Effects of Correlation on the Structure of Impurity Bands

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The effects of electron-electron interaction on the electronic density of states has been considered for a dilute system of scattering centers distributed randomly in an electron gas of moderate density. Using as a starting point an independent-electron t-matrix method, a modified t matrix in the presence of the electron-electron interaction is obtained. To illustrate the effects of correlation, the formalism has been applied to the simple case of a linear chain of attractive δ-function potentials distributed randomly. The electrons are assumed to interact via a repulsive δ-function potential. The density of states in the impurity band is evaluated and compared with the results for independent electrons. It is found that the inclusion of electron-electron interaction produces a significant broadening and downward energy shift of the impurity band.

INTRODUCTION

Many papers have appeared dealing with the electronic structure of disordered systems. Because of the difficulty of the subject, for which there exists no general one-electron theory, these treatments have, for the most part, considered the electrons as noninteracting. Wolff[1] has treated the modification of a free-electron band in the presence of both the electron-impurity and the electron-electron interactions. However, he considers the case of very high impurity and electron densities (relative to the effective Bohr radius of the impurity), so that no localized states arising from single-impurity bound states can occur. The transport properties of interacting electrons in a system of random impurities have also been treated extensively by Langer,[2] Betbeder-Matibet and Nozières,[3] and more recently by Sigel and Argyres[4] and Sigel.[5] Here we describe a calculation of the effect of particle-particle interaction on the density of single-particle states in the band which arises from a bound state of an isolated impurity. To describe the impurity band without many-particle effects the t-matrix approach of des Cloizeaux[6] is used. This is based on infinite-order perturbation theory and consequently many-body effects can be included in a straightforward way using standard propagator formalism.[7]

CALCULATION

We start by writing the Hamiltonian for a system of fixed volume Ω at $T \approx 0$ containing N_e particles interacting with N_a impurities distributed at random. We assume the impurities to be infinitely massive. Then

$$H=\sum_{i=1}^{N_e} T_i+\sum_{i=1}^{N_e} V_a(\vec{r}_i)+\frac{1}{2}\sum_{i,j=1;\, i\neq j}^{N_e} v_e(\vec{r}_i-\vec{r}_j) - \sum_{i=1}^{N_e} V_{0a}-\frac{1}{2}\sum_{i=1}^{N_e} V_{0e}\ , \tag{1}$$

where

$$T_i=-(\hbar^2/2m_e)\nabla_i^2 \tag{2}$$

is the kinetic-energy operator for the ith particle and

$$V_a(\vec{r}_i)=\sum_{\alpha=1}^{N_a} v_a(\vec{r}_i-\vec{R}_\alpha) \tag{3}$$

is the potential energy of the ith particle due to the interactions $v_a(\vec{r}_i-\vec{R}_\alpha)$ between the ith particle and the impurities distributed among the sites $\vec{R}_\alpha$. All physical quantities are to be averaged over the (random) distribution of the $\vec{R}_\alpha$. We consider the system as being "neutral," i.e., assume that there are potential sources which compensate for the potential energy of a particle in the average potential fields V_{0a} of the impurities and V_{0e} of the particle gas. The perturbation calculation is carried out using the second-quantized form of H:

$$H=\sum_{\vec{k}} E'_{\vec{k}} a^*_{\vec{k}} a_{\vec{k}}+\sum_{\vec{k},\vec{k}',\sigma}\sum_{\alpha=1}^{N_a} e^{-i(\vec{k}-\vec{k}')\cdot\vec{R}_\alpha}\langle\vec{k}|v_a(\vec{r})|\vec{k}'\rangle a^*_{\vec{k},\sigma}a_{\vec{k}',\sigma}$$
$$+\frac{1}{2}\sum_{\vec{k},\vec{k}',\vec{q},\sigma,\sigma';\vec{k}\neq\vec{k}'}\langle\vec{k}|v_e(\vec{r})|\vec{k}'\rangle a^*_{-\vec{k}+\vec{q},\sigma'}a^*_{\vec{k},\sigma}a_{-\vec{k}'+\vec{q},\sigma'}a_{\vec{k}',\sigma},$$

where

$$E'_{\vec{k}}=E_{\vec{k}}-V_{0a}$$

and

$$E_{\vec{k}}=\hbar^2k^2/2m_e\ .$$

The effect of the constant term $-V_{0e}$ in Eq. (1) is to remove the diagonal elements $\langle\vec{k}|v_e|\vec{k}\rangle$ from the particle-particle portion of H. Hence $\vec{k}\neq\vec{k}'$ in Eq. (1). The constant term $-V_{0a}$ in Eq. (1) simply shifts the scale of single-particle energies:

$$E = E' + V_{0a} = E' + N_a \langle \vec{k} | v_a | \vec{k} \rangle ,$$

where E' is the energy referred to the unshifted energy scale. (However, when v_a is long ranged, e.g., Coulombic, this energy shift is divergent – V_{0a} has to be included implicitly by removing the diagonal elements from the particle-impurity interaction.)

We wish to obtain the single-particle propagator $G(\vec{k}, \omega)$ for the system. The density of single-particle states will then be given by

$$D(E) = \pi^{-1} \operatorname{Im} \textstyle\sum_{\vec{k}} G(\vec{k}, E), \quad E < E_F$$

$$= -\pi^{-1} \operatorname{Im} \textstyle\sum_{\vec{k}} G(\vec{k}, E), \quad E > E_F. \qquad (4)$$

(Unless otherwise indicated, the index $\vec{k}$ includes implicitly the spin quantum number $\sigma = \pm \frac{1}{2}$.) First, we consider the case without particle-particle interaction ($v_e = 0$). The Hamiltonian becomes a sum of N_e independent one-particle Hamiltonians $H_i = T_i + V_a(\vec{r}_i)$ and it is sufficient to obtain $G(\vec{k}, \omega)$ for the system of one-particle plus impurities. The propagator can be written as a summation of an infinite series of multiple-scattering diagrams involving the free-particle propagator $G_0(\vec{k}, \omega)$. Denoting $G(\vec{k}, \omega)$ by the diagram of Fig. 1(a) and $G_0(\vec{k}, \omega)$ by that of Fig. 1(b) we have the summation shown in Fig. 1(c). We proceed by replacing the potential v_a by the particle-impurity t matrix $t_a(\omega)$, which is the sum of all multiple scatterings of the particle by the impurity α [Fig. 2(a)].

des Cloizeaux has introduced the notion of artic-

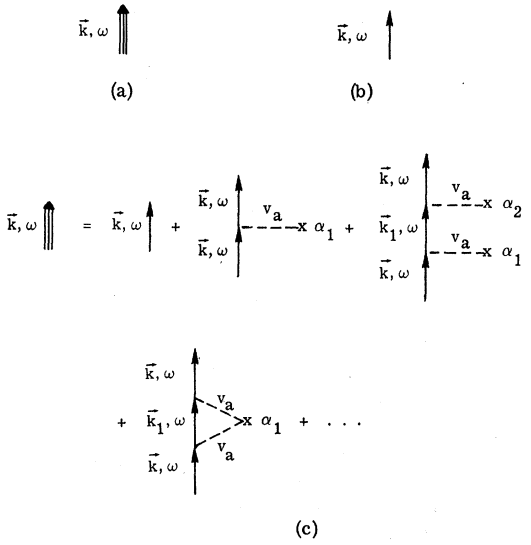

FIG. 1. (a) Diagrammatic representation of the single-particle propagator $G(\vec{k}, \omega)$; (b) diagram of the propagator $G_0(\vec{k}, \omega)$ for a free particle; (c) perturbation expansion of G in terms of G_0.

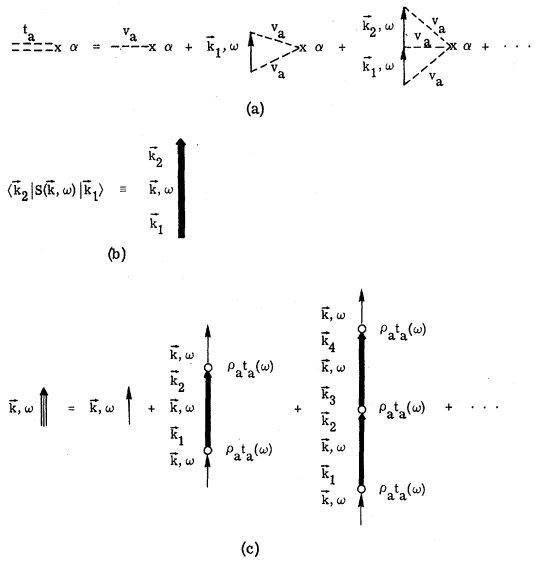

FIG. 2. (a) Definition of the particle-impurity t matrix t_a; (b) matrix element $\langle \vec{k}_2 | S(\vec{k}, \omega) | \vec{k}_1 \rangle$ of the self-propagator $S(\vec{k}, \omega)$; (c) expansion of G in terms of S.

ulation points in these diagrams.[6] By definition an articulation point is associated with an interaction of the particle with the impurity α if all scattering centers β ($\beta \neq \alpha$) encountered by the particle before this interaction are different from all scattering centers γ ($\gamma \neq \alpha$) encountered after this interaction. As a consequence of the averaging process each diagram can then be reduced into a product of irreducible parts by cutting the propagator lines connected to each articulation point in the diagram. Propagation between articulation points can be described by a "self-propagator" $S(\vec{k}, \omega)$, with matrix element $\langle \vec{k}_2 | S(\vec{k}, \omega) | \vec{k}_1 \rangle$, and, upon associating the operator $\rho_a t_a(\omega) \equiv (N_a/\Omega) t_a(\omega)$ with each articulation point denoted by O, the diagrammatic expansion of $G(\vec{k}, \omega)$ can be redrawn as shown in Fig. 2(c), leading to

$$G(\vec{k}, \omega) = G_0(\vec{k}, \omega) + G_0^2(\vec{k}, \omega) \times \langle \vec{k} | \rho_a t_a(\omega) [1 - \rho_a S(\vec{k}, \omega) t_a(\omega)]^{-1} | \vec{k} \rangle . \qquad (5)$$

The self-propagator S can in turn be expanded in powers of the impurity density with the leading term, of order ρ_a^2, containing the contribution of scattering by pairs of impurities.

In considering the effects of electron-electron interaction we are particularly interested in the broadening and shift of the impurity band at moderate-to-high electron densities. Consequently we look at the effect on a particle of a *single* impurity in the presence of all the other particles. This approach leads to a modification of the particle-impurity t matrix while neglecting correlation effects on the scattering of the particle between

different impurities. To each "skeleton" particle-particle scattering diagram contributing to the propagator in the absence of this impurity, we obtain the corresponding diagram in its presence by replacing everywhere the free-particle propagator with the "dressed" propagator appropriate to the system of a particle plus one impurity [Fig. 3(a)].

Let us consider irreducible diagrams, i.e., those which cannot be cut into two others by cutting a dressed propagator line. We denote by $\Sigma(\vec{k},\vec{k}',\omega)$ the sum of all irreducible diagrams, taking the particle from state $\vec{k}'$ to state $\vec{k}$, with energy $\hbar\omega$ [Fig. 3(b)]. Because the presence of the impurity disrupts the homogeneity of the particle gas, the term $\Sigma(\vec{k},\vec{k}',\omega)$ differs from the usual self-energy by being nondiagonal. For this reason Dyson's equation for the modified propagator $G_{a\text{-}e}(\vec{k},\vec{k}',\omega)$ for the system of particle gas plus one impurity cannot be summed into closed form [Fig. 3(c)]. The effective t matrix t_a^{eff} is defined in Fig. 4 in terms of $G_{a\text{-}e}$ and the propagator $G_e(\vec{k},\omega)$ in the presence of the particle gas only. To obtain t_a^{eff} we must know Σ. To make the situation tractable let us in fact approximate Σ by $\delta_{\vec{k},\vec{k}'}\Sigma_e(\vec{k},\omega)$, where Σ_e is the (diagonal) self-energy without the impurity. The resulting expression for $G_{a\text{-}e}$ is shown in Fig. 5(a). This can be resummed in terms of G_e as in Fig. 5(b).

The propagator G_e can be expanded in terms of G_0 and Σ_e as in Fig. 6, the closed-form expression

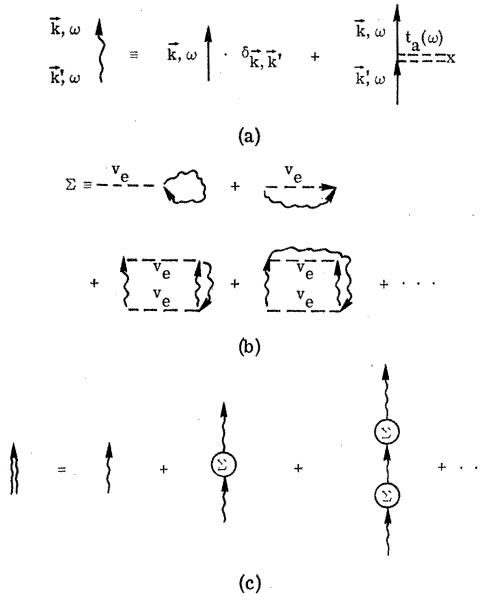

FIG. 3. (a) Definition of the dressed propagator for a particle in the presence of a single impurity; (b) definition of the self-energy Σ in the presence of one impurity and the particle gas; (c) expansion of the propagator $G_{a\text{-}e}$ (double wiggly line) for the system of particle gas plus one impurity.

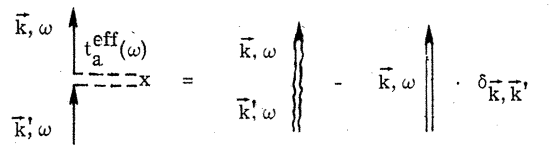

FIG. 4. Definition of the effective particle-impurity t matrix in terms of $G_{a\text{-}e}$ and the propagator G_e (double straight line) for the pure particle gas.

of which is

$$G_e(\vec{k},\omega) = G_0(\vec{k},\omega)/[1-\Sigma_e(\vec{k},\omega)G_0(\vec{k},\omega)]\,. \qquad (6)$$

Let us now consider the simple case of a disordered linear chain of attractive δ-function potentials. In this case we have

$$v_a(x-X_\alpha) = -v_0^a\,\delta(x-X_\alpha),$$

and the t matrix is

$$\langle k|\,t_a(\omega)\,|k'\rangle = \left(-\frac{v_0^a}{\Omega}\right)\Big/\left[1-\frac{iv_0^a}{2(\omega+i0)^{1/2}}\right], \quad \omega<0$$

in atomic units ($\hbar=1$, $m_e=\frac{1}{2}$, $e^2/4\pi\epsilon_0=2$). This has a singularity at the bound-state energy $E_b=-(v_0^a/2)^2$ of a particle in the field of one impurity. The fact that the matrix element of t_a is independent of initial and final momenta simplifies matters considerably since the expression in Fig. 5(b) for $G_{a\text{-}e}(\vec{k},\vec{k}',\omega)$, the propagator for the system of particles plus one impurity, can be summed into closed form:

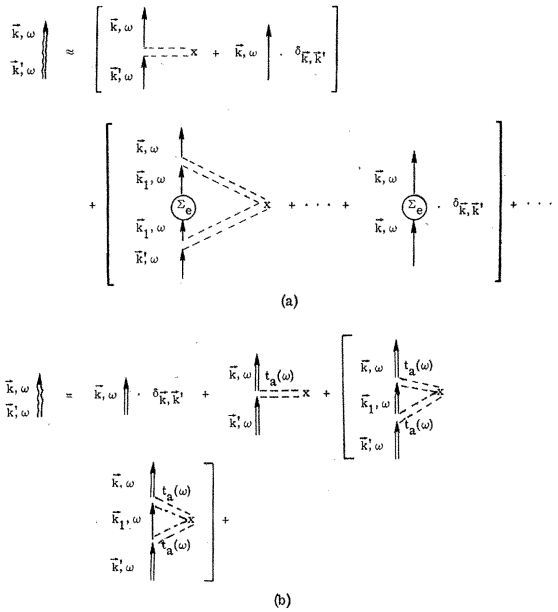

FIG. 5. (a) Expansion for $G_{a\text{-}e}(\vec{k},\vec{k}',\omega)$ when $\Sigma(\vec{k},\vec{k}',\omega)$ is approximated by $\delta_{k,k'}\Sigma_e(\vec{k},\omega)$; (b) resummation of the series in (a) in terms of $G_e(\vec{k},\omega)$.

$$G_{a-e}(k,k',\omega)=G_e(k,\omega)\delta_{k,k'}+G_e(k',\omega)t_a(\omega)G_e(k,\omega)$$
$$+G_e(k',\omega)t_a(\omega)\{\sum_{k_1}[G_e(k_1,\omega)-G_0(k_1,\omega)]\}t_a(\omega)G_e(k,\omega)+\cdots$$
$$=G_e(k,\omega)\delta_{k,k'}+G_e(k',\omega)\Big(\sum_{n=0}^{\infty}t_a^{n+1}(\omega)\mathcal{S}^n(\omega)\Big)G_e(k,\omega)$$
$$=G_e(k,\omega)\delta_{k,k'}+G_e(k',\omega)t_a(\omega)[1-t_a(\omega)\mathcal{S}(\omega)]^{-1}G_e(k,\omega), \tag{7}$$

where

$$\mathcal{S}(\omega)=\sum_{k_1}[G_e(k_1,\omega)-G_0(k_1,\omega)]$$
$$=\sum_{k_1}\left[\frac{G_0(k_1,\omega)\Sigma_e(k_1,\omega)G_0(k_1,\omega)}{1-\Sigma_e(k_1,\omega)G_0(k_1,\omega)}\right], \tag{8}$$

and $t_a(\omega)$ has been written for $\langle k|t_a(\omega)|k'\rangle$. From Fig. 4 we see that

$$t_a^{\mathrm{eff}}(\omega)=[1-\Sigma_e(k',\omega)G_0(k',\omega)]^{-1}t_a(\omega)$$
$$\times[1-t_a(\omega)\mathcal{S}(\omega)]^{-1}[1-\Sigma_e(k,\omega)G_0(k,\omega)]^{-1},$$

and is dependent upon k' and k. To facilitate comparison with the results using the bare t matrix, this dependence is ignored:

$$t_a^{\mathrm{eff}}(\omega)\approx t_a(\omega)[1-t_a(\omega)\mathcal{S}(\omega)]^{-1}. \tag{9}$$

The quantity $\mathcal{S}(\omega)$ has been evaluated when the particles or "electrons" interact via a repulsive δ function:

$$v_e(x_i-x_j)=v_0^e\delta(x_i-x_j). \tag{10}$$

The self-energy was calculated in the ladder approximation; to lowest order (Fig. 7) in the particle-particle t matrix $t_e(\vec{q},\zeta)$ we have

$$\Sigma_e(\vec{k},\omega)=-\frac{i}{2\pi}\times 2\sum_{\vec{q}}\int_{-\infty}^{\infty}d\zeta[\langle\vec{k}|t_e(\vec{q},\zeta)|\vec{k}\rangle$$
$$-\langle\vec{k}|v_e|\vec{k}\rangle]G_0(\vec{q}-\vec{k},\zeta-\omega)+\frac{i}{2\pi}$$
$$\times\sum_{\vec{q}}\int_{-\infty}^{\infty}d\zeta\langle\vec{q}-\vec{k}|t_e(\vec{q},\zeta)|\vec{k}\rangle G_0(\vec{q}-\vec{k},\zeta-\omega). \tag{11}$$

In this case $\langle\vec{k}|t_e(\vec{q},\zeta)|\vec{k}'\rangle$ depends only on q and ζ and can be obtained in closed form as

$$t_e(q,\zeta)=\left(\frac{v_0^e}{\Omega}\right)\left[1-\left(\frac{v_0^e}{\Omega}\right)\lim_{\delta\to 0}\Big(\sum_{\substack{k>k_F\\|q-k|>k_F}}[\zeta-k^2-(q-k)^2+i\delta]^{-1}\right.$$
$$\left.-\sum_{\substack{k\le k_f\\|q-k|\le k_f}}[\zeta-k^2-(q-k)^2-i\delta]^{-1}\Big)\right]^{-1}. \tag{12}$$

DISCUSSION

The expression which results, when the free-particle propagator $G_0(\vec{k},\omega)$ appearing in Eq. (5) is replaced by $G_e(\vec{k},\omega)$ and the bare particle-impurity t matrix t_a by t_a^{eff}, is

$$G(\vec{k},\omega)=G_e(\vec{k},\omega)+G_e^2(\vec{k},\omega)$$
$$\times\langle\vec{k}|\rho_a t_a^{\mathrm{eff}}(\omega)[1-\rho_a S(\vec{k},\omega)t_a^{\mathrm{eff}}(\omega)]^{-1}|\vec{k}\rangle. \tag{13}$$

This equation reduces to the correct limit when either v_a or v_e vanishes. Upon computing G_e from Eq. (6) and t_a^{eff} from Eq. (9), the resulting density of states (per unit length) obtained for negative energies is shown in Fig. 8, together with the result for independent electrons. In both cases we have used $v_0^a=2$ Ry$-a_0$ and $\rho_a=\frac{1}{3}a_0^{-1}$, while in the former case we have taken $v_0^e=v_0^a$ and $\rho_e=1a_0^{-1}$. The lowest-order expansion in ρ_a of the self-propagator was used.[8] Also shown is a machine calculation for independent electrons, reported in Ref. 6. We see that the effect of particle-particle interaction on the impurity band is to displace it to lower energies as well as to broaden it. For the parameter values used here the full width at half-maximum with particle interaction (~ 0.42 Ry) is comparable to that occurring in the machine calculation for independent particles (~ 0.30 Ry). To estimate the shift of the impurity band with respect to the Fermi level, the following approximate relation for a filled band ($\rho_e>2\rho_a$) was used in obtaining E_F:

$$\int_{-\infty}^{E_F}\Omega^{-1}[D(E)-D_e(E)]\,dE\sim 2\rho_a \tag{14a}$$

or

$$\int_{-\infty}^{E_F}\Omega^{-1}D_e(E)\,dE\sim\rho_e-2\rho_a, \tag{14b}$$

where $D_e(E)$ is the contribution to the state density from the first term in Eq. (13). Equation (14a) is a good approximation in the independent-particle theory, for which $\int_{-\infty}^{0}\Omega^{-1}D(E)\,dE\approx 2\rho_a$. In general

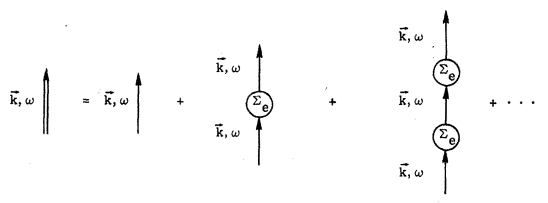

FIG. 6. Expansion of G_e in terms of G_0 and Σ_e, leading to Eq. (6).

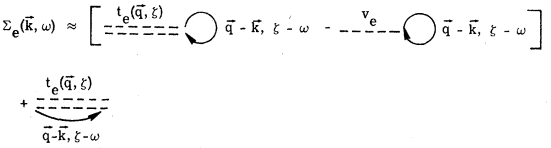

FIG. 7. Diagrammatic expression for the particle self-energy to lowest order in the particle-particle t matrix t_e (ladder approximation).

we would expect it to be applicable in the tight-binding limit (ρ_a small relative to the bound-state radius of an isolated impurity) for v_e small compared to v_a. Using Eq. (14b) we obtain $E_F \sim 0.27$, $E_F' \sim -0.03$ Ry, so that the shift is

$$(E_B' - E_F') - (E_B - E_F) \sim -0.49 \text{ Ry}.$$

The integrated-state density up to $E = E_F'$ is

$$\int_{-\infty}^{E_F'} \Omega^{-1} D(E)\, dE = 0.74\, \frac{\text{states}}{a_0} < \rho_e \quad .$$

Thus Eq. (14a) underestimates the shifted Fermi level E_F' in this case ($v_e = v_a$),

The above results indicate that while broadening of the impurity and conduction bands due to interparticle interaction increases their overlap, there is a net downward shift of the center of the impurity band with respect to the Fermi level.

In three dimensions we anticipate the effect of particle-particle interaction on an impurity band to be more pronounced than in one dimension. This is so because in three dimensions it is known that strong screening of an impurity at high electron densities can cause it to ionize completely, whereas a one-dimensional potential well always possesses at least one bound state. We feel that the over-all results of this calculation are reasonable. In treating a more realistic (e.g., three-dimensional) case, however, the computational problem becomes rather formidable. An accurate determination of $\Sigma_e(\vec{k},\omega)$ for the Coulomb interaction for a wide range of ω, for example, is difficult at intermediate-to-low electron density, where correlations are important. Such a calculation would be of interest in any situation where one probes the state density arising from tightly bound outer electron states of impurities and/or atoms of a disordered host.

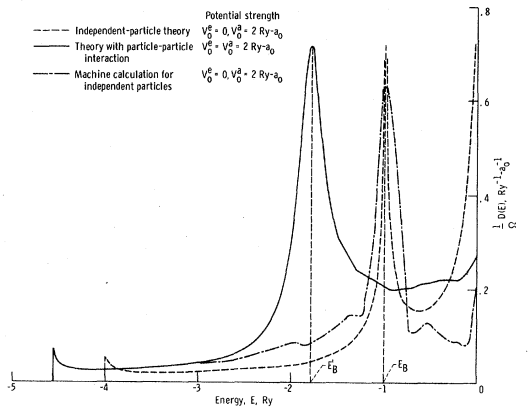

FIG. 8. Single-particle density of states, per unit length, in the impurity band for a linear chain of random scatterers. Scatterer density $\rho_a = \frac{1}{3} a_0^{-1}$, particle density $\rho_e = 1 a_0^{-1}$.

[1]P. A. Wolff, Phys. Rev. 126, 405 (1962).

[2]J. S. Langer, Phys. Rev. 120, 714 (1960); 124, 1003 (1961); 127, 5 (1962); 128, 110 (1962).

[3]O. Betbeder-Matibet and P. Nozières, Ann. Phys. (N. Y.) 37, 17 (1966).

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[5]J. L. Sigel, Phys. Rev. 186, 182 (1969).

[6]J. des Cloizeaux, Phys. Rev. 139, A1531 (1965).

[7]For example, D. Pines, *The Many-Body Problem* (Benjamin, New York, 1962); P. Nozières, *Theory of Interacting Fermi Systems* (Benjamin, New York, 1964).

[8]The self-propagator $S(\vec{k},\omega)$ consists of the sum of two terms $A(\omega) + B(\vec{k},\omega)$ and, to lowest order in ρ_a, only the first term has been retained as giving, in this particular case, the dominant contribution to $D(E)$ in the neighborhood of the maximum in the impurity band. (See Ref. 6.)