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Impurity Bands and Perturbation Theory

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Perturbation theory can be applied to calculate the density of states of an electron moving in a random potential produced by impurity centers, but for small concentrations the usual approximations are unreliable and do not predict correctly the shape of the impurity band. A new chain of approximations is obtained by expressing the Green's function of the electron in terms of a "self-propagator." It is shown that this method leads to more realistic results.

I. INTRODUCTION

GOOD theories of random processes are needed in many areas of physics, but owing to mathematical difficulties, little progress has been made in this domain in the past. Indeed, many papers have been devoted to the study of the motion of electrons in random potentials and especially to the scattering of free electrons and the formation of impurity bands, but usually these effects have been considered separately and treated by different methods. For instance, the scattering of an electron can be easily calculated by perturbation theory and the first-order approximation gives quite reasonable results.[1] On the other hand, the formation of impurity bands can be conveniently investigated in the strong-binding limit.[2]

Our aim here is to build a formalism leading to reasonable approximations for all values of the electron energy. Perturbation theory is used as a starting point and we want to predict the shape of impurity bands as well as scattering effects. In this paper, we are mainly concerned with the difficulties which are introduced by the random character of the impurity distribution. For this reason all the correlation effects due to electron-electron interactions are neglected in spite of their importance, and we deal with independent-electron models only.

In order to obtain finite results, we must sum the contributions of infinite series of diagrams. Unfortunately, there is no obvious way of knowing which diagrams are the most important. Actually, it will be shown that, for small densities of impurities, all the current approximations lead to unphysical results. Thus new physical ideas are needed to get a good picture of the situation. In the following, we visualize an electron as wandering from atom to atom and in order to describe this process, we introduce a "self-propagator." The one-particle Green's function is expressed in terms of this propagator and not in terms of the usual self-energy. A new series of approximations can be found in this way and we show that a first-order calculation of the propagator leads to nice results in the limit of small densities. For this purpose, we use a soluble linear model; for reasons of simplicity, it is assumed that the potential consists of attractive δ functions distributed at random.

II. MOTION OF AN ELECTRON IN A RANDOM POTENTIAL: FAILURE OF THE APPROXIMATIONS FOR LOW DENSITIES

In order to describe the motion of an electron in a random potential and to calculate the spectrum of the system, it is convenient to use one-electron Green's functions. For reasons of simplicity, we study here one-dimensional problems only, but the generalization of our method to the three-dimensional case is trivial. Our Hamiltonian will be written

$$H=-\partial^2/\partial x^2+\sum_j V(x-x_j). \qquad (1)$$

Here, xj indicates the position of an impurity center; these centers are randomly distributed and their density is denoted by N.

Special attention will be paid to the simple case

$$V(x)=-2\delta(x) \qquad (2)$$

which will be called the δ model and will be used as a test for all the theories which we describe in the following. In fact, for this model, the density of states by

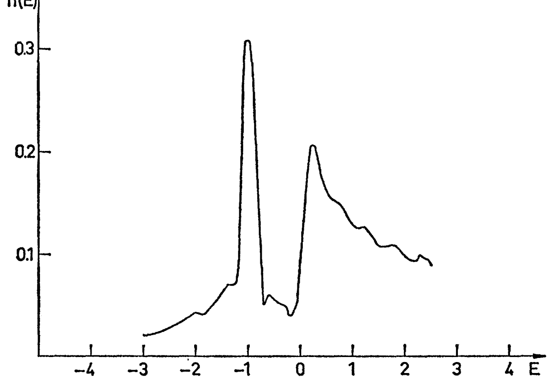

FIG. 1. The density of states $n(E)$, obtained for $N=\frac{1}{3}$ by calculating $\mathfrak{N}(E)=\int_{-\infty}^{E} n\,(E)dE$, as indicated in Sec. II, with a chain of 9000 impurity centers. Note that the impurity band remains fairly narrow.

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[1] Detailed studies and references to earlier publications can be found in the work of J. S. Langer, Phys. Rev. **128**, 110 (1962); **127**, 5 (1962); **120**, 714 (1960).

[2] An interesting classification of the energy levels in the tight binding limit has been given by I. M. Lifshitz, Zh. Eksperim. i Teor. Fiz. **44**, 1129 (1963) [English transl.: Soviet Phys—JETP **17**, 1159 (1963)]; Advan. Phys. **13**, 483 (1964).

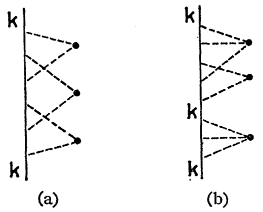

FIG. 2. Typical diagrams for the Green's function. (a) Σ-irreducible diagrams. The interactions of the electron with the impurity centers M_1, M_2, and M_3 are entangled. (b) Σ-reducible diagram. The diagram can be split into two parts containing, respectively, M_1 and M_2, M_3.

unit length $n(E)$ can be obtained directly by using a computer. A simple method[3] consists in calculating for a long chain of length L containing NL centers, the number $\mathfrak{N}(E)$ of zeros of a wave function of energy E. In the limit, of large L, we have

$$\mathfrak{N}(E)=L\int_{-\infty}^{E} n(E)dE. \tag{3}$$

This method has been used for $N=\frac{1}{3}$ and a chain of randomly distributed impurity centers. The result is shown in Fig. 1. More sophisticated methods[4] are also available, but these techniques apply only to the one-dimensional case. Therefore, in order to deal with physical situations, we must examine more general perturbation methods.

The Green's function is defined by

$$G(k,\omega)=\langle k|(\omega-H)^{-1}|k\rangle \tag{4}$$

and the density of states is given by

$$n(E)=-\frac{1}{2\pi^2}\,\mathrm{Im}\int_{-\infty}^{+\infty} G(k,\,E+i0)dk. \tag{5}$$

In the absence of interaction, we have, of course,

$$G_0(k,\omega)=(\omega-k^2)^{-1}, \tag{6}$$

$$n_0(E)=(2\pi(E)^{1/2})^{-1}, \quad (E>0). \tag{7}$$

The function $G(k,\omega)$ can be expanded as usual in terms of the interaction and typical diagrams are shown in Fig. 2. The contributions of each diagram are averaged with respect to the positions of the impurity centers. For this reason, the Green's function is diagonal in the momentum space. A factor N^p appears in the contribution of a diagram if p different impurity centers appear on this diagram (for instance $p=3$ for the diagrams of Fig. 2). Therefore $G(k,\omega)$ can be expanded with respect to N but the terms of this expansion have strong singularities which must be eliminated by summing up infinite series of these terms. Actually, as a result of the averaging process, the momentum k must appear several times on the electron line of a diagram, if all the interactions do not overlap with each other; in this case, we say that the diagram is Σ reducible (for instance, in Fig. 2, diagram (a) is Σ irreducible, but diagram (b) can be split into two irreducible parts). Now, the Green's function can be expressed in terms of the irreducible Σ parts:

$$G(k,\omega)=G_0(k,\omega)+G_0(k,\omega)\Sigma(k,\omega)G_0(k,\omega)+\cdots. \tag{8}$$

More explicitly, we have

$$G(k,\omega)=(\omega-k^2-\Sigma(k,\omega))^{-1}. \tag{9}$$

$\Sigma(k,\omega)$ itself can be expanded in terms of the density N and the diagrammatic representation of the first-order term $\Sigma_0(k,\omega)$, proportional to the diagonal part of the t matrix, corresponding to one impurity, is given in Fig. 3.

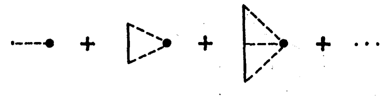

FIG. 3. First-order self-energy $\Sigma_0(k,\omega)$.

Now we may wonder whether $\Sigma_0(k,\omega)$ is a good approximation to $\Sigma(k,\omega)$ in the limit of small densities. For our δ model, we have

$$\Sigma_0(k,\omega)=\sigma(\omega)=-2N(\omega)^{1/2}/(\omega^{1/2}-i). \tag{10}$$

The pole of this expression for $\omega=-1$ corresponds to the bound state of an electron in the field of one impurity. By replacing $\Sigma(k,\omega)$ by $\sigma(\omega)$ in Eq. (9), we get a value of $G(k,\omega)$ which, for $E<0$, leads to the following level density:

$$n(E)=\frac{1}{2\pi}\left[\frac{1-|E|^{1/2}}{|E|^{1/2}(|E|-|E|^{1/2}-2N)}\right]^{1/2}$$
$$-1>E>-(\tfrac{1}{2}+2N+\tfrac{1}{2}(1+8N)^{1/2}). \tag{11}$$

In principle, this function should give an approximate expression for the level density in the impurity band but the result is obviously wrong (see Fig. 4). The level density $n(E)$ must be strongly peaked on the value $E=-1$ and the broadening of the impurity level must

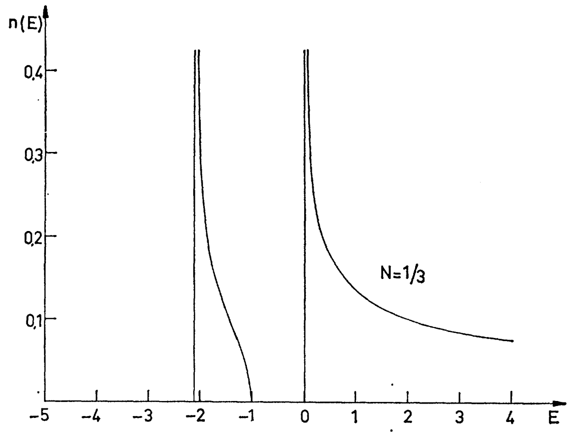

FIG. 4. First-order calculation of the density of states $n(E)$.

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[3] H. M. James and A. S. Ginzbarg, J. Phys. Chem. **57**, 840 (1953).

[4] M. Lax and J. C. Phillips, Phys. Rev. **110**, 41 (1958); H. Frisch and S. Lloyd, *ibid.* **120**, 1175 (1960).

be symmetric, in the strong coupling limit. This fact can be demonstrated in many ways. For instance, a can be easily verified when the impurities form it periodic lattice. In the random case, the same conclusion can be reached by assuming that each center interacts only with its nearest neighbor. This crude, but realistic, approximation gives for small values of $|E+1|$

$$n(E)=\tfrac{1}{2}N^2(|E|+1)^{-1+N}, \qquad (12)$$

an expression which bears no resemblance to Eq. (11). Finally, this approximate symmetry of the impurity band for low values of N appears clearly on the spectra calculated by exact methods (see Fig. 1).

Thus, simple perturbation methods seem to give very bad results for negative values of the energy, and it is not difficult to show that the situation is hardly improved by calculating $\Sigma(k,\omega)$ up to second order. Therefore, it seems quite necessary to use a self-consistent approximation.

The so called Brueckner or Matsubara-Toyazawa approximation[5] seems very appealing and has been described in the literature as "a scheme quite adequate for most practical problems." In this approximation, when a center interacts with an impurity, the influence of all other impurities is taken into account by using a self-consistent Green's function (see diagrams of Fig. 5). In the δ model, this propagator can be simply written

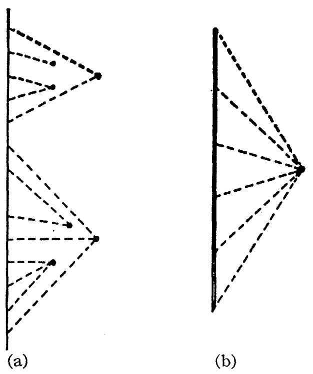

FIG. 5. Brueckner approximation: (a) A typical diagram, (b) general representation of a diagram contributing to $\Sigma(\omega)$. The black line corresponds to the self-consistent Green's function.

$$G(k,\omega)=[\omega-k^2-\Sigma(\omega)]^{-1}. \qquad (13)$$

By setting

$$\gamma(\omega)=[\omega^2-\Sigma(\omega)]^{1/2}, \qquad (14)$$

we obtain the self-consistent equation

$$\gamma^2(\omega)=\omega+2N\gamma(\omega)/[\gamma(\omega)-i] \qquad (15)$$

which determines $\Sigma(\omega)$. The corresponding level density $n(E)$ is given in terms of $\gamma(\omega)$:

$$n(E)=(1/2\pi)\operatorname{Re}[\gamma(E+i0)]^{-1}. \qquad (16)$$

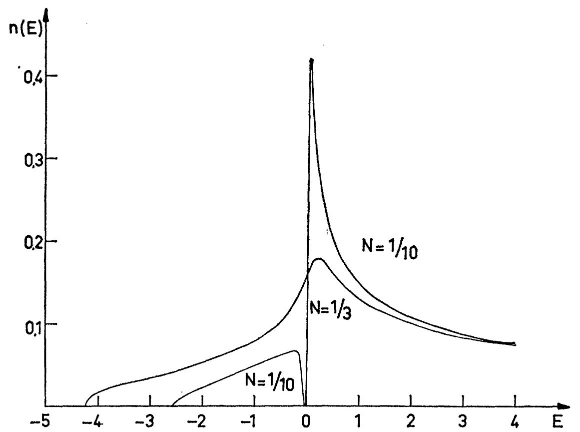

FIG. 6. The density of states in the Brueckner approximation for $N=\frac{1}{3}$ and $N=\frac{1}{10}$. For $N=\frac{1}{10}$, the gap between the impurity band-band and the conduction-band is already very small; for $N=\frac{1}{3}$, the impurity band is completely smeared out.

Therefore, in this case, by using Cardan's formula, $n(E)$ can be calculated immediately. Qualitatively, the results are reasonable; for small values of N a narrow symmetrical impurity band is obtained and this band is separated from the conduction band by a gap; this gap disappears as expected when N increases. However, quantitatively, the method is very bad, as can be seen by comparing the results obtained for $N=\frac{1}{3}$ by using this approximation (see Fig. 6) and the nearly exact results calculated for the same density of impurity centers (see Fig. 1).

Thus, for small values of N, this approximation fails to give a physical picture of the formation of impurity bands; the broadening predicted by this theory is much too large. For large values of N, this method may be useful, but for small values of N, the problem must be carefully re-examined.

III. METHOD OF THE SELF-PROPAGATOR

In order to build a new chain of approximations, we start from the basic idea that each electron is wandering

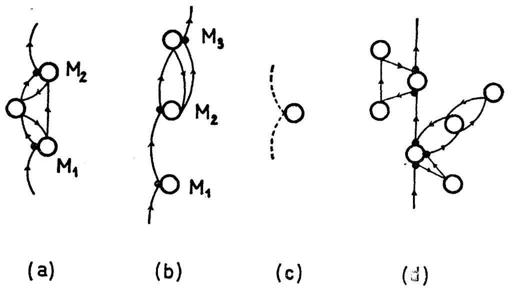

FIG. 7. Simplified diagrams. The articulation points are indicated on the atom circles by dots. Here the drawings (a) and (b) correspond, respectively, to the diagrams (a) and (b) of Fig. 1 (and also to other diagrams having the same structure). The contribution associated with diagram (c) is the matrix $t(\omega)$, and is the sum of the contributions corresponding to all the diagrams of Fig. 2. The diagram (d) corresponds to the diagram (a) of Fig. 4.

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[5] J. R. Klauder, Ann. Phys. (N. Y.) 14, 43 (1961); F. Yonezawa, Progr. Theoret. Phys. (Kyoto) 31, 357 (1964).

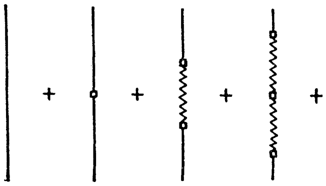

FIG. 8. Expansion of $G(k,\omega)$. The articulation points are represented by squares and the operators $S(k,\omega)$ by a wavy line.

from atom to atom, and therefore, that the Green's function should be expressed in terms of diagrams corresponding to this picture. Consequently, we introduce a new set of diagrams by suppressing, in our previous diagrams, all the interaction lines. Now, in these simplified diagrams, the atoms are represented by small circles (see Fig. 7); successive interactions of an electron with an atom A are symbolized by a point on the corresponding circle; and if an electron interacts with an atom A and immediately after with an atom B, we draw a line directed from A to B. Thus, each new diagram corresponds to a collection of the old diagrams. The contribution of one of these new diagrams can be calculated as follows: To each line joining two atoms, we associate the propagator $G_0(k,\omega)$, and to each point of contact of the electron line with an atom circle, we associate the t-matrix $t(\omega)$ [the diagonal part of which is $N^{-1}\Sigma_0(k,\omega)$].

We can now define the S reducibility of these new diagrams by introducing the notion of articulation point. By definition, a point belonging to an atom circle A is an articulation point if all centers M' $(M'\neq A)$ which are met by the electron before reaching A at this point, are different from the centers M'' $(M''\neq A)$ which are reached by the electron after leaving M. This definition can be illustrated by the drawing of Fig. 7, where the articulation points are indicated by dots.

Now, we can split a diagram into irreducible S parts by cutting the lines which are connected to this point. There are two kinds of irreducible parts. The irreducible parts of the first kind have both ends rooted on the same center M; the sum of their contributions (the ends are excluded) can be represented by an operator $N\mathcal{A}(\omega)$ independent of the wave number k. On the contrary, an irreducible part of the second kind connects two different centers M and M' and carries a momentum k. The sum of the corresponding contribution can be represented by an operator $\mathcal{B}(k,\omega)$. The self-propagator is defined by

$$\mathcal{S}(k,\omega)=\mathcal{A}(\omega)+\mathcal{B}(k,\omega). \tag{17}$$

Now, it is easy to express $G(k,\omega)$ in terms of this operator; we attribute to each articulation point the factor $Nt(\omega)$, where $t(\omega)$ is the one-impurity t operator and we describe the motion of an electron between two articulation points by $\mathcal{S}(k,\omega)$. A graphic representation of $G(k,\omega)$ is given in Fig. 8, and we can write accordingly

$$\begin{aligned}G(k,\omega)=G_0(k,\omega)&+G_0(k,\omega)\langle k|Nt(\omega)|k\rangle G_0(k,\omega)\\&+G_0(k,\omega)\langle k|Nt(\omega)\mathcal{S}(k,\omega)Nt(\omega)|k\rangle G_0(k,\omega)\\&+G_0(k,\omega)\langle k|Nt(\omega)\mathcal{S}(k,\omega)Nt(\omega)\mathcal{S}(k,\omega)Nt(\omega)|k\rangle G_0(k,\omega)+\cdots\end{aligned} \tag{18}$$

or, more simply,

$$G(k,\omega)=G_0(k,\omega)+G_0^2(k,\omega)\langle k|Nt(\omega)[1-N\mathcal{S}(k,\omega)t(\omega)]^{-1}|k\rangle. \tag{19}$$

This relation is rather similar to Eq. (9) and both are rigorous, but $\mathcal{S}(k,\omega)$ and $\Sigma(k,\omega)$ are not related in a simple way; actually, Σ reducibility and S reducibility are very different notions. This new expression of $G(k,\omega)$ can be used as the starting point of a new approximation, since $\mathcal{S}(k,\omega)$ can be expanded in terms of N. It will be shown now that, in the lowest order approximation and for small values of N, this kind of expansion leads to fairly good results.

For the δ model, simplifications occur in the expression of $G(k,\omega)$. In this case, the matrix elements of $t(\omega)$ are independent of the momentum transfer:

$$N\langle k|t(\omega)|u\rangle=\sigma(\omega). \tag{20}$$

Therefore, by setting

$$S(k,\omega)=\sum_{uv}\langle u|\mathcal{S}(k,\omega)|v\rangle, \tag{21}$$

we can write

$$G(k,\omega)=G_0(k,\omega)+G_0^2(k,\omega)\frac{\sigma(\omega)}{1-\sigma(\omega)S(k,\omega)}, \tag{22}$$

or more explicitly, by using Eqs. (6) and (10),

$$G(k,\omega)=\frac{1}{\omega-k^2}+\frac{1}{(\omega-k^2)^2}\,\frac{2N(\omega)^{1/2}}{\omega^{1/2}-i+2N(\omega)^{1/2}S(k,\omega)}. \tag{23}$$

$S(k,\omega)$ is the sum of two terms,

$$S(k,\omega)=A(\omega)+B(k,\omega). \tag{24}$$

The lower order terms are independent of N and correspond to the full interaction of an electron with two centers (see Fig. 9). A straightforward calculation gives

$$\begin{aligned}A_0(\omega)=-i\left(\frac{\omega^{1/2}-i}{2\omega}\right)&[2\ln(\omega^{1/2}-i)\\&-\ln(\omega^{1/2})-\ln(\omega^{1/2}-2i)],\end{aligned} \tag{25}$$

$$B_0(k,\omega)=\sum_{n=0}^{\infty}\frac{2n+1}{(2n+1)^2\omega-k^2}\left(\frac{i}{\omega^{1/2}-i}\right)^{2n}. \tag{26}$$

By replacing $S(k,\omega)$ by the sum of these two terms in

Eq. (22), we obtain the first-order approximation which will be examined now.

As the interaction of an electron with two centers is treated in an exact way, the present approximation should give results in agreement with the crude nearest-neighbor approximation. This remark can be checked by calculating $n(E)$ in the vicinity of the value $E=-1$. In this case

$$A_0(E)\simeq-(|E|^{1/2}-1)\ln||E|^{1/2}-1| \\ -\tfrac{1}{2}i\pi||E|^{1/2}-1|, \quad (27)$$

$$B_0(k,E)\simeq\tfrac{1}{2}\pi||E|^{1/2}-1|\tanh(\tfrac{1}{2}\pi k) \\ \times\sin(k\ln||E|^{1/2}-1|) \\ -\tfrac{1}{2}i\pi(|E|^{1/2}-1)\cos(k\ln||E|^{1/2}-1|). \quad (28)$$

The function $B_0(k,E)$ is a function which oscillates strongly and it is easy to show that its contribution to the calculation of $n(E)$ for small values of $|E+1|$ is negligible. In this approximation, we get

$$n(E)=N^2\,(2||E|^{1/2}-1|[1-2N\ln||E|^{1/2}-1|]^2)^{-1}. \quad (29)$$

This expression has a form which is not very different from Eq. (12) since both expressions are nearly proportional to $N^2/||E|-1|$ except at the singularity point. Moreover, we verify easily that

$$\int_{-4}^{0} n(E)dE=N, \quad (30)$$

a result which was expected *a priori.*

In this approximation, the function $n(E)$ retains a singularity for $E=-1$ and also, as can be easily shown, for $E=0$. This unsatisfactory behavior shows that our method can only be applied in the low-density region. However, in its range of validity, it gives fairly good results as it appears by comparison of our results, calculated for $N=\frac{1}{3}$ and plotted in Fig. 10 with the exact calculations of Fig. 1. Thus for low values of the density of impurity centers N, this method seems to lead to realistic approximations[6] and therefore can be used to study more complicated problems.

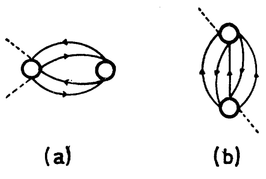

FIG. 9. Diagrams representing $S_0(k,\omega)=A_0(\omega)+B_0(k,\omega)$: (a) $A_0(\omega)$; (b) $B_0(\omega)$.

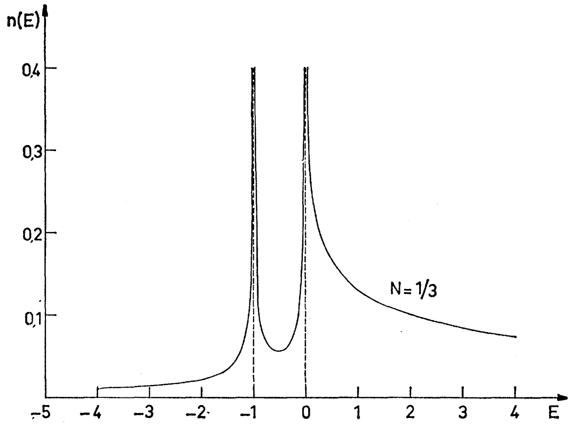

FIG. 10. The density of states obtained for $N=\frac{1}{3}$ by using the "self-propagator" method to the lowest order approximation.

IV. CONCLUSION

The motion of an electron in a potential produced by random atoms can be studied by perturbation theory but in different ways. When the density of atoms is large, the "Brueckner method" seems adequate. On the contrary, if the atoms are dilute, good results can be obtained by using the "self-propagator" method which has been described in the preceding section.

Now in order to deal with practical questions, two main problems remain to be solved. First, we need new approximations which could be valid both for low and high densities. For this purpose, it is necessary to take into account, in an accurate way, the interaction of an electron with the nearest atoms as well as the interaction with distant atoms. On the other hand, the correlation effects which have been neglected here are rather important in the low-density limit and must be properly treated. In principle, these problems can be easily solved by perturbation theory, but difficulties arise from our requirements of convergence and simplicity: An approximation must be both realistic and easy to compute. Of course, the new mathematical models would find a wide range of applications in the study of random processes such as the conductivity of electrons in impurity bands, or the electrical properties or liquids.

ACKNOWLEDGMENTS

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[6] However, for $E\leq 4$, the approximation breaks down completely and in this domain our approximate Green's function has a real role which is spurious.