The generalized atomic hopping problem—occupancy correlation functions*

Peter A. Fedders and O. F. Sankey
Department of Physics, Washington University, St. Louis, Missouri 63130
(Received 30 November 1976)

We develop a formalism for calculating the occupancy correlation functions associated with atomic hopping processes where atoms at certain lattice sites can hop to nearby vacant lattice sites. Although the problem is trivial if $\Gamma_{\alpha\beta} = \Gamma_{\beta\alpha}$, where $\Gamma_{\alpha\beta}$ is the hopping rate from site α to site β, it becomes a true many-body problem if $\Gamma_{\alpha\beta} \neq \Gamma_{\beta\alpha}$. The formalism yields a diagrammatic expansion of the moments of the correlation functions. Certain classes of moment diagrams can then be approximately summed to yield the correlation functions themselves. Applications to the hopping of interstitial hydrogen in metals as well as the usual atomic migration are discussed.

I. INTRODUCTION

In this paper we develop a formalism to treat the general hopping problem where one has a number of particles which can singly occupy discrete lattice sites and which can hop to nearby vacant lattice sites. The rate equation for the occupancy of a site can be written

$$\left(\frac{dn_\alpha}{dt}\right)_0 = -\sum_\beta \Gamma_{\alpha\beta} n_\alpha (1-n_\beta) + \sum_\beta \Gamma_{\beta\alpha} n_\beta (1-n_\alpha) \ , \tag{1}$$

where Greek letters denote lattice sites, $\Gamma_{\alpha\beta}$ is the hopping rate for a particle at the site α to jump to a vacant site β, and n_α denotes the occupancy of the site α ($n_\alpha = 1$ if the site α is occupied and $n_\alpha = 0$ if the site α is vacant). For the special case where $\Gamma_{\alpha\beta} = \Gamma_{\beta\alpha}$, the right-hand side of Eq. (1) is linear in the n's and one can trivially solve for two-point correlation functions of the form

$$\langle n_\alpha(t) n_\beta(0) \rangle \ , \tag{2}$$

where $\langle x \rangle$ denotes the ensemble average of x. However if $\Gamma_{\alpha\beta} \neq \Gamma_{\beta\alpha}$, the problem is a true many-body problem and cannot be solved trivially. This situation can easily obtain if some lattice sites have deeper effective potential wells than other sites do.

The precise meaning of Eq. (1) is that in a small time Δt the change in probability of the site α being occupied is given by (i) $-\Gamma_{\alpha\beta}(\Delta t)$ summed over all vacant sites β if the site α is occupied, and by (ii) $+\Gamma_{\beta\alpha}(\Delta t)$ summed over all occupied sites β if the site α is vacant. Thus the notation $(d/dt)_0$ does not indicate a true time derivative but rather the change in probability of the quantity operated on in a small time Δt, divided by Δt. The fact that Eq. (1) is not an equation in the usual sense can be seen by noting that

$$\left(\frac{d}{dt}\right)_0 (n_\alpha n_\beta) \neq n_\alpha \left(\frac{dn_\beta}{dt}\right)_0 + \left(\frac{dn_\alpha}{dt}\right)_0 n_\beta \ . \tag{3}$$

That is, if Eq. (1) is substituted into the right-hand side of Eq. (3), one does not obtain the change in probability per unit time that both sites α and β are occupied. An equality in Eq. (3) would be correct only if the changes in n_α and n_β were independent of each other. This is not so because particles can hop between the site α and β. We wish to note that the troubles discussed above persist even in the special case where $\Gamma_{\alpha\beta} = \Gamma_{\beta\alpha}$. Since the right-hand side of Eq. (1) is linear in the n's in this special case, the equation can be iterated repeatedly with no difficulties. Thus one can trivially calculate correlation functions of the form of Eq. (2). However, for calculations of correlation functions with more than one n at a given time, one faces the same difficulties that are present in the more general problem.

There are a number of interesting physical problems where a theory for the general hopping problem is or may be of use. For example, there is evidence that in many metal hydrides, some interstitial lattice sites (preferred ones) are occupied by the protons for longer times than are other (unpreferred) lattice sites, but that the protons still spend some time in the unpreferred sites. The existence of preferred and unpreferred sites automatically implies asymmetric hopping rates. In fact the possibility of preferred and unpreferred sites has been suggested by Lütgemier, Bohn, and Arons as an explanation of their experiments on Nb-D systems.[1] Further, in the α phase, hydrogen nuclei in Ta are believed to occupy all tetrahedral sites randomly.[2,3] However, neutron-diffraction patterns of the β phase indicate that only 1 out of 12 tetrahedral sites are appreciably occupied.[4] If this is so it seems quite likely that the hydrogen hop into and out of the unpreferred sites even though they spend most of

their time on the preferred sites. There have also been suggestions that both tetrahedral and octahedral sites are occupied with different concentrations in some metal hydride phases.

The formalism developed in this paper can also be used to describe host atomic hopping in lattices with inequivalent sites. With some modifications it could be used to treat impurity problems with atomic hopping where atoms tend to prefer or avoid lattice sites near an impurity. With more-drastic modifications the formalism might be used to study divacancies or vacancy attraction by including terms of the right hand side of Eq. (1) that describe the preference of a vacancy to hop next to another vacancy.

Finally, there is the distinct but related problem of calculating the correlation functions for specific particles. Such correlation functions are measured in tracer experiments and some NMR experiments. While n_α relates to the probability that the site α is occupied by some particle, let $p_{i\alpha}$ relate to the probability that the specific particle i is at the site α. That is, $p_{i\alpha}=1$ if the particle i is at the site α and $p_{i\alpha}=0$ otherwise. The rate equation for $p_{i\alpha}$, in analogy with Eq. (1), is

$$\left(\frac{dp_{i\alpha}}{dt}\right)_0 = -\sum_\beta \Gamma_{\alpha\beta} p_{i\alpha}(1-n_\beta) + \sum_\beta \Gamma_{\beta\alpha} p_{i\beta}(1-n_\alpha) \ , \tag{4}$$

with the $(d/dt)_0$ having the same meaning as before. In contrast to Eq. (1), this equation cannot be solved trivially to yield pair-correlation functions even if $\Gamma_{\alpha\beta}=\Gamma_{\beta\alpha}$. This problem will be treated in the following paper.[5]

Since we are considering a true many-body problem, there is little hope of finding an exact analytical solution. In the remainder of this section we shall transform Eq. (1) into a form which includes an effective-field term and an interaction or scattering term on the right-hand side. In Sec. II we develop the theory by deriving diagrammatic rules for calculating all possible configurations after n hops. From these rules we then derive diagrammatic expressions for all of the moments of correlation functions of the form of Eq. (2). Finally, in Sec. III, we discuss some methods for summing up infinite classes of moments into time-dependent correlation functions. While the mathematical arguments of Secs. II and III are not abstruse, they are somewhat tedious and cumbersome. However the results are quite compact and easy to use.

It is convenient to make a change of variables from the n_α to variables whose average values are zero and that are in some sense orthonormal. We note that $\langle n_\alpha\rangle = c_\alpha$, where c_α is the concentration of particles at the site α or equivalently the probability that the site α is occupied. Thus we define

$$\xi_\alpha = (n_\alpha - c_\alpha)/a_\alpha, \quad a_\alpha = [c_\alpha(1-c_\alpha)]^{1/2} \ . \tag{5}$$

With these definitions one can easily show that

$$\langle \xi_\alpha\rangle = 0, \quad \langle \xi_\alpha \xi_\beta\rangle = \delta_{\alpha,\beta} \ , \tag{6}$$

since $\langle (n_\alpha)^2\rangle = \langle n_\alpha\rangle$. Further, the ensemble average of any product ξ's is zero if any site is represented only once in the product. Thus the ξ's are the desired set of variables. Equation (1) can be easily written in terms of the new variables as

$$\left(\frac{d\xi_\alpha}{dt}\right)_0 = -\sum_\beta \omega_{\alpha\beta}\xi_\beta - \sum_\beta \Omega_{\alpha\beta}\xi_\alpha\xi_\beta \ , \tag{7}$$

where

$$\omega_{\alpha\beta} = \omega_{\beta\alpha} = \delta_{\alpha\beta}\sum_\gamma [\Gamma_{\alpha\gamma}(1-c_\gamma) + \Gamma_{\gamma\alpha}c_\gamma] - \frac{[\Gamma_{\alpha\beta}c_\alpha + \Gamma_{\beta\alpha}(1-c_\alpha)]a_\beta}{a_\alpha} \ , \tag{8}$$

$$\Omega_{\alpha\beta} = -a_\beta(\Gamma_{\alpha\beta} - \Gamma_{\beta\alpha}) \ . \tag{9}$$

In deriving these equations we have used the equilibrium condition of detailed balance

$$\Gamma_{\alpha\beta}c_\alpha(1-c_\beta) = \Gamma_{\beta\alpha}c_\beta(1-c_\alpha) \ . \tag{10}$$

The meaning of $(d/dt)_0$ remains the same and is literally defined only in terms of the n's.

By neglecting the last term on the right-hand side of Eq. (7) we obtain a linear equation in the ξ's or n's. Since such an equation can be iterated indefinitely without complications, the solution for pair correlation functions is trivial.[6] This approximation is a mean-field or effective-field approximation and is the best approximation that one can expect from linearized equations. Essentially the approximation consists of approximating the occupancy of any site β that a particle at α might hop to by c_β. From comparing $\Omega_{\alpha\beta}$ to $\omega_{\alpha\beta}$, one can see that the mean-field approximation becomes exact if $\Gamma_{\alpha\beta}\to\Gamma_{\beta\alpha}$ or if all of the concentrations approach zero as the ratios of the Γ's remain fixed. This second condition is not surprising since at low concentrations essentially all sites that a particle might hop to are vacant.

II. MOMENTS

Consider the two-point occupancy correlation functions defined as

$$D(\alpha,\beta;t) = \langle \xi_\alpha(t)\xi_\beta(0)\rangle\Theta(t) \ , \tag{11}$$

where Θ is the step function. This quantity is proportional to the time dependent part of the probability that the site α is occupied at time t if the site β was occupied at time $t=0$. The function is normalized so that $D(\alpha,\beta;0)=\delta_{\alpha,\beta}$ and the variables have been chosen so that $D(\alpha,\beta;t)$ vanishes at $t\to\infty$. Since we expect exponential-like solutions, we define moments of D as

$$M_n(\alpha,\beta)=\left(\frac{-d}{dt}\right)^n D(\alpha,\beta;t)\Big|_{t=0} , \tag{12a}$$

$$D(\alpha,\beta;t)=\sum_{n=0}^{\infty} M_n(\alpha,\beta)\,\frac{(-t)^n}{n!}\,\Theta(t) . \tag{12b}$$

Since all of the moments of the correlation functions are defined in the limit as $t\to 0$, one can relate the nth moment to the nth order hopping probability

$$M_n(\alpha,\beta)=\left\langle\left[\left(\frac{-d}{dt}\right)_0^n \xi_\alpha\right]\xi_\beta\right\rangle , \tag{13}$$

where

$$\left(\frac{d}{dt}\right)_0^n \xi=\left(\frac{d}{dt}\right)_0\left[\left(\frac{d}{dt}\right)_0^{n-1}\xi\right] . \tag{14}$$

However, since $(d/dt)_0^n\xi$ involve products of up to $n+1$ of the ξ's, we must be able to calculate $(d/dt)_0$ on products of arbitrary numbers of ξ's.

First consider $(d/dt)_0$ acting on only a pair of variables at different sites

$$-\left(\frac{d}{dt}\right)_0(\xi_\alpha\xi_\beta)=-\left(\frac{1}{a_\alpha a_\beta}\right)\left(\frac{d}{dt}\right)_0 \times[n_\alpha n_\beta-c_\alpha n_\beta-c_\beta n_\alpha+c_\alpha c_\beta], \tag{15}$$

where $\alpha\neq\beta$. Now divide the operation $(d/dt)_0$ into a correlated (c) part and an uncorrelated (uc) part. The correlated part is defined as that part referring to hops that involve both of the sites α and β. The part left over is the uncorrelated part which will involve the site α or the site β but not both. Obviously

$$\left(\frac{d}{dt}\right)_{uc}[n_\alpha n_\beta-c_\alpha n_\beta-c_\beta n_\alpha+c_\alpha c_\beta] =(n_\alpha-c_\alpha)\left(\frac{dn_\beta}{dt}\right)_{uc}+(n_\beta-c_\alpha)\left(\frac{dn_\alpha}{dt}\right)_{uc} , \tag{16}$$

where $(dn_\alpha/dt)_{uc}$ is the part from Eq. (1) that does not involve the site β. Thus, we get

$$\left(\frac{dn_\alpha}{dt}\right)_{uc}=\sum_{\gamma\neq\beta}\left[\Gamma_{\alpha\gamma}n_\alpha(1-n_\gamma)-\Gamma_{\gamma\alpha}n_\gamma(1-n_\alpha)\right] . \tag{17}$$

By combining Eq. (17) and the corresponding expression for $(dn_\beta/dt)_{uc}$, one obtains

$$-\left(\frac{d}{dt}\right)_{uc}(\xi_\alpha\xi_\beta)=\sum_{\gamma\neq\beta}\left[\omega_{\alpha\gamma}(\beta)\xi_\gamma\xi_\beta+\Omega_{\alpha\gamma}\xi_\alpha\xi_\gamma\xi_\beta\right] +\sum_{\delta\neq\alpha}\left[\omega_{\beta\delta}(\alpha)\xi_\alpha\xi_\delta+\Omega_{\beta\delta}\xi_\beta\xi_\delta\xi_\alpha\right] , \tag{18}$$

where

$$\omega_{\alpha\gamma}(\beta)=\omega_{\alpha\gamma}-\delta_{\alpha\gamma}[\Gamma_{\alpha\beta}(1-c_\beta)+\Gamma_{\beta\alpha}c_\beta] . \tag{19}$$

We now calculate the correlated part of Eq. (15). Contributions to this part can come from one of two possibilities: (i) if a particle originally at the site α hops to a vacant site β, the quantity in the square brackets of Eq. (15) changes by $(c_\beta-c_\alpha)$, the hopping rate for this process is $\Gamma_{\alpha\beta}$, and it can occur only if $n_\alpha(1-n_\beta)$ is one. (ii) If a particle originally at the site β hops to the vacant site α, the quantity in the square brackets of Eq. (15) changes by $(c_\alpha-c_\beta)$, the hopping rate for this process is $\Gamma_{\beta\alpha}$, and it can occur only if $n_\beta(1-n_\alpha)$ is one. By combining these possibilities one obtains

$$-\left(\frac{d}{dt}\right)_c(\xi_\alpha\xi_\beta) =(c_\alpha-c_\beta)[\Gamma_{\alpha\beta}n_\alpha(1-n_\beta)-\Gamma_{\beta\alpha}n_\beta(1-n_\alpha)]/a_\alpha a_\beta . \tag{20}$$

Finally, by combining Eqs. (18) and (20), one obtains

$$-\left(\frac{d}{dt}\right)_0(\xi_\alpha\xi_\beta)=\sum_{\gamma\neq\beta}(\omega_{\alpha\gamma}\xi_\gamma\xi_\beta+\Omega_{\alpha\gamma}\xi_\alpha\xi_\gamma\xi_\beta) +\sum_{\delta\neq\alpha}(\omega_{\beta\delta}\xi_\alpha\xi_\delta+\Omega_{\beta\delta}\xi_\beta\xi_\delta\xi_\alpha) +\Omega_{\alpha\beta}\xi_\alpha+\Omega_{\beta\alpha}\xi_\beta+V_{\alpha\beta}\xi_\alpha\xi_\beta , \tag{21}$$

where

$$V_{\alpha\beta}=V_{\beta\alpha} =(c_\alpha-c_\beta)(\Gamma_{\beta\alpha}-\Gamma_{\alpha\beta}) +\omega_{\alpha\beta}(a_\alpha^2+a_\beta^2)/a_\alpha a_\beta . \tag{22}$$

Note that since $\alpha\neq\beta$ and $V_{\alpha\alpha}=\Omega_{\alpha\alpha}=0$, none of the products of the ξ's in Eq. (21) involve the same site twice.

The five terms on the right-hand side of Eq. (21) can be viewed as follows. The first term is just $-(d\xi_\alpha/dt)_0\xi_\beta$ except that none of the terms from $-(d\xi_\alpha/dt)_0$ can involve the site β. The second term is similar with α and β interchanged. The last three terms are new terms which arise because of the correlation between the sites α and β. It is now clear how to construct the analytical expression for

$$-\left(\frac{d}{dt}\right)_0\prod_{i=1}^{n}\xi_{\alpha_i} . \tag{23}$$

First there are n terms, one for each value of i, that are formed from $(-d\xi_{\alpha_i}/dt)_0$ times the $(n-1)$ remaining ξ's. These terms can be written using Eq. (7),

$$\sum_i \left(\sum_\beta{}' (\omega_{\alpha_i\beta}\xi_\beta + \Omega_{\alpha_i\beta}\xi_{\alpha_i}\xi_\beta) \prod_{j\neq i} \xi_{\alpha_j} \right) , \tag{24}$$

where the prime on the summation means that β cannot be equal to any of the set $\{\alpha_i\}$. The other terms, corresponding to the last three terms on the right-hand side of Eq. (18), are

$$\sum_p \left((\Omega_{\beta\beta'}\xi_\beta + \Omega_{\beta'\beta}\xi_{\beta'} + V_{\beta\beta'}\xi_\beta\xi_{\beta'}) \prod_r \xi_{\alpha_r} \right) , \tag{25}$$

where the summation on p is over all unordered pairs of sites β and β' that can be made from the set $\{\alpha_i\}$, and the product over r is over the remainder of the set $\{\alpha_i\}$ that is not included in p. That is, since the sites α_i for $1 \leq i \leq n$ are all distinct, one need only consider the correlated parts of $(-d/dt)_0$ pairwise. This is so because if one considers the possibility of a particle at the site α_1 hopping to the site α_2, the occupancy of sites $\alpha_3, \alpha_4, \ldots$ cannot matter.

The equations which we have derived are probably too complex to be of any use directly. Fortunately, however, the equations can be expressed diagrammatically in an extremely simple manner. Consider the basic event diagrams displayed in Fig. 1 and the analytical expressions associated with them. A single dot (•) is defined as one event. The rules derived above for calculating $(-d/dt)_0^n \xi_\alpha$ can be expressed diagrammatically as follows: (i) Form all distinct connected diagrams with n events that can be made up from n basic event diagrams connected together and that start on the left with a single line labeled α. The diagrams can be made up by connecting more and more diagrams to the right of existing lower order diagrams. (ii) Associated the proper analytical expression from Fig. 1 with each event. Thus each distinct diagram has a product of n analytical expressions associated with it. (iii) There will be a number of lines on the right with indices β_i that do not terminate at a dot. Multiply the expression by ξ_{β_i} for each one of these. (iv) Sum over all internal sites indices (all sites not labeled α) with the restriction that no two sites at the same "time" or horizontal coordinate can be equal. For example if two lines labeled α_1 and α_2 occur at the same horizontal (time) coordinate, sums are restricted so that $\alpha_1 \neq \alpha_2$.

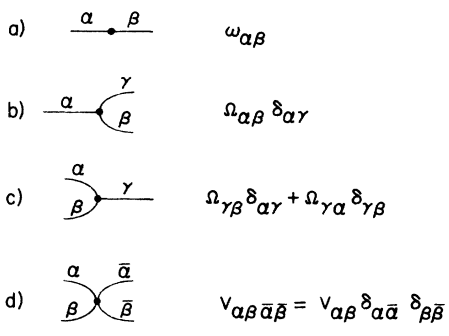

FIG. 1. Basic event diagrams and their corresponding analytical expressions.

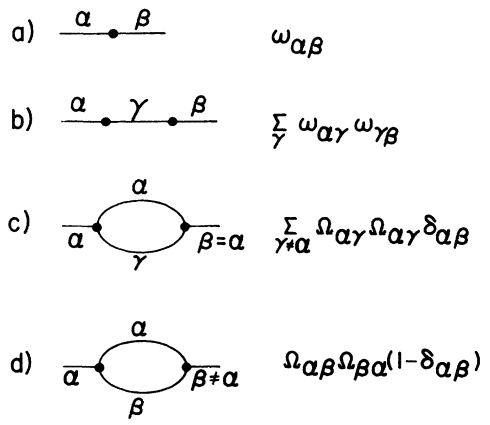

FIG. 2. Diagrammatic representations and analytical expressions for (a), the one diagram that contributes to $M_1(\alpha,\beta)$, and (b), (c), and (d), the three diagrams that contribute to $M_2(\alpha,\beta)$.

Diagrams and analytical expressions for the moments can now easily be deduced. From Eqs. (6) and the sentence following that equation, one can easily see that the only diagrams contributing to $M_n(\alpha,\beta)$ are those that end on the right with a single line labeled β. Thus the rules for calculating $M_n(\alpha,\beta)$ are as follows: (i) form all distinct connected diagrams with n events from the set of basic event diagrams. These diagrams should start on the left with a single line labeled α and end on the right with a single line labeled β. These diagrams will be made up of n basic event diagrams and will thus contain n dots. (ii) Label the internal lines with dummy site indices and associate the proper analytical expression with each diagram. (iii) Sum over all dummy site indices with the restriction that no sites at the same time (or horizontal position) can be equal. In Fig. 2 we have displayed the only diagram that contributes to $M_1(\alpha,\beta)$ and the three diagrams that contribute to $M_2(\alpha,\beta)$ along with the appropriate analytical expressions. The quantity $V_{\alpha\beta}$ does not enter into $M_n(\alpha,\beta)$ for $n \leq 2$.

III. SUMMATION TECHNIQUES

The diagrammatic representation for the moments developed in the last section is very similar to the diagrammatic representation for moments of the high-temperature spin paramagnet developed by Reiter[7] and others. In fact the use of such diagrams in the spin problem has motivated our approach in this paper and some of the techniques used in this section.

For example, experience with the related spin problem shows that it is extremely convenient to define a self energy or memory function. In the present problem it is most convenient to define this function $K(\alpha,\beta;t)$ by the equation

$$i\frac{d}{dt}D(\alpha,\beta;t)+i\int_0^\infty d\bar{t}\sum_\gamma K(\alpha,\gamma;\bar{t}) \times D(\gamma,\beta;t-\bar{t})=i\delta_{\alpha,\beta}\delta(t)\ . \quad (26)$$

This equation can easily be Fourier transformed in time to yield

$$\omega D(\alpha,\beta;\omega)+i\sum_\gamma K(\alpha,\gamma;\omega)D(\gamma,\beta;\omega)=i\delta_{\alpha\beta}\ , \quad (27)$$

where all quantities $A(t)$ are Fourier transformed as

$$A(\omega)=\int_{-\infty}^{\infty}dt\,A(t)e^{i\omega t}\ . \quad (28)$$

Further, we expand $K(t)$ in terms of its moments as

$$K(\alpha,\beta;t)=L_1(\alpha,\beta)\delta(t) -\sum_{n=0}^{\infty}L_{n+2}(\alpha,\beta)\frac{(-t)^n}{n!}\Theta(t)\ . \quad (29)$$

By substituting Eqs. (12b) and (29) into Eq. (26) one obtains the following relationship between the L's and M's:

$$M_{n+1}(\alpha,\beta)=\sum_\gamma\sum_{m=1}^{n+1}L_m(\alpha,\gamma)M_{n+1-m}(\gamma,\beta)\ . \quad (30)$$

As discussed with respect to the spin problem,[8] Eq. (30) has a very convenient topological meaning. The meaning is that if $\{M_n(\alpha,\beta)\}$ is a set of connected diagrams, then $\{K_n(\alpha,\beta)\}$ is the subset $\{M_n(\alpha,\beta)\}$ that consists of irreducible diagrams. An irreducible diagram is one that cannot be separated into two pieces by cutting only one line between events. Thus the diagram in Fig. 2(b) is reducible while the other three diagrams in Fig. 2 are irreducible. The rules for calculating $L_n(\alpha,\beta)$ are thus the same as the rules for calculating $M_n(\alpha,\beta)$ except that only irreducible diagrams are included.

From our definition of $D(\alpha,\beta;t)$, it is easily seen that $M_0(\alpha,\beta)=\delta_{\alpha,\beta}$. Further, Fig. 2(a) is the only diagram with one event so

$$M_1(\alpha,\beta)=L_1(\alpha,\beta)=\omega_{\alpha\beta}\ . \quad (31)$$

If we stop here we obtain

$$K_1(\alpha,\beta;t)=\omega_{\alpha\beta}\delta(t)\ . \quad (32)$$

By substituting Eq. (32) into Eq. (26) and comparing the result with Eq. (7), it is easily seen that approximating $K(\alpha,\beta;t)$ by $K_1(\alpha,\beta;t)$ yields the mean-field theory described in Sec. I.

At this point we observe that the equations for a lattice are much simpler if we Fourier transform in space. If a unit cell of the lattice contains b sites, then the D's, K's, M's, and L's will be $b\times b$ matrices in reciprocal or $\vec{q}$ space. If we denote basis indices by Latin letters which go from 1 to b, equations like Eqs. (27) will read

$$\omega D(i,j;\vec{q};\omega)+i\sum_k K(i,k,\vec{q};\omega)D(k,j;\vec{q},\omega)=i\delta_{ij}\ , \quad (27')$$

where

$$D(i,j,\vec{q};\omega)=\sum_l e^{-i\vec{q}\cdot\vec{R}_l}D(\alpha,\beta;\omega)\ , \quad (27a')$$

where α is the site i in the cell l and β is the site j in the cell zero. The rest of the equations in this section transform similarly and, for example,

$$\omega(i,j,\vec{q})=\sum_l e^{-i\vec{q}\cdot\vec{R}_l}\omega_{\alpha\beta}\ , \quad (27b')$$

using the same notation as in Eq. (27a'). Methods have been developed for generating self-consistent integral equations for spectral functions in the spin problem which effectively sum up infinite classes of moment diagrams with similar topological structures.[8] Before applying these methods to the present problem we will mention that a method of Padé approximants[9] and high-frequency expansions appears to converge quickly in some limits for the similar problem discussed in the following paper,[5] and may work well for the present problem. In order to use the method we note that the nontrivial or interacting part of $K(\omega)$, denoted $K'(\omega)$, where

$$K'(i,j,\vec{q},\omega)=K(i,j;\vec{q},\omega)-\omega(i,j,\vec{q})\ , \quad (33)$$

can be expanded at high frequencies as

$$K'(i,j,\vec{q},\omega)=\sum_{n=0}^{\infty}\left(\frac{-i}{\omega}\right)^{n+1}L_{n+2}(i,j,\vec{q}) \quad (34)$$

by using Eq. (29). Since $K'(\omega)$ vanishes as $1/\omega$ as $\omega\to\infty$, we expand it as a ratio of polynomials in ω with one power higher in the denominator than the numerator,

$$K'_n(i,j,\vec{q},\omega)=\sum_{k=0}^{n}a_k(i,j,\vec{q})\omega^k\left(\sum_{k=0}^{n+1}b_k(i,j,\vec{q})\omega^k\right)^{-1}\ , \quad (35)$$

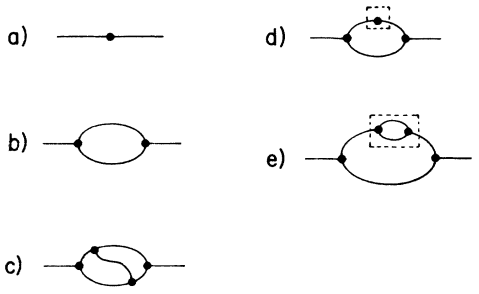

FIG. 3. Examples of skeleton diagrams (a), (b), and (c) and nonskeleton diagrams (e) and (f). The lower-order pieces of diagrams (e) and (f) that identify them as nonskeleton are enclosed in dashed boxes.

where $n=0,1,2,\ldots$ denotes the nth order Padé approximant. The coefficients a_k and b_k are determine by matching the first $2n+2$ terms of the expansions in Eqs. (34) with the high-frequency expansion of Eq. (35).

Finally we shall describe how to write down self-consistent integral equations for $D(\alpha,\beta;\omega)$ which sum up infinite classes of topologically similar moments diagrams. We shall only state the procedure and not derive it because the derivation is almost identical to the derivation in Ref. 8. The method sums up all moment diagrams that have the topological structure of certain skeleton diagrams. A skeleton diagram is an irreducible diagram which cannot be made up by piecing together lower-order diagrams. In Fig. 3, diagrams (a), (b), and (c) are skeleton diagrams. Diagrams (d) and (e) are not because they are constructed from lower-order diagrams enclosed in the dashed boxes.

The rules for the nth order contribution to $K(\alpha,\beta;t)$ in the self-consistent integral equation scheme are as follows: (i) Draw all distinct skeleton diagrams made up of the basic event diagrams starting on the left with a single line, ending on the right with a single line, and containing n events. (ii) Label the first dot on the left with time t, the last dot on the right by time 0, and all internal dots by times t_i. Label all lines where they go into and out of dots by distinct site indices. Thus each internal line has a distinct site index at each end. The incoming line on the left is labeled α and the outgoing line on the right is labeled β. (iii) Associated the appropriate analytical expression given in Fig. 1 with each dot. Replace every line going from (γ',t_i) to (γ'',t_j) by $D(\gamma',\gamma'';t_i-t_j)$. (iv) Integrate over all internal times t_i, sum over all internal sites, and multiply by $(-1)^{n+1}$. This procedure yields an integral equation for K in terms of D which must be solved self-consistently with Eq. (26) which gives D in terms of K.

The above procedure does have one potentially serious drawback. It ignores the restrictions about site labels at the same "time" being equal. However, in the following paper we show that at least under some conditions, this introduces very little error.

Although we have not included any specific examples in this paper the examples in the following paper, which treats a very similar problem, should illustrate the method. At present we are applying this formalism to the hopping of interstitial hydrogen in bcc lattices in the β phase with inequivalent hopping rates.

---

*Supported in part by the NSF under Grant No. DMS 75-18100.

[1]H. Lütgemier, H. G. Bohn, and R. R. Arons, J. Magn. Resonance 8, 80 (1972).
[2]J. J. Rush, R. C. Livingston, and L. A. de Graaf, J. Chem. Phys. 59, 6570 (1973).
[3]J. W. Rowe, J. J. Rush, and H. E. Flotow, Phys. Rev. B 9, 5039 (1974).
[4]V. F. Petrunin, V. A. Somenkov, S. Shilshtein, and A. A. Chertkov, Sov. Phys.-Crystallogr. 15, 137 (1970).
[5]O. Sankey and P. A. Fedders, following paper, Phys. Rev. B 15, 3586 (1977).
[6]By trivial we mean that the problem can be solved by a transform or matrix inversion.
[7]G. F. Reiter, Phys. Rev. B 5, 222 (1972).
[8]C. W. Myles and P. A. Fedders, Phys. Rev. B 9, 4872 (1974).
[9]For a discussion of Padê approximants see, for example, George A. Baker, Jr. and John L. Gammel, *The Padê Approximant in Theoretical Physics* (Academic, New York, 1970).