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Tight-Binding Models of Amorphous Systems: Liquid Metals

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A tight-binding approach to the electronic structure of disordered systems is developed for a simple one-orbital model of a liquid metal. An equation is derived for a one-electron continuum Green's function from which the electronic density of states can be obtained. Utilizing an analogy between this Green's function and the *T* matrix of multiple-scattering theory, results are obtained corresponding to the quasicrystalline approximation (QCA) of Lax and the self-consistent approximation (SCA) of Schwartz and Ehrenreich. Moments of the spectral function are also analyzed. Calculations were made using random and hard-sphere pair distribution functions. The QCA in this model is quite inadequate, and the SCA, while a considerable improvement, proves to involve a questionable approximation to the three-body distribution function.

I. INTRODUCTION

In a recent Letter[1] (I) a method was introduced for the study of electronic states in disordered systems based on tight-binding or linear-combination-of-atomic-orbitals (LCAO) representations. In this paper a more detailed account is given of the method, and the results are extended and further analyzed. As in I we shall restrict ourselves to the case of a single atomic *S* orbital per site, and approximations which depend upon the spherically symmetric radial distribution function of atoms about a given one. Thus we deal with a simple model of a liquid metal. It is hoped in later work to extend the results to include more orbitals, for a more realistic liquid-metal calculation, and to consider in greater detail the arrangement of atoms about a given one, so as to be able to deal with the tetrahedral coordination in amorphous semiconductors or the bridging in SiO_2.

One motivation for using an LCAO approach is that it has had some success recently in the band theory[2] of semiconductors and even simple metals, and especially transition metals.[3] There has also been recent work on defects in semiconductors,[4] and in SiO_2,[5] based on semiempirical LCAO approximations. The main features of these calculations which make them more realistic than the early tight-binding theory are the inclusion of all overlaps, i.e., many neighbors, and the consideration of the nonorthogonality of the basis. We shall incorporate both of these features in the present calculation.

A second motivation is the success of tight-binding models in the study of substitutional alloys. In particular the coherent-potential approximation (CPA) of Soven,[6] takes a simple form in these systems.[7,8] Relevant to the liquid-metal problem is a "lattice-liquid" model in which the atoms occupy a fraction of the sites of a lattice. This system has been investigated by Kirkpatrick.[9] Again, Weaire and Thorpe[10] have used a simple tight-binding model to gain insight into the electronic states, and in particular the energy gap, of tetrahedrally coordinated systems such as amorphous semiconductors.

In the theory of liquid metals, there have been several approaches to improving upon the nearly-free-electron results of Ziman.[11] One of these involves evaluating the electron self-energy by treating the pseudopotential as a perturbation[12,13] and derives from the Green's-function formulation of Edwards.[12] Another involves using multiple-scattering techniques[14-16] based primarily on the quasicrystalline approximation (QCA) of Lax.[14] We shall be concerned here mainly with the latter methods. The QCA has been shown[16] to correspond in the alloy case to the average-*T*-matrix approximation[17] (ATA) which does not have the self-consistent propagator renormalization of the CPA, and which was believed to give spurious gaps[6] in the energy spectrum. Consequently efforts have been made[16,18,19] to obtain, for the liquid metal, results analagous to the CPA. While for the random-liquid case[16,18] there is general agreement, for more realistic pair distribution functions there are differences. The best result appears to be the self-consistent approximation (SCA) of Schwartz and Ehrenreich,[16] which reduces to the CPA for the alloy case. However, in general the equations are very difficult to solve, so that it has not been possible to analyze the differences, or the improvements over the QCA, in detail. The tight-binding model, being simpler, can hopefully give insights into the relative merits of the various approximations.

Actually, recent work of Schwartz *et al.*[20] has shown that the spurious energy gaps associated with the average-*T*-matrix approximation are the consequence of a further approximation made by Beeby,[6] and also used by Velicky *et al.*[7] This version of the ATA we shall term ATA′, and we shall discuss the relationship of these approximations to the present work in Sec. VI.

A tight-binding formulation was made by Beeby and Edwards[21] based on a T-matrix expansion, and they obtained a result similar to our analog of the QCA.[1] Takeno[22] has obtained the QCA analog by methods closer to those we use, but which seem to involve ambiguities in the configurational averaging which we have eliminated. Cyrot-Lackman[23] has examined the moments of the density of states for an LCAO model. The last two authors have assumed orthogonal orbitals.

In this article we develop the general formalism in Sec. II resulting in an equation for the continuum Green's function[1] which can be configurationally averaged in a well-defined way, and from which the density of states can be determined. In Sec. III we demonstrate the analogy between this Green's function and the T matrix of multiple-scattering theory and obtain a result corresponding to the quasicrystalline approximation, which we shall term the QCA′. In Sec. IV we exploit the above analogy to derive the SCA′, which corresponds to the self-consistent approximation of Schwartz and Ehrenreich, and we reduce the result to an integral equation with a self-consistently determined kernel. Section V gives some results involving moments of the spectral function, and Sec. VI gives the specialization of the theory to the cases of the lattice and the lattice liquid with some comments on the average-T-matrix approximation. Numerical results are presented in Sec. VII for the random liquid and in Sec. VIII for a hard-sphere liquid. Finally we discuss the implication of our results in Sec. IX.

II. BASIC EQUATION FOR THE GREEN'S FUNCTION; DENSITY OF STATES

The model we use has been outlined in I, but we shall develop it again in a more leisurely and thorough manner. We consider a collection of atoms in some distribution and assume that the wave function is expanded in terms of atomic orbitals $\phi_j(\vec{r}) = \phi(\vec{r} - \vec{R}_j)$ located on the various atomic sites. Actually, we shall find it most convenient to deal with the one-electron Green's function $\mathcal{G}_t(\vec{r}, \vec{r}\,')$ for the system. In terms of the Green's function we can obtain the density of states by standard means.[7,12] We assume an LCAO expansion for $\mathcal{G}_t$,

$$\mathcal{G}_t(\vec{r}, \vec{r}\,') = \sum_{ij} \phi_i(\vec{r}) \mathcal{G}_{ij} \phi_j^*(\vec{r}\,') \quad . \tag{2.1}$$

Following the notation of Schwartz and Ehrenreich[16] we shall use script letters for quantities such as $\mathcal{G}$ depending on an individual distribution of atoms—i.e., member of the ensemble—and italic letters for the statistical averages. Thus

$$\langle \mathcal{G}_t(\vec{r}, \vec{r}\,') \rangle = G_t(\vec{r}, \vec{r}\,') \quad . \tag{2.2}$$

The Green's function satisfies the equation

$$(\omega - \mathcal{H}) \mathcal{G}_t(\vec{r}, \vec{r}\,') = \delta(\vec{r} - \vec{r}\,') \quad , \tag{2.3}$$

where $\mathcal{H}$ is the one-electron Hamiltonian for the system. If we multiply Eq. (2.3) by $\phi_i^*(\vec{r})$ on the left and $\phi_m(\vec{r}\,')$ on the right and integrate using Eq. (2.1), we have

$$\sum_{lj} \int \phi_i^*(\vec{r})(\omega - \mathcal{H}) \phi_l(\vec{r})\, d\vec{r}\, \mathcal{G}_{lj} \int \phi_j^*(\vec{r}\,') \phi_m(\vec{r}\,')\, d\vec{r}\,' = \int \phi_i^*(\vec{r}) \phi_m(\vec{r})\, d\vec{r} \quad . \tag{2.4}$$

Introducing overlap and transfer matrices

$$\mathcal{S}_{ij} = S(\vec{R}_i - \vec{R}_j) = \int \phi_i^*(\vec{r}) \phi_j(\vec{r})\, d\vec{r} \quad , \tag{2.5}$$

$$\mathcal{H}_{ij} = \int \phi_i^*(\vec{r}) \mathcal{H} \phi_j(\vec{r})\, d\vec{r} \quad , \tag{2.6}$$

we have

$$\sum_{lj} (\omega \mathcal{S}_{il} - \mathcal{H}_{il}) \mathcal{G}_{lj} \mathcal{S}_{jm} = \mathcal{S}_{im} \quad . \tag{2.7}$$

For any distribution of atoms, $\mathcal{S}_{ij}$ can be shown to be positive definite and to have an inverse.[24] We therefore have for $\mathcal{G}_{ij}$ the equation

$$\sum_{l} (\omega \mathcal{S}_{il} - \mathcal{H}_{il}) \mathcal{G}_{lj} = \delta_{ij} \quad . \tag{2.8}$$

This is the basic equation of the present work.[1] It suffers, however, from the following signal disadvantage. The quantity $\mathcal{G}_{ij}$ cannot be statistically averaged in a meaningful way because the basis depends upon the distribution of atoms. We can statistically average $\mathcal{G}_t(\vec{r}, \vec{r}\,')$, but it is more convenient at this point to introduce the quantity

$$\mathcal{G}(\vec{r}, \vec{r}\,') = \sum_{ij} \delta(\vec{r} - \vec{R}_i) \mathcal{G}_{ij} \delta(\vec{r}\,' - \vec{R}_j) \quad , \tag{2.9}$$

which is the continuum Green's function. $\mathcal{G}$ is essentially $\mathcal{G}_{ij}$ in which atom i is restricted to be located at point $\vec{r}$ and atom j at point $\vec{r}\,'$. $\mathcal{G}_t$ can be readily obtained from $\mathcal{G}$:

$$\mathcal{G}_t(\vec{r}, \vec{r}\,') = \int \mathcal{G}(\vec{R}, \vec{R}\,') \phi(\vec{r} - \vec{R}) \phi(\vec{r}\,' - \vec{R}\,')\, d\vec{R}\, d\vec{R}\,' . \tag{2.10}$$

We can now contemplate calculating the statistical average of $\mathcal{G}(\vec{r}, \vec{r}\,')$, which will be denoted by $G(\vec{r}, \vec{r}\,')$ and is a continuous function of $\vec{r}$ and $\vec{r}\,'$, except near $\vec{r} = \vec{r}\,'$ where it behaves like a δ function. We first must obtain an equation for $\mathcal{G}(\vec{r}, \vec{r}\,')$ based on Eq. (2.8).

At this point let us make two simplifying assumptions for Eq. (2.8). In general, the matrix element $\mathcal{H}_{ij}$ will depend on the distribution of other atoms about atoms i and j since it depends on potentials due to the various atoms. Let us assume however that for $i \neq j$, $\mathcal{H}_{ij}$ is a function only of the distance between atoms i and j, i.e.,

$$\mathcal{H}_{ij} = H(\vec{R}_{ij}) \quad . \tag{2.11}$$

This is either a two-center approximation or, more generally, we use an averaged distribution of other atoms about i and j to compute $\mathcal{H}_{ij}$. Similarly for $i=j$, let us assume $H_{ii}=H_0$, a constant independent of the distribution of neighbors.

Another assumption we might wish to make is to neglect $\mathcal{S}_{ij}$ for $i\neq j$. (Note that $\mathcal{S}_{ii}=1$ by definition.) The justification for this would be the fact that the atoms do not come closer to each other than a certain minimum distance. But as mentioned in the Introduction, experience has shown that the overlaps are important, so we shall not make this approximation, except as a special case. However we can lump the overlap term in with $\mathcal{H}_{ij}$ as follows for $i\neq j$:

$$\mathcal{H}'_{ij}=H'(\vec{R}_{ij})=\mathcal{H}_{ij}-\omega\,\mathcal{S}_{ij}\ , \tag{2.12}$$

and therefore develop the equation as though we had assumed orthogonal orbitals.

Equation (2.8) then becomes

$$(\omega-H_0)\,\mathcal{G}_{ij}-\sum_{l\neq i} H'(\vec{R}_{il})\mathcal{G}_{lj}=\delta_{ij}\ . \tag{2.13}$$

Let us multiply by $\delta(\vec{R}-\vec{R}_i)\delta(\vec{r}\,'-\vec{R}_j)$ and sum over i and j, using Eq. (2.9). Then

$$(\omega-H_0)\,\mathcal{G}(\vec{r},\vec{r}\,')-\sum_{\substack{ij\\ l\neq i}} \delta(\vec{r}-\vec{R}_i)H'(\vec{R}_{il})\mathcal{G}_{lj}\delta(\vec{r}\,'-\vec{R}_j)$$
$$=\rho(\vec{r})\delta(\vec{r}-\vec{r}\,')\ , \tag{2.14}$$

where we have introduced the density function

$$\rho(\vec{r})=\sum_i \delta(\vec{r}-\vec{R}_i)=\sum_i \rho_i(\vec{r})\ . \tag{2.15}$$

If in the second term we introduce $\int\delta(\vec{r}\,''-\vec{R}_l)\,d\vec{r}\,''=1$ and then replace $H'(\vec{R}_{il})$ by $H'(\vec{r}-\vec{r}\,'')$, we have

$$\sum_{\substack{ij\\ l\neq i}} \int \delta(\vec{r}-\vec{R}_i)H'(\vec{r}-\vec{r}\,'')\delta(\vec{r}\,''-\vec{R}_l)$$
$$\times\mathcal{G}_{lj}\delta(\vec{r}\,'-\vec{R}_j)\,d\vec{r}\,''\ .$$

If we add and subtract the $i=l$ term and use Eqs. (2.9) and (2.16), the equation for $\mathcal{G}(\vec{r},\vec{r}\,')$ becomes

$$[\omega-H_0+H'(0)]\,\mathcal{G}(\vec{r},\vec{r}\,')-\rho(\vec{r})\int H'(\vec{r}-\vec{r}\,'')$$
$$\times\mathcal{G}(\vec{r}\,'',\vec{r}\,')\,d\vec{r}\,''=\delta(\vec{r}-\vec{r}\,')\rho(\vec{r})\ . \tag{2.16}$$

This equation is the main result of this section. We note that the dependence on the positions of the atoms occurs solely through the density $\rho(\vec{r})$, while the interaction $H'(\vec{r}-\vec{r}\,')$ is a continuum quantity. In the following sections we shall apply multiple-scattering theory to this equation. Let us first close this section by obtaining an expression for the density of states in terms of $\mathcal{G}(\vec{r},\vec{r}\,')$.

The density of states, which we shall calculate per atom, is obtained from the one-electron Green's function as follows[7,12]:

$$N(\omega)=-(1/\pi N)\,\mathrm{Im}\int\langle\mathcal{G}_t(\vec{r},\vec{r})\rangle\,d\vec{r}$$
$$=-(1/\pi N)\,\mathrm{Im}\int G_t(\vec{r},\vec{r})\,d\vec{r}\ , \tag{2.17}$$

the latter form being from Eq. (2.2). If we use Eq. (2.1) for $\mathcal{G}_t$, we have

$$N(\omega)=-\frac{1}{\pi N}\,\mathrm{Im}\left\langle\sum_{ij}\mathcal{S}_{ij}\mathcal{G}_{ij}\right\rangle\ . \tag{2.18}$$

Alternatively, we can use Eq. (2.10) to obtain

$$N(\omega)=-(1/\pi N)\,\mathrm{Im}\int S(\vec{R}-\vec{R}\,')G(\vec{R},\vec{R}\,')\,d\vec{R}\,d\vec{R}\,'\ , \tag{2.19}$$

where $G(\vec{R},\vec{R}\,')=\langle\mathcal{G}(\vec{R},\vec{R}\,')\rangle$ is the statistical average of our continuum Green's function. If we assume spatial homogeneity for our ensemble, then $G(\vec{r},\vec{r}\,')=G(\vec{r}-\vec{r}\,')$ depends only upon the distance between $\vec{r}$ and $\vec{r}\,'$. (The same holds for G_t.) Then Eq. (2.19) becomes

$$N(\omega)=-(1/\pi n)\,\mathrm{Im}\int S(\vec{r})G(\vec{r})\,d\vec{r}\ , \tag{2.20}$$

where n is the density. If we introduce the Fourier transform of $G(\vec{r})$

$$G_{\vec{k}}=\int e^{i\vec{k}\cdot\vec{r}}\,G(\vec{r})\,d\vec{r} \tag{2.21}$$

and similarly for S, the expression for the density of states can also be written

$$N(\omega)=-(1/\pi n)\,\mathrm{Im}\int S_{\vec{k}}G_{\vec{k}}\,d\vec{k}/8\pi^3\ . \tag{2.22}$$

Equation (2.22) will be the most useful means of calculating the density of states in various approximations. Notice the explicit occurrence of the overlap integral $S_{\vec{k}}$. This acts as a natural cutoff for the $\vec{k}$ integral in Eq. (2.22), and hence it is most important to keep it in the calculation. If we do wish to use the approximation $\mathcal{S}_{ij}=\delta_{ij}$, we must go back to Eq. (2.18), and the density of states depends upon $\mathcal{G}_{ii}$. To obtain this quantity, we must isolate the part of $G(\vec{r},\vec{r}\,')$ which depends on $\delta(\vec{r}-\vec{r}\,')$, and this is just the large-$\vec{k}$ limit of $G_{\vec{k}}$. Thus we find

$$N(\omega)\big|_{\mathcal{S}_{ij}=\delta_{ij}}=-(1/\pi n)\,\mathrm{Im}G_{\vec{k}}\big|_{\vec{k}\to\infty}\ . \tag{2.23}$$

III. MULTIPLE-SCATTERING EXPANSION AND QUASICRYSTALLINE APPROXIMATION

Equation (2.16) can be rewritten, using an operator notation for $\mathcal{G}$, ρ, and H':

$$\mathcal{G}=\rho/\omega'+(\rho/\omega')H'\mathcal{G}\ , \tag{3.1}$$

where

$$\omega'=\omega-H_0+H'(0)\ . \tag{3.2}$$

We can also expand the right-hand side of Eq. (3.1):

$$\mathcal{G}=\frac{\rho}{\omega'}+\frac{\rho}{\omega'}H'\frac{\rho}{\omega'}+\frac{\rho}{\omega'}H'\frac{\rho}{\omega'}H'\frac{\rho}{\omega'}+\cdots\ . \tag{3.3}$$

As noticed previously, the quantity in Eqs. (3.1) and (3.3) pertaining to the atoms is ρ/ω', while H' is a "medium" quantity.

These equations are formally analogous to the expansion of the T matrix for the case of a free electron in a disordered array of scatters. Using barred quantities for this latter case, which is the more usual approach to liquid metals, we can write[16] for the Green's function

$$\bar{\mathcal{G}}=\bar{\mathcal{G}}_0+\bar{\mathcal{G}}_0\bar{\mathcal{T}}\bar{\mathcal{G}}_0 \ , \tag{3.4}$$

$$\begin{aligned}\bar{\mathcal{T}}&=\bar{\mathcal{V}}+\bar{\mathcal{V}}\bar{\mathcal{G}}_0\bar{\mathcal{T}}\\ &=\bar{\mathcal{V}}+\bar{\mathcal{V}}\mathcal{G}_0\bar{\mathcal{V}}+\bar{\mathcal{V}}\mathcal{G}_0\bar{\mathcal{V}}\mathcal{G}_0\bar{\mathcal{V}}+\cdots \ .\end{aligned} \tag{3.5}$$

Here $\bar{\mathcal{G}}_0$ is the free-electron Green's function and $\bar{\mathcal{V}}=\sum_i \bar{v}_i$ is the scattering potential. We note the analogy between our $\mathcal{G}$ and $\bar{\mathcal{T}}$, with the potential $\bar{\mathcal{V}}$ replaced by $\rho/\omega'=\sum_i \rho_i/\omega'$ and the free-electron Green's function $\bar{\mathcal{G}}_0$ replaced by the medium interaction H'. The correspondence is summarized in Table I. It is well known[6,20] that Eq. (3.5) can be reexpanded in terms of the T matrix for a single scattering center,

$$\bar{t}_i=\bar{v}_i+\bar{v}_i\bar{\mathcal{G}}_0\bar{t}_i \ , \tag{3.6}$$

to give

$$\bar{\mathcal{T}}=\sum_i \bar{t}_i+\sum_{i\neq j}\bar{t}_i\mathcal{G}_0\bar{t}_j+\sum_{\substack{i\neq j\\ j\neq k}}\bar{t}_i\bar{\mathcal{G}}_0\bar{t}_j\bar{\mathcal{G}}_0\bar{t}_k+\cdots \ , \tag{3.7}$$

where no two successive indices in the sum are the same. In our case the analog of t_i is simply

$$\tau_i=\frac{\rho_i}{\omega-H_0}=\frac{\rho_i}{\omega'}+\frac{\rho_i}{\omega'}H'(0)\tau_i \ , \tag{3.8}$$

so that the expansion becomes

$$\mathcal{G}=\sum_i \tau_i+\sum_{i\neq j}\tau_i H'\tau_j+\sum_{\substack{i\neq j\\ j\neq k}}\tau_i H'\tau_j H'\tau_k+\cdots \ . \tag{3.9}$$

This result was obtained in I in a slightly different manner. τ_i is essentially an atomic Green's function or locator.[25,26]

TABLE I. Corresponding quantities in present theory and multiple-scattering theory.[a]

Tight-binding theory	Multiple-scattering theory
$\mathcal{G}$, G	$\mathcal{T}$, T
ρ/ω'	$\mathcal{V}$
ρ_i/ω'	v_i
$\tau_i=\rho_i/(\omega-H_0)$	t_i
$\mathcal{J}=H'+H'\mathcal{G}H'$ $I=H'+H'GH'$	$\mathcal{G}$, G
D	Σ
d_i	σ_i
q_i	t_i

[a]L. Schwartz and H. Ehrenreich, Ref. 16.

Let us now examine the statistical average of the expansion of Eq. (3.9), which depends on the averages

$$n=\sum_i \langle\rho_i(\vec{r})\rangle \ , \tag{3.10}$$

$$n^2 g(\vec{r}-\vec{r}\,')=\sum_{ij}{}' \langle\rho_i(\vec{r})\rho_j(\vec{r}\,')\rangle \ , \tag{3.11}$$

$$n^3 g(\vec{r},\vec{r}\,',\vec{r}\,'')=\sum_{ijl}{}' \langle\rho_i(\vec{r})\rho_j(\vec{r}\,')\rho_l(\vec{r}\,'')\rangle \ . \tag{3.12}$$

Here n is the density, $g(\vec{r}-\vec{r}\,')$ the radial distribution function, and $g(\vec{r},\vec{r}\,',\vec{r}\,'')$ a three-particle distribution function. The prime on the summation indicates that no two indices are equal. Then

$$\begin{aligned}G(\vec{r},\vec{r}\,')&=\frac{\delta(\vec{r}-\vec{r}\,')}{\omega-H_0}+\frac{n^2}{(\omega-H_0)^2}H'(\vec{r}-\vec{r}\,')g(\vec{r}-\vec{r}\,')\\ &+\frac{n^3}{(\omega-H_0)^3}\int\left(\frac{\delta(\vec{r}-\vec{r}\,')}{n}g(\vec{r}-\vec{r}\,'')+g(\vec{r},\vec{r}\,',\vec{r}\,'')\right)\\ &\times H'(\vec{r}-\vec{r}\,'')H'(\vec{r}\,''-\vec{r}\,')\,d\vec{r}\,''+\cdots \ .\end{aligned} \tag{3.13}$$

In making this expansion, we need to treat separately terms in which two or more indices coincide.

Consider now an approximation for the above expansion in which we neglect all correlations between positions of atoms in the sums of Eq. (3.9) except those between atoms corresponding to successive indices. Thus in the third term of Eq. (3.13) we replace the term in large parentheses by $g(\vec{r}-\vec{r}\,'')g(\vec{r}\,''-\vec{r}\,')$. Then if we write $H'(\vec{r})g(\vec{r})$ as $\tilde{H}'(\vec{r})$, we have

$$\begin{aligned}G^{\mathrm{QCA}}(\vec{r},\vec{r}\,')&=\frac{n\delta(\vec{r}-\vec{r}\,'')}{\omega-H_0}+\left(\frac{n}{\omega-H_0}\right)^2\tilde{H}'(\vec{r}-\vec{r}\,')\\ &+\left(\frac{n}{\omega-H_0}\right)^3\int\tilde{H}'(\vec{r}-\vec{r}\,'')\tilde{H}(\vec{r}\,''-\vec{r}\,')\,d\vec{r}\,''+\cdots \ .\end{aligned} \tag{3.14}$$

Considering now the Fourier transform $G_{\vec{k}}$, we can readily sum this to obtain[27]

$$G_{\vec{k}}^{\mathrm{QCA}}=\frac{n}{\omega-H_0-nH'_{\vec{k}}} \ , \tag{3 15}$$

$$n\tilde{H}'_{\vec{k}}=n\int e^{i\vec{k}\cdot\vec{r}}g(\vec{r})\tilde{H}'(\vec{r})\,d\vec{r} \ . \tag{3.16}$$

As we shall see in Sec. IV, this result, which we call QCA$'$, is the analog of the QCA of Lax.[14] We notice that $n\tilde{H}_{\vec{k}}$ is an obvious generalization of the Bloch sum, which in fact enables us to deal with interactions as long range as we like. The lack of any broadening, however, makes this approximation somewhat unrealistic, so we now turn to the task of improving upon it.

IV. SELF-CONSISTENT APPROXIMATION

There have been several attempts[16,18,19] to obtain results for the liquid-metal case analogous to the coherent-potential approximation for the substitutional alloy. In the tight-binding substitutional-alloy model the self-energy (assumed site diagonal) is readily projected into a contribution from each lattice site so that the perturbation $(V-\Sigma)$ consists of a contribution from each scatterer, and a self-consistent single-site approximation—the CPA—can be obtained. In the liquid-metal case such a clearcut division cannot be made. Assigning $1/N$ of the self-energy to each scatterer as in the work of Faulkner[18] and Gyorffy[19] appears to be unsatisfactory. Schwartz and Ehrenreich,[16] rather than try to localize the perturbation, related the self-energy to a contribution from each scatterer, and manipulated the Green's-function equation so as to obtain a self-consistent set after a decoupling approximation was made. The result reduces to the CPA for the substitutional alloy. We shall follow their method transposed to apply to our case.

We first present another derivation of the QCA′. Let us write the Green's function as

$$\mathcal{G}=\sum_i \mathcal{G}_i \;, \tag{4.1}$$

$$\mathcal{G}_i(\vec{r},\vec{r}\,')=\sum_j \delta(\vec{r}-\vec{R}_i)\,\mathcal{G}_{ij}\delta(\vec{r}\,'-\vec{R}_j) \;.$$

Then from Eq. (2.16) or (3.1) we have

$$[\omega-H_0+H'(0)]\mathcal{G}_i=\rho_i+\rho_i H'\sum_j \mathcal{G}_j \;. \tag{4.2}$$

We can cancel the $j=i$ term to obtain

$$(\omega-H_0)\mathcal{G}_i=\rho_i+\rho_i H'\sum_{j\neq i} \mathcal{G}_j \;. \tag{4.3}$$

Let us now introduce conditional averages[14,16] of quantities depending on the position of the atoms. Defining a distribution function $f(\vec{R}_1,\ldots,\vec{R}_N)$ for the ensemble such that $\int f(\vec{R}_1,\ldots,\vec{R}_N)\,d\vec{R}_1\cdots d\vec{R}_N=1$, we define

$$\langle A\rangle=\int A(\vec{R}_1,\ldots,\vec{R}_N)f(\vec{R}_1,\ldots,\vec{R}_N)\,d\vec{R}_1\cdots d\vec{R}_N \;, \tag{4.4}$$

$$\begin{aligned}\langle A\rangle_i&=\frac{\int A(\vec{R}_1,\ldots,\vec{R}_N)f(\vec{R}_1,\ldots,\vec{R}_N)\,d\vec{R}_1\cdots d\vec{R}_N/d\vec{R}_i}{\int f(R_1,\ldots,R_N)\,dR_1\cdots dR_N/dR_i}\\&=\Omega\int A(\vec{R}_1,\ldots,\vec{R}_N)f(\vec{R}_1,\ldots,\vec{R}_N)\\&\qquad\times d\vec{R}_1\cdots d\vec{R}_N/d\vec{R}_i \;,\end{aligned} \tag{4.5}$$

$$\begin{aligned}\langle A\rangle_{ij}=\Omega^2[g(\vec{R}_{ij})]^{-1}\int A(\vec{R}_1,\ldots,\vec{R}_N)f(\vec{R}_1,\ldots,\vec{R}_N)\\\times d\vec{R}_1\cdots d\vec{R}_N/d\vec{R}_i\,d\vec{R}_j \;.\end{aligned} \tag{4.6}$$

Here, for example, $\langle A\rangle_i$ is the average of A with the position of the ith atom held fixed, and Ω is the volume of the system.

We then average Eq. (4.3) over the positions of all atoms other than i to obtain

$$(\omega-H_0)\langle\mathcal{G}_i\rangle_i=\rho_i+\frac{1}{\Omega}\sum_{j\neq i}\rho_i H'\int g(\vec{R}_{ij})\langle\mathcal{G}_j\rangle_{ij}\,d\vec{R}_j \;. \tag{4.7}$$

Our analog of the quasicrystalline approximation is obtained by neglecting the i dependence of $\langle\mathcal{G}_j\rangle_{ij}$, i.e.,

$$\langle\mathcal{G}_j\rangle_{ij}\cong\langle\mathcal{G}_j\rangle_j \quad (\text{QCA}') \;. \tag{4.8}$$

In the coordinate representation form of Eq. (4.7) [see Eq. (2.16)] we have $H'(\vec{r}-\vec{r}\,'')g(\vec{R}_{ij})$ multiplied by δ functions which fix $\vec{R}_i$ at $\vec{r}$ and $\vec{R}_j$ at $\vec{r}\,''$. We can therefore write this as $\tilde{H}'(\vec{r}-\vec{r}\,'')$. If we now average over $\vec{R}_j$ and sum over i, noting that the $j=i$ term in Eq. (4.7) gives no contribution, we have

$$(\omega-H_0)G^{\text{QCA}}=n+n\tilde{H}'G^{\text{QCA}} \;. \tag{4.9}$$

This is the same result as we obtained in Sec. III.

Let us now derive the SCA′. In Schwartz and Ehrenreich's treatment they make use of the exact Green's function. In our case the analogous quantity is the "interaction operator, "

$$I=H+HGH \;. \tag{4.10}$$

They also calculate a self-energy. In our case the analogous quantity is obtained by looking at Eq. (3.1),

$$\mathcal{G}=(\rho/\omega)(1+H\mathcal{G}) \;. \tag{4.11}$$

We have dropped the primes on H' and ω' in both (4.10) and (4.11) and shall restore them at the end of the section. ρ/ω is a sum of atomic Green's functions ρ_i/ω, which are locators,[25] but defined in a slightly different way from those in Eq. (3.8). Let us now define a quantity D such that the exact averaged Green's function satisfies

$$G=D(1+HG) \;. \tag{4.12}$$

We shall call D the medium locator[25] or simply the locator, and it is the analog of the self-energy in the work of Schwartz. In fact the present treatment bears some resemblance to the locator approach of Shiba[26] to the alloy problem. D can be written in several ways using Eq. (4.10):

$$D=GHI^{-1}=H^{-1}-I^{-1} \;. \tag{4.13}$$

In what follows we shall develop an approximation like Eq. (4.8), but for the locator rather than the Green's function. The locator D can be decomposed into contributions from individual atoms by writing

$$d_i=\langle\mathcal{G}_i\rangle_i HI^{-1} \tag{4.14}$$

in terms of which

$$D=\frac{1}{\Omega}\sum_i\int d_i\,dR_i=n\int d_i\,dR_i \;. \tag{4.15}$$

Here we have replaced the summation by N times a typical term. We shall make this same replacement several times below. We now transform the right-hand side of Eq. (4.14) by writing Eq. (4.2) averaged with atom i held fixed, in the form

$$\langle \mathcal{G}_i \rangle_i = (\rho_i/\omega)(1 + H\langle \mathcal{G} \rangle_i) \quad . \tag{4.16}$$

Let us denote $\langle \mathcal{G} \rangle_i$, the Green's function with atom i fixed, by G_i. We then have

$$d_i = (\rho_i/\omega)(1 + HG_i)HI^{-1} \quad . \tag{4.17}$$

In terms of G_i we can define I_i and D_i, the interaction operator and locator with atom i fixed:

$$I_i = H + HG_iH \quad , \tag{4.18}$$

$$D_i = G_iHI_i^{-1} = H^{-1} - I_i^{-1} \quad . \tag{4.19}$$

Now G_i can be written in analogy with Eq. (4.7):

$$G_i = \langle \mathcal{G}_i \rangle_i + n \int g(\vec{R}_{ij}) \langle \mathcal{G}_j \rangle_{ij} \, d\vec{R}_j \quad , \tag{4.20}$$

so that we have for D_i

$$\begin{aligned} D_i &= G_iHI_i^{-1} \\ &= \langle \mathcal{G}_i \rangle_i HI_i^{-1} + n \int g(\vec{R}_{ij}) \langle \mathcal{G}_j \rangle_{ji} HI_i^{-1} \, d\vec{R}_j \quad . \end{aligned} \tag{4.21}$$

The first term can be rewritten by using a relation obtained from Eqs. (4.16) and (4.18),

$$\langle \mathcal{G}_i \rangle_i = (\rho_i/\omega) I_i H^{-1} \quad , \tag{4.22}$$

so that Eq. (4.21) becomes

$$\begin{aligned} D_i &= \rho_i/\omega + n \int g(\vec{R}_{ij}) d_j^i \, d\vec{R}_j \quad , \\ d_j^i &\equiv \langle \mathcal{G}_j \rangle_{ji} HI_i^{-1} \quad . \end{aligned} \tag{4.23}$$

We now make the approximation of the SCA′ which is to ignore the fact that atom i is fixed in d_j^i so that

$$d_j^i \cong d_j \quad . \tag{4.24}$$

Then subtracting Eq. (4.15) from (4.23), we have

$$D_i - D = \rho_i/\omega + n \int h(\vec{R}_{ij}) d_j \, d\vec{R}_j \quad , \tag{4.25}$$

where $h(\vec{r}) = g(\vec{r}) - 1$.

Equations (4.17) and (4.25), together with the relations (4.18) and (4.19) between G_i and D_i, form a closed set which is the SCA′ result. We can simplify these equations by defining a quantity q_i

$$q_i = I^{-1}H(G_i - G)HI^{-1} \tag{4.26}$$

in terms of which I_i can be written

$$I_i = I + Iq_iI \quad . \tag{4.27}$$

We can now rewrite Eq. (4.17) in terms of q_i using Eq. (4.27),

$$d_i = (\rho_i/\omega)(1 + Iq_i) \quad . \tag{4.28}$$

We can also relate D_i to q_i by using Eqs. (4.19), (4.27), and (4.13),

$$(D_i - D)(1 + Iq_i) = q_i \quad . \tag{4.29}$$

The set of equations for the SCA′ at this stage consists of Eqs. (4.28), (4.29), (4.25), (4.15), and the definitions (4.10) and (4.12). Substituting Eq. (4.25) into Eq. (4.29) and using Eq. (4.28), we can rewrite and collect the SCA′ equations as follows:

$$d_i = (\rho_i/\omega)(1 + Iq_i) \quad , \tag{4.30}$$

$$q_i = d_i - \tilde{d}_i(1 + Iq_i) \quad , \tag{4.31}$$

$$\tilde{d}_i = -n \int h(\vec{R}_{ij}) d_j \, d\vec{R}_j \quad , \tag{4.32}$$

$$D = n \int d_i \, dR_i \quad , \tag{4.33}$$

$$G = (D^{-1} - H)^{-1} \quad , \tag{4.34}$$

$$I = H + HGH \quad . \tag{4.35}$$

Equations (4.30)–(4.33) can also be obtained by taking over Eqs. (2.36), (2.53), (2.5a), and (2.5b) in the paper by Schwartz and Ehrenreich,[16] and making the changes indicated in Table I.

Let us now reduce the SCA′ equation to a simpler and more useful form, making use of the δ-function nature of ρ_i. Let us first note that $\vec{R}_i$ is the only unique point in the system, and therefore we can assume that, using a coordinate representation,

$$q_i(\vec{r}, \vec{r}\,') = q(\vec{r} - \vec{R}_i, \vec{r}\,' - \vec{R}_i) \tag{4.36}$$

and similarly for d_i and $\tilde{d}_i$. If we also note that $G(\vec{r}, \vec{r}\,') = G(\vec{r} - \vec{r}\,')$ and similarly for H, D, and I, due to translational invariance, we can write Eq. (4.30) as

$$d_i(\vec{r}, \vec{r}\,') = \frac{\delta(\vec{r} - \vec{R}_i)}{\omega} \times \left(\delta(\vec{r} - \vec{r}\,') + \int I(\vec{r}\,'') q(\vec{r}\,'', \vec{r}\,' - \vec{r}) d\vec{r}\,'' \right) \quad . \tag{4.37}$$

From Eq. (4.33) we have

$$D(\vec{r} - \vec{r}\,') = (n/\omega)[\delta(\vec{r} - \vec{r}\,') + \int I(\vec{r}\,'') q(\vec{r}\,'', \vec{r}\,' - \vec{r}) d\vec{r}\,''] \quad . \tag{4.38}$$

From Eqs. (4.38), (4.37), and (4.32), we can then write

$$d(\vec{r} - \vec{r}\,') = [\delta(\vec{r})/n] D(\vec{r} - \vec{r}\,') \quad , \tag{4.39}$$

$$\tilde{d}(\vec{r}, \vec{r}\,') = -h(\vec{r}) D(\vec{r} - \vec{r}\,') \quad . \tag{4.40}$$

Then Eq. (4.31) becomes

$$q(\vec{r}, \vec{r}\,') = [\delta(\vec{r})/n + h(\vec{r})] D(\vec{r} - \vec{r}\,') + \int h(\vec{r}) D(\vec{r} - \vec{r}_1) \times I(\vec{r}_1 - \vec{r}_2) q(\vec{r}_2, \vec{r}\,') \, d\vec{r}_1 \, d\vec{r}_2 \quad . \tag{4.41}$$

This with Eq. (4.38) and the definitions (4.34) and (4.35) form the self-consistent set, which we shall further simplify. We Fourier transform Eq. (4.41) and write

$$q(\vec{k}, \vec{k}\,') = F(\vec{k}, \vec{k}\,') D_{\vec{k}\,'} \quad . \tag{4.42}$$

The integral equation for F is then

$$nF(\vec{k},\vec{k}')=1+nh(\vec{k}-\vec{k}')+n\int h(\vec{k}-\vec{k}'')H_{\vec{k}''}G_{\vec{k}''}F(\vec{k}'',\vec{k}')\,d\vec{k}''/8\pi^3\ . \qquad (4.43)$$

We have here used Eq. (4.13) to replace DI by HG. The Fourier transform for D is from Eq. (4.38),

$$D_{\vec{k}}=\frac{n}{\omega}+\frac{n}{\omega}\int I_{\vec{k}'}F(\vec{k}',\vec{k})\frac{d\vec{k}'}{8\pi^3}D_{\vec{k}}\ . \qquad (4.44)$$

Solving for $D_{\vec{k}}^{-1}$, substituting into Eq. (4.34), and eliminating I with Eq. (4.35), we have

$$G_{\vec{k}}^{-1}=\omega/n-\int(H_{\vec{k}'}+H_{\vec{k}'}^2G_{\vec{k}'})F(\vec{k}',\vec{k})\,d\vec{k}'/8\pi^3-H_{\vec{k}}\ . \qquad (4.45)$$

Let us write this in the form

$$nG_{\vec{k}}^{-1}=\omega-n\tilde{H}_{\vec{k}}-\Sigma_{\vec{k}}-H(0)\ , \qquad (4.46)$$

where $\Sigma_{\vec{k}}$ is a self-energy correction to the QCA result:

$$\Sigma_{\vec{k}}=n\int(H_{\vec{k}'}+H_{\vec{k}'}^2G_{\vec{k}'})F(\vec{k}',\vec{k})\,d\vec{k}'/8\pi^3+nH_{\vec{k}}-n\tilde{H}_{\vec{k}}-H(0)\ . \qquad (4.47)$$

To simplify this let us multiply Eq. (4.43) by $H_{\vec{k}}$ and integrate over $\vec{k}$:

$$\int nH_{\vec{k}}F(\vec{k},\vec{k}')\,d\vec{k}/8\pi^3=H(0)+\int nH_{\vec{k}}h(\vec{k}-\vec{k}')\,d\vec{k}/8\pi^3+n\int H_{\vec{k}}h(\vec{k}-\vec{k}'')H_{\vec{k}''}G_{\vec{k}''}F(\vec{k}'',\vec{k}')\,d\vec{k}''/8\pi^3\ . \qquad (4.48)$$

From the definition of $\tilde{H}_{\vec{k}}$ we have

$$\int H_{\vec{k}}h(\vec{k}-\vec{k}')\,(d\vec{k}/8\pi^3)=\tilde{H}_{\vec{k}'}-H_{\vec{k}'}\ ; \qquad (4.49)$$

using this relation and adding Eq. (4.48) to (4.47), we have finally

$$\Sigma_{\vec{k}}=n\int\tilde{H}_{\vec{k}'}H_{\vec{k}'}G_{\vec{k}'}F(\vec{k}',\vec{k})\,d\vec{k}'/8\pi^3\ . \qquad (4.50)$$

Let us now collect the results and restore the primes omitted in Eq. (4.11). The self-consistent set of equations becomes[27]

$$G_{\vec{k}}=n(\omega-H_0-n\tilde{H}'_{\vec{k}}-\Sigma_{\vec{k}})^{-1}\ , \qquad (4.51)$$

$$\Sigma_{\vec{k}}=n\int\tilde{H}'_{\vec{k}'}H'_{\vec{k}'}G_{\vec{k}'}F(\vec{k}',\vec{k})\,d\vec{k}'/8\pi^3\ , \qquad (4.52)$$

$$nF(\vec{k},\vec{k}')=1+nh(\vec{k}-\vec{k}')+n\int h(\vec{k}-\vec{k}'')H'_{\vec{k}''}G_{\vec{k}''}F(\vec{k}'',\vec{k}')\,d\vec{k}''/8\pi^3\ . \qquad (4.53)$$

This is the final result of this section. We see that the SCA′ results in an integral equation with a self-consistently determined kernel. Because of isotropy this equation can be put in a one-dimensional form and solved numerically, as we shall show in Sec. VIII.

V. MOMENTS

In I we found that an improvement over QCA′ can be found by calculating the second moment of the spectral function $-(1/\pi)\,\mathrm{Im}G$. It also will be of interest here to compare the second moment obtained from the SCA′ with exact results. We shall initially assume orthogonal orbitals, though in Secs. VII and VIII we shall find that results so obtained are useful for the case of $H(\vec{r})\propto S(\vec{r})$.

The Green's function can be expanded in the form[7]

$$G_{\vec{k}}=n\sum_{n=0}\frac{\omega_{\vec{k}}^{(n)}}{(\omega-H_0)^{n+1}}\ , \qquad (5.1)$$

where $\omega_{\vec{k}}^{(n)}$ is the nth moment of the spectral function about H_0:

$$\omega_{\vec{k}}^{(n)}=n^{-1}\int[-(1/\pi)\,\mathrm{Im}G_{\vec{k}}](\omega-H_0)^n d\omega\ . \qquad (5.2)$$

Thus the moment expansion is the same as our expansion of Eq. (3.9). We have

$$\omega_{\vec{k}}^{(0)}=1\ , \qquad (5.3)$$

$$\omega_{\vec{k}}^{(1)}=n\tilde{H}_{\vec{k}}\ , \qquad (5.4)$$

$$\omega_{\vec{k}}^{(2)}=FT\left[n^2\int\left(\frac{\delta(\vec{r}-\vec{r}')}{n}g(\vec{r}-\vec{r}'')+g(\vec{r},\vec{r}'',\vec{r}')\right)\times H(\vec{r}-\vec{r}'')H(\vec{r}''-\vec{r}')\,d\vec{r}''\right]\ , \qquad (5.5)$$

$$\omega_{\vec{k}}^{(3)}=FT\left[n^3\int\left(\frac{\delta(\vec{r}-\vec{r}_2)}{n}g(\vec{r},\vec{r}_1,\vec{r}')+\frac{\delta(\vec{r}_1-\vec{r}')}{n}\times g(\vec{r},\vec{r}_2,\vec{r}')+\frac{\delta(\vec{r}-\vec{r}')}{n}g(\vec{r},\vec{r}_1,\vec{r}_2)+\frac{\delta(\vec{r}-\vec{r}_2)\delta(\vec{r}'-\vec{r}_1)g(\vec{r}-\vec{r}')}{n^2}+g(\vec{r},\vec{r}_1,\vec{r}_2,\vec{r}')\right)\times H(\vec{r}-\vec{r}_1)H(\vec{r}_1-\vec{r}_2)H(\vec{r}_2-\vec{r}')\,d\vec{r}_1\,d\vec{r}_2\right]. \qquad (5.6)$$

If we wish to calculate the moments of the density of states for orthogonal orbitals, we obtain these by letting $\vec{k}\to\infty$, or taking the coefficient of the $\delta(\vec{r}-\vec{r}')$ term:

$$\omega^{(0)}=1\ , \qquad (5.7)$$

$$\omega^{(1)}=0\ , \qquad (5.8)$$

$$\omega^{(2)}=n\int g(\vec{r})H(\vec{r})^2 d\vec{r}, \qquad (5.9)$$

$$\omega^{(3)}=n^2\int g(0,\vec{r},\vec{r}')H(\vec{r})H(\vec{r}-\vec{r}')H(\vec{r}')\,d\vec{r}\,d\vec{r}'\ . \qquad (5.10)$$

We notice that for an attractive interaction the third moment is negative, indicating an unsymmetrical density of states.[23]

The quasicrystalline approximation gives $\omega_{\vec{k}}^{(n)}=(n\tilde{H}_{\vec{k}})^n$, and so only the zeroth and first moments are given correctly. To improve upon this, in I we used the superposition approximation,

$$g(\vec{r},\vec{r}'',\vec{r}')=g(\vec{r}-\vec{r}'')g(\vec{r}''-\vec{r}')g(\vec{r}-\vec{r}')\ , \qquad (5.11)$$

to obtain the result for the second moment

$$\omega_{\vec{k}}^{(2)}=(\omega_{\vec{k}}^{(1)})^2+\gamma_{\vec{k}}^2\ , \qquad (5.12)$$

$$\gamma_{\vec{k}}^2 = n\int \tilde{H}_{\vec{k}'} H_{\vec{k}'}\, d\vec{k}'/8\pi^3 + n^2\int h(\vec{k}-\vec{k}')\tilde{H}_{\vec{k}'}^2\, d\vec{k}'/8\pi^3 . \tag{5.13}$$

If we now calculate the first few moments in the SCA′, we find that the zeroth and first moments are given exactly, and the second moment is given by Eq. (5.12) with

$$\gamma_{\vec{k}}^2 = n\int [1+nh(\vec{k}-\vec{k}')]\tilde{H}_{\vec{k}'} H_{\vec{k}'}\, d\vec{k}'/8\pi^3 \quad . \tag{5.14}$$

This differs slightly from the superposition-approximation result, and the difference has important consequences for the hard-sphere liquid, as we shall see.

An examination of Eq. (5.5) shows that the SCA′ result obtains when we use the approximation

$$g(\vec{r},\vec{r}'',\vec{r}') = [1+h(\vec{r}-\vec{r}'')] \times [1+h(\vec{r}-\vec{r}')+h(\vec{r}''-\vec{r}')] \, . \tag{5.15}$$

This same factorization occurs in the T-matrix expansion studied by Schwartz and Ehrenreich.[16] It is interesting to note that for the lattice case (with, e.g., $h \to -\delta_{ij}$) this is exact, and is simply a scheme for enumerating the site exclusions. It would be interesting to extend this to higher terms to see if our result could be derived by a method such as that used by Blackman, Esterling, and Beck.[28]

If we consider briefly the case of nonorthogonal orbitals, we can show that the zeroth moment of the density of states is exactly 1. For the relation between the moments and the coefficients of an expansion in (here) $1/\omega$ also applies to $\sum_j \mathcal{S}_{ij}\mathcal{G}_{ji}$. According to Eq. (2.8) we have for large ω

$$\sum_j \mathcal{S}_{ij}\mathcal{G}_{ji} \sim 1/\omega + O(1/\omega^2) \quad . \tag{5.16}$$

But from Eq. (2.18) the spectral function corresponding to this is just the density of states per atom. We thus have the sum rule

$$\omega^{(0)} = \int N(\omega)\, d\omega = 1 \quad . \tag{5.17}$$

If we define a new Green's function

$$\tilde{\mathcal{G}}_{ij} = \sum_l \mathcal{S}_{il}\mathcal{G}_{lj} \quad , \tag{5.18}$$

we can write

$$\omega\tilde{\mathcal{G}}_{ij} = \delta_{ij} + \mathcal{H}_{im}\mathcal{S}_{ml}^{-1}\tilde{\mathcal{G}}_{lj} \quad , \tag{5.19}$$

and in principle we can calculate moments of $\tilde{\mathcal{G}}$ from this. However these involve the inverse of $\mathcal{S}_{ij}$, which is not known exactly, so that we must content ourselves with approximations for the nonorthogonal case.

The sum rule in Eq. (5.17) is in fact not obeyed in the QCA′, when the orbitals are not orthogonal. Thus, letting ω become large in Eq. (3.15), we have $\tilde{H}_{\vec{k}}' \sim -\omega\tilde{S}_{\vec{k}}$, and from Eq. (2.22) we have

$$\omega^{(0)} = \lim_{\omega\to\infty}\frac{\omega}{n}\int S_{\vec{k}}G_{\vec{k}}\frac{d\vec{k}}{8\pi^3} = \int\frac{S_{\vec{k}}}{1+n\tilde{S}_{\vec{k}}}\frac{d\vec{k}}{8\pi^3} \, . \tag{5.20}$$

For orthogonal orbitals $\tilde{S}_{\vec{k}} = 0$ and the result is just $S(0)=1$. Otherwise, the integral is, in general, different from 1 and in particular for the random lattice $\tilde{S}_{\vec{k}} = S_{\vec{k}} > 0$, so that $\omega^{(0)}$ is less than 1.

For the SCA′, however, we can show that in the special case of the random liquid the sum rule is satisfied. To prove this we take $h(r)=0$ in Eqs. (4.51)–(4.53) [see Eqs. (7.2) and (7.3)] and let ω become large. We have $H_{\vec{k}}' \sim -\omega S_{\vec{k}}$ and it is consistent to assume that $\Sigma \sim c\omega$. Then

$$G_{\vec{k}} \sim n\omega^{-1}/(1-c+nS_{\vec{k}}) \quad , \tag{5.21}$$

$$c = \int\frac{nS_{\vec{k}}^2}{1-c+nS_{\vec{k}}}\frac{d\vec{k}}{8\pi^3} \quad . \tag{5.22}$$

The integral can be rewritten to give

$$c = \int\left(1-\frac{1-c}{1-c+nS_{\vec{k}}}\right)S_{\vec{k}}\frac{d\vec{k}}{8\pi^3} \quad . \tag{5.23}$$

The $S_{\vec{k}}$ integral is again $S(0)=1$, so that Eq. (5.22) becomes

$$1-c = (1-c)\int\frac{S_{\vec{k}}}{1-c+nS_{\vec{k}}}\frac{d\vec{k}}{8\pi^3} \quad . \tag{5.24}$$

Unless $c=1$, the integral on the right-hand side must equal 1, and from Eqs. (5.20) and (5.21) this is just $\omega^{(0)}$. $c=1$ would give an infinite result for $\omega^{(0)}$, and so must be excluded.

VI. THE LATTICE AND LATTICE-LIQUID CASE

The quasicrystalline approximation is exact in the case of a lattice, and this result carries over into the tight-binding model, as can be readily seen by using the pair distribution function for a lattice

$$g(\vec{r}) = \frac{1}{n}\sum_{\vec{R}\neq 0}\delta(\vec{r}-\vec{R}) \quad , \tag{6.1}$$

where $\vec{R}$ goes over lattice points. We have then

$$n\tilde{H}_{\vec{k}} = \sum_{\vec{R}\neq 0} H(\vec{R})e^{i\vec{k}\cdot\vec{R}} = \epsilon_{\vec{k}} \quad , \tag{6.2}$$

$$n\tilde{S}_k = \sum_{R\neq 0} S(\vec{R})e^{i\vec{k}\cdot\vec{R}} = s_{\vec{k}} \quad . \tag{6.3}$$

Here $\epsilon_{\vec{k}}$ is the Bloch energy measured from H_0, and $s_{\vec{k}}$ is a normalization correction. The Green's function is

$$G_{\vec{k}} = \frac{n}{\omega(1+s_{\vec{k}})-H_0-\epsilon_{\vec{k}}} \quad . \tag{6.4}$$

$G_{\vec{k}}$ is now periodic in $\vec{k}$.

It is interesting to reduce the expression for the density of states to an integral over one Brillouin zone (BZ). We have

$$N(\omega) = -\frac{1}{\pi}\,\mathrm{Im}\int\frac{nS_{\vec{k}}}{\omega(1+s_{\vec{k}})-H_0-\epsilon_{\vec{k}}}\frac{d\vec{k}}{8\pi^3}$$
$$= -\frac{1}{\pi}\,\mathrm{Im}\int_{\mathrm{BZ}}\frac{\sum_{\vec{K}'} nS_{\vec{k}+\vec{K}}}{\omega(1+s_{\vec{k}})-H_0-\epsilon_{\vec{k}}}\frac{d\vec{k}}{8\pi^3} \quad , \tag{6.5}$$

where the $\vec{K}$ are the reciprocal-lattice vectors. But using

$$\sum_{\vec{K}} e^{i\vec{K}\cdot\vec{r}} = \frac{1}{n}\sum_{\vec{R}} \delta(\vec{r}-\vec{R}) \ , \tag{6.6}$$

we can write

$$\sum_{\vec{K}} nS_{\vec{k}+\vec{K}} = n\sum_{\vec{K}} \int S(\vec{r})\, e^{i(\vec{k}+\vec{K})\cdot\vec{r}}\, d\vec{r}$$

$$= \sum_{\vec{R}} S(\vec{R})\, e^{i\vec{k}\cdot\vec{R}} = 1 + s_{\vec{k}} \ , \tag{6.7}$$

so that in Eq. (6.5), we have effectively a one-BZ Green's function

$$\tilde{G}_{\vec{k}} = \frac{1}{\omega - (H_0 + \epsilon_{\vec{k}})/(1+s_{\vec{k}})} \ , \tag{6.8}$$

which gives the correct normalization for the density of states.

Let us now examine the QCA′ for the lattice liquid, in which the atoms occupy a fraction x of the lattice points. For this case we have

$$g(\vec{r}) = \frac{x}{n}\sum_{i\neq 0} \delta(\vec{r}-\vec{R}_i) \tag{6.9}$$

and

$$G_{\vec{k}} = \frac{n}{\omega(1+xs_{\vec{k}}) - H_0 - x\epsilon_{\vec{k}}} \ . \tag{6.10}$$

The one-BZ Green's function is

$$\tilde{G}_{\vec{k}} = \frac{1+s_{\vec{k}}}{\omega(1+xs_{\vec{k}}) - H_0 - x\epsilon_{\vec{k}}} \ . \tag{6.11}$$

For orthogonal orbitals, $s_{\vec{k}} = 0$, and $G_{\vec{k}}$ gives a band the same shape as the $x = 1$ case, but reduced in width. The lattice liquid corresponds to the split-band limit of the substitutional alloy, and the QCA′ corresponds to what has been termed the average-T-matrix approximation,[6,7] but which actually[20] is a more restricted result. This deserves some more discussion.

The T-matrix expansion, Eq. (3.7), has been applied to the tight-binding model of the substitutional alloy,[6,7] for which the i correspond to lattice sites. The ATA is obtained by averaging t_i over the scatterers, i.e., the atoms A or B, which can occupy site i. This has been discussed in detail by Schwartz *et al.*[20] Suppose, however, we make the analogous approximation to Eq. (3.9), where again i refers to the site, and where τ_i goes into the locator for site i,

$$L_i = 1/(\omega - \epsilon_i) \ , \tag{6.12}$$

where $\epsilon_i = \epsilon_A$ or ϵ_B, the diagonal energy for A and B atoms. If we average the locator, we have

$$\langle L\rangle = \frac{x}{\omega-\epsilon_A} + \frac{1-x}{\omega-\epsilon_B} \ , \tag{6.13}$$

and we readily obtain for the alloy

$$G_{\vec{k}} = \frac{1}{\langle L\rangle^{-1} - \epsilon_{\vec{k}}} \ . \tag{6.14}$$

This is exactly the approximation called ATA by Velicky *et al.*,[7] but which we shall call ATA′. It is perhaps more rightfully called an average locator approximation. Also, it is in the spirit of approximations used in the Hubbard[29] model for correlation in narrow energy bands by Hubbard[29] in his first paper and by Roth.[30]

If we specialize to the split-band limit $\epsilon_B \to \infty$, and identify ϵ_n with H_0, this expression is the same as the orthogonal orbitals limit of Eq. (6.11), except for normalization. Thus the QCA′ of our tight-binding liquid metal reduces in the lattice-liquid case to the ATA′.

Let us now specialize the SCA′ to the lattice-liquid case. Here it is not sufficient simply to use the lattice pair distribution function, but the integrals in Eqs. (4.32) and (4.33) must be replaced by sums. The simplest way to proceed is to regard the $\vec{r}$ space as the lattice, replacing integrals by sums, n by x, and $g(\vec{r})$ by $1-\delta_{ij}$. We can either work from Eqs. (4.30)–(4.35) or (4.51)–(4.53). Choosing the latter, we have for $H_0 = 0$ and orthogonal orbitals

$$G_{\vec{k}} = x/(\omega - x\epsilon_{\vec{k}} - \Sigma) \ , \tag{6.15}$$

$$\Sigma = x\int_{\mathrm{BZ}} \epsilon_{\vec{k}}^2 G_{\vec{k}} (d\vec{k}/8\pi^3) F \ , \tag{6.16}$$

$$xF = 1 - x - x\int_{\mathrm{BZ}} \epsilon_{\vec{k}''} G_{\vec{k}''} (d\vec{k}''/8\pi^3) F \ , \tag{6.17}$$

where, since $h \to -1$, F is independent of $\vec{k}$ and $\vec{k}'$, and Σ is independent of $\vec{k}$.

Let us now redefine the self-energy:

$$\omega - \Sigma' = (\omega - \Sigma)/x \ , \tag{6.18}$$

so that the Green's function is written as

$$G_{\vec{k}} = 1/(\omega - \Sigma' - \epsilon_{\vec{k}}) \ , \tag{6.19}$$

which is the form used by Velicky, Kirkpatrick, and Ehrenreich.[7] It is then easily shown that

$$\int_{\mathrm{BZ}} \epsilon_{\vec{k}} G_{\vec{k}}\, d\vec{k}/8\pi^3 = (\omega - \Sigma')G_0 - 1 \ , \tag{6.20}$$

$$\int_{\mathrm{BZ}} \epsilon_{\vec{k}}^2 G_{\vec{k}}\, d\vec{k}/8\pi^3 = (\omega - \Sigma')^2 G_0 - (\omega - \Sigma') \ , \tag{6.21}$$

where

$$G_0 = \int_{\mathrm{BZ}} G_{\vec{k}}\, d\vec{k}/8\pi^3 \ . \tag{6.22}$$

Substituting Eqs. (6.20) and (6.21) into (6.16) and (6.17) and eliminating F, we find

$$\Sigma' = -(1-x)/G_0 \tag{6.23}$$

which is the CPA result for the split-band limit.[7]

This result is consistent with the fact that the CPA can be derived starting from an atomic or locator point of view, as has been shown by Shiba[26] and Ducastelle.[31]

We can generalize this in an obvious way to include nonorthogonality. It can be shown that for the nonorthogonal CPA the sum rule for the density of states, Eq. (5.17) is obeyed. The proof is very similar to the SCA′ random-liquid case which was given in Sec. V. The nonorthogonal ATA′, on the other hand, does not obey the sum rule.

VII. RESULTS FOR RANDOM LIQUID

For the special case of a random liquid we have $g(\vec{r}) = 1$ or $h(r) = 0$, and our results simplify considerably. Since $\tilde{H}_{\vec{k}} = H_{\vec{k}}$, we have for the QCA′

$$G_{\vec{k}}^{\mathrm{QCA}} = n/(\omega - H_0 - nH'_{\vec{k}}) \quad . \tag{7.1}$$

For the SCA, the solution of the integral equation (4.53) is now trivial, and the other equations reduce to

$$G_{\vec{k}} = n/(\omega - H_0 - nH'_{\vec{k}} - \Sigma) \quad , \tag{7.2}$$

$$\Sigma = \int H'^2_{\vec{k}} G_{\vec{k}}\, d\vec{k}/8\pi^3 \quad , \tag{7.3}$$

with Σ now independent of $\vec{k}$. Finally, for the second moment, Eq. (5.13) reduces to

$$\gamma^2 = n \int H^2_{\vec{k}}\, d\vec{k}/8\pi^3 \quad , \tag{7.4}$$

which is also independent of $\vec{k}$. This is exact, and the SCA′ gives the same result.

As reported in I, we have carried out calculations using a Gaussian interaction, and we will here present these results in greater detail. We have also found an exactly soluble special case which is described in Appendix A.

Proceeding with the Gaussian case, then, we take

$$H(r) = H_1 e^{-\lambda r^2} \quad . \tag{7.5}$$

In Fig. 1 we have plotted

$$nH_{\vec{k}} = H_1 n(\lambda/\pi)^{3/2} e^{-k^2/4\lambda} \quad , \tag{7.6}$$

and also the rms width γ. $nH_{\vec{k}}$ is effectively the electron energy for orthogonal orbitals in the QCA′. If we include γ, we can regard it as the imaginary part of the electron self-energy. The parameters we use are $\lambda = 2$, $n = 0.859$, and $H_1 = -1$, with $H_0 = 0$.

For the SCA′ we must solve Eqs. (7.2) and (7.3) self-consistently. We evaluated the integral by the method outlined in Appendix B for nearly singular integrals and then iterated the self-energy. Convergence was considerably improved by using Newton's method. The results are shown in Fig. 2, for the real and imaginary parts of the self-energy Σ.

Turning now to the density of states for orthogonal orbitals, which is actually somewhat artificial for the random liquid because the atoms by assumption do not keep apart, we use Eq. (2.23). We notice that for the QCA′ the result is simply $N(\omega) = \delta(\omega)$. That is, in the QCA′ we have zero bandwidth. We can see from Eq. (2.23) that this result persists for other liquidlike pair distribution functions for which $n\tilde{H}_{\vec{k}} \to 0$ as $k \to \infty$. This is in marked contrast with the lattice liquid for which the ATA′ gives a band narrowed by x. For the lattice liquid, $n\tilde{H}_{\vec{k}}$ is periodic in $\vec{k}$, so that even for large $\vec{k}$ we must average over a Brillouin zone.

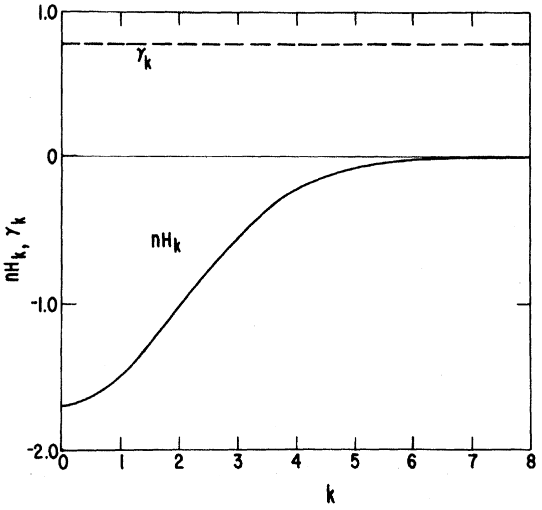

FIG. 1. Energy $nH_{\vec{k}}$ and rms width $\gamma_{\vec{k}}$ for random liquid with Gaussian interaction, with $\lambda = 2$, $n = 0.859$, $H_0 = 0$, and $H_1 = -1$.

The next approximation we consider is the broadened QCA′ in which the spectral function $-(1/\pi)\,\mathrm{Im}\,G_{\vec{k}}$ is approximated by a Gaussian with rms deviation $\gamma_{\vec{k}}$:

$$-\frac{1}{\pi}\,\mathrm{Im}\,G_{\vec{k}} = \frac{1}{(2\pi)^{1/2}\gamma_{\vec{k}}}\, e^{-(\omega - n\tilde{H}_{\vec{k}})/2\gamma^2_{\vec{k}}} \quad . \tag{7.7}$$

For orthogonal orbitals, the resulting density of states is just a Gaussian centered on $\omega = 0$.

For the SCA′, the result is more interesting. The density of states for orthogonal orbitals is given by

$$N(\omega) = -\frac{1}{\pi}\,\mathrm{Im}\,\frac{1}{\omega - \Sigma} = \frac{-\Sigma''}{(\omega - \Sigma')^2 + \Sigma''^2} \quad . \tag{7.8}$$

This is plotted in Fig. 3. Note the asymmetry which is as predicted by the third moment in Eq. (5.10).

If now we consider nonorthogonal orbitals, in general the results are more difficult to obtain. However for the special case in which $H(\vec{r})$ is proportional to the overlap $S(\vec{r})$, the results can be simply related to orthogonal orbitals results. We assume $H(r) = H'_2 S(\vec{r})$, or $H'(\vec{r}) = S(\vec{r})(H'_2 - \omega_R)$, where ω_R corresponds to the "right" ω. Going back to Eq. (2.16), we can write it in the form

$$\left(\frac{\omega_R - H_0}{H'_2 - \omega_R} + S(0)\right) \mathcal{G}(\omega_R) - \rho S \mathcal{G}(\omega_R) = \frac{\rho}{H'_2 - \omega_R} \quad . \tag{7.9}$$

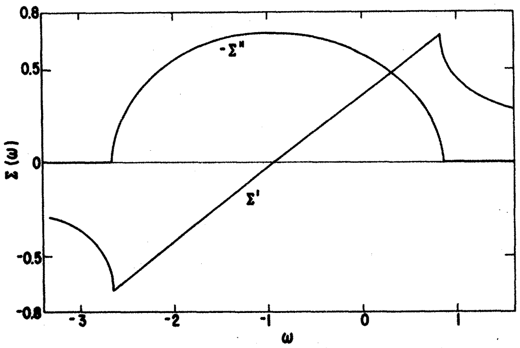

FIG. 2. Self-energy $\Sigma = \Sigma' + i\Sigma''$ for random liquid of Fig. 1, in the SCA′.

Thus if the $\mathcal{G}^0(\omega)$ is the orthogonal orbitals Green's function for the dimensionless interaction $S(r)$,

$$(\omega + 1 - \rho S)\mathcal{G}^0(\omega) = \rho \ , \tag{7.10}$$

we have

$$\mathcal{G}(\omega) = \frac{1}{H_2' - \omega_R}\, \mathcal{G}^0\left(\frac{\omega_R - H_0}{H_2' - \omega_R}\right) \ . \tag{7.11}$$

Averaging over the ensemble, we use $\omega = (\omega_R - H_0)/(H_2' - \omega_R)$, and write $H_2 = H_2' - H_0$, so that we have implicitly

$$G(\vec{r}, \vec{r}\,', \omega_R) = \frac{1+\omega}{H_2}\, G^0(\vec{r}, \vec{r}\,', \omega) \ , \tag{7.12}$$

$$\omega_R = H_0 + H_2 \frac{\omega}{1+\omega} \ . \tag{7.13}$$

Since Eqs. (7.11)–(7.13) are exact, they enable us to calculate the Green's function in any of the approximations from the orthogonal orbitals Green's function with $H(\vec{r})$ replaced by $S(\vec{r})$. Equation (7.12) has a dependence on H_0 which can be eliminated by measuring ω_R from H_0 (but notice that H_2 depends on H_0).

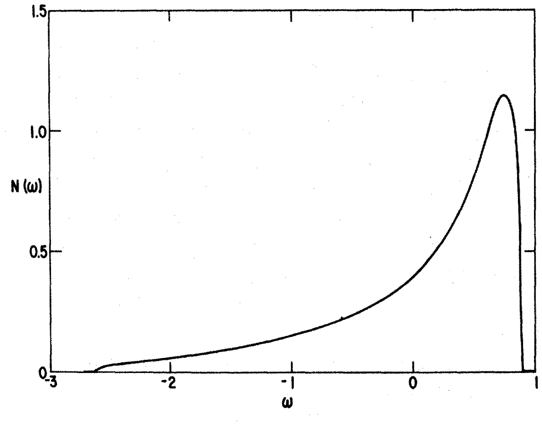

FIG. 3. Density of states for random liquid of Fig. 1 for orthogonal orbitals in the SCA′.

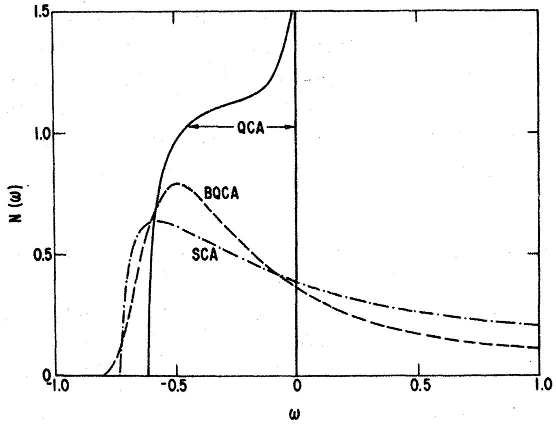

FIG. 4. Density of states for random liquid of Fig. 1 for $H \propto S$ with $H_2 = -1$, in the QCA′, broadened QCA′, and SCA′.

From Eq. (7.12) we see that as $\omega \to -1$ from above, $\omega_R \to \infty$ (for $H_1 < 0$). We can show that the energy band ends before this limit is reached, since in Eq. (7.10) ρ and S are both positive definite operators so that all the eigenvalues of $\rho S - 1$ are greater than -1. Therefore we need not concern ourselves with the unphysical region $\omega < -1$.

For the Gaussian interaction used in this section G^0 is the same as the G we have calculated, except that we must take $H_1 = +1$ in Eqs. (7.5) and (7.6). We calculate the density of states from Eq. (2.22), and the results for the three approximations are given in Fig. 4 for the previous parameters and $H_2 = -1$. We see that for this case the QCA′ does give a finite bandwidth but, as noted in I, gives a singularity at the top of the band. This is removed by the inclusion of broadening.

We can also see that the area under the QCA′

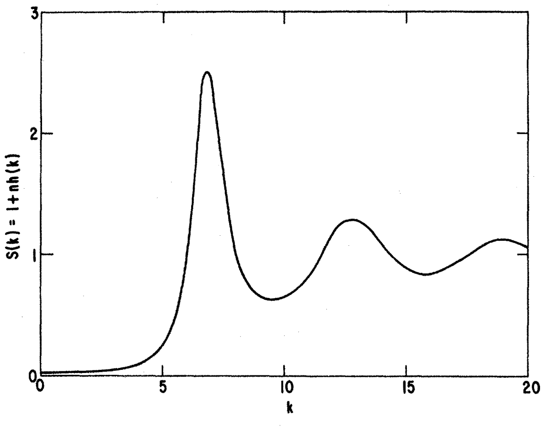

FIG. 5. Structure factor for hard-sphere liquid from Ref. 32, with packing fraction 0.45.

curve is not 1. This is consistent with our finding in Sec. V. For the SCA′ random-lattice case we have proved in that section that the area is equal to 1. The broadened QCA′ (BQCA′) seems to have an area intermediate between the two other curves.

VIII. RESULTS FOR HARD-SPHERE LIQUID

We now consider the more realistic case of a hard-sphere liquid. We take for the pair distribution function the exact solution of the Percus–Yevick equation which has been shown by Ashcroft and Leckner[32] to give good results for the structure factor of liquid alkalis. The structure factor

$$S(\vec{k}) = 1 + nh(\vec{k}) \tag{8.1}$$

was calculated from Ashcroft and Leckner's paper using a hard-sphere packing fraction of 0.45, and is plotted in Fig. 5.

We use the Gaussian interaction Eqs. (7.5) and (7.6) of Sec. VII. In Fig. 6 is shown $n\tilde{H}_{\vec{k}}$, which can be written

$$n\tilde{H}_{\vec{k}} = nH_{\vec{k}} + n \int h^0(\vec{k}, \vec{k}')H_{\vec{k}'}\, d\vec{k}'/8\pi^3 \ , \tag{8.2}$$

where

$$h^0(k, k') = \int h(\vec{k} - \vec{k}')\, d\Omega_{\vec{k}\vec{k}'}/4\pi \tag{8.3}$$

is the $l = 0$ component of a spherical-harmonic expansion of $h(k - k')$, and is plotted in Fig. 7. We also show in Fig. 6 that the rms width $\gamma_{\vec{k}}$ in the superposition approximation, Eq. (5.13). The parameters are $\lambda = 2$, $H_1 = -1$, and the packing fraction of 0.45 corresponds to $n = 0.859$, in units for which the hard-sphere diameter is 1.

Turning now to the SCA′, we must solve the integral equation for F and iterate to obtain Σ.

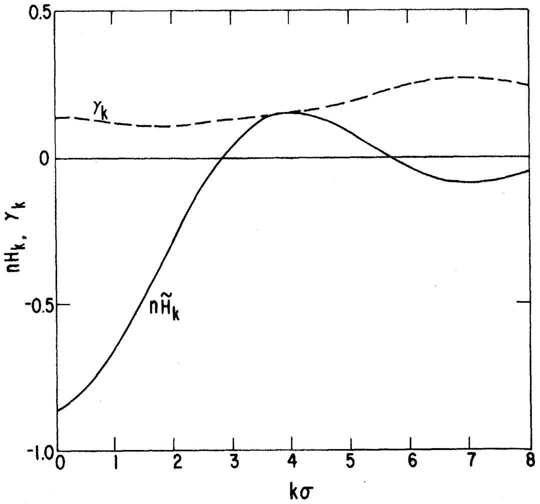

FIG. 6. Energy nH_k and rms width $\gamma_{\vec{k}}$ for hard-sphere liquid with Gaussian interaction, with $\lambda = 2$, $n = 0.859$, $H_0 = 0$, and $H_1 = -1$.

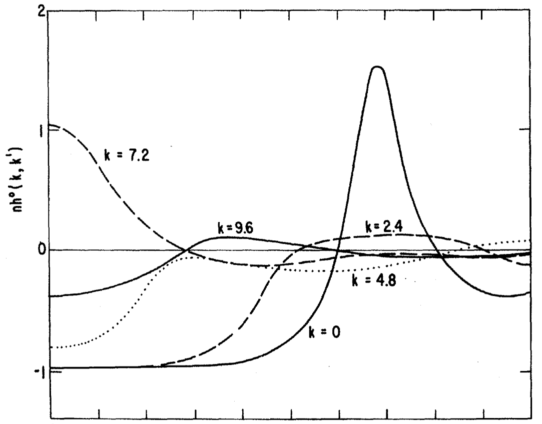

FIG. 7. $l = 0$ component $h^0(k, k')$ of $h(\vec{k} - \vec{k}')$ which is part of the kernel in Eq. (8.5).

From Eq. (4.52) we need only the average $F^0(k, k')$ of F, so that we can write Eqs. (4.52) and (4.53) in the form

$$\Sigma_{\vec{k}} = \Sigma^1_{\vec{k}} \equiv \int \frac{n\tilde{H}_{\vec{k}'}H_{\vec{k}'}nF(k', k)}{\omega - nH_{\vec{k}'} - \Sigma_{\vec{k}'}} \frac{d\vec{k}'}{8\pi^3} \ , \tag{8.4}$$

$$nF^0(k, k') = 1 + nh^0(k, k')$$

$$+ n \int \frac{h^0(k, k'')H_{\vec{k}''}nF^0(k'', k')}{\omega - nH_{\vec{k}''} - \Sigma_{\vec{k}''}} \frac{d\vec{k}''}{8\pi^3} \ . \tag{8.5}$$

The integrals were approximated by the method of Appendix B, and the resulting equation for F was solved by matrix inversion. Equations (8.4) and (8.5) then give $\Sigma_{\vec{k}} = \Sigma^1_{\vec{k}}[\Sigma_{\vec{k}}]$. We used the iteration scheme

$$\Sigma^{n+1}_{\vec{k}} = A\Sigma^1_{\vec{k}}[\Sigma^n_{\vec{k}}] + (1 - A)\Sigma^1_{\vec{k}}[\Sigma^{n-1}_{\vec{k}}] \ , \tag{8.6}$$

where convergence was helped when needed by adjusting A.

The initial attempts at implementing this scheme were not successful. The iteration did not converge well and seemed to be giving a spectral function which changed sign. In order to investigate the situation we calculated the second moment of the spectral function, as given by the SCA′ [Eq. (5.14)], which as we saw in Sec. V differs from the superposition approximation result. In Fig. 8 we plot $\gamma^2_{\vec{k}}$ for the two cases, and we see that the SCA′ result for $\gamma^2_{\vec{k}}$ dips below the axis, which indeed implies a spectral function which changes sign.

The problem here is that most of the interaction function $e^{-\lambda r^2}$ appears inside the excluded volume of the hard spheres. While $g(\vec{r}, \vec{r}'', \vec{r}')$ in the superposition approximation vanishes in the excluded volume, in the approximation of Eq. (5.15)

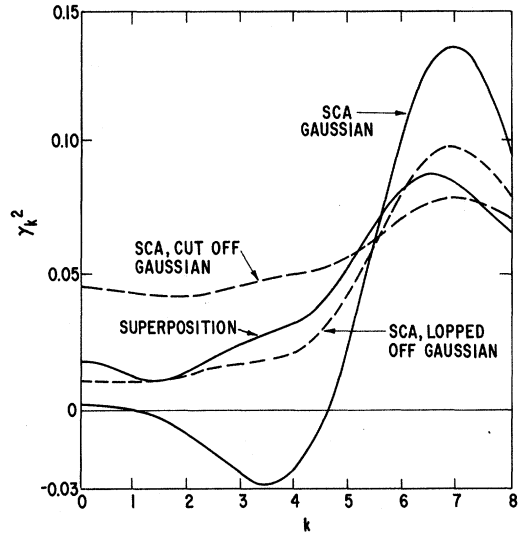

FIG. 8. Difference $\gamma_{\vec{k}}^2$ between second moment of spectral function and square of first, for several approximations.

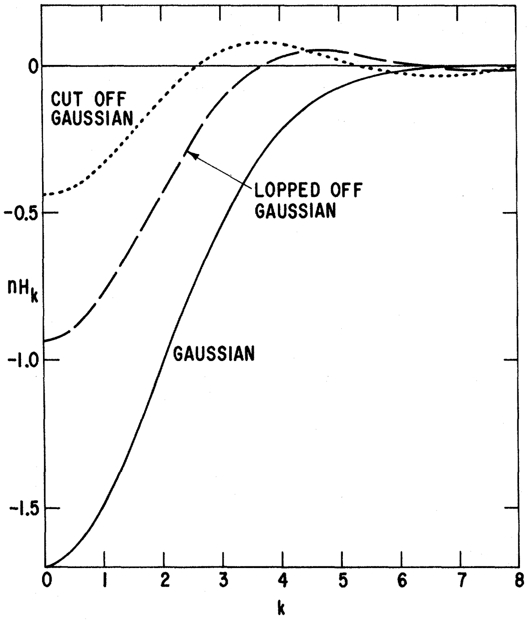

FIG. 10. $nH_{\vec{k}}$ for the three cases of Fig. 9.

it does not, and this appears to be the cause of the difficulty.

To test this hypothesis we have calculated $\gamma_{\vec{k}}^2$ for a Gaussian interaction cut off at the hard-sphere diameter, and Fig. 8 shows that $\gamma_{\vec{k}}^2$ remains positive in this case. The problem with using the cut-off Gaussian is that the sharp cutoff in real space introduces oscillations in k space, so that $H_{\vec{k}}$ no longer acts as a good convergence factor in the integrals. We have also considered a "lopped-off" Gaussian, in which $H(r) = H(1)$ for $r < 1$. In Fig. 9, $r^2H(r)$ is shown for the three cases. The lopped-off Gaussian has only a break in the derivative at the hard-sphere diameter, and hence $H_{\vec{k}}$ was found to fall off reasonably well with $\vec{k}$. Figure 8 shows that $\gamma_{\vec{k}}^2$ for this case is positive and rather similar to the superposition approximation result. Therefore we have used this interaction in the calculation. $nH_{\vec{k}}$ is shown for the three cases in Fig. 10.

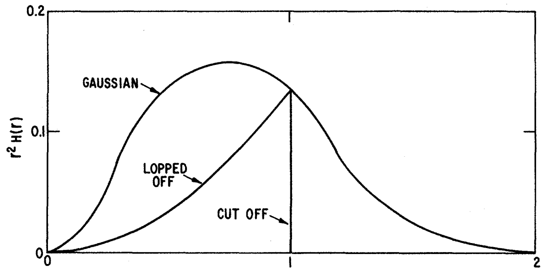

FIG. 9. $r^2H(r)$ for Gaussian, cut-off Gaussian, and lopped-off Gaussian interactions.

In solving the system of equations we found that for $\omega < 0$, two to five iterations, mainly with $A = 1$, were sufficient to give successive $\Sigma_{\vec{k}}$'s with rms deviations of 0.001. For negative ω the convergence became worse, particularly near the upper band edge. Even with $A = 0.5$, we needed 20 iterations. The upper band edge could, however, be located by approaching it from above. The integral was cut off at $k_m = 8$ and an interval Δk of 0.4 was used. Test calculations with $k_m = 11.2$, $\Delta k = 0.4$, and $k_m = 8.4$, $\Delta k = 0.3$ were performed at $\omega = 0.6$. The density of states agreed to within 2% with the regular calculation. The results for $\Sigma_{\vec{k}}$ in the test calculations followed the regular results reasonably closely. The regular calculation took about 45 min (0.2 min per iteration) on a GE 660 computer.

In Figs. 11 and 12 we have plotted the real and imaginary parts of $\Sigma_{\vec{k}}$ for various values of ω. The most striking feature is the large influence of the first peak in the structure factor on $\Sigma_{\vec{k}}$. Near the band edge $\text{Im}\Sigma_{\vec{k}}$ is roughly proportional to $S(\vec{k})$ which is reminiscent of Ziman's[11] result for the scattering rate for nearly free electrons.

In Fig. 13 we show the infinite-$\vec{k}$ limit of Σ, which is given by Eq. (8.4) with $nF \rightarrow 1$. In Fig. 14 we show the orthogonal orbitals density of states, obtained from Eq. (7.8). We have changed the scale in this figure by taking $H_1 = -e^2 = -7.39$, so that $H(1) = 1$. This is for a comparison which we will make below with results for the face-centered-cubic lattice. The density of states is rather strange looking, with a very large peak in it. This

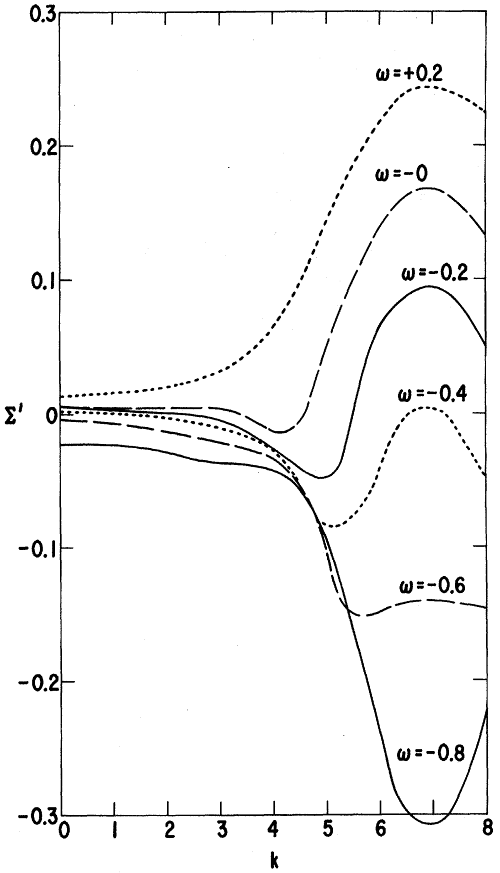

FIG. 11. Real part of self-energy $\Sigma_{\vec{k}}$ vs k for values of ω as shown, for hard-sphere liquid of Fig. 6.

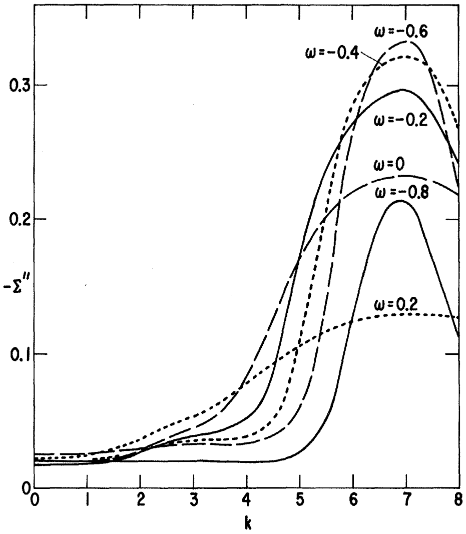

FIG. 12. Imaginary part of self-energy $\Sigma_{\vec{k}}$ vs k for values of ω as shown, for hard-sphere liquid of Fig. 6.

is connected with the dip in ImΣ in Fig. 13, which in turn appears to be due to oscillations in the integrand of Eq. (8.4). We do not know whether this has any significance.

As in the random-liquid case the QCA′ and BQCA results for the orthogonal orbitals density of states are a δ function and a Gaussian, respectively, the latter with rms width $0.265H_1$.

We now present results for the density of states with $H \propto S$ which are obtained from Eqs. (7.11) and (2.22) using in the latter equation a Gaussian (not lopped off) for S. The QCA′ and BQCA′ cases are given in Fig. 15 and the SCA′ result in Fig. 16. For both of these plots we take $H_2 = -e^2$. We notice that the results are quite similar for the bottom of the band, except for the band tail in the BQCA′ case. The upper part of the band looks quite different, however, in the three approximation. The SCA′ gives an appreciably wider band than QCA′, and as previously noted, the singularities are not there.

If we examine $H(\vec{r})$ in the context of the fcc lattice which would result from close packing the hard spheres of the model liquid, we find that for the parameters we have chosen, the second-neighbor contribution to $\sum_R H(\vec{R})$ is only 6% of the nearest-neighbor part. It is therefore of interest to compare our results with those for the fcc lattice liquid with a fraction $x = 0.45$ of the sites occupied. Unfortunately, the CPA has not been calculated for this lattice, but it is relatively simple to obtain results for the ATA′, which are given in Fig. 17 for both the orthogonal orbitals and $H \propto S$ cases with $H(1) = -1$ and $S(1) = e^{-2} = 0.135$. These were calculated from Eq. (6.11) using the density of states calculated by Jelitto.[33] The width of the band is in rough accord with the tight-binding

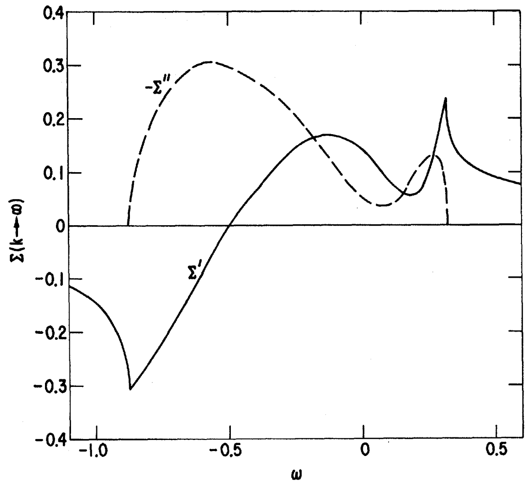

FIG. 13. Infinite-k limit of self-energy Σ for hard-sphere liquid of Fig. 6.

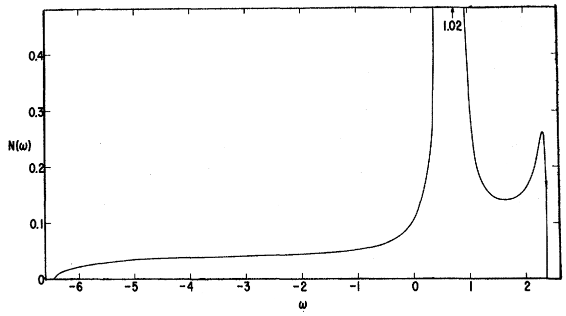

FIG. 14. Density of states for hard-sphere liquid of Fig. 6 but with $H_1=-e^2$, for orthogonal orbitals in the SCA′.

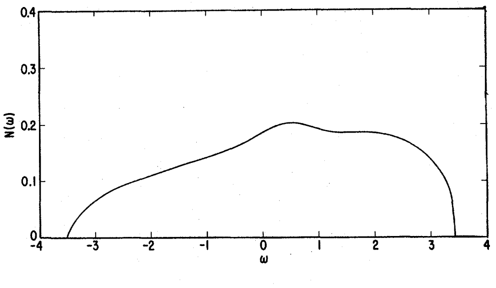

FIG. 16. Same as Fig. 15 in the SCA′.

liquid-metal result for both cases (but, of course, for orthogonal orbitals the QCA′ gives a δ function), and the lower part of the band is similar, while there are more variations in the upper part of the band.

IX. DISCUSSION

We have formulated a theory for electronic states in disordered systems based on LCAO representations, and have applied it to a simple model of a liquid metal. We have, on the one hand, borrowed from conventional multiple-scattering theory and, on the other hand, used our model to test several approximations used in that theory.

The quasicrystalline approximation has turned out to be disappointing in that it gives a dispersion law with no damping. If we assume orthogonal orbitals and use Eq. (2.23), the unphysical result of zero bandwidth obtains, despite the bandlike dispersion relation. The result for nonorthogonal orbitals is somewhat more reasonable, but contains singularities and is not correctly normalized. Hence it is clear that for a good account of electronic structure some improvement over the QCA′ is essential for our model. In carrying this conclusion over to the conventional multiple-scattering theory, we note that, while the QCA′ reduces to the ATA′ in the alloy case, the QCA reduces to the ATA. The ATA, without the prime, has been shown[20] to be a much better approximation for the alloy problem than the ATA′. Our conclusions regarding the QCA′ may therefore not necessarily carry over to the QCA.

Schwartz and Ehrenreich's self-consistent approximation also has had its disappointments for us. This is because the approximation to the three-body distribution function, Eq. (5.15), does not treat the excluded volume properly. We have actually made a severe test of it, but have only obtained results by modifying the interaction within the excluded volume. Whether this problem carries over to the conventional multiple-scattering theory is not known. However, it certainly raises difficulties for extending our theory to more realistic systems. It would be desirable to find an approximation which treats the three-body distribution function more accurately.

A simpler approach which is worth further exploration is the method of moments which gave fair agreement with the SCA for the lower part of the band, except for the Gaussian tail. While a tail of localized states should be present, we have tried the Gaussian approximation to the spectral function in the simple cubic lattice liquid, and found that the method gives too long a tail—extending in fact beyond the known limits[7–9] of the band.

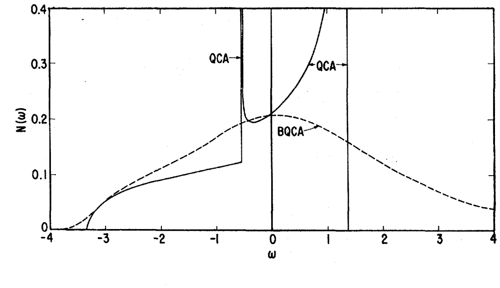

FIG. 15. Density of states for hard-sphere liquid of Fig. 6 but with $H_2=-e^2$, for $H\propto S$ in the QCA′ and broadened QCA′.

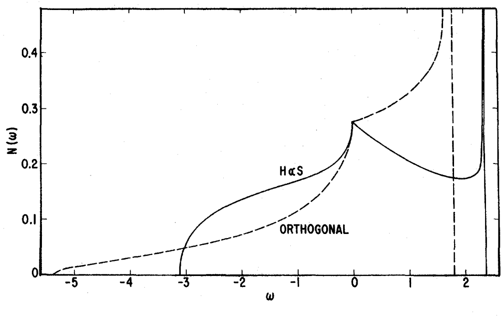

FIG. 17. Density of states for fcc lattice liquid for both orthogonal orbitals and $H\propto S$, for $x=0.45$, $H(1)=-1$, and $S(1)=0.135$.

We should therefore examine other analytic forms for the spectral function.

We have found that including nonorthogonality has had an important effect upon the results. Actually, the differences between Figs. 14 and 16 for the hard-sphere SCA are greater than we might have expected. We should have thought that the large peak due to G_{ii} should have been more prominent in the $S \propto H$ case. It would be worthwhile to investigate more closely the relationship between Eqs. (2.22) and (2.23) for approximate Green's function.

After dealing with the above difficulties we hope to apply the theory to more realistic models and to tetrahedrally coordinated systems.

ACKNOWLEDGMENTS

The author has benefited from conversations with M. H. Cohen, A. J. Bennett, and R. Messmer.

APPENDIX A: SOLUBLE CASE FOR RANDOM-LIQUID SCA′

We consider the following interaction:

$$H(r) = H_1 3\,\frac{\sin k_0 r - k_0 r \cos k_0 r}{(k_0 r)^3}\ , \tag{A1}$$

which has the Fourier transform

$$\begin{aligned} H_{\vec{k}} &= H_1 v_0\ , \quad k < k_0 \\ &= 0\ , \qquad k > k_0 \end{aligned} \tag{A2}$$

where v_0 is the volume $6\pi^2/k_0^3$. Then Eq. (7.3) can be integrated exactly to give

$$\Sigma = \frac{nH_1^2 v_0}{\omega - H_0 - nH_1 v_0 - \Sigma}\ . \tag{A3}$$

This can be readily solved for Σ. If we let $y = nv_0$, take $H_0 = 0$, and choose units in which $H_1 = -1$, we have

$$\Sigma = \tfrac{1}{2}\{\omega + y \pm [(\omega \pm y)^2 - 4y]^{1/2}\}\ . \tag{A4}$$

For $\omega + y > 2y^{1/2}$, Σ is real and we choose the root so that $\Sigma \to 0$ as $\omega \to \pm\infty$. For $|\omega + y| < 2y^{1/2}$, Σ has a negative imaginary part, and this corresponds to the allowed band. The density of states from Eq. (2.23) is

$$N(\omega) = -\frac{1}{\pi}\,\mathrm{Im}\,\frac{1}{\omega - \Sigma} = \frac{[4y - (\omega + y)^2]^{1/2}}{2\pi y(1 - \omega)}\ . \tag{A5}$$

This is asymmetrical and of roughly the form as Fig. 2. The band limits are

$$\omega_\pm = -y \pm 2y^{1/2}\ , \tag{A6}$$

and we note that

$$1 - \omega_+ = (1 - y^{1/2})^2 > 0\ , \tag{A7}$$

so that except for the case $y = 1$, there are no singularities in the density of states. For $y = 1$, we have

$$N(\omega) = \frac{1}{2\pi}\left(\frac{3+\omega}{1-\omega}\right)^{1/2}\ . \tag{A8}$$

Turning now to the $S \propto H$ case, with S given by Eq. (A1) where $H_1 \to +1$, the density of states is given by Eqs. (2.22), (7.12), and (7.13) with $H_2 = -1$ and $H_0 = 0$:

$$N(\omega_R) = (1 + \omega)\int_0^{k_0} v_0\left(-\frac{1}{\pi}\,\mathrm{Im}G^0\right)\frac{k^2\,dk}{2\pi^2}\ , \tag{A9}$$

$$\omega_R = -\omega/(1+\omega)\ . \tag{A10}$$

G^0 is obtained by letting $H_1 = +1$ in Eq. (A3) for Σ,

$$\Sigma^0 = \tfrac{1}{2}\{\omega - y \pm [(\omega - y)^2 - 4y]^{1/2}\}\ . \tag{A11}$$

Then for $k < k_0$,

$$G^0 = n/(\omega - y - \Sigma^0)\ , \tag{A12}$$

from which we find

$$N(\omega_R) = \frac{1+\omega}{2\pi y}\,[4y - (\omega - y)^2]^{1/2}\ . \tag{A13}$$

In terms of ω_R this becomes

$$N(\omega_R) = \frac{|1-y|}{2\pi y}\,\frac{1}{(1+\omega_R)^2} \times\left[\frac{4y}{(1-y)^4} - \left(\omega_R - \frac{y(3-y)}{(1-y)^2}\right)^2\right]^{1/2}\ . \tag{A14}$$

The band now goes between the limits

$$\omega_R^\pm = \frac{y(3-y) \pm 2y^{1/2}}{(1-y)^2}\ . \tag{A15}$$

The band is again asymmetrical, but skewed in the opposite direction from Eq. (A5). For the special case $y = 1$, we have

$$N(\omega_R) = \frac{1}{2\pi}\,\frac{1}{(1+\omega_R)^2}\,(3 + 4\omega_R)^{1/2}\ . \tag{A16}$$

Here the upper limit is infinite, but the expression is integrable. It can, in fact, be verified that the density of states is normalized to 1 for $H \propto S$ as well as for orthogonal orbitals.

APPENDIX B: NUMERICAL EVALUATION OF NEARLY SINGULAR INTEGRALS

In numerically solving the integral equation (8.5) as well as evaluating various integrals in the theory, we found it necessary to improve upon the Simpson's-rule calculation of an integral of the form

$$I = \int \frac{f(\vec{k})}{\omega - nH_{\vec{k}} - \Sigma_{\vec{k}}}\,\frac{d\vec{k}}{8\pi^3}\ , \tag{B1}$$

where $\Sigma_{\vec{k}}$ has a negative imaginary part whose magnitude we do not initially know. If $\mathrm{Im}\Sigma_{\vec{k}}$ is sufficiently large, the pole in Eq. (A1) is far from the real axis and we have no problem. But if $\mathrm{Im}\Sigma_{\tilde{k}}$ is small, the integrand is nearly singular. We wish to find a method for evaluating Eq. (A1) in either case.

Simpson's rule involves approximating the integrand in an interval $2h$ by a quadratic. We generalize this by using a ratio of two quadratics Specifically, we write, using y or $x=y-(2n+1)h$ as the variable of integration,

$$I_n=\int_{2nh}^{(2n+2)h}\frac{A(y)}{B(y)}\,dy\cong\int_{-h}^{h}\frac{dx^2+ex+f}{ax^2+bx+c}\,dx\ , \tag{B2}$$

where

$$\begin{aligned} a&=\tfrac{1}{2}\,(B_{2n+2}+B_{2n}-2B_{2n+1}),\\ b&=\tfrac{1}{2}\,(B_{2n+2}-B_{2n}),\\ c&=B_{2n+1}, \end{aligned} \tag{B3}$$

and similarly for d, e, and f. Here, e.g., $B_{2n}=B(2nh)$, and we have omitted indices from a, b, etc. for simplicity.

The integrals can be evaluated by elementary means to give

$$I_n=dI_{n3}+eI_{n2}+fI_{n1}\ , \tag{B4}$$

where

$$\begin{aligned} I_{n1}&=\frac{h}{a}\,\frac{1}{(x_+-x_-)}\,\ln\frac{(1-x_+)(1+x_-)}{(1+x_+)(1-x_-)}\ ,\\ x_\pm&=[-b\pm(b^2-4ac)^{1/2}]/2a\ ,\\ I_{n2}&=\frac{h}{2a}\,\ln\frac{a+b+c}{a-b+c}-\frac{b}{2a}I_{n1}\ ,\\ I_{n3}&=\frac{2h}{a}-\frac{b}{a}I_{n2}-\frac{c}{a}I_{n1}\ . \end{aligned} \tag{B5}$$

We can rewrite Eq. (B4) in the form

$$I_n=\tfrac{1}{2}A_{2n}(I_{n3}-I_{n2})+A_{2n+1}(I_{n1}-I_{n3})+\tfrac{1}{2}A_{2n+2}(I_{n3}+I_{n2})\ , \tag{B6}$$

in which case the coefficients of the A's are the generalization of the triple $\frac{1}{6}h\,(1, 4, 1)$ of Simpson's rule. For the entire integral we have

$$\begin{aligned} &\int_0^{2Nh}\frac{A(x)}{B(x)}\,dx=\sum_{n=0}^{N}A_nW_n\ ,\\ &W_{2n+1}=I_{n1}-I_{n3}\ ,\\ &W_{2n}=\tfrac{1}{2}\,(I_{n3}-I_{n2}+I_{n-1,3}+I_{n-1,2}), \end{aligned} \tag{B7}$$

where $I_{0j}=I_{Nj}=0$.

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