldots, p$ are the state vectors of the ion l in state α. The set of states chosen is arbitrary, but as discussed in Ref. I and shown here, the best choice is the set of orthonormal effective-field states, which is assumed throughout the paper.

From (2.1) is follows that the multiplication rule for SBO is

$$\hat{L}^{l}_{\alpha\alpha'}\hat{L}^{l}_{\beta'\beta} = \delta_{\alpha'\beta'}\hat{L}^{l}_{\alpha\beta} \ . \tag{2.2}$$

Using (2.2) and the basic symmetry properties of the single-ion wave functions it follows that

$$[\hat{L}^{l}_{\alpha\alpha'}, \hat{L}^{m}_{\beta'\beta}]_{\pm} = \delta^{lm}(\delta_{\alpha'\beta'}\hat{L}^{l}_{\alpha\beta} \pm \delta_{\alpha\beta}\hat{L}^{l}_{\beta'\alpha'}) \ . \tag{2.3}$$

The plus sign is used if both operators have fermion character, and the minus sign if one or both operators have boson character. The SBO $\hat{L}^{l}_{\alpha\alpha'}$ has fermion character if the difference between the number of electrons in state $|l\alpha\rangle$ and in state $|l\alpha'\rangle$ is odd, and it has boson character if this difference is even.[9] Thus the operator $\hat{L}^{l}_{\alpha\alpha'}$ for $\alpha \neq \alpha'$ can have either character, but $\hat{L}^{l}_{\alpha\alpha}$ is always of boson character. The diagonal SBO satisfy the normalization condition

$$\sum_{\alpha} \hat{L}^{l}_{\alpha\alpha} = \hat{1} \ . \tag{2.4}$$

I consider a general Hamiltonian $\hat{H}$ consisting of single-site and two-site interaction terms for systems having a finite number of discrete energy levels. As in I, $\hat{H}$ has the form

$$\hat{H} = \sum_{f,l} h^{l}_{f}\hat{A}^{l}_{f} + \frac{1}{2}\sum_{g,l}\sum_{g',m} J^{lm}_{gg'}\hat{B}^{l}_{g}\hat{B}^{m}_{g'} \ , \quad \text{with } J^{ll}_{gg'} = 0 \ . \tag{2.5}$$

The matrix operators $\hat{A}^{l}_{f}$ and $\hat{B}^{l}_{g}$ are elements of the set $\{\hat{A}^{l}_{f}, f = 1, \ldots, N_f; \hat{B}^{l}_{g}, g = 1, \ldots, N_g\}$ necessary to form the Hamiltonian. The superscripts denote the site (ion) $l, m = 1, \ldots, N$. The scalars h^{l}_{f} are the effective-field strengths, and $J^{lm}_{gg'}$ are the interaction constants.

In terms of SBO defined in the effective-field states the Hamiltonian (2.5) takes the form

$$\hat{H} = \sum_{\mu,l} \epsilon^{l}_{\mu}\hat{L}^{l}_{\mu\mu} + \frac{1}{2}\sum_{\mu\mu',l}\;\sum_{\nu\nu',m} W^{lm}_{\mu'\mu,\nu\nu'}\Delta\hat{L}^{l}_{\mu'\mu}\Delta\hat{L}^{m}_{\nu\nu'} + (\text{const}) \ , \tag{2.6}$$

where $\Delta\hat{L}_{\mu'\mu} = \hat{L}_{\mu'\mu} - \delta_{\mu\mu'}\langle\hat{L}_{\mu\mu}\rangle$ is the fluctuation operator introduced for convenience for all operators, even though we define $\Delta\hat{L}_{\mu'\mu} = \hat{L}_{\mu'\mu}$ for $\mu \neq \mu'$. The single-system effective-field energies are $\epsilon^{l}_{\mu} = \epsilon^{l}_{\mu} + \zeta n^{l}_{\mu}$, with n^{l}_{μ} the number of electrons in state $|l\mu\rangle$, and ζ the chemical potential. The combined intersystem-interlevel coupling constants $W^{lm}_{\mu'\mu\nu\nu'}$, are given by

$$W^{lm}_{\mu'\mu,\nu\nu'} = W^{lm}_{\mu^{+},\nu} = \sum_{g,g'} J^{lm}_{gg'}B^{g}_{\mu^{+}}B^{g'}_{\nu} \ , \tag{2.7}$$

in which double subscripts have been replaced by the notation $\mu = (\mu, \mu')$ and $\mu^{+} = (\mu', \mu)$. Whenever the subscripts are arbitrary, this compact notation will be assumed throughout the paper. The constants B^{g}_{μ} are matrix elements of $\hat{B}^{l}_{g}$ in the effective-field states.

In the compact subscript notation, the two-operator retarded SBO Green's function is defined by[7]

$$G^{nm}_{\alpha\beta^{+}}(t-t') = \langle\langle\hat{L}^{n}_{\alpha}(t)|\hat{L}^{m}_{\beta^{+}}(t')\rangle\rangle = \begin{cases} -i\langle[\hat{L}^{n}_{\alpha}(t), \hat{L}^{m}_{\beta^{+}}(t')]_{\pm}\rangle & \text{for } t > t', \\ 0 \quad \text{for } t < t', \end{cases} \tag{2.8}$$

where the bracket $\langle\cdots\rangle$ denotes a thermal average. The spectral representation of this SBO Green's function has the equation of motion

$$EG^{nm}_{\alpha\beta^+}(E) = (1/2\pi)\langle[\hat{L}^n_\alpha,\hat{L}^m_{\beta^+}]_\pm\rangle + \langle\langle[\hat{L}^n_\alpha,\hat{H}]_-|\hat{L}^m_{\beta^+}\rangle\rangle_E \ , \tag{2.9}$$

and it is related to the corresponding time-dependent correlation functions through the relation[1]

$$\langle\hat{L}^m_{\beta^+}(t')\hat{L}^n_\alpha(t)\rangle = \int_{-\infty}^{\infty}\frac{dE}{i}[G^{nm}_{\alpha\beta^+}(E-i0) - G^{nm}_{\alpha\beta^+}(E+i0)] \times f^\pm(E)e^{-iE(t-t')} \ , \tag{2.10}$$

where

$$f^\pm(E) = (e^{E/k_BT} \pm 1)^{-1} \ . \tag{2.11}$$

Introducing an operator-character parameter $\eta^{\mathrm{ln}}_{\nu\mu}$ defined by the commutator equation

$$\hat{L}^l_\nu\hat{L}^n_\mu = \eta^{\mathrm{ln}}_{\nu\mu}\hat{L}^n_\mu\hat{L}^l_\nu \quad \text{for } l \neq n \ , \tag{2.12}$$

it follows from Hamiltonian (2.6) that the Green's-function equation of motion (2.9) is

$$\begin{aligned}(E-\Delta\epsilon^l_\alpha)G^{nm}_{\alpha\beta^+}(E) = {} & \frac{1}{2\pi}\langle[\hat{L}^n_\alpha,\hat{L}^m_{\beta+}]_\pm\rangle + \sum_{\mu,\nu,l}\langle\langle[V^{nl}_{\alpha'\mu,\nu}(\eta^{\mathrm{ln}}_{\nu,\alpha'\mu})\hat{L}^n_{\alpha\mu} - \eta^{nl}_{\alpha,\nu}V^{nl}_{\mu\alpha,\nu}(\eta^{\mathrm{ln}}_{\nu,\mu\alpha})\hat{L}^n_{\mu\alpha'}]\Delta\hat{L}^l_\nu|\hat{L}^m_{\beta+}\rangle\rangle_E \\ & + \sum_{\mu,\nu,l}(\eta^{nl}_{\alpha\nu}-1)(W^{nl}_{\mu\mu,\nu} + W^{\mathrm{ln}}_{\nu,\mu\mu})\langle\hat{L}^n_{\mu\mu}\rangle\langle\langle\hat{L}^n_\alpha\Delta\hat{L}^l_\nu|\hat{L}^m_{\beta+}\rangle\rangle_E \\ & + \sum_{\substack{\mu,l \\ l,l'\neq n}}\sum_{\nu,l'} W^{ll'}_{\mu^+,\nu}(\eta^{nl}_{\alpha\mu}\eta^{nl'}_{\alpha\nu}-1)\langle\langle\Delta\hat{L}^l_{\mu+}\Delta\hat{L}^{l'}_\nu\hat{L}^n_\alpha|\hat{L}^m_{\beta^+}\rangle\rangle_E \ ,\end{aligned} \tag{2.13}$$

where

$$V^{nl}_{\mu,\nu}(\eta^{\mathrm{ln}}_{\nu,\mu}) = \tfrac{1}{2}(W^{nl}_{\mu,\nu} + \eta^{\mathrm{ln}}_{\nu,\mu}W^{\mathrm{ln}}_{\nu,\mu})$$

and (2.14)

$$\Delta\epsilon^l_\alpha = \Delta\epsilon^l_{\alpha\alpha'} = \epsilon^l_{\alpha'} - \epsilon^l_\alpha \ .$$

For Hamiltonians of the form (2.5) in which the interaction does not mix operators of different character, the last two terms in Eq. (2.13) are absent. In these cases, which include the Hubbard Hamiltonian[9] and spin Hamiltonians, the signs of all $\eta^{\mathrm{ln}}_{\nu\mu}$ appearing in Eq. (2.13) will be identical, in agreement with Hubbard IV.[9]

III. RPA EQUATION AND SOLUTIONS

The simplest linearization of Eq. (2.13) is the random phase approximation in which thermal fluctuations of the SBO appearing on the left-hand side of the three-operator Green's functions are neglected, i.e.,

$$\langle\langle\hat{L}^n_{\mu\mu'}\Delta\hat{L}^l_\nu|\hat{L}^m_{\beta^+}\rangle\rangle_E \approx \delta_{\mu\mu'}\langle\hat{L}^n_{\mu\mu}\rangle G^{lm}_{\nu\beta^+}(E) \ , \tag{3.1}$$

noting that $\langle\Delta\hat{L}^l_\nu\rangle = 0$. The assumption that $\langle\hat{L}_{\mu\mu'}\rangle << \langle\hat{L}_{\mu\mu}\rangle$ is reasonably justified only for SBO defined in the effective-field states. Applying (3.1) to (2.13), and noting that only excitations of the same character are coupled,[9] yields the RPA equation

$$(E-\Delta\epsilon^n_\alpha)G^{nm}_{\alpha\beta^+} = \Delta P^\pm_\alpha\left(\frac{\delta^{nm}}{2\pi}\delta_{\alpha\beta} + \sum_{\nu,l}V^{nl}_{\alpha^+,\nu}(\mp)G^{lm}_{\nu\beta^+}\right) \ , \tag{3.2}$$

where

$$\Delta P^\pm_\alpha = P_\alpha \pm P_{\alpha'}, \quad \text{with } P_\alpha = \langle\hat{L}_{\alpha\alpha}\rangle \ . \tag{3.3}$$

The upper or lower sign is chosen according to whether $\hat{L}^n_{\alpha\alpha'}$ has Fermi or Bose character, respectively. The most-general linearization possible for Eq. (2.13) is easily constructed in terms of SBO by applying the method of Roth,[18] in which the arbitrary linearization coefficients can be evaluated in principle by conserving the second moment of the spectral intensity function.[19,20] Unfortunately, the resulting Green's-function equations of motion cannot be solved analytically for systems with many levels. In contrast, analytic solutions can often be constructed for the RPA equations (3.2). The remainder of the paper deals with solutions of the RPA equations.

For systems fixed on a translationally invariant lattice, Eq. (3.2) is simplified by Fourier transforming to the momentum representation. Using the transformations defined in I gives the RPA interlevel matrix equation in k space

$$(E-\Delta\epsilon_\alpha)G^k_{\alpha\beta^+} = \Delta P^\pm_\alpha\left(\frac{1}{2\pi}\delta_{\alpha\beta} + \sum_\nu V^k_{\alpha^+,\nu}(\mp)G^k_{\nu\beta^+}\right) \ , \tag{3.4}$$

where explicitly

$$V^k_{\alpha^+,\nu}(\mp) = \frac{1}{2}\sum_{g,g'}(J^k_{gg'} \mp J^{-k}_{g'g})B^g_{\alpha^+}B^{g'}_\nu \ . \tag{3.5}$$

Generalization of Eq. (3.4) to the case of multiple sublattices, such as in antiferromagnets, is straightforward, and is found in I. For the lower sign case, the RPA equation (3.4) is algebraically analogous to the equation for the SBO Green's functions obtained in the diagram technique of Yang and Wang by summing over the chainlike diagrams.[11] If the averages P_α are replaced by $D_\alpha = \langle \hat{L}_{\alpha\alpha} \rangle_0$, where D_α is an ensemble average taken with respect to the effective field Hamiltonian, Eq. (3.4) becomes identical with their chain formula.

In general, for systems having p levels, Eq. (3.4) couples $p(p-1)$ Green's functions together. An analytic solution of this RPA equation by inversion of the interlevel matrix of dimension $p(p-1)$ is only feasible for systems with p very small,[7,21] or when many of the coupling constants $V^k_{\alpha^+,\nu}$ are zero.[16] A much simpler approach is to make use of the explicit form of the coupling constants in terms of the matrix elements B^g_ν.

Introducing an interlevel-averaged Green's function defined by

$$\mathcal{G}^k_{\beta^+}(g') = \sum_\nu B^{g'}_\nu G^k_{\nu\beta^+} \ , \tag{3.6}$$

and operating on Eq. (3.4) with $\sum_\alpha B^g_\alpha (E-\Delta\epsilon_\alpha)^{-1}$ yields the coupling-constant matrix equation

$$\sum_{g'} [\delta_{gg'} - X^k(g',g)]\, \mathcal{G}^k_{\beta^+}(g') = \frac{1}{2\pi} Z_{\beta^+}(g) \ . \tag{3.7}$$

The inhomogeneous term is given by

$$Z_{\beta^+}(g) = B^g_\beta \, \Delta P^\pm_\beta (E - \Delta\epsilon_\beta)^{-1} \ , \tag{3.8}$$

and X^k is a matrix with elements

$$X^k(g',g) = \sum_\alpha Y^k_{\alpha^+}(g') B^g_\alpha \, \Delta P^\pm_\alpha (E-\Delta\epsilon_\alpha)^{-1} \ , \tag{3.9}$$

with

$$Y^k_{\alpha^+}(g') = \frac{1}{2} \sum_f (J^k_{fg'} \mp J^{-k}_{g'f}) B^f_{\alpha^+} \ . \tag{3.10}$$

The functions $\mathcal{G}^k_{\beta^+}(g)$ are determined by inversion of a matrix of dimension N_g. Substituting the resulting expressions for $\mathcal{G}^k_{\beta^+}$ into Eq. (3.4) gives the complete solution of the RPA equations for all $G^k_{\alpha\beta^+}$. The advantage of this approach is that often $N_g \ll p(p-1)$, or X^k is a diagonal matrix. In either case, Eq. (3.7) is easily solved. For example, in the Heisenberg ferromagnet the coupling constants that determine the RPA quasiparticle excitations are

$$V^k_{\alpha^+,\alpha} = -\tfrac{1}{2} J^k b^2_\alpha \delta_{\alpha',\alpha-1} \tag{3.11}$$

and the matrix X^k is of dimension one. The parameters in Eq. (3.11) are given in the Appendix, where the Heisenberg ferromagnet with arbitrary spin S is treated. In the Hubbard model quasihole excitations are mainly determined by[22]

$$V^k_{\alpha^+,\nu} = \sum_{gg'} T^k_{gg'} (\alpha' | c^\dagger_g | \alpha)(\nu | c_g{'} | \nu') \ , \tag{3.12}$$

where $c^\dagger_g$ creates an electron in atomic orbital g, characterized by some appropriate set of quantum numbers. For example, $g = (l, m, \sigma)$ for a single-electron orbital, where l is the angular momentum, m is the orbital projection, and σ are the electron-spin quantum numbers. Similarly for quasielectron excitations

$$V^k_{\alpha^+,\nu} = -\sum_{gg'} T^{-k}_{g'g} (\nu | c^\dagger_g | \nu')(\alpha' | c_{g'} | \alpha) \ . \tag{3.13}$$

For the Hubbard s-band model, $V^k_{\alpha^+,\alpha} = \pm T^k$, and the matrix X^k is diagonal. In other cases, a reasonable approximation of the hopping matrix elements $T^k_{gg'}$ can sometimes be made, which greatly reduces the problem of inverting the matrix X^k.[17]

As an illustration of the problems arising in the solutions of the RPA equation (3.4), I consider the class of Hamiltonians for which the matrix X^k is diagonal, i.e., $X^k(g,g') = \delta_{gg'} X^k(g)$, and for which each given set of level indices (α, α') has at most one nonzero matrix element $B^{g(\alpha,\alpha')}_{\alpha\alpha'}$ associated with it. This class includes the anisotropic Heisenberg ferromagnet and the Hubbard s-band Hamiltonians.

For the cases under consideration, the solution of Eq. (3.7) is given by

$$\mathcal{G}^k_{\beta^+} = \mathcal{G}^k_{\beta^+}(g) = \frac{1}{2\pi} Z_{\beta^+}(g) \times \left[1 - \sum_\alpha Y_{\alpha+}(g) B^g_\alpha \, \Delta P^\pm_\alpha (E - \Delta\epsilon_\alpha)^{-1} \right] \ , \tag{3.14}$$

where $g = g(\beta, \beta')$. Since there is only one g associated with each (β, β') the g designation will be suppressed in the sequel, but it should be remembered that $g(\beta, \beta')$ restricts the sum over α in the denominator of Eq. (3.14).

Clearing fractions in Eq. (3.14) gives $\mathcal{G}^k_{\beta^+}$ as the ratio of polynomials in E, the numerator being of one degree less than the denominator. The roots ω^r_k of the denominator are quasiparticle excitation energies between states in the bands formed from the interaction dispersed effective-field levels ϵ_α. Assuming that these roots are distinct, or at worst degenerate at a few isolated points in k space, Eq. (3.14) may be expanded in partial fractions.[23] This expansion gives

$$\mathcal{G}^k_{\beta^+} = (2\pi)^{-1} B_\beta \Delta P^\pm_\beta \sum_r R^\pm_\beta(k,r)(E - \omega^r_k)^{-1} \ . \tag{3.15}$$

The excitation energies ω^r_k are determined from the characteristic equation

$$\prod_r (E-\omega_k^r)=\prod_\nu (E-\Delta\epsilon_\nu) - \sum_\alpha Y^k_{\alpha^+}[g(\beta)]B_\alpha^{g(\beta)}\,\Delta P_\alpha^\pm \times \prod_{\nu\neq\alpha}(E-\Delta\epsilon_\nu) \;, \tag{3.16}$$

where $\prod_{\nu\neq\alpha}(E-\Delta\epsilon_\nu)$ is the product necessary to clear fractions in Eq. (3.14), excluding the term $E-\Delta\epsilon_\alpha$. The functions $R_\beta^\pm(k,r)$ are defined by

$$R_\beta^\pm(k,r)=\prod_{\nu\neq\beta}(\omega_k^r-\Delta\epsilon_\nu) \times \left[\prod_{r'\neq r}(\omega_k^r-\omega_k^{r'})\right]^{-1} \;. \tag{3.17}$$

They satisfy the normalization

$$\sum_r R_\beta^\pm(k,r)=1 \quad\text{for any } \beta \;. \tag{3.18}$$

Substituting expression (3.15) for $\mathcal{G}^k_{\beta^+}$ into (3.4) yields the interlevel Green's function

$$G^k_{\alpha\beta^+}=\frac{\Delta P_\alpha^\pm}{2\pi}\left\{\delta_{\alpha\beta}(E-\Delta\epsilon_\alpha)^{-1}+V^k_{\alpha^+,\beta}\,\Delta P_\beta^\pm \times \sum_r \frac{R_\beta(k,r)}{\omega_k^r-\Delta\epsilon_\alpha}\left[(E-\omega_k^r)^{-1} - (E-\Delta\epsilon_\alpha)^{-1}\right]\right\} \;. \tag{3.19}$$

When $V^k_{\alpha^+\beta}=0$, the only nonzero Green's function is $G^k_{\alpha\alpha^+}$ which has an effective-field pole $\Delta\epsilon_\alpha$. The reason is that the RPA equation of motion (3.4) contains only terms to linear order in the matrix elements $B_{\alpha'\alpha}$ of the interaction Hamiltonian, which does not directly connect levels α and α' if $B_{\alpha'\alpha}=0$. To disperse such an excitation, a higher decoupling involving powers of the interaction Hamiltonian would have to be used. Effective-field excitations, also present in diagrammatic methods,[12,24] are due to approximations.

The surprising feature of Eq. (3.19) is that when $V^k_{\alpha^+\alpha}\neq 0$, the Green's function $G^k_{\alpha\alpha^+}$ may have poles not only at the dispersed excitation energies ω_k^r but also simultaneously at the effective-field excitation energy $\Delta\epsilon_\alpha$. It can be shown using the characteristic equation (3.16) that this mixing of dispersed and nondispersed poles in $G^k_{\alpha\alpha^+}$ occurs whenever there exists degeneracy in the effective-field excitations appearing in Eq. (3.16). Such degeneracy occurs in the isotropic Heisenberg ferromagnet, and in the Hubbard *s*-band model in the limit of vanishing electron-electron interaction I for electrons on the same site. In the absence of effective field excitation degeneracy, for example the Heisenberg ferromagnet with single-ion anisotropy [see (A13)], the poles of $G^k_{\alpha\alpha^+}$ and $\mathcal{G}^k_{\alpha^+}$ are identical and dispersed. However, the numerators are quite different; thus these two Green's functions generate different correlation functions.

In inhomogeneous media one might expect poles of the single-ion type to represent an approximation to a localized excitation due to scattering of a wavelike excitation. However in the homogeneous media considered here, these poles appear to be spurious. They should be present only in the limit as the interaction goes to zero. In this limit the dispersed excitations reduce directly to the corresponding single-ion excitations.

In contrast to the spurious pole situation in $G^k_{\alpha\alpha^+}$ when $V^k_{\alpha^+\alpha}\neq 0$, the averaged Green's function $\mathcal{G}^k_{\beta^+}$ given by (3.15), which is a linear combination of only the interlevel Green's functions for which $B_{\alpha^+}\neq 0$, contains only dispersed poles ω_k^r. These averaged Green's functions play an important role in calculating correlation functions in Sec. IV, but first I consider what happens when Eq. (3.19) is used to determine such functions.

Thermal averages of single-ion operators are determined from the correlation functions associated with G^{nm}. Substituting (3.19) into (2.10) and transforming back to coordinate representation, the time-independent correlation functions are determined in RPA by the interlevel equations

$$\langle \hat{L}^m_{\beta^+}\hat{L}^n_\alpha\rangle=\Delta P_\alpha^\pm\left\{\delta^{nm}\delta_{\alpha\beta}f^\pm(\Delta\epsilon_\alpha)+\Delta P_\beta^\pm N^{-1}\sum_{k,r}\frac{V^k_{\alpha^+\beta}R_\beta(k,r)}{\omega_k^r-\Delta\epsilon_\alpha}\left[f^\pm(\omega_k^r)-f^\pm(\Delta\epsilon_\alpha)\right]e^{i\vec{k}\cdot(\vec{n}-\vec{m})}\right\} \;. \tag{3.20}$$

Examination of Eq. (3.20) shows that it gives an overcomplete set of nonlinear algebraic equations for the autocorrelation functions $\langle \hat{L}^n_{\beta^+}\hat{L}^n_\beta\rangle$ which determine the set $\{P_\beta\}$ of thermal-average occupation probabilities. The source of this redundancy is that $P_\beta=\langle \hat{L}_{\beta\beta}\rangle$ can be calculated from any autocorrelation function $\langle \hat{L}^n_{\beta\alpha}\hat{L}^n_{\alpha\beta}\rangle$ for $\alpha=1,\ldots,P$, except $\alpha=\beta$. This redundancy exists in any order of approximation, including an exact calculation; however, in the latter case any complete set of $\langle \hat{L}^n_{\beta\alpha}\hat{L}^n_{\alpha\beta}\rangle$, with the normalization condition (2.4), gives a unique value for all P_β. This is easily demonstrated by neglecting the interaction part of Hamiltonian (2.6), in which case the first term in (3.20) represents an exact solution for the effective-field Hamiltonian.

In approximations of higher order than the effective-field approximation, the equation-of-motion method and the diagrammatic-expansion method can treat different interlevel excitations to different orders of approximation. For example, in the Heisenberg ferromagnet $B_{\beta\pm 1,\beta} \neq 0$, but $B_{\beta\alpha}=0$ for $|\beta-\alpha| > 1$; thus Eq. (3.20) has a completely different algebraic form in determining $P'_\beta = \langle \hat{L}_{\beta\alpha} \hat{L}_{\alpha\beta} \rangle$ for $|\beta-\alpha| > 1$ from its form in determining $P_\beta = \langle \hat{L}_{\beta,\beta-1} \hat{L}_{\beta-1,\beta} \rangle$. One obtains different results if P'_β is used instead of P_β in calculating thermodynamic parameters. This lack of uniqueness also prevails in the diagrammatic technique of Yang and Wang.[11] In their treatment of the spin-1 Heisenberg ferromagnet[12] in complete set $\{P_1, P_0, P_{-1}\}$ where 1,0,1 label the projection states of $\hat{S}_Z$, was calculated, but $P'_\beta = \langle L^n_{1-1} L^n_{-11} \rangle$ was ignored because the Green's function which determines P'_1 is not linked with the set of Green's functions which determine $\{P_1, P_0, P_{-1}\}$. It remains to be shown in the diagrammatic method that P'_β can be calculated equal to P_β. Also in the RPA equation (3.20), the P'_β are not linked to the P_β when the Hamiltonian does not contain matrix elements between nonadjacent states, i.e., when $B_{\beta\alpha}=0$ for $|\beta-\alpha| > 1$.

In addition to the autocorrelation functions $\langle \hat{L}^n_{\beta\alpha} \hat{L}^n_{\alpha\beta} \rangle$ which determine $\{P_\beta\}$, Eq. (3.20) contains $\langle L^n_{\beta'\beta} \hat{L}^n_{\alpha\alpha'} \rangle$ with $\alpha \neq \beta$. In accordance with the multiplication rule (2.2), referred to as the "monotopic restriction" in I, all functions $\langle \hat{L}^n_{\beta'\beta} \hat{L}^n_{\alpha\alpha'} \rangle = 0$ for $\alpha \neq \beta$. However, applying the multiplication rule to Eq. (3.20) shows that this equation is not satisfied for $\alpha \neq \beta$, unless $\Delta P^\pm_\alpha = 0$. This is not only physically unreasonable, but it is in contradiction with the nonzero values of $\Delta P^\pm_\alpha$ which also follow from Eq. (3.20) when $\alpha=\beta$.

This lack of internal consistency occurs in the chainlike diagram formula given by Yang and Wang.[11,12] These authors show in an explicit calculation on the spin-1 Heisenberg ferromagnet that the chainlike diagrams for the autocorrelation functions do not include all terms to first order in their expansion-parameter reciprocal interaction volume. They prove, however, that when all diagrams to first order are summed, the functions $\langle \hat{L}^n_{\beta'\beta} \hat{L}^n_{\alpha\alpha'} \rangle = 0$ for $\alpha \neq \beta$.

Can the RPA equations be used in some way to give a unique and reasonable value for the set $\{P_\beta\}$ of occupation probabilities without violating basic operator rules? In the many previous papers utilizing Green's functions of angular momentum operators, RPA decoupling results in equations for autocorrelation functions which are linear combinations of the SBO autocorrelation function equations. These equations involving thermal averages of products of angular-momentum operators are solved by introducing exact relationships among the operators. This procedure using exact operator relations in conjunction with the approximate RPA equations produces different results depending on which linear combination of SBO Green's functions is used. The reason is that the errors inherent in the RPA are propagated with different weighting factors in different linear combinations. In Sec. IV it is shown that there is one a particular linear combination of SBO Green's functions which does not lead to any inconsistancies.

IV. CORRELATION FUNCTIONS

The RPA equations do, in fact, have a solution which yields unique values for the set $\{P_\beta\}$ of thermal average occupation probabilities, and which does not violate the basic operator multiplication rules. The particular linear combination of SBO Green's functions that accomplishes this is $\mathcal{G}^k_{\beta+}$ defined by Eq. (3.6). Using $\mathcal{G}^k_{\beta+}$ given by Eq. (3.15), or operating on Eq. (3.20) with $\sum_\alpha B_\alpha$, leads to the correlation-function equation

$$\sum_\alpha B_\alpha \{ \langle \hat{L}^m_{\beta+} \hat{L}^n_\alpha \rangle - \delta_{\alpha\beta} \Delta P^\pm_\alpha \Phi^\pm_\alpha (n-m) \} = 0 \ , \qquad (4.1)$$

with

$$\Phi^\pm_\alpha (n-m) = N^{-1} \sum_{k,r} R^\pm_\alpha (k,r) f^\pm(\omega^r_k) e^{i\vec{k}\cdot(\vec{n}-\vec{m})} \ . \qquad (4.2)$$

This linear combination of SBO correlation functions is that formed from matrix elements of the operator $\hat{B}^n$ which appears in the interaction Hamiltonian. Equation (4.1) has the unique feature that it is the only linear combination containing only dispersed excitation energies as arguments of the distribution function $f^\pm$.

Multiplying Eq. (4.1) by an arbitrary scalar A_β and summing over β gives

$$\langle \hat{A}^m \hat{B}^n \rangle = \sum_\beta A_\beta B_\beta \Delta P^\pm_\beta \Phi^\pm_\beta (n-m) \ , \qquad (4.3)$$

where $\hat{A}^m$ is an arbitrary operator, associated with site m having matrix elements A_β. Usually the only correlation functions of physical interest are those for which $\hat{A}^m = (\hat{B}^m)^\dagger$. For example, in the Heisenberg ferromagnet, Eq. (4.3) gives an expression for $\langle \hat{S}^m_- \hat{S}^n_+ \rangle$, and in the Hubbard s-band model it yields $\langle (\hat{c}^m)^\dagger \hat{c}^n \rangle$. In order to calculate the correlation functions $\langle \hat{A}^m \hat{B}^n \rangle$, the occupation probabilities need to be determined. This is accomplished from Eq. (4.1) by setting $m = n$.

When $m=n$ in Eq. (4.1), application of multiplication rule (2.2) and the assumption $\langle \hat{L}_{\alpha\beta} \rangle << P_\alpha$ reduces Eq. (4.1) to an equation involving only occupation probabilities. Reintroducing the expanded subscript notation, the result is

$$P_\beta / P_\alpha = r^\pm_{\alpha\beta} = \Phi^\pm_{\alpha\beta}(0) [1 \mp \Phi^\pm_{\alpha\beta}(0)]^{-1}$$

$$\text{for all } \alpha \text{ and } \beta$$

$$\text{such that} B_{\alpha\beta} \neq 0 \ . \qquad (4.4)$$

For the class of Hamiltonians leading to Eq. (3.14), the function Φ is given by

$$\Phi^{\pm}_{\alpha\beta}(0) = N^{-1} \sum_{k,r} \prod_{\nu,\nu'\neq\alpha,\beta} (\omega_k^r - \Delta\epsilon_{\nu\nu'}) \times \left[\prod_{r'\neq r} (\omega_k^r - \omega_k^{r'}) \right]^{-1} f^{\pm}(\omega_k^r) \quad . \tag{4.5}$$

For other Hamiltonians for which the matrix X^k defined by Eq. (3.9) is not diagonal, Eq. (4.1) and hence Eq. (4.4) have the same form as presented here in the diagonal case. The only modification is that some coefficients a_k^r appear in Φ.

Equation (4.4) defines the ratio $r^{\pm}_{\alpha\beta}$ of occupation probabilities between levels α and β which are directly connected by nonzero matrix elements $B^g_{\alpha\beta}$ of the interaction Hamiltonian. It is shown, as an example, in the Appendix that the application of Eq. (4.4) to the isotropic Heisenberg ferromagnet of arbitrary spin leads very quickly to the same thermodynamics as results from complicated procedures based on spin angular-momentum operator Green's functions in the RPA.[2,4] In addition, under the condition that thermal averages of nondiagonal operators are neglected, Eq. (4.4) is the solution of any autocorrelation function commutator equation having the form

$$\langle \hat{A}\hat{B} \rangle = \langle [\hat{C},\hat{A}]_{\pm} \rangle \quad , \tag{4.6}$$

where A is an arbitrary operator, and $\hat{B}$ and $\hat{C}$ are defined by

$$\hat{B} = \sum_{\alpha} B_\alpha \hat{L}_\alpha \quad \text{and} \quad \hat{C} = \sum_{\alpha} B_\alpha \Phi^{\pm}_{\alpha} \hat{L}_\alpha \quad . \tag{4.7}$$

The usual procedure for solving an equation having the form (4.6) is to choose $\hat{A}$ to be members of some complete set $\{\hat{A}^f\}$ of operators $\hat{A}^f$ such that Eq. (4.6) forms a closed set of equations. The solution of these equations can be used to determine any thermal average $\langle \hat{A}^f \hat{B} \rangle$. Although this procedure is possible, in principle, for any system with discrete levels, the selection of the set $\{\hat{A}^f\}$ may be difficult and it is not unique. There may be several sets $\{\hat{A}^f\}$, used in conjunction with exact relationships among the operators $\hat{A}^f$, $\hat{B}$, and $\hat{C}$ to close Eq. (4.6), which give the same values of thermal averages (see the Appendix). Assuming that the operators $\hat{B}$ and $\hat{C}$ are fixed, it is evident that the solution [Eq. (4.6)] cannot depend on the arbitrary operator $\hat{A}$ if exact operations are used. Solving Eq. (4.6) is simply a matter of making the judicious choice for $\hat{A}$ to minimize algebra. Choosing $\hat{A} = \hat{L}_{\beta^+}$ and applying the multiplication rule equation (2.2), with the assumption $\langle \hat{L}_{\alpha\beta} \rangle << P_\beta$ for $\alpha \neq \beta$, yields the solution of Eq. (4.6) in the form of occupation-probability ratios $r^{\pm}_{\alpha\beta}$ given by Eq. (4.4).

Even when Eq. (4.4) gives enough ratios to determine the complete set $\{P_\beta\}$, it may not represent all the ratios generated by the RPA equations. Equation (3.20) also yields, consistent with the SBO multiplication rule, the ratios

$$P_\beta / P_\alpha = q_{\alpha\beta} = f^{\pm}(\Delta\epsilon_{\alpha\beta})[1 \mp f^{\pm}(\Delta\epsilon_{\alpha\beta})]^{-1} = e^{-\Delta\epsilon_{\alpha\beta}/k_B T} \quad \text{for all } B_{\alpha\beta} = 0 \quad . \tag{4.8}$$

Equation (4.8) defines the ratio $q_{\alpha\beta}$ for all levels not directly connected by matrix elements in the interaction Hamiltonian, and as such these ratios are functions of the effective-field excitations $\Delta\epsilon_{\alpha\beta} = \epsilon_\beta - \epsilon_\alpha$.

Equations (4.4) and (4.8) together represent the complete solution of the RPA autocorrelation-function equation (3.20) consistent with the SBO multiplication rule. For a system with p levels, Eq. (4.4) and (4.8) constitute a redundant set of $\frac{1}{2}p(p-1)$ equations for the ratios P_β/P_α with $\alpha, \beta = 1, \ldots, p$, corresponding to all possible interlevel excitations. In addition to these ratio equations, the constraint (2.4) requires the normalization

$$\sum_{\alpha=1}^{p} P_\alpha = 1 \quad . \tag{4.9}$$

In the effective-field approximation all occupation probability ratios are given by Eq. (4.8), and it is readily shown using $q_{\alpha\beta} = q_{\alpha\gamma} q_{\gamma\beta}$ that of the $\frac{1}{2}p(p-1)$ ratio equations only $p-1$ are independent. Combining these $(p-1)$-independent equations with the normalization condition (4.9) yields a unique set $\{P_\beta; \beta = 1, \ldots, p\}$. In the RPA the situation is complicated by the presence of two types of excitations, resulting in different functional forms $q_{\alpha\beta}$ and $r^{\pm}_{\alpha\beta}$ for the ratios $p_\beta/p_\alpha = Q_{\alpha\beta}$ depending on the levels α and β, and one is faced with the problem of selecting $p-1$ ratios from $\frac{1}{2}p(p-1)$. Since the RPA values of $Q_{\alpha\beta}$ may not be equal to $Q_{\alpha\gamma}Q_{\gamma\beta}$, where γ is some intermediate state, selecting different ratio equations could give different results for $\{P_\beta\}$.

In accordance with the normalization Eq. (4.9), the set of occupation probabilities is given by

$$P_\alpha = \left[1 + \sum_{\beta\neq\alpha} Q_{\alpha\beta} \right]^{-1} \quad \text{for } \alpha = 1, \ldots, p \quad . \tag{4.10}$$

Equations (4.10) are internally consistent only if all the values used for the $Q_{\alpha\beta}$'s satisfy a product rule $Q_{\alpha\beta} = Q_{\alpha\gamma} Q_{\gamma\beta}$, appropriate to transition probabilities. The true $Q_{\alpha\beta}$'s, which are defined as probability ratios, satisfy such a product rule and hence there are only $(p-1)$-independent ratios. The RPA values for the ratios do not satisfy this product rule and one must select $p-1$ values for the ratios to obtain internal consistency in Eqs. (4.10). Once an appropriate set of RPA values for $p-1$ ratios $Q_{\alpha\beta}$ is chosen, the remaining ratios are given in terms of products of the chosen values. These various products are readily determined from an effective-field energy-level diagram, or more laboriously they can be found by inserting the $p-1$ chosen values for ratios in Eqs. (4.10), replacing the remaining $Q_{\alpha\beta}$'s by p_β/p_α and solving self-consistently for p_β/p_α.

It is worth mentioning that the use of averaging procedures to involve more than $p-1$ of the RPA ratio equations in the determination of the set $\{p_\beta\}$ leads to inconsistencies.

The problem of selecting $p-1$ RPA values for probability ratios is often resolved by the following physical arguments. Assume $|l\alpha\rangle$ and $|l\beta\rangle$ are localized eigenstates of a single-ion system at site l. If neither of these states is linked by an interaction to states of other ions, $|l\alpha\rangle$ and $|l\beta\rangle$ are eigenstates of the Hamiltonian, and the occupation probability ratio P_β/P_α is correctly given by $q_{\alpha\beta}$ in Eq. (4.8). However, if either one of the states $|l\alpha\rangle$ or $|l\beta\rangle$ is connected in the interaction Hamiltonian to states of ions on other sites $n\neq l$, it is no longer an eigenstate of H and a direct thermal transition of the type $q_{\alpha\beta}$ is not appropriate. In this latter case, transitions are more correctly described by dispersed quasiparticle excitations, which in the RPA are manifested by the mean-mode excitation probabilities $r^{\pm}_{\alpha\beta}$ in Eq. (4.4). In general transitions are characterized in the RPA by a combination of quasiparticle excitations occuring through various paths dictated by some set of nonzero matrix elements of $\hat{B}$. For example, in the Heisenberg ferromagnet of spin S the only nonzero matrix elements of $\hat{B}$ are those connecting adjacent energy states, which in the RPA leads to $p-1=2S$ independent ratios $Q_{\alpha,\alpha-1}=r^{-}_{\alpha,\alpha-1}$. Transitions between nonadjacent states are described by a series of independent quasiparticle excitations (see the Appendix). In the Hubbard s-band model the above reasoning can be used to select a set of $p-1=3$ values of $Q_{\alpha\beta}=r^{+}_{\alpha\beta}$, which gives very reasonable thermodynamics.

For cases in which the selection of $Q_{\alpha\beta}=r^{\pm}_{\alpha\beta}$ when either $|l\alpha\rangle$ or $|l\beta\rangle$ is not an eigenstate of $\hat{H}$ or $Q_{\alpha\beta}=q_{\alpha\beta}$ when both states are eigenstates of $\hat{H}$ does not reduce the number of independent RPA values for $Q_{\alpha\beta}$ to $p-1$, one must rely on other physical criteria. Such is the case of electron excitations in the two-band Hubbard model, where known limits of weak and strong interactions can be used to eliminate certain $r^{+}_{\alpha\beta}$'s.[25]

The thermodynamics of single-ion systems is completely determined by Eq. (4.10). Assuming that $\langle \hat{L}_{\alpha\beta}\rangle << P_\beta$, the thermal average of a single-ion operator $\hat{O}$ with matrix elements $O_{\alpha\beta}$ in the effective field states is given by

$$\langle \hat{O}\rangle = \sum_\alpha O_{\alpha\alpha}P_\alpha \ , \tag{4.11}$$

with P_α defined in the RPA by Eq. (4.10). For nonlocalized electron excitations, the chemical potential ζ, implicit in $\Delta\epsilon_{\alpha\beta}$, is determined by the additional constraint $n_e=\sum_\alpha n_\alpha P_\alpha$. The number of electrons in each system l is n_e, and n_α is the number per state $|l\alpha\rangle$.

The same prescription which led from the RPA equation (3.14) to the probability formula (4.10) may also be applied to the general RPA equation (3.7). One obtains a commutator equation of the form of Eq. (4.6), whose solution gives equations for the ratios $r^{\pm}_{\alpha\beta}$ associated with dispersed excitations. Using these ratios together with those associated with undispersed excitations, the occupation probabilities are calculated from Eq. (4.10).

V. CONCLUSIONS

A prescription for determining the thermodynamics of interacting many-level systems from random-phase-approximated Green's functions has been presented using standard-basis operators. The general RPA equations of motion for SBO Green's functions are analogous to the chain-diagram equations of SBO perturbation theory. Solution of the set of coupled equations for the SBO interlevel Green's functions is greatly facilitated for systems with many levels by constructing a particular linear combination of the interlevel Green's functions using matrix elements of the transition operators in the interaction Hamiltonian. This linear combination is essential in determining the solution of the corresponding autocorrelation function equations consistent with the monotopic restrictions. An explicit formula is given for calculating internally consistent values of the set $\{P_\beta\}$ of level occupation probabilities from the over complete set of RPA values for the ratios P_β/P_α.

It is worth emphasizing that calculation of autocorrelation functions from any other linear combination of SBO Green's functions leads to violations of the monotopic restrictions. There have been a number of previous RPA calculations on magnetic systems using spin angular-momentum operators in which the equations chosen to calculate autocorrelation functions were not equivalent to the particular linear combination of SBO functions which satisfies the monotopic restrictions. Such choices, which are in direct contradiction with the basic multiplication rules of the SBO are hardly justifiable.

In the Appendix it is shown that the method presented here gives almost trivially the RPA thermodynamics of the Heisenberg ferromagnet of general spin S, which has been previously determined only after lengthy calculation. Application of this method to the Hubbard s-band Hamiltonian also yields quickly the thermodynamics, which exhibits the correct behavior in the fully itinerant and fully localized electron limits.[25]

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APPENDIX: HEISENBERG FERROMAGNET

The Heisenberg ferromagnnet is chosen to illustrate the theory presented in this paper, because its thermodynamics has been studied extensively, particularly using Green's functions decoupled in the RPA.[3-8] The Hamiltonian of the Heisenberg ferromagnet with uniaxial single-ion anisotropy, represented in the eigenstates of the Z component of the spin angular-momentum operator in terms of $\hat{S}_Z$, $\hat{S}_+$, and $\hat{S}_-$ is given by

$$\hat{H} = -\sum_{l}[D(\hat{S}_Z^l)^2 + h\hat{S}_Z^l] - \frac{1}{2}\sum_{l,m} J^{lm}[\hat{S}_Z^l\hat{S}_Z^m + \tfrac{1}{2}(\hat{S}_+^l\hat{S}_-^m + \hat{S}_-^l\hat{S}_+^m)] \ . \tag{A1}$$

The parameters are anisotropy strength D, external field h, and exchange J^{lm}. The operators $\hat{S}_\pm$ are the raising and lowering angular-momentum operators.

Using the transformations

$$(\hat{S}_Z)^n = \sum_\alpha \alpha^n \hat{L}_{\alpha\alpha} \ ,$$

$$\hat{S}_+ = \sum_\alpha b_\alpha \hat{L}_{\alpha,\alpha-1} \ , \tag{A2}$$

and

$$\hat{S}_- = \sum_\alpha b_\alpha \hat{L}_{\alpha-1,\alpha} \ ,$$

where

$$b_\alpha = [(S+\alpha)(S-\alpha+1)]^{1/2}$$

$$\text{for } \alpha = -S, -S+1, \ldots, S \ ,$$

the Hamiltonian in SBO representation is

$$\hat{H} = \sum_{\mu,l} \epsilon_\mu \hat{L}_{\mu\mu}^l - \frac{1}{2}\sum_{\mu,l}\sum_{\nu,m} J^{lm} \times [\mu\nu\Delta\hat{L}_{\mu\mu}^l\Delta\hat{L}_{\nu\nu}^m + \tfrac{1}{2}b_\mu b_\nu \times(\hat{L}_{\mu,\mu-1}^l\hat{L}_{\nu-1,\nu}^m + \hat{L}_{\mu-1,\mu}^l\hat{L}_{\nu,\nu-1}^m)] \ . \tag{A3}$$

The effective-field energies ϵ_μ are given by

$$\epsilon_\mu = -\mu(D\mu + h + J^0\langle\hat{S}_Z\rangle) \ , \tag{A4}$$

with J^0 the $k=0$ component of the Fourier transform J^k of J^{lm}.

Comparing (A3) with the general Hamiltonian (2.6) and using (2.7) and (3.5) gives

$$V_{\alpha'\alpha,\nu\nu'}^k = -\tfrac{1}{2}J^k B_{\alpha'\alpha}^- B_{\nu\nu'}^+ \ ,$$

$$\text{with} \tag{A5}$$

$$B_{\alpha\beta}^+ = B_{\beta\alpha}^- = b_\alpha\delta_{\beta,\alpha-1} \ ,$$

where inversion symmetry was assumed, i.e., $J^k = J^{-k}$.

To clarify the connection between the SBO autocorrelation-correlation function equations in Sec. IV and previous calculations using spin angular-momentum operators, the isotropic case $D=0$ will be considered first. Using expressions (A4) and (A5) in equations (3.16) and (4.5) gives for the commutator equation (4.6) the form

$$\langle\hat{A}\hat{S}_+\rangle = \langle[\hat{S}_+,\hat{A}]_-\rangle\Phi \ . \tag{A6}$$

The function $\Phi = N^{-1}\sum_k f^-(\omega_k)$ is the average occupation number of the dispersed excitation modes $\omega_k = h + (J^0 - J^k)\langle S_Z\rangle$. To solve (A6) the arbitrary operator $\hat{A}$ can be chosen successively from the set of spin operators $\{(\hat{S}_Z)^n\hat{S}_\pm, n=0,\ldots,2S-1\}^2$, or from the set $\{(\hat{S}_-)^n(\hat{S}_+)^{n-1}, n=0,\ldots,2S-1\}^4$. The set of $2S$ equations is used in conjunction with the constraint equation $\prod_\alpha(S_Z-\alpha)=0$ (Refs. 2 and 4) to determine the thermal average moments $\langle(S_Z)^n\rangle$. An alternate procedure is to set $\hat{A} = \exp(\hat{a}S_Z)\hat{S}_-$ and to solve the resultant differential equation in the variable a.[26] All of these choices for $\hat{A}$ give the same formula for $\langle\hat{S}_Z\rangle$ first derived for arbitrary S by Callen.[26] It is

$$\langle\hat{S}_Z\rangle = [S-(S+1)r+(S+1-Sr)r^{2S+1}] \times(1-r)^{-1}(1-r^{2S+1})^{-1} \ , \tag{A7}$$

where

$$r = \Phi(1+\Phi)^{-1} \ . \tag{A8}$$

In contrast to the complicated derivations of (A7) from (A6) using angular-momentum operators,[2,4,26] the derivation using SBO is simple. The matrix elements of $\hat{S}_+$ are $B_{\alpha\beta}^+ = b_\alpha\delta_{\beta,\alpha-1}$; hence in accordance with (4.4), which solves any commutator equation of the type (4.6), Eq. (A6) gives the ratios

$$P_{\alpha-1}/P_\alpha = r \quad \text{for } \alpha = -S+1, \ldots, S \ , \tag{A9}$$

with r defined in (A8). Equation (A9) is a recursion relation for a system with $2S+1$ equally spaced energy levels. Iterating (A9) gives the ratio $P_\beta/P_\alpha = r_{\alpha\beta} = r^{\alpha-\beta}$ for $\beta=-S,\ldots,S$. Since there are no matrix elements $B_{\alpha\beta}$ connecting nonadjacent states, the only excitation mode in the RPA is a series of quasiparticle excitations each having mean-mode occupancy Φ and excitation probability r. Noting that there are no isolated states, we set $Q_{\alpha\beta} = r^{\alpha-\beta}$ in formula (4.10) giving

$$P_\alpha = r^{S-\alpha}(1-r)(1-r^{2S+1})^{-1} \quad \text{for } \alpha=-S,\ldots,S \tag{A10}$$

The thermal average moments of $\hat{S}_Z$ follow immediately from (A2) and (A10). They are

$$\langle(\hat{S}_Z)^n\rangle = r^S(1-r)(1-r^{2S+1})^{-1}\sum_{\alpha=-S}^{S}\alpha^n r^{-\alpha} \quad . \qquad \text{(A11)}$$

Noting that

$$\sum_\alpha \alpha^n r^{-\alpha} = r^{-1}\frac{d}{dr^{-1}}\sum_\alpha \alpha^{n-1} r^{-\alpha}$$

gives the moment formula

$$\langle(\hat{S}_Z)^n\rangle = r^S(1-r)(1-r^{2S+1})^{-1}\left(r^{-1}\frac{d}{dr^{-1}}\right)^n$$

$$\times[(r^S-r^{-(S+1)}))1-r)^{-1}] \quad . \qquad \text{(A12)}$$

For $n=1$, Eq. (A12) reduces to the Callen result (A7).

In the presence of single-ion anisotropy $D\neq 0$, the single-ion energy levels are not evenly spaced, resulting in a set of $2S$ different RPA quasiparticle excitations ω_k^r defined from Eq. (3.16) by

$$\prod_r(E-\omega_k^r) = \prod_{\nu=-S}^{S}(E-\Delta\epsilon_\nu)+\frac{J^k}{2}\sum_{\alpha=-S}^{S}b_\alpha^2(P_\alpha-P_{\alpha-1})$$

$$\times\prod_{\nu\neq\alpha}(E-\Delta\epsilon_\nu)) \quad , \qquad \text{(A13)}$$

where

$$\Delta\epsilon_\nu = h + J^0\langle\hat{S}_Z\rangle + (2\nu-1)D \quad .$$

The probability-ratio equations for $D\neq 0$ are given by

$$P_{\alpha-1}/P_\alpha = r_\alpha \quad , \qquad \text{(A14)}$$

with $r_\alpha = r^-_{\alpha,\alpha-1}$ defined by Eq. (4.4). Due to the term $-\alpha^2 D$ in the effective-field energy ϵ_α, the ratio r_α depends on α in $\Phi^-_{\alpha,\alpha-1}(k,r)$ defined in Eq. (4.5). Hence one cannot make an Ansatz of the form $P_\beta/P_\alpha = e^{-(\alpha-\beta)X}$, as was possible in the isotropic case, and the Callen-Shtrikman common probability arguments[27] are not valid, except in the limit $D/J^0 \ll 1$.

Equation (A14) can be solved by iteration to find $Q_{\alpha\beta} = r_{\alpha\beta}$ in the formula (4.10) for P_α. The result is

$$P_\alpha = r_{\alpha+1}\cdots r_S(1+r_S+r_{S-1}r_S$$

$$+\cdots+r_{-S+1}\cdots r_{S-1}r_S)^{-1}$$

$$\text{for } \alpha=-S,\ldots,S \quad . \qquad \text{(A15)}$$

At this point is is seen that the determination of the set $\{P_\alpha\}$ is reduced by the method presented here to the resolution to the characteristic equation (A13) for the roots ω_k^r, followed by self-consistent solution of Eq. (A15). Such a calculation will be presented elsewhere.

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