

## Short-range order and the electronic structure of a one-dimensional liquid metal

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The energy spectrum of a one-dimensional array of  $\delta$ -function potentials is studied as a function of the degree of short-range order in the arrangement of the scatterers. The integrated density of states is evaluated numerically and the results are used to compare alternate theoretical formalisms. In particular, we consider Lax's quasicrystalline approximation (QCA) and the more recent self-consistent approaches of Gyorffy and Schwartz and Ehrenreich. Surprisingly, we find that only the non-self-consistent QCA yields a reasonable description of the electronic spectrum. The failure of the self-consistent schemes appears to be due to an incomplete treatment of the multiple-occupancy corrections.

### I. INTRODUCTION

Recent authors have devoted considerable attention to the electronic structure of disordered systems. To a large extent, this research has been concerned with the description of substitutional binary alloys within the framework of the coherent-potential approximation (CPA).<sup>1-3</sup> The success of the CPA in clarifying the qualitative features of the alloy problem has prompted attempts by various authors to develop generalizations of this approach to the case of *structurally* disordered systems and in particular to the liquid-metal problem. While several distinct approximation schemes have been proposed<sup>4-10</sup> there is at present no general agreement as to their relative merits. The purpose of this paper is to describe a simple model Hamiltonian which has at least some of the features of a realistic liquid but which, nevertheless, is sufficiently tractable that detailed calculations can be performed with relatively little effort. It is hoped that this model will provide a reliable mechanism for the comparison of alternate theoretical formalisms.

It should be emphasized at the outset that there are important differences between the liquid and alloy problems. In the alloy the atomic constituents are arranged at random on a periodic lattice and the disorder is *substitutional*. By contrast, in a liquid the disorder is *structural* and the spatial arrangement of the scatterers no longer exhibits any long-range order. Despite this lack of long-range order, it is generally assumed that density correlations in the liquid play an important role over distances on the order of several interatomic spacing and, at the very least, that they prevent any overlap of the atomic potentials. The existence of this short-range order implies that care must be taken in developing a *self-consistent* description of the system. Specifically, suppose that the liq-

uid's average properties are represented by an effective medium. An incorrect embedding of the atoms in this medium can lead, in effect, to a spurious overlap of the scattering potentials and, therefore, to serious errors in the electronic density of states. In the language of the alloy problem (where the scatterers are also nonoverlapping) these errors are avoided only by including what are generally referred to as multiple-occupancy corrections.<sup>3</sup> Physically, the part of the medium belonging to a given site must be removed before that site's atomic potential is embedded in the medium. The multiple-occupancy corrections provide a formal link between the self-consistent descriptions of the liquid and alloy problems.<sup>11</sup> Indeed, the essential feature of the CPA is the fact that it includes these corrections exactly and it is this aspect of the theory that must be generalized to the liquid metal.

The existing theoretical approaches to the problem of short-range order may all be loosely classified as single-site approximations in the sense that the atoms surrounding a given site are represented only in terms of that site's average environment. Formally each approximation scheme then depends on just the average two-site distribution function  $g(x)$ ; all higher-order correlation effects are implicitly evaluated in terms of  $g(x)$ . In Sec. II we consider the properties of a simple one-dimensional liquid.<sup>12</sup>  $N$  atoms, each of which is represented by an attractive  $\delta$ -function potential are assumed to occupy a line of length  $L$ . Short-range order is built into the model with the assumption that the probability for finding nearest neighbors separated by a distance  $x$  is zero for  $x$  less than a *hard-rod* length  $a$  and decreases exponentially for  $x > a$ .<sup>13</sup> Given these assumptions, an analytic expression for the pair correlation function  $g(x)$  can be derived, and the implementation of the var-

ious single-site approximations is greatly simplified. More important, however, is the fact that the electronic spectrum for this model can be evaluated exactly for a finite but large ( $N \sim 10^4$ ) linear chain.<sup>14</sup> As the parameter  $\alpha = aN/L$  is varied between zero and unity these exact results allow us to monitor the effects of short-range order on the electronic spectrum and also to test the validity of the alternate approximation schemes. In the limit  $\alpha \rightarrow 0^+$ , the average arrangement of scattering is random (i. e., there is no short-range order) and the present model reduces to that discussed by Klauder<sup>15</sup> and others.<sup>4,16</sup>

In Sec. III the results of three single-site approximations are compared with the exact machine calculations. The approximate methods we consider are the quasicrystalline approximation (QCA) of Lax<sup>17</sup> and Ziman,<sup>18</sup> and the more recent approaches of Gyorffy<sup>5</sup> and Schwartz and Ehrenreich.<sup>6</sup> The QCA is a non-self-consistent scheme and is, in some sense, analogous to the average  $t$ -matrix description of the binary alloy.<sup>11,19</sup> By contrast, the Gyorffy and Schwartz-Ehrenreich approaches are self-consistent and were both proposed as generalizations of the CPA to the liquid problem. In the random limit it can be shown that the Gyorffy and Schwartz-Ehrenreich approximations reduce to equations shown by Faulkner<sup>4</sup> to be the CPA for an uncorrelated liquid.<sup>20</sup> However, since in this limit the atoms are allowed to overlap, multiple-occupancy corrections do not contribute, and the fact that a given approximation scheme reduces to the CPA does not necessarily imply that it will properly describe the effects of short-range order in a correlated system.

The calculations presented in Sec. III indicate that only the QCA provides a reasonable description of the alloy over the entire range of parameters for which exact results are available. Indeed, in the case of greatest interest, i. e., when the short-range order is most important, the quasicrystalline and exact results are essentially identical. The deficiencies of the two self-consistent methods show up in the negative-energy part of the spectrum. The states in this region are associated with atomic bound states and form a narrow tight-binding band. This is the energy range in which the scattering is strong and in which multiple-occupancy effects are most essential. We find, however, that both self-consistent schemes seriously overestimate the width of the negative-energy peak in the density of states, an error that would appear to be due to a spurious overlap of the atomic orbitals, i. e., to a failure to properly treat the multiple-occupancy effects. (Note that, since the QCA is based on a perturbation series in which the atoms are embedded in free space rather than the effective medium, multiple-occupancy correc-

tions do not arise, and the resulting description of the negative-energy states is not unreasonable.)

## II. MODEL

### A. Definition of the model

We consider a disordered one-dimensional array consisting of  $N$  atomic scattering centers on a line of length  $L$ . The one-electron Hamiltonian is

$$\mathcal{H} = p^2 + \sum_{n=1}^N v_n(x) \quad (2.1)$$

and the individual atomic potentials are taken as

$$v_n(x) = -\lambda \delta(x - x_n), \quad \lambda > 0. \quad (2.2)$$

An isolated potential of this form leads to a single bound state at the energy  $E_0 = -\frac{1}{4}\lambda^2$ .<sup>21</sup>

In addition to the mean ionic density  $n = N/L$ , the extent to which the average positions of the ions are correlated must also be specified. In particular, we require the pair distribution function  $g(x)$ . A convenient feature of one-dimensional systems is the fact that  $g(x)$  can be expressed in terms of just the nearest-neighbor distribution  $p_1(x)$ . This is seen most easily if we consider separately the cases  $x > 0$  and  $x < 0$ . Suppose that an atom is known to be at the origin. The probability distributions for the left- and right-hand nearest neighbors are  $p_1^+(x) = p_1(x) \theta(x)$  and  $p_1^-(x) = p_1(x) \theta(-x)$ , respectively. The left- and right-hand second-nearest-neighbor distributions are then

$$\begin{aligned} p_2^+(x) &= \int_0^{+\infty} dx_1 p_1^+(x_1) p_1^+(x - x_1) \\ &= \int_0^{+\infty} dx_1 dx_2 p_1^+(x_1) p_1^+(x_2) \delta(x_1 + x_2 - x), \end{aligned} \quad (2.3)$$

and the combined probability for finding either atom at  $x$  is simply  $p_1^+(x) + p_2^+(x)$  depending on whether  $x > 0$  or  $x < 0$ . In general,

$$\begin{aligned} p_n(x) &= \int_0^{+\infty} dx_1 p_1^+(x_1) p_{n-1}^+(x - x_1) \\ &= \int_0^{+\infty} dx_1 \cdots dx_n p_1^+(x_1) \cdots p_1^+(x_n) \\ &\quad \times \delta(x_1 + \cdots + x_n - x), \end{aligned} \quad (2.4)$$

and the complete two-particle distribution is given by  $g(x) = g^+(x) + g^-(x)$ , where

$$g^+(x) = \sum_{n=1}^{\infty} p_n^+(x) = g^+(-x). \quad (2.5)$$

Finally, introducing the Fourier transforms

$$g^{\pm}(k) = \int_0^{+\infty} dx e^{-ikx} g^{\pm}(x) = g^{\mp}(-k) \quad (2.6a)$$

and

$$p_n^*(k) = \int_0^{\pm\infty} dx e^{-ikx} p_n^*(x) = p_n^*(-k), \quad (2.6b)$$

we observe that Eqs. (2.4) and (2.5) allow us to write  $g^*(k)$  as

$$g^*(k) = \sum_{n=1}^{\infty} p_n^*(k) = \sum_{n=1}^{\infty} [p_1^*(k)]^n = p_1^*(k) [1 - p_1^*(k)]^{-1}. \quad (2.7)$$

The nearest-neighbor distribution functions for the hard rod liquid are given by<sup>13</sup>

$$p_1^*(x) = \frac{\theta(\pm x - a)}{l - a} \exp\left(\frac{-(\pm x - a)}{l - a}\right) \quad (2.8a)$$

$$= \frac{\theta(\pm x - a)}{l(1 - \alpha)} \exp\left(\frac{-(\pm x - a)}{l(1 - \alpha)}\right). \quad (2.8b)$$

Here  $\alpha$  denotes the length of the hard rod surrounding each site (see Fig. 1),  $l = L/N$  is the average length per atom and, in the second equation, we have introduced the short-range-order parameter

$$\alpha = a/l. \quad (2.9)$$

In the random limit,  $\alpha \rightarrow 0^+$  and there is no longer a minimum allowed separation of the scattering sites. In the perfect crystal,  $\alpha = 1$  and the atoms exhibit perfect long-range order. Note that the distributions (2.8) are properly normalized and are sharply peaked in the ordered limit  $\alpha \rightarrow 1^-$ .

Combining Eqs. (2.6), (2.7), and (2.8) the Fourier transforms  $p_1^*(k)$  and  $g^*(k)$  are given by

$$p_1^*(k) = e^{\mp ika} [1 \pm ikl(1 - \alpha)]^{-1} \quad (2.10a)$$

and

$$g^*(k) = \frac{e^{\mp ika}}{1 - e^{\mp ika} \pm ikl(1 - \alpha)}. \quad (2.10b)$$

A quantity of particular interest in the theory is  $h(x) \equiv g(x) - n$  obtained by removing the uninteresting asymptotic contribution to  $g(x)$ .  $h(x)$  approaches zero for  $|x| \gg a$  and its Fourier transform is thus well behaved near  $k=0$ . Indeed, adding  $g^*(k)$  and  $g^-(k)$  and subtracting the  $\delta$  function at  $k=0$  we obtain

$$h(k) = \frac{2[\cos ka - kl(1 - \alpha) \sin ka - 1]}{(1 - \cos ka)^2 + [\sin ka + kl(1 - \alpha)]^2}. \quad (2.11)$$

Note that in the crystal limit  $\alpha = 1^-$ ,  $h(k=0) = -1$ , in accord with the usual compressibility sum rule

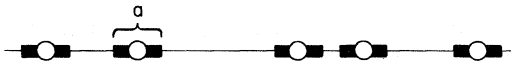


FIG. 1. Schematic representation of the hard-rod liquid. The "radius" of each rod is  $\frac{1}{2}a$  and the minimum separation of the atomic potentials is  $a$ .

$$\int_{-\infty}^{\infty} dx [g(x) - n] = -1. \quad (2.12)$$

## B. Exact results

Machine calculations for the present model are based on the solution of the Schrödinger equation

$$\left(-\frac{d^2}{dx^2} - \sum_n \lambda \delta(x - x_n)\right) \psi(x; E) = E \psi(x; E), \quad (2.13)$$

where the positions of the potentials  $\{x_n\}$  are determined by the statistical mechanics of a hard-rod fluid.<sup>13</sup>

The calculation of the energy spectrum of an arbitrarily long chain of potentials is simplified by the fact that the total number of eigenstates with energy less than  $E$  can be determined (to within  $\pm 1$  state) by choosing arbitrary boundary conditions at the left-hand side of the chain and integrating Eq. (2.13) through to the right-hand side.<sup>14</sup> The number of states with energy less than  $E$  [i.e., the integrated density of states  $n(E)$ ] is just the number of nodes of  $\psi(x; E)$ . In practice the integration can be reduced to a process of multiplying transfer matrices. The transfer matrix  $T_\delta$  which takes the wave function and its derivative at the left-hand side of the  $n$ th  $\delta$ -function potential into their corresponding values on the right-hand side is

$$T_\delta = \begin{bmatrix} 1 & 0 \\ \lambda & 1 \end{bmatrix} \quad (2.14)$$

(independent of  $n$ ). Thus

$$\begin{bmatrix} \psi(x_n^+) \\ \psi'(x_n^+) \end{bmatrix} = T_\delta \begin{bmatrix} \psi(x_n^-) \\ \psi'(x_n^-) \end{bmatrix}. \quad (2.15)$$

In addition, we require the transfer matrix  $T_f$ , which takes the wave function and its derivative at the right-hand side of a potential into their corresponding values at the left-hand side of the next potential,

$$T_f = \begin{bmatrix} \cosh(\kappa d_n) & \kappa^{-1} \sinh(\kappa d_n) \\ \kappa \sin(\kappa d_n) & \cosh(\kappa d_n) \end{bmatrix} (E < 0), \quad (2.16)$$

$$T_f = \begin{bmatrix} \cos(\kappa d_n) & \kappa^{-1} \sin(\kappa d_n) \\ -\kappa \sin(\kappa d_n) & \cos(\kappa d_n) \end{bmatrix} (E > 0). \quad (2.17)$$

Here  $d_n = x_{n+1} - x_n$  and  $\kappa = (|E|)^{1/2}$ .

The distances between the wells,  $d_n = x_{n+1} - x_n$ , are random quantities assigned by the computer with a probability distribution consistent with the hard-rod nearest-neighbor correlation function (2.8).

The behavior of the exact integrated density of states for the hard rod liquid is summarized in Figs. 2(a) and 2(b). Results are shown for two values of the density and three values of the short

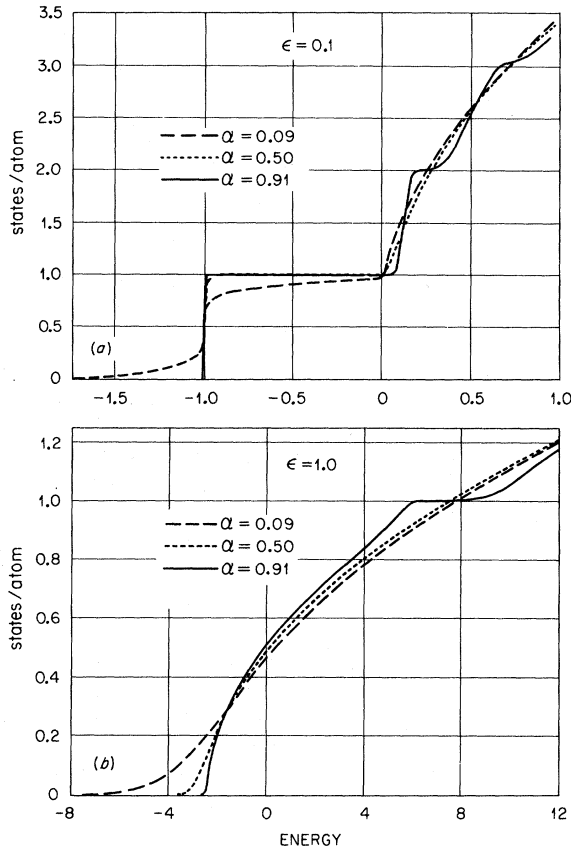


FIG. 2. Exact integrated electronic density of states is shown as a function of the short-range-order parameter  $\alpha$  and the density  $\epsilon$ : (a)  $\epsilon = 0.1$ ,  $\alpha = 0.09$ ,  $0.50$ , and  $0.91$ ; (b)  $\epsilon = 1.0$ ,  $\alpha = 0.09$ ,  $0.50$ , and  $0.91$ .

range order parameter  $\alpha$ . The density is most conveniently measured in terms of a length scale fixed by the decay of an isolated atomic bound-state wave function<sup>21</sup>:

$$\psi_0(x) \sim e^{-x/\lambda^2}.$$

Accordingly, we introduce the dimensionless parameter  $\epsilon = 2n/\lambda$ . Our units of energy are chosen such that the bound-state energy  $E = -(\frac{1}{2}\lambda)^2 = -1.0$ .

Consider first the low-density results ( $\epsilon = 0.1$ ). For all values of  $\alpha$  there exists a well-defined tight-binding-like band in the vicinity of  $E_0 = -1.0$ . As expected, the width of this band is sensitive to fluctuations in the effective overlap of the atomic orbitals and is greatest when the parameter  $\alpha$  is small. Note, however, that even in the case  $\alpha = 0.09$  most of this band's weight is contained within a narrow region centered around  $E_0$ . At positive energies, the qualitative behavior of the integrated density of states is seen to depend quite strongly on the value of the parameter  $\alpha$ . For  $\alpha = 0.09$  and  $0.50$  the results are basically free-electron-like and scale as  $E^{1/2}$ . Increasing  $\alpha$  to  $0.91$ , we note

the appearance of *pseudo*-band-gaps in the electronic spectrum. This structure may be viewed as a remnant of the perfect crystal band gaps which occur at the energies

$$E_n = (n\pi/l)^2 \quad (n = 1, 2, \dots). \quad (2.18)$$

The present results indicate the extent to which these gaps survive in a system which has no long-range order, but in which density correlations are, nevertheless, important.

Turning next to the results for high density ( $\epsilon = 1.0$ ), we note that the negative energy part of the spectrum has broadened considerably and has, in fact, merged with the positive energy continuum. This broadening is due to the enhancement of the bound-state overlap integrals. At positive energies the spectrum is again free-electron-like for  $\alpha = 0.09$  and  $0.50$ , and shows a *pseudogap* for  $\alpha = 0.91$ . Note, however, that, in accord with (2.18), the position of the gap has shifted to higher energies.

### III. SINGLE-SITE APPROXIMATIONS

#### A. General equations

The equilibrium properties of a liquid metal are described by the single-particle Green's function

$$G(z) = \langle (z - \mathcal{H})^{-1} \rangle \equiv [z - p^2 - \Sigma(z)]^{-1}. \quad (3.1)$$

Here the angular brackets indicate an ensemble average over the allowed configurations of the atomic scattering centers,  $z$  denotes an arbitrary (complex) energy, and the second equality defines the electron self-energy operator  $\Sigma(z)$ . In terms of  $G(z)$ , the mean electronic density of states per atom may be written

$$\rho(E) = -(N\pi)^{-1} \text{Im Tr}[G(E^*)]. \quad (3.2)$$

The evaluation of  $\Sigma(z)$  proceeds most directly within the framework of multiple scattering theory.<sup>17</sup> In this approach  $\Sigma(z)$  is calculated in terms of the auxiliary operator  $\sigma_n$ .<sup>6</sup> Thus<sup>22</sup>

$$\begin{aligned} \Sigma(x - x') &= n \int_{-\infty}^{\infty} dx_n \sigma_n(x, x') \\ &= n \int_{-\infty}^{\infty} dx_n \sigma(x - x_n, x' - x_n), \end{aligned} \quad (3.3)$$

and the problem then reduces to that of developing reliable approximations for the calculation of  $\sigma_n$ . There is a class of approximations, generally termed *single-site approximations*, that are all, in some sense, based on the neglect of fluctuation effects in the calculation of the average scattering by a given site. These approximation schemes have in common the feature that the electronic properties of the liquid are determined by three input units: the atomic potentials  $v_n(x)$ , their mean density  $n$ , and the pair-distribution functions  $g(x)$ .

The earliest of the single-site approximations is

Lax's quasicrystalline approximation (QCA).<sup>17</sup> In this approach  $\sigma_n$  is determined by the integral equation

$$\sigma_n = t_n^{(0)} + t_n^{(0)} G_0 \int_{-\infty}^{\infty} dx_m h(n|m) \sigma_m, \quad (3.4a)$$

where  $G_0(z) = (z - p^2)^{-1}$  is the free-electron Green's function,

$$t_n^{(0)} = (1 - v_n G_0)^{-1} v_n \quad (3.4b)$$

is the scattering operator for a single atomic potential in the vacuum, and  $h(n|m) \equiv h(x_n - x_m)$  is defined by Eq. (2.11).<sup>23</sup> Equations (3.4) are non-self-consistent in the sense that the self-energy is specified in terms of unperturbed Green's function  $G_0(z)$ . They can of course be made self-consistent by simply replacing  $G_0(z)$  by  $G(z)$ . Thus,

$$\sigma_n = t_n + t_n G \int_{-\infty}^{\infty} dx_m h(n|m) \sigma_m, \quad (3.5a)$$

where

$$t_n = (1 - v_n G)^{-1} v_n \quad (3.5b)$$

is the scattering operator for a single atom embedded in the effective medium described by  $G(z)$ . Equations (3.5) are equivalent to those originally proposed by Gyorffy.<sup>5</sup> Their present form is due to Korringa and Mills.<sup>24</sup> An alternate self-consistent scheme was proposed by Schwartz and Ehrenreich (SE).<sup>6</sup> Their equations are

$$\sigma_n = v_n + \sigma_n G v_n + \sigma_n G \int_{-\infty}^{\infty} dx_m h(n|m) \sigma_m \quad (3.6a)$$

$$= [1 - (v_n - \bar{\sigma}_n) G]^{-1} v_n, \quad (3.6b)$$

where

$$\bar{\sigma}_n = - \int_{-\infty}^{\infty} dx_m h(n|m) \sigma_m. \quad (3.7)$$

In the random limit,  $h(n|m) \rightarrow 0$ , the Gyorffy-Korringa-Mills<sup>24</sup> (G-KM) and Schwartz-Ehrenreich<sup>6</sup> equations both reduce to<sup>4</sup>

$$\Sigma(k, z) = n t(k, k) \quad (3.8)$$

and the self-energy is expressed in terms of the forward-scattering matrix element of the self-consistent atomic scattering operator. This result is to be compared with the corresponding limit for the QCA

$$\Sigma(k, z) = n t^{(0)}(k, k). \quad (3.9)$$

Physically, the random limit can only be attained on the case of very low atomic densities. In this connection, we note that the QCA result (3.9) is just the first-order term in a perturbation series expansion of  $\Sigma(z)$  in powers  $n$ .<sup>11</sup> To lowest order in  $n$ , Eqs. (3.8) and (3.9) are, of course, identical.

However, because  $t(k, k)$  is computed in terms of  $G(z)$ , the self-consistent result (3.8) contains selected contributions of all orders in  $n$ . The extent to which these higher order terms improve the description of the electronic spectrum can be checked only by explicit calculations.

#### B. Specific equations

Specializing now to the one-dimensional hard-rod  $\delta$ -function liquid, it can easily be shown that the solution to the various single-site approximations are all of the form

$$\sigma_n(x, x') = \delta(x - x_n) f(x' - x_n; z). \quad (3.10)$$

Once the function  $f(x)$  has been determined, its Fourier transform  $f(k; z)$  is directly related to the quantity  $\langle k | \Sigma(z) | k \rangle \equiv \Sigma(k, z)$  via Eq. (3.2).

The application of the QCA to the present model is greatly simplified since the analytic form of the unperturbed Green's function is known:

$$G_0(|x|) = \int_{-\infty}^{\infty} \frac{dk}{2\pi} \frac{e^{ikx}}{E - k^2} = \frac{-i}{2\kappa} e^{i\kappa|x|}. \quad (3.11)$$

Here  $\kappa = E^{1/2}$  or  $i|E|^{1/2}$  depending on whether  $E$  is positive or negative. Thus, combining Eqs. (3.4b) and (2.2), the matrix elements of the atomic scattering operators are given by

$$t_n^{(0)}(x, x') = \delta(x - x_n) \tau^{(0)}(E) \delta(x' - x_n), \quad (3.12)$$

where

$$\tau^{(0)}(E) = -\lambda [1 + \lambda G_0(|x| = 0)]^{-1} = -2\lambda\kappa / (2\kappa - i\lambda). \quad (3.13)$$

Substituting Eqs. (3.10)–(3.13) into (3.4a), we obtain the following closed expression for  $\Sigma(k, E)$ :

$$\Sigma(k, E) = n \tau^{(0)}(E) [1 - \tau^{(0)}(E) G_0''(k, E)]^{-1}, \quad (3.14)$$

where

$$\begin{aligned} G_0''(k, E) &= \int_{-\infty}^{\infty} dx e^{-ikx} G_0(|x|) h(|x|) \\ &= \int_{-\infty}^{\infty} \frac{dq}{2\pi} G_0(q, E) h(k - q) \\ &= \frac{-i}{2\kappa} [g^-(\kappa + k) + g^-(\kappa - k)] - [i(E - k^2)]^{-1}. \end{aligned} \quad (3.15b)$$

Turning next to the G-KM equations, we note that the self-consistent scattering operators  $t_n$  of Eq. (3.5b) can again be written as in (3.12), but that its single matrix element is now of the form

$$\tau(E) = -\lambda [1 + \lambda G(|x| = 0)]^{-1}, \quad (3.16a)$$

with

$$G(|x| = 0) = \int \frac{dk}{2\pi} [E - k^2 - \Sigma(k, E)]^{-1}. \quad (3.16b)$$

The G-KM self-energy is then given by

$$\Sigma(k, E) = n\tau(E)[1 - \tau(E)G''(k, E)]^{-1}, \quad (3.17)$$

where

$$G''(k, E) = \int_{-\infty}^{\infty} \frac{dq}{2\pi} G(q, E)h(k-q). \quad (3.18)$$

Note, however, that in the present case it is not possible to write  $G''$  in a closed form analogous to the QCA result (3.15b). Equations (3.16)–(3.18) must be solved self-consistently,  $G''(k, E)$  being computed at each stage in terms of  $\Sigma(k, E)$  given by the previous iteration.

Finally, in the case of the SE equations, inserting the trial solution (3.10) into (3.6a) yields the following self-consistency requirement:

$$\begin{aligned} \Sigma(k, E) = & -n\lambda \left( 1 + n^{-1} \int_{-\infty}^{\infty} \frac{dq}{2\pi} \Sigma(q, E)G(q, E) \right) \\ & \times [1 - n^{-1} \tilde{G}''(k, E)]^{-1}, \end{aligned} \quad (3.19)$$

where

$$\tilde{G}''(k, E) = \int_{-\infty}^{\infty} \frac{dq}{2\pi} \Sigma(q, E)G(q, E)h(k-q). \quad (3.20)$$

### C. Results

To examine the relative utility of the quasicrystalline, G-KM, and SE approximations, all three were applied to the simplest case, that of low density ( $\epsilon = .1$ ) and relatively little short-range order ( $\alpha = 0.09$ ). As indicated above, the single-site approximations are, at the very least, expected to be valid in the low-density regime. In addition, the fact that the parameter  $\alpha$  has been taken to be small guarantees that the spectrum is not complicated by the correlation effects discussed in connection with Figs. 2(a) and 2(b). It is of interest then to note that, even in this simple case, there are important differences between the three approximations. While all three reproduce the proper free-electron-like behavior at positive energies, neither of the self-consistent schemes yields a description of the tightly bound negative energy states which is as reasonable as that of the non-self-consistent QCA. Indeed, the results plotted in Fig. 3 show that the two self-consistent schemes lead to densities of states that are spread over much too wide a range of energies. This is most apparent in the case of the G-KM curves but is also evident in the SE results. By contrast, the quasicrystalline density of states is confined to a narrow energy region in the vicinity of  $E_0 = -1.0$ . The most obvious shortcoming of the QCA is the fact that it does not properly describe the tails on either side of the peak in the exact spectrum. As we noted earlier, these tails are due to extreme fluctuations in the effective overlap integrals and it is thus not sur-

prising that they are beyond the scope of a simple non-self-consistent mean-field description.

The failure of the self-consistent approximations in the strong-scattering regime is not entirely unexpected. Indeed, similar behavior is evident in Klauder's analysis of the random linear chain.<sup>25,26</sup> Klauder's approximation number five has been shown by Faulkner<sup>4</sup> to be the random limit of the CPA. Nevertheless, it yields much too broad a spectrum for the negative energy states. This is a difficulty which may well be shared by all theories which reduce to the CPA in the random limit. In addition, Schwartz and Siggia<sup>27</sup> have shown that a self-consistent version of the average  $t$ -matrix approximation (analogous to Gyorffy's self-consistent version of the QCA) produces an excessively broadened impurity band in the disordered alloy. In each case, the embedding of an atomic potential in the self-consistent medium allows an artificial overlap of the original potential with those effectively represented by the medium, and thus leads to an overestimate of the average bandwidth. As we noted in the introduction, this amounts to a failure to treat the multiple-occupancy corrections properly.

Having established the inadequacy of the self-consistent single-site approximations (at least within the context of the present model) let us consider the predictions of the QCA in more detail. In Figs. 4 and 5 the quasicrystalline and exact results are compared over the entire range of energies. Results are shown in Fig. 4 for  $\epsilon = 0.1$  and two values of  $\alpha$ . Most interesting is the case  $\alpha = 0.91$  where the effects of short-range order are clearly in evidence. Here the quasicrystalline and exact results are essentially indistinguishable. The QCA predicts both the narrowing of the negative-energy tight-binding states and the existence of the *pseudo*-band-gaps in the positive energy range. In connection with the latter effect, the curves shown in Fig. 6 illustrate that even the detailed structure in the positive-energy density of states is reproduced by the QCA. Finally, in Fig. 5 the QCA is compared

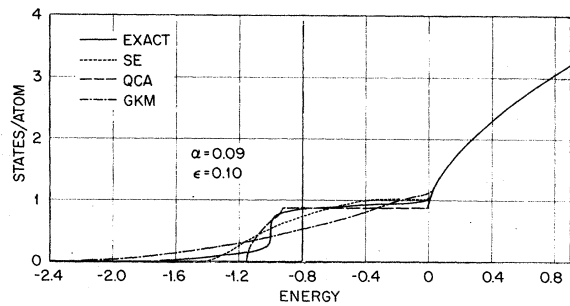


FIG. 3. Three single-site approximations are compared with the exact results in the case  $\alpha = 0.09$ ,  $\epsilon = 0.1$ . Only the negative energy part of the spectrum is shown.

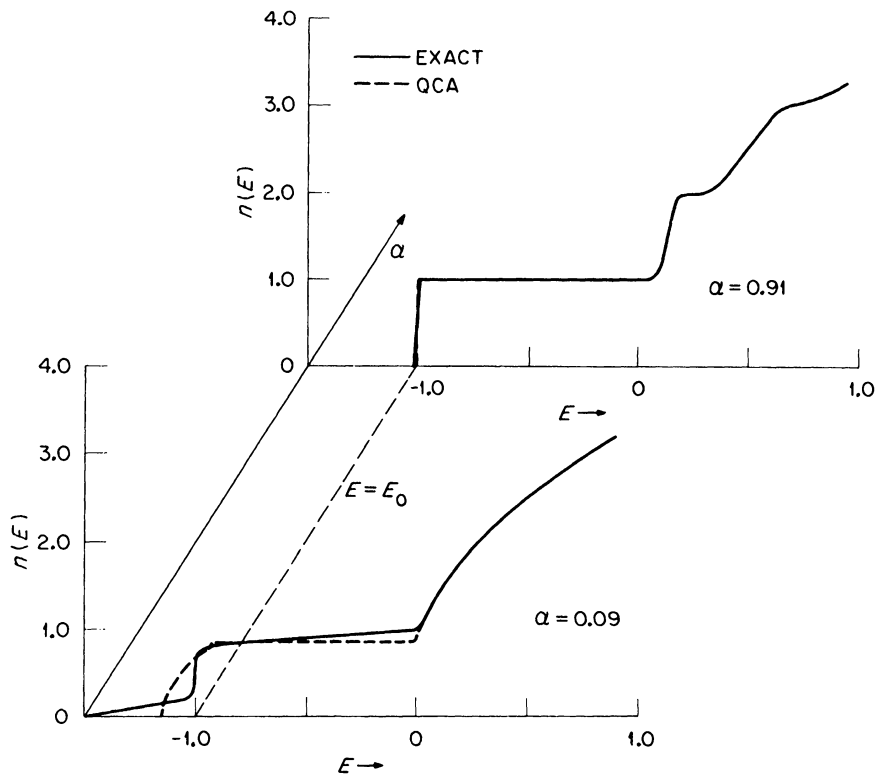


FIG. 4. Comparison of the QCA and exact integrated state densities:  $\epsilon = 0.1$ ,  $\alpha = 0.09$  and  $0.91$ .

with the exact results in the high-density regime ( $\epsilon = 1.0$ ). In the random limit ( $\alpha = 0.09$ ), the QCA properly predicts the broadening of the negative

energy states although, as expected, the smearing of the spectrum is underestimated. Increasing  $\alpha$  to  $0.91$ , the agreement between the quasicrystalline

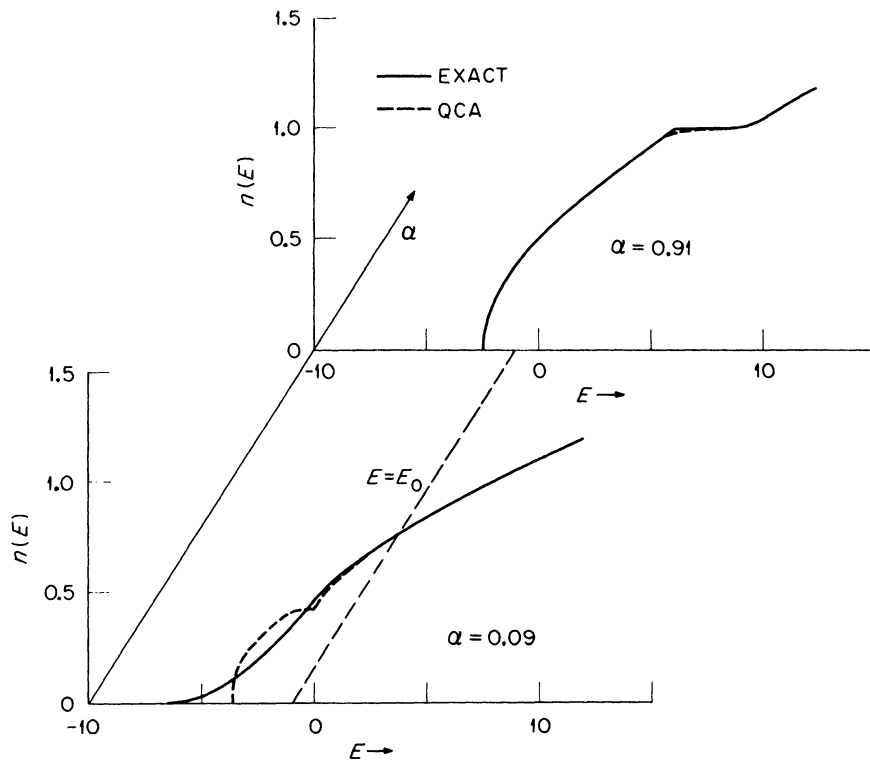


FIG. 5. Comparison of the QCA and exact integrated state densities:  $\epsilon = 1.0$ ,  $\alpha = 0.09$  and  $0.91$ .

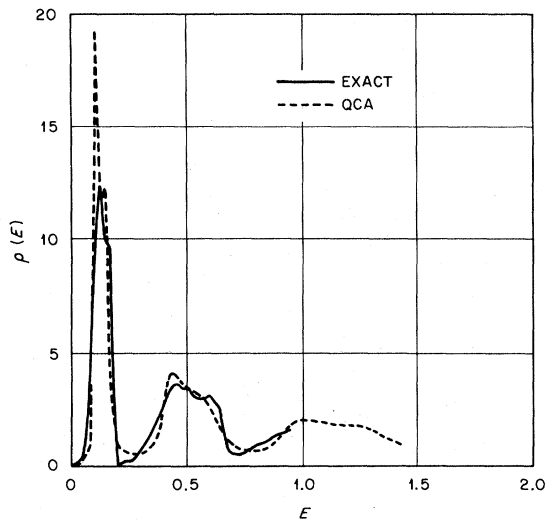


FIG. 6. Comparison of the QCA and exact densities of states in the vicinity of a *pseudo*-band-gap. Results are shown for  $\alpha = 0.91$  and  $\epsilon = 0.1$ .

and exact curves is again excellent on both the negative- and positive-energy sides.

#### IV. DISCUSSION

Two conclusions may be drawn from the results presented in this paper. First, that the present model provides an important test of the extent to which a given self-consistent theory of the liquid has treated correctly the multiple-occupancy problem. In this connection we remark that it would be of interest to compare our results with those obtained from Roth's effective-medium approxima-

tion<sup>9</sup> (EMA). While the formal analysis of Yonezawa, Roth, and Watabe<sup>28</sup> indicates that the EMA does include the multiple occupancy corrections, its validity would best be tested by a comparison with the exact results now available. Second, and perhaps more important, the accuracy of the QCA in the present case would seem to imply that further calculations based on this method are warranted. While it is admittedly dangerous to generalize from one to three dimensions, we see no reason why the QCA would fail to give reasonable results in the case of a more realistic model of the liquid, for example, the muffin-tin model discussed by Ziman.<sup>18</sup> Since the application of the QCA is relatively straightforward, such calculations would determine most directly the extent to which this approach is capable of explaining the existing experimental data. Thus, even if the multiple-occupancy problem is eventually solved, the resulting self-consistent equations may well be so complicated that their application to realistic models would be impractical. This is essentially the case in the alloy problem where the most realistic models have been analyzed only in terms of the non-self-consistent average *t*-matrix approximations rather than the more accurate, but less easily implemented, CPA.<sup>29</sup> At the very least, a consistent application of the QCA would isolate those instances in which qualitative discrepancies would suggest the need for a more sophisticated analysis.

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<sup>20</sup>In the case of the random one-dimensional  $\delta$ -function liquid the CPA can be derived unambiguously. Consider the corresponding alloy in which a fraction *c* of the lattice sites  $x_n$  are occupied by potentials of the form  $\lambda\delta(x - x_n)$  and the remaining sites are vacant. Now, take limit that the lattice constant *a* and the concentration *c* both approach zero in such a way that the average number of scattering centers per unit length approaches a constant *n*. In this limit it can be shown that the CPA equations for the alloy reduce to those derived for the



liquid in Ref. 4 [cf. J. S. Faulkner, Phys. Rev. **135**, A123 (1964)].

<sup>21</sup>K. Gottfried, *Quantum Mechanics* (Benjamin, New York, 1966), p. 50.

<sup>22</sup>The matrix elements  $\langle x | A | x' \rangle$  of an arbitrary operator  $A$  will be denoted as  $A(x, x')$ . Thus  $\langle x | \sigma_n | x' \rangle = \sigma_n(x, x')$  and  $\langle k | G(z) | k' \rangle = \Omega \delta_{k,k'} G(k, z)$ .

<sup>23</sup>This version of the QCA is derived as Eq. (3.6) of Ref. 6.

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<sup>25</sup>See curve number 5 in Fig. 3 of Ref. 15.

<sup>26</sup>While Klauder's approximation (five) is equivalent to the random limit of the G-KM and SE approximations, we emphasize that his non-self-consistent approximation (four) is *not* equivalent to the random limit of the QCA. Specifically, in our units, Klauder's result is

$$\rho_4(E) = (2\pi n)^{-1} \operatorname{Re} \left( (E + n\lambda) - \frac{n}{+1/\lambda + (i/\lambda)[(4/\lambda^2)(E + n\lambda)]^{1/2}} \right)^{-1/2},$$

whereas the random limit of the QCA leads to the result

$$\rho(E) = (2\pi n)^{-1} \operatorname{Re} \left( E - \frac{n}{-1/\lambda + (i/\lambda)[(4/\lambda^2)E]^{1/2}} \right)^{-1/2}.$$

These equations differ in three ways: an energy shift  $E \rightarrow E + n\lambda$ , the sign of the  $1/\lambda$  term, and the sign of the exponent of the factor  $4E/\lambda^2$ . Machine calculations show explicitly that these equations lead to different results, and further, that the first equation does, in fact, reproduce the curves shown in Figs. 3 and 4 of Ref. 15.

<sup>27</sup>L. Schwartz and E. Siggia, Phys. Rev. B **5**, 383 (1972), see Fig. 5(b).

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