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# *STRUCTURE OF THE ENERGY SPECTRUM OF IMPURITY BANDS IN DISORDERED SOLID SOLUTIONS*

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A study is made of the structure of the impurity bands in the energy spectrum of elementary excitations in disordered solid solutions at small concentrations. The systematics of the states corresponding to an impurity band are studied. The behavior of the spectral density near singular points is ascertained, and the exact form of the concentration broadening of the levels is determined in limiting cases.

THE structure of the energy spectrum is a central and hitherto unsolved problem of the quantum theory of the condensed state of systems which do not possess spatial periodicity. Disordered solid solutions are one example of systems of this sort. As will be shown below, the problem of the energy spectrum of the excitations in a disordered solid solution can be rather fully investigated in the case of a small concentration of impurities. If, as is always the case, the spectrum of excitations of a given type (phonon, electronic, spin, and so on) has a band structure, the addition of disordered impurities leads, on one hand, to increases of the widths and changes of the spectral density in the bands, and on the other hand to the possibility of the appearance of new impurity bands. These will appear when an individual impurity atom in an infinite crystal causes the appearance of an isolated local level.

For the case of the phonon spectrum this question has been investigated in papers by the author [1,2] and by the author and Stepanova.[3] The method developed there is essentially much more general (as was pointed out in [2]), but since the exposition was not given in the terms that have now become standard, and the results were formulated concretely for the phonon spectrum, these results have evidently remained little known.

In the present paper the structure of an impurity band of excitations at small concentrations of the impurity is studied under extremely general assumptions. In the first section we obtain and study in general form results associated with the structure of the impurity band as a whole. The second section gives the solution of the more complicated problem of the behavior of the spectral density near singular points in an impurity band, and the development of an exact theory of the spreading of the levels with increasing concentration. These questions were not dealt with at all in the papers cited [1-3].

## 1. THE STRUCTURE OF THE SPECTRUM

1. Statement of the Problem. If $\hat{H}_0$ is the Hamiltonian of a given type of quasi-particles in an ideal crystal and $U_0$ is the operator for the local perturbation caused by one impurity center at the origin of coordinates, the Hamiltonian of the quasi-particles in the crystal with impurities is of the form

$$\hat{H} = \hat{H}_0 + \sum_j \hat{T}_{\mathbf{r}_j} \hat{U}_0, \tag{1}$$

where $T_{\mathbf{r}}$ is the operator which shifts the coordinate of the impurity center by the vector $\mathbf{r}$. The points $\mathbf{r}_j$ are random and only their probability law is given: if c is the concentration of impurities, the probability that two particles are at the points $\mathbf{r}_1$, $\mathbf{r}_2$ is $c^2 W(\mathbf{r}_2 - \mathbf{r}_1)$; the probability that three particles are at the points $\mathbf{r}_1$, $\mathbf{r}_2$, $\mathbf{r}_3$ is $c^3 W(\mathbf{r}_2 - \mathbf{r}_1, \mathbf{r}_3 - \mathbf{r}_1)$; and so on. Thus for $|\mathbf{r}_i - \mathbf{r}_k| \to \infty$ the correlation functions $W \to 1$.

While the wave functions of the operator (1) depend essentially on the concrete distribution of the impurity atoms and it has no meaning to speak of their average values, arbitrary quantities of the type $\mathrm{Sp}\,\Phi(\hat{H})/N$ are "self-averaging," i.e., have reliable values for an infinite crystal. In particular this is true of the spectral density

$$\nu(E, c) = \mathrm{Sp}\,\mathrm{Im}\,\hat{G}/\pi N, \quad \hat{G} = (E - \hat{H})^{-1}, \quad E = E - i0 \tag{2}$$

(N is the number of cells in the crystal, $N \to \infty$; in what follows the volume of a cell is taken to be unity).

Our problem is to determine $\nu(E, c)$. It turns out that for the impurity bands the results can be formulated in rather general terms not connected with the concrete nature of the quasi-particles.

Let $E_0$ be a local level in the case of one impurity center ($\hat{H}_1 = \hat{H}_0 + \hat{U}_0$). The presence of other impurity centers at distances $\mathbf{r}_1, \mathbf{r}_2, \ldots$ from the given one leads to shift and splitting of this level, $E_i = E_0 - \epsilon_i$, and in the case of an infinite number of randomly distributed impurity centers to the production of an entire band in the spectrum—an impurity band. It is obvious that the level shifts $\epsilon_i$ will decrease rapidly with the distance to the impurity center nearest to the one considered. Therefore the spectral density in the neighborhood of the point $\epsilon = 0$ ($\epsilon = E_0 - E$) is mainly determined by large distances between impurity centers, and the density far from this point, by small distances. At large distances, of the order of the mean distance between centers, $\bar{r} \sim c^{-1/3}$, the positions of individual levels are determined by the entire configuration of the impurities, which leads to a concentration broadening of the main level $\epsilon = 0$. In the limit of small concentrations $c \to 0$ the point $\epsilon = 0$ is a singular point of the spectral density $\nu(\epsilon, c)$.

If two impurity atoms are a small distance apart, then owing to the discreteness of the possible positions of the impurity atoms the corresponding levels must also be discrete. The interactions with distant impurity centers, however, leads to a concentration broadening of these levels, just as it does for the level $\epsilon = 0$. Therefore we shall begin with the study of the structure of an impurity band as a whole, which can be carried out rather simply, and shall then go on to the exact theory of the concentration broadening of levels.

2. *Structure of an Impurity Band as a Whole. Limits of Applicability of the Method of Expanding in Powers of the Concentration.* A general idea of the structure of the spectrum of an impurity band as a whole can be obtained by means of the method of expanding in powers of the concentration. [2,3]

The majority of thermodynamic quantities for the elementary excitations can be represented in the form

$$\varphi(c) = \int \nu(E, c)\, \Phi(E)\, dE = \operatorname{Sp} \Phi(\hat{H}) / N,$$

$$\varphi_0 = \operatorname{Sp} \Phi(\hat{H}_0) / N, \tag{3}$$

where the function $\Phi(z)$ is subject only to restrictions of a very general character. We introduce the quantities

$$\varphi_1 = \operatorname{Sp}[\Phi(\hat{H}_1) - \Phi(\hat{H}_0)], \quad \varphi_2^{\mathbf{r}} = \operatorname{Sp}[\Phi(\hat{H}_2^{\mathbf{r}}) - \Phi(\hat{H}_0)], \tag{4}$$

where $\hat{H}_1, \hat{H}_2^{\mathbf{r}}, \ldots$ are the respective Hamiltonians of the form (1) for the presence of one, two, or more impurity centers.1)

By means of the quantities $\varphi_1, \varphi_2^{\mathbf{r}}, \ldots$ we can construct an expansion of the functional $\varphi(c)$ in powers of $c$:

$$\varphi(c) = \varphi_0 + c\varphi_1 + \frac{c^2}{2} \sum_{\mathbf{r}} W(\mathbf{r}) (\varphi_2^{\mathbf{r}} - 2\varphi_1) + \ldots \tag{5}$$

Equation (5) has a rather obvious physical meaning, and follows from direct calculation:

$$\left.\frac{\partial \varphi}{\partial c}\right|_{c=0} = \lim \frac{\varphi(\Delta c) - \varphi(0)}{\Delta c} = \lim_{N \to \infty} \frac{\operatorname{Sp}[\Phi(\hat{H}_1) - \Phi(\hat{H}_0)] / N}{1 / N} = \varphi_1,$$

$$\left.\frac{\partial^2 \varphi}{\partial c^2}\right|_{c=0} = \lim_{N \to \infty} \frac{\overline{\operatorname{Sp}\{\Phi(\hat{H}_2^{\mathbf{r}}) - \Phi(\hat{H}_0)\} / N}}{1 / N^2} = \sum_{\mathbf{r}} W(\mathbf{r}) \{\varphi_2^{\mathbf{r}} - 2\varphi_1\}.$$

It is obvious that $\varphi_2^{\mathbf{r}} \to 2\varphi_1$, and this has been used in the second of these formulas. We do not write out the terms proportional to $c^3, \ldots$, since they are obtained in just as elementary a way (cf. [3]).

For the case of a phonon spectrum explicit expressions for the functionals $\varphi_n$ have been obtained in [3]. The contribution to $\varphi(c)$ from the impurity band is, however, quite elementary in form in the general case.

Let $\Phi(z)$ be different from zero only for $z$ lying inside the energy range of the impurity band; then, as follows from the definition (4),

$$\varphi_0 = 0, \qquad \varphi_1 = \Phi(E_0),$$

$$\varphi_2^{\mathbf{r}} = \Phi(E_0 - \varepsilon_1(\mathbf{r})) + \Phi(E_0 - \varepsilon_2(\mathbf{r}))$$

and so on. The quantities $\epsilon_1(\mathbf{r})$ and $\epsilon_2(\mathbf{r})$ are the shifts of the energies of the split level $E_0$ when there are two impurity centers at the distance $\mathbf{r}$ apart. Always hereafter, except when a special statement is made, we shall measure energies from the main local impurity level $E_0$ ($\epsilon = E_0 - E$). Then Eq. (5) takes the form

$$\varpi(c) = \int \nu(\varepsilon, c)\, \Phi(\varepsilon)\, d\varepsilon = c\Phi(0) + \frac{c^2}{2} \int w(\mathbf{r}) \{\Phi(\varepsilon_1) + \Phi(\varepsilon_2) - 2\Phi(0)\}\, d\mathbf{r} + \ldots$$

$$(\varepsilon_i(\mathbf{r})|_{r \to \infty} \to 0). \tag{6}$$

We have gone over from the sum over $\mathbf{r}$ in Eq. (5) to an integral and have introduced instead of the discrete quantities $W_{\mathbf{r}}$ a distribution $w(\mathbf{r})$, which has $\delta$-function peaks at the lattice sites. At large distances $r$ one may obviously neglect this structure of $w$ and simply set $w(\mathbf{r}) = 1$.

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1)As was shown in [1], expressions of the type (3) are finite in spite of the fact that for each separate term $\operatorname{Sp}\Phi(\hat{H}) = \infty$.

For a sufficiently smooth function $\Phi(z)$ the expansion (6) converges rapidly and is quite effective for the calculation of $\varphi(c)$. According to Eq. (2) the function $\Phi$ for the spectral density $\nu(\epsilon, c)$ is the imaginary part of the resolvent operator $\hat{G} = (E - \hat{H})^{-1}$. This means that $\Phi(\epsilon_j) = \operatorname{Im} \pi^{-1}(\epsilon - \epsilon_j - i\Gamma_0)$, where $\Gamma_0$ is the "bare" damping owing to the interaction in the ideal crystal. If we neglect this damping, then $\Phi(\epsilon_j) = \delta(\epsilon - \epsilon_j)$ and the formula (6) gives for the spectral density in the impurity band

$$\nu(\varepsilon, c) = c\delta(\varepsilon) + c^2\psi(\varepsilon) + \ldots;$$

$$\psi(\varepsilon) = \frac{d}{d\varepsilon}(\Omega_1 + \Omega_2), \qquad \Omega_j(\varepsilon) = -\int\limits_{\varepsilon_j(\mathbf{r}) > \varepsilon} w(\mathbf{r})\, d\mathbf{r}. \tag{7}$$

For small values of $\epsilon$, i.e., for large distances $\mathbf{r}$, $w(\mathbf{r}) = 1$. If for simplicity we assume that the interaction with the impurities is spherically symmetric, i.e., if we set $\epsilon_i = \epsilon_i(r)$, then

$$\psi(\varepsilon) = -\frac{4\pi}{3}\frac{d}{d|\varepsilon|}(r_1^3 + r_2^3),$$

where $r_i = r_i(\epsilon)$ is the root of the equation $\epsilon_i(r_i) = \epsilon$. For example, if $\epsilon(r) \sim r^{-k}$, then $\nu(\epsilon, c) \sim c^2 |\epsilon|^{-(3/k+1)}$. For the exponential law of decrease $\epsilon(r) \sim e^{-\alpha r}$ we have $\nu(\epsilon, c) \sim c^2 |\epsilon|^{-1} \ln^2 |\epsilon|$.

The energy-level shifts corresponding to the average distance $\bar{r} = c^{-1/3}$ between impurities are of the order $\epsilon \sim \epsilon(r) \sim \epsilon(c^{-1/3})$. Therefore the expansion (7) is valid as long as $|\epsilon| \gg |\epsilon(c^{-1/3})|$ and the contributions from "collisions" of higher order than binary between the impurity centers are small. Inside the region $|\epsilon| \lesssim |\epsilon(c^{-1/3})|$, where all of the distances between impurities are of the same order $\bar{r} \sim c^{-1/3}$, the terms from nonbinary interactions give the main contribution and lead to a concentration broadening of the level $\epsilon = 0$ ($E = E_0$). An exact theory of the concentration broadening of a level will be given in later sections of this paper. We can, however, make some simple estimates in a quite elementary way.

Owing to the rapid decrease of the local perturbation $U_0(r)$ the random shift $\epsilon$ of the level is determined in order of magnitude by the distance $r$ to the nearest impurity center, $\epsilon = \epsilon(r)$. For $r \ll \bar{r}$ this assumption is practically exact, since the probability of a triple "collision" of impurity centers is proportional to the next power of $c$ ($c \ll 1$). For $r \ll \bar{r}$ the estimate is valid only in order of magnitude. If $r = r(\epsilon)$ is the root of the equation $\epsilon(r) = \epsilon$, then $V = V(\epsilon) = (4\pi/3)r^3(\epsilon)$ is the volume of the region of space in which $|\epsilon(r)| > |\epsilon|$. At large distances we can obviously neglect the discreteness of the possible positions of the impurity centers (the discreteness of the lattice), and also the correlations between them, i.e., we can suppose that the probability that the nearest impurity center is in the volume $dV$ is $c\,dV$. This means that the probability that the nearest impurity center is in a spherical shell of radius $r = r(\epsilon)$ is

$$p(\varepsilon)\, d\varepsilon = e^{-\Omega} d\Omega, \qquad \Omega = cV(\varepsilon) = \tfrac{4}{3}\pi c r^3(\varepsilon). \tag{8}$$

It is obvious that $p(\epsilon)$ is the desired spectral density for small $\epsilon$, normalized to one impurity atom, i.e., $\nu(\epsilon, c) = cp(\epsilon, c)$, $[p(\epsilon) = p(\epsilon, c)]$,

$$p(\varepsilon) = ce^{-cV(\varepsilon)} |dV(\varepsilon)/d\varepsilon|. \tag{9}$$

Thus for the power law $\epsilon(r) \sim r^{-k}$, $V(\epsilon) = (U_1/\epsilon)^{3/k}$ we have

$$\nu(\varepsilon, c) = c^2 A |\varepsilon|^{-(3/k+1)} \exp\{-c|U_1/\varepsilon|^{3/k}\}, \qquad A = 3k^{-1} U_1^{3/k}. \tag{9a}$$

As can be seen from Eq. (9), the width of the maximum of $p(\epsilon)$, i.e., the value of the concentration broadening $\Delta$, can be found from the condition $cV(\Delta) \sim 1$, i.e., $\Delta \sim \epsilon(c^{-1/3})$. In the case of (9a) this gives $\Delta \sim U_1 c^{k/3}$.

For $\epsilon(r) \sim \xi_0 e^{-\alpha r}$ we have $V(\epsilon) \sim \alpha^{-3} \times \ln^3 |\xi_0/\epsilon|$, and our estimate for the width $\Delta$ is given by $\ln(\xi_0/\Delta) \sim \alpha c^{-1/3}$. As we shall see, all of these results remain qualitatively correct in the exact theory.

The estimates just given were for small $\epsilon$, i.e., distances $r \gg 1$. For sufficiently large values of $\epsilon$, corresponding to distances $r \sim 1$, we must take into account the fact that the values of $\mathbf{r}$ are discrete [i.e., that $w(\mathbf{r})$ has sharp peaks at the lattice sites], and use the general formula (6), which we now write in the form

$$\int \nu(\varepsilon, c)\, \Phi(\varepsilon)\, d\varepsilon = c\Phi(0) + \frac{c^2}{2}\sum_{\mathbf{r}} W(\mathbf{r})\, \{\Phi(\varepsilon_1(\mathbf{r})) + \Phi(\varepsilon_2(\mathbf{r})) - 2\Phi(0)\} + \ldots \tag{10}$$

A literal application of this formula with a finite number of terms would mean that each point $\epsilon_{1,2}(\mathbf{r})$, corresponding to a discrete value of $\mathbf{r}$, would be a discrete level of the impurity band of "intensity" $c^2$ [i.e., it would give a contribution $c^2 \delta(\epsilon - \epsilon(\mathbf{r}))$ in $\nu(\epsilon, c)$]. The point $\epsilon = 0$ is a limit point of condensation of these levels. On the other hand, each discrete level $\epsilon_{1,2}(\mathbf{r})$ is a limit point for the levels $\epsilon(\mathbf{r}_1, \mathbf{r}_2)$ which correspond to triple "collisions" of the impurities and are of "intensity" $c^3$, and so on (see Fig. 1, a). As we have seen, however, the interaction with distant

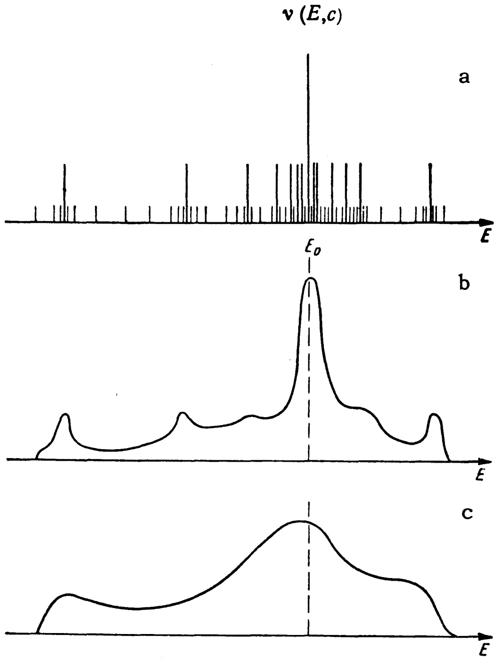

FIG. 1

impurities [inclusion of which is beyond the scope of the approximation (7)] leads to a concentration broadening of each discrete level $\epsilon(\mathbf{r})$. Therefore the picture of a "fine structure" of the band, consisting of a series of separated maxima, is preserved only in the energy range where the distance between adjacent levels satisfies $\delta\epsilon \gg \Delta$ ($\Delta$ is the width of the concentration broadening). Since the volume $V(\epsilon)$ is the number of levels with energies $\epsilon_j > \epsilon$, the distance between adjacent discrete levels can be determined from the condition $\delta\epsilon dV(\epsilon)/d\epsilon \sim 1$. Thus a fine structure of the band exists for

$$\varepsilon\,(c^{-1/3})\; dV\,(\varepsilon)/d\varepsilon < 1.$$

For example, with the power law $\epsilon(r) \sim r^{-k}$, $V(\epsilon) = (U_1/\epsilon)^{3/k}$, we have $\Delta \sim U_1 c^{k/3}$, and the condition for resolvability of the maxima is $\epsilon > U_1 c^{k^2/3(k+3)}$.

As the concentration is increased the maxima gradually merge and the fine structure of the band disappears (see Fig. 1, b, c).

## 2. THEORY OF CONCENTRATION BROADENING OF LEVELS

1. General Considerations and Estimates. We shall suppose for simplicity that the perturbation $U_0$ is a centrally symmetric potential $U_0(r) < 0$ ($\int |U_0| r^2 dr < \infty$), which yields at least one local level $E_0$. In the simplest case the Hamiltonian of a quasi-particle in the ideal crystal $[\hat{H}_0 = E(\hat{k})]$ is $E(\mathbf{k}) = \hat{k}^2/2\mu = -\Delta/2\mu$ ($\hbar = 1$). The case of a general form of the perturbation $U_0$ and an arbitrary periodic dispersion law $E(\mathbf{k})$ can be studied in just the same way, but the calculations are more cumbersome. Accordingly we set

$$\hat{H} = \hat{k}^2/2\mu + \sum_j U(|\mathbf{r} - \mathbf{r}_j|). \tag{11}$$

For sufficiently large distances between the impurity centers the level shifts $\epsilon_j$ consist of two terms: $\epsilon_j = \epsilon_j^{(1)} + \xi_j$; $\epsilon_j^{(1)}$ is the "classical" part associated with the general lowering of the potential in the neighborhood of a given center owing to the action of the others; if one of the centers is at the origin, the random lowering of the potential is[2]

$$\varepsilon^{(1)} = \sum_{r_j \neq 0} U(r_j). \tag{12}$$

The "quantum" or "wave" part $\xi_j$ is the relative shift of the local level in the given potential well $U(r)$. This shift is caused by overlapping of the wave functions of the local states associated with the individual impurity centers. Since the wave functions of the local states fall off exponentially, we have in order of magnitude $\xi_i \sim \xi(r) \sim \xi_0 \exp(-\alpha r)$, where $1/\alpha$ is the radius of the local state and $r$ is the distance to the nearest impurity atom.

Therefore there are two possible cases: if at distances $r \sim c^{-1/3}$ the potential $U(r)$ falls off more slowly than $e^{-\alpha r}$, the entire picture is determined by the random "classical" displacement of the bottom of the well,

$$\varepsilon_i = \sum_j U(r_j).$$

For short-range forces $U(r) \ll e^{-\alpha r}$, on the other hand, everything is determined by the quantum shift of the levels, $\xi(r)$.

We shall study each of these cases separately. Before going on to the exact theory, however, we call attention to one simple fact which follows from the estimate (8). In the classical case $\epsilon(r) = -U(r) > 0$, and therefore the entire distribution lies in the region $\epsilon > 0$ ($E < E_0$). In the quantum case two impurity centers a distance $r$ apart give a symmetrical splitting of the level $\epsilon = 0$, so that there are two collective states with the energies

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[2] The potential in the neighborhood of the point $r = 0$

$$\sum_j U(|\mathbf{r}_j - \mathbf{r}|) = U(r) + \sum_{r_j \neq 0} \{U(r_j) + (\mathbf{r}\nabla)\, U_j + \dots\}$$

contains in addition to the quantities $U(r_j)$ a deformation part $(\mathbf{r}\nabla)\, U_j$, but for $r_j \gg 1$ this part is small in comparison with $U(r_j)$.

$$\varepsilon_{1,2} = \pm \xi(r), \qquad \xi(r) = \xi_0 e^{-\alpha r}.$$

Thus the spectral density is different from zero on both sides of the point $\epsilon = 0$ (see Fig. 2). Therefore the "quantum" contribution to the energy spectrum for $\epsilon < 0$ ($E > E_0$) is important even when it is small.

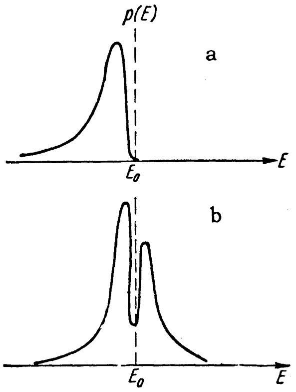

FIG. 2. Concentration broadening of the level $E_0$: a – "classical" case; b – "wave" case.

2. Exact Theory of Concentration Broadening in the Classical Case. In the classical case the random shift of the level is of the form

$$\varepsilon = \sum u_i, \qquad u_i = -U(r_i) > 0, \tag{13}$$

where the $u_i$ are independent random quantities. If the crystal contains N cells, the probability $w(u)$ of the inequality $u_i > u$ is the ratio of the volume $V(u)$ introduced earlier to the entire volume of the crystal:

$$w(u) = V(u)/N, \qquad V(u) = \frac{4\pi}{3} r^3(u), \quad -U(r) = u. \tag{14}$$

The total number of impurity centers is $n = cN$. Therefore the average value $\overline{\epsilon}$ is

$$\overline{\varepsilon} = cN \int_0^N u \frac{dV}{N} = -c \int_0^\infty U(\mathbf{r})\, d\mathbf{r} = c\varepsilon_0,$$

$$\varepsilon_0 = -4\pi \int_0^\infty r^2\, U(r)\, dr. \tag{15}$$

As can be seen from Eq. (15) the average level displacement $\overline{\epsilon} = c\epsilon_0$ for small c is of course much larger than the interaction $U(c^{-1/3})$ at the average distances which determine the broadening.

To determine the probability density $p(\epsilon)$ we construct the generating function

$$F(z) = \overline{e^{-\varepsilon z}} = \int_0^\infty p(\varepsilon)\, e^{-\varepsilon z}\, d\varepsilon.$$

Using the fact that the $u_i$ are independent, we have

$$F(z) = \lim \prod_j \overline{(e^{-u_j z})_N} = \lim_{N\to\infty} \left( \int_0^N e^{-uz} dV/N \right)^{cN}$$

$$= \lim \left( 1 - \int_0^\infty (1 - e^{-zu})\, dV/N \right)^{cN} = e^{-c\varphi(z)},$$

$$\varphi(z) = \int_0^\infty (1 - e^{zU(r)})\, 4\pi r^2\, dr \equiv z \int_0^\infty e^{-zu} V(u)\, du. \tag{16}$$

We note that for $z = -1/kT$ the function $\varphi(z)$ has the meaning of the first virial coefficient in a gas of particles with the pair-interaction energy $U(r)$. Accordingly

$$\int_0^\infty p(\varepsilon)\, e^{-\varepsilon z}\, d\varepsilon = e^{-c\varphi(z)}, \tag{17}$$

from which we have by the inversion formula[3)]

$$p(\varepsilon) = \frac{1}{2\pi i} \int_{-i\infty+0}^{i\infty+0} e^{\varepsilon z - c\varphi(z)}\, dz. \tag{18}$$

Let us consider the case of a power-law decrease of the potential at large distances, $U(r) \sim r^{-k}$, or in other words $U(V) = -U_1 V^{-k/3}$, $U_1 > 0$, i.e., according to Eq. (10), $u = U_1 V^{-k/3}$, $V(u) = (u/U_1)^{-3/k}$.

For $z \gg U_1^{-1}$ the behavior of $\varphi(z)$ is determined by the decrease of $u(V)$ at large distances (i.e., $V \gg 1$), while for $z \ll U_1^{-1}$ $\varphi(z)$ contains a term coming from the integration of the potential at small distances:

$$\varphi(z) = \begin{cases} \gamma z^{3/k} + z\varepsilon_0, & z \lll \varepsilon_0^{-1}, \qquad \overline{\varepsilon} = c\varepsilon_0, \quad \varepsilon_0 \sim U_1 \\ \gamma z^{3/k}, & z \ggg \varepsilon_0^{-1}, \qquad \gamma = U_1^{3/k}\,\Gamma(1 + 3/k) \end{cases}. \tag{19}$$

In the range of energies of interest to us, $\epsilon \ll U_1$, the important region for the integral (18) is $z \gg U_1^{-1}$, and therefore

$$p(\varepsilon)\, d\varepsilon = \rho(y)\, dy, \qquad y = c\gamma\varepsilon^{-3/k}; \tag{20}$$

$$\rho(y) = \frac{3}{k} \frac{i}{2\pi y} \int_{-i\infty+0}^{i\infty+0} \exp\{\zeta - y\zeta^{3/k}\} d\zeta, \quad y \ggg c. \tag{20a}$$

Accordingly,

$$p(\varepsilon) = \rho(y) \left| \frac{dy}{d\varepsilon} \right| = \frac{3}{k}\, c\gamma\rho(y)\, \varepsilon^{-3/k-1}. \tag{21}$$

As can be seen from Eq. (21) the function $p(\epsilon)$ is sharply asymmetrical relative to its maximum, which is at the point

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[3)] We note that if in Eq. (18) we expand the integrand in powers of c and interchange the integrations over z and r [using Eq. (16)], we at once get the expansion (7).

$$\varepsilon_m = \left(\frac{c\gamma}{y_m}\right)^{k/3} = U_1 c^{k/3}\left(\frac{\Gamma(1+3/k)}{y_m}\right)^{k/3}, \quad \frac{y_m \rho'(y_m)}{\rho(y_m)} = 1 + \frac{k}{3}.$$

The center of gravity of the distribution lies at the point $\overline{\epsilon} = c\epsilon_0$, and is displaced far from the narrow maximum of width $\Delta \sim U_1 c^{k/3}$, although in the limit $c \to 0$ the entire integrated intensity is concentrated in this maximum.

The expression (20) leads to the same level width as the qualitative formulas (8) and (9), which are similar to Eq. (20) in structure, but the shape of the maximum, which is determined by the function $\rho(y)$, differs from that in Eq. (6) [where $\rho(y)\,dy = e^{-\Omega}d\Omega$, $y = \Omega\Gamma(1 + 3/k)$].

In particular, in the important case $U(r) \sim r^{-6}$, which is characteristic of van der Waals forces, we have in Eq. (21) $3/k = 1/2$, which gives

$$\rho(y) = \frac{2}{\sqrt{\pi}} e^{-y^2}, \quad p(\varepsilon) = \frac{2c\gamma}{\sqrt{\pi}} \varepsilon^{-3/2} \exp\left(-\frac{c^2\gamma^2}{\varepsilon}\right).$$

Although our formula for the spectral density of a level broadened owing to classical concentration broadening has been derived for the ground level $\epsilon = 0$, the derivation remains essentially correct for any discrete level which arises owing to the presence of two (or more) impurity levels located close to each other. In fact, the random lowering of the potential by the action of distant impurities, as found from Eq. (13), does not depend on the number of centers located near the origin which give rise to the given discrete level. This fact also results from the exact calculation.

All of our formulas (16)—(20) can be extended without difficulty to the case of discrete points at which the impurities are located. In this case the quantities $u_i = -U(r_i)$ in Eq. (13) take discrete values corresponding to the discrete points $\mathbf{r}_i$ which are the lattice sites. If in Eq. (14) we introduce instead of the volume $V(u)$ the quantity $N(u)$, the number of lattice sites that lie in that volume (the volume per site is unity), all of the arguments are unchanged, but in Eqs. (13) and (14) $\varphi(z)$ is now determined not by Eq. (16), but by the corresponding sum over discrete points:

$$\varphi(z) = \sum_{\mathbf{r}} (1 - e^{zU(\mathbf{r})}), \qquad U(\mathbf{r}) < 0. \tag{22}$$

We can obtain the form of the function $p(\epsilon)$ near a sufficiently distant discrete point with $\epsilon = -U(r_0)$ if we write the expression $e^{-c\varphi(z)}$ in the approximate form

$$\begin{aligned} e^{-c\varphi(z)} = {} & [1 - c(1 - e^{zU(\mathbf{r}_0)})] \exp\Big\{-c \sum_{\mathbf{r}\neq\mathbf{r}_0} (1 - e^{zU(\mathbf{r})})\Big\} \\ & \cong \exp\Big\{-c\int (1 - e^{zU})\, d\mathbf{r}\Big\} \\ & + c\exp\Big\{zU(\mathbf{r}_0) - c\int(1 - e^{zU})\, d\mathbf{r}\Big\}. \end{aligned} \tag{23}$$

When this is substituted in Eq. (18) the second term in Eq. (23) leads to the former distribution, except that it is shifted by the amount $U(r_0)$ $[p(\epsilon + U(r_0))]$, in agreement with what we have said above.

Our second comment is as follows. The "classical" broadening which we have obtained is due neither to the true damping (i.e., the lifetime) nor to collectivization of the states. Therefore the states remain local states, and this broadening is not connected in any way with the transition probabilities and does not contribute to the mobility of the quasi-particles. We shall return to this matter a bit later.

3. Concentration Broadening in the Quantum (Wave) Case. Let us go on to the study of the opposite limiting case of short-range forces, for which the shifting and splitting of the levels are occasioned only by the overlap of the wave functions.[4] In the case of a large radius of the local state such a situation can in principle arise not only when the potential falls off faster than $e^{-\alpha r}$ ($\alpha^{-1}$ is the radius of the local state), but also if the decrease of $U(r)$ is less rapid, provided the average distances $\overline{r} \sim c^{-1/3}$ are not too large, so that $U(\overline{r}) \ll \xi_0 e^{-\alpha r}$. For simplicity, however, we shall suppose that the potential is a short-range one, i.e., we shall assume for the wave function of a local state

$$\hat{U}_0\psi(\mathbf{r}) = -\beta u(\mathbf{r})(\psi, u),$$

$$(\psi, u) = \int \psi(\mathbf{r})\, u(\mathbf{r})\, d\mathbf{r}, \qquad \int u\, d\mathbf{r} = 1, \qquad \beta > 0,$$

which corresponds to replacing the function $\psi(\mathbf{r})$ inside the narrow potential well $U(r) = -\beta u(r)$ by its mean value in the well $[(\psi, u) = \int U\psi\, dr / \int U\, dr]$. All of the further results can be derived in a much more general case, but these simplest assumptions shorten the calculations.[5]

We start from the equation for the wave functions in the form

$$(\hat{E}(\mathbf{k}) - E)\psi - \beta \sum u^{(j)}(\psi, u^{(j)}) = 0,$$

$$u^{(j)} = u(\mathbf{r} - \mathbf{r}_j), \tag{24}$$

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[4] Strictly speaking, it is with a wave picture that we are concerned, and not with a quantum picture. For example, the spectrum of an impurity band of lattice vibrations contains no quantum characteristics, and the elastic vibrations themselves play the part of wave functions.

[5] In particular, it can be shown that the fundamental equation (31) for the energy levels always holds asymptotically, provided only that $u(r)e^{\alpha r} \to 0$ for $r \to \infty$.

or in the $\mathbf{k}$ representation $[u_{\mathbf{k}}^{(j)} = u_{\mathbf{k}}(\mathbf{r} - \mathbf{r}_j) = u_{\mathbf{k}}e^{-i\mathbf{k}\mathbf{r}_j})$,

$$\psi_{\mathbf{k}} - \beta \sum_j \tau_j \frac{u_{\mathbf{k}}^{(j)}}{E(\mathbf{k}) - E} = 0, \qquad \tau_j = (\psi, u_j). \tag{24a}$$

Taking the scalar product of Eq. (24a) and $u_{\mathbf{k}}^{(i)}$, we get

$$\tau_i - \sum_k J_{ik}\tau_k = 0, \qquad J_{ik} = J(E, \mathbf{r}_i - \mathbf{r}_k),$$

$$J(E, \mathbf{r}) = \beta \int \frac{|u_{\mathbf{k}}|^2 e^{i\mathbf{k}\mathbf{r}} d\mathbf{k}}{E(\mathbf{k}) - E}. \tag{25}$$

The eigenvalues of $\hat{H}$ are determined from the equation

$$D(\delta_{ik} - J_{ik}(E)) = 0. \tag{26}$$

All of the further procedure is based on an analysis of certain limiting properties of the roots of (36) and on the systematics of the eigenvalues of the random operator $\hat{H}$. Because of the local nature of the potential $u(r)$ its Fourier components $u_{\mathbf{k}}$ are constant down to values $k \sim 1$ (the volume of a cell is unity). Therefore for large values of $r$

$$J(E, \mathbf{r}) = \beta |u_0|^2 \int \frac{e^{i\mathbf{k}\mathbf{r}} d\mathbf{k}}{E(\mathbf{k}) - E}, \qquad |u_0|^2 = (2\pi)^{-3}. \tag{27}$$

Furthermore, for large $\mathbf{r}$, for which only small values of $\mathbf{k}$ are important, in the spherically symmetric case $E(\mathbf{k}) = k^2/2\mu$ and we have for $E < 0$

$$J(E, r) = Ae^{-\alpha r}/r, \qquad \alpha^2 = -2\mu E, \qquad A = \mu\beta/2\pi^2. \tag{28}$$

On the other hand, for $\mathbf{r} = 0$ the decrease of $u_{\mathbf{k}}$ for large $\mathbf{k}$ is important:

$$J(E, 0) = \beta \int \frac{|u_{\mathbf{k}}|^2 d\mathbf{k}}{E(\mathbf{k}) - E}. \tag{29}$$

The position of the fundamental isolated local level $E_0$ which arises from one impurity center is in this case determined by the equation

$$1 - \beta \int \frac{|u_{\mathbf{k}}|^2 d\mathbf{k}}{E(\mathbf{k}) - E_0} = 0, \qquad E_0 = -\frac{\alpha^2}{2\mu}. \tag{30}$$

For energies $E = E_0 - \epsilon = -(\alpha^2/2\mu + \epsilon)$ close to $E_0$, the condition (30) shows that the diagonal elements of the determinant (26) are

$$1 - \beta \int \frac{|u_{\mathbf{k}}|^2 d\mathbf{k}}{E(\mathbf{k}) - E_0 + \varepsilon} = -B\varepsilon,$$

$$B = \beta \int \frac{|u_{\mathbf{k}}|^2 d\mathbf{k}}{[\alpha^2/2\mu + E(\mathbf{k})]^2}.$$

Thus for large distances $r_{jk} = |\mathbf{r}_j - \mathbf{r}_k|$ between all of the impurity atoms the secular equation (20) takes the form

$$\begin{vmatrix} \varepsilon & \lambda e^{-\alpha r_{12}}/r_{12} & \lambda e^{-\alpha r_{13}}/r_{13} & \ldots \\ \lambda e^{-\alpha r_{12}}/r_{12} & \varepsilon & \lambda e^{-\alpha r_{23}}/r_{23} & \ldots \\ \lambda e^{-\alpha r_{13}}/r_{13} & \lambda e^{-\alpha r_{23}}/r_{23} & \varepsilon & \ldots \\ \ldots & \ldots & \ldots & \ldots \end{vmatrix} = 0; \qquad \lambda = \frac{A}{B}.$$

Since the volume per impurity atom is $c^{-1}$, we can introduce coordinates $\mathbf{x} = \mathbf{r}c^{1/3}$ and regard the impurity atoms as distributed with uniform probability density $\rho(\mathbf{x}) = 1$ per unit volume in $\mathbf{x}$-space. Finally, introducing the quantity $\alpha c^{-1/3} = t \gg 1$, which is the large parameter of the theory, we have

$$D\left(\eta\delta_{ik} + \frac{e^{-tx_{ik}}}{x_{ik}}(1 - \delta_{ik})\right) = 0, \qquad x_{ik} = |\mathbf{x}_i - \mathbf{x}_k|,$$

$$\eta = \frac{\varepsilon c^{-1/3}}{\lambda} \tag{31}$$

The desired quantity is the density of the distribution of roots of the equation (31) for random distances $x_{ik}$.

Before proceeding to average over the random points $x_i$ we must investigate the systematics of the eigenvalues $\eta$ and the states associated with them. This is in itself an interesting problem, and is necessary for an understanding of the whole situation in disordered systems. An argument which permits a relatively simple development of such a systematics is as follows: the probability that a given impurity atom $\mathbf{x}_0$ has two equally distant nearest neighbors $(x_{01} = x_{02})$, or, more exactly, that these distances differ so slightly that $e^{t(x_{01}-x_{02})} \sim 1$, will be $\sim 1/t$. Therefore in the limiting case we can assume that all of the quantities $x_{jk}$ are such that a coincidence of $x_{jk_1}$, $x_{jk_2}$, ... for neighboring impurity atoms is excluded, so that for $t \to \infty$ expressions of the type of $e^{-t(x_{01}-x_{02})}$ will approach either zero or infinity with probability approaching unity. Meanwhile it is just a coincidence of $x_{jk_1}$, $x_{jk_2}$, ... that leads to special resonance situations, which are particularly characteristic of periodic structures: for example, a chain composed of $n$ equally spaced centers leads to an almost uniform distribution of levels in a band $\Delta\eta \sim e^{-tx}/x$ ($x$ is the distance between the centers), and the corresponding states are completely collectivized. As we shall see, such situations, which in the limiting case are infinitely improbable, are here completely excluded.

The result that will be obtained is as follows: if we introduce the quantity $s = -t^{-1}\ln|\eta| = c^{1/3}\alpha^{-1}\ln|\eta|$, i.e., the energy of the levels on a logarithmic scale, the possible values of the levels $s_j$ are linear combinations of the distances $x_{ik}$ ($s_j = \Sigma a_{ik}x_{ik}$, $a_{ik} = 0, \pm 1, \pm 2$), in which both the number of terms and the coefficients $a_{ik}$ are determined by certain inequalities for the quantities $x_{ik}$. Therefore the spectral density $P(s)ds$ does not contain the concentration, nor any other specific characteristics of the problem, and is a universal function, which is now to be determined.

4. Systematics of the Levels and States. Determination of the Spectral Density. Before formulating the general rules of the systematics of the levels, we shall consider some simple examples. If there are just two impurity centers a distance $x$ apart, then because they are equivalent both states are resonance states. In this case Eq. (31) gives

$$\eta^2 = e^{-2xt}/x^2, \qquad \eta_{1,2} = \pm e^{-tx}/x.$$

The two states $\eta_1$ and $\eta_2$ belong to the centers 1 and 2 to equal extents.

When there are three centers let the distances be $x_{12}$, $x_{23}$, $x_{31}$, arranged in increasing order. Then Eq. (31) is of the form

$$\eta^3 - \frac{\exp\{-2tx_{12}\}}{x_{12}^2}\eta + 2\frac{\exp\{-t(x_{12}+x_{23}+x_{31})\}}{x_{12}x_{23}x_{31}} = 0.$$

Up to infinitesimals of order $e^{-kt}$ $(k > 0)$ this equation has two resonance roots

$$\eta_{1,2} = \pm \exp\{-tx_{12}\}/x_{12},$$

which correspond to "pairing" of the states near centers 1 and 2, and a root

$$\eta_3 = 2\exp\{-t(x_{23} + x_{31} - x_{12})\}/x_{12}x_{23}x_{31},$$

which mainly corresponds to the local state near center $x_3$, slightly "contaminated" with states 1 and 2. If we represent $|\eta|$ in the form $|\eta| = e^{-st}$, we have (to logarithmic accuracy)

$$s_{1,2} = x_{12}, \qquad s_3 = x_{23} + x_{31} - x_{12}. \tag{32}$$

There are several possible cases for four centers (see Fig. 3). For example, if $x_{12}$ and $x_{34}$ are smaller than any of the cross distances between (1, 2) and (3, 4) (namely, $x_{13}$, $x_{23}$, $x_{14}$, $x_{24}$), then

$$\text{a)}\ s_{1,2} = x_{12}, \qquad s_{3,4} = x_{34}, \tag{33a}$$

i.e., there are two pairs of resonance levels, just as if each pair of centers were isolated. Possible cases for other inequalities among the distances are

$$\text{b)}\ s_{1,2} = x_{12}, \qquad s_3 = x_{23} + x_{31} - x_{12}, \\ s_4 = x_{12} + 2x_{34} - x_{23} - x_{31} \tag{33b}$$

(when $x_{12}$ is the smallest of the $x_{jk}$ and $x_{12} + x_{23} + x_{31}$ is the smallest of the sums $x_{ik} + x_{kl} + x_{li}$, $i \neq k \neq l$), and

$$\text{c)}\ s_{1,2} = x_{12}, \qquad s_{3,4} = x_{13} + x_{24} - x_{12} \tag{33c}$$

(when $x_{12} = \min x_{ik}$, $x_{13} + x_{24} = \min(x_{ik} + x_{lm})$, $i \neq k \neq l \neq m$).

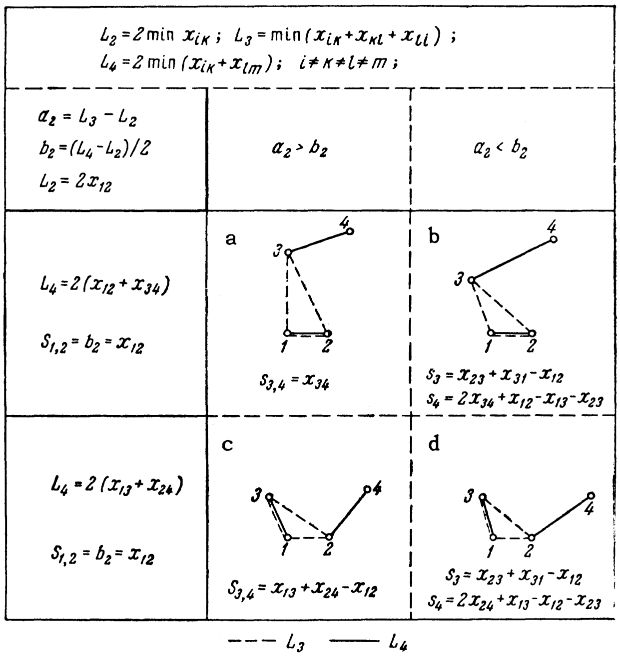

FIG. 3

In case b) the states $s_1$, $s_2$ are collectivized states between centers 1 and 2, and $s_3$ and $s_4$ are "contaminated" local levels at the respective centers 3 and 4. In case c) states $s_1$, $s_2$ are collectivized between centers 1 and 2, and $s_3$, $s_4$ are collectivized mainly between centers 3 and 4, which are not nearest neighbors. Figure 4 illustrates the simplest case of rearrangement of the spectrum for smooth motion of one center relative to two others.

We proceed to the exposition of the general principle of the classification of levels and states.

Let us consider Eq. (31) for any finite number $n$ of impurity centers[6]

$$D\left(\delta_{jk} + \frac{\exp\{-tx_{jk}\}}{x_{jk}}(1 - \delta_{jk})z\right) = 0, \qquad z = 1/\eta.$$

Expansion of this determinant in powers of $z$ gives

$$1 + \sum_{m=2}^{n} \Lambda_m z^m = 0. \tag{34}$$

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[6] Formally, the transition to an infinite crystal must be made in the following sequence: we break the entire volume of the crystal up into a large number of equal parts, which on the average contain $n$ randomly distributed impurity atoms. Then the spectral density of the entire crystal (normalized to unit volume) is the average of the spectral densities of these parts. Since for sufficiently large $n$ the results obtained below for the probabilities are already independent of $n$, we can take the limit $n \to \infty$ in these results.

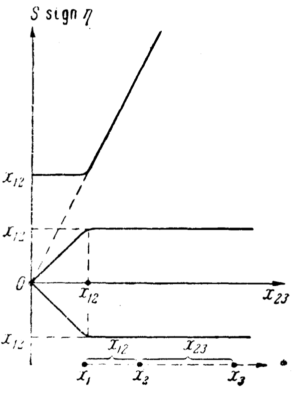

FIG. 4. Positions of levels s as functions of $x_{23}$ for fixed $x_{12}$.

Each of the coefficients $\Lambda_m$ is the sum of all possible terms of the type $e^{-t\mathscr{L}_m}$:

$$\mathscr{L}_m = \sum_{\Gamma} l(\Gamma^{(j)}), \quad \sum j = m.$$

Here $\Gamma^{(j)}$ is the outline of a polygon with j vertices chosen from the points $x_k$, so that no vertex is encountered twice (i.e., the polynomials have no vertices in common), and $l(\Gamma^{(j)})$ is the perimeter of the polygon. If

$$L_m = \min \sum_{\Gamma} l(\Gamma^{(j)}), \qquad \sum_{j} = m, \tag{35}$$

then in the limiting case

$$t^{-1} \ln |\Lambda_m| = -L_m.$$

If $|\eta| = e^{-ts}$, then $|z| = e^{ts}$, and consequently each term in Eq. (34) is of the form

$$t^{-1} \ln |\Lambda_m z^m| = ms - L_m. \tag{36}$$

For an arbitrary s all of the terms are small quantities of different orders (in the sense of $e^{-kt}$), and the entire determinant is determined by a single term $t^{-1} \ln D(s) = \max(ms - L_m)$. Therefore Eq. (34) can have a solution only when as s is varied the exponents in some two terms of the series are equal (such equality for a larger number of terms is infinitely improbable). Let us consider the sequence of exponents in Eqs. (34) and (36):

$$0,\ 2s - L_2,\ 3s - L_3, \ldots$$

If we introduce the notations $L_{m+1} - L_m = a_m$, $L_{m+2} - L_m = 2b_m$, then from the geometrical meaning of the quantities $L_m$ we have the inequalities

$$a_m + a_{m+1} = 2b_m > 0, \qquad b_{m+1} > b_m. \tag{37}$$

As s increases, starting from 0, the first root occurs at $2s = L_2$; this root corresponds to the two levels

$$\eta_{1,2} = \pm |\eta|, \qquad s = -\ln |\eta| / t.$$

As s increases further, according to the inequalities (37) successive roots occur at points determined either by the equation

$$ms - L_m = (m+2)s - L_{m+2}, \qquad 2s = 2b_m, \tag{I}$$

or by the equation[7]

$$ms - L_m = (m+1)s - L_{m+1}, \qquad s = a_m. \tag{II}$$

The first case occurs when $b_m < a_m$ and corresponds to the appearance of a pair of equal roots of Eq. (I). There are two corresponding collectivized states with energies $\eta_{1,2} = \pm |\eta|$.

In the second case, which occurs for the reversed inequality $a_m < b_m$, there are different roots $s_m$ instead of the two equal roots of (I). To each such root there corresponds a local state at one of the centers with a definite sign of the energy.

The equations we have obtained lead to a constructive geometrical systematics of the roots $s_m$. This systematics is particularly simple in the one-dimensional case, which is considered in the appendix.

In the investigation of the equations (I) and (II) it is important that the quantity $L_m = \min \mathscr{L}_m$ cannot involve contours $\Gamma^{(2k)}$ with even numbers of vertices for $k > 1$. In fact, $l(\Gamma^{(2k)}) = x_{12} + x_{23} + \ldots + x_{2k,1}$, and for $k > 1$ any such contour can be broken up into a sum of "diangles," i.e., sides without common vertices, with a smaller total perimeter $[2(x_{12} + x_{34} + \ldots + x_{2k-1,2k})]$. Therefore, for example, the most frequent case of equations of type (I) is that in which the difference $L_{2m+2} - L_{2m}$ comes from only one quantity $2x_{j_0k_0}$, which is the smallest segment as compared with all its neighbors (i.e., $x_{j_0k_0} < x_{j_0l}, x_{k_0l}$ for all $l \neq j_0, k_0$). The result is that the corresponding level depends on only one of the distances, $x_{j_0k_0}$, and is insensitive to all the others. Depending on the inequalities satisfied by the $x_{jk}$ for the impurities surrounding the given center, the quantities $s_j$ (which are the energy levels on a logarithmic scale) are determined by one, two, or a larger number of the distances $x_{ik}$. By choosing

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[7] This last result also can be seen from the following simple arguments: the equation for a root s

$$ms - L_m = (m+k)s - L_{m+k}$$

corresponds to an equation for the eigenvalues $\eta$

$$\eta^k = \exp(-t(L_{m+k} - L_m)),$$

and therefore, because $\eta$ is real ($\hat{H}$ is Hermitian), only the cases $k = 1, 2$ are possible.

for each case a suitable numbering of the points $x_i$ we can represent the roots s in the form

$$s = \begin{cases} x_{12} & x_{1l},\ x_{2l} > x_{12};\ l > 2 \\ x_{23} + x_{31} - x_{12} & x_{12} < x_{23},\ x_{31};\ x_{1l} > x_{13};\ x_{2l} > x_{23}; \\ & x_{3l} > x_{23} + x_{31} - x_{12} = s;\ l > 3 \\ \cdots & \cdots \\ \Sigma a_{jk} x_{jk} & a_{jk} = 0,\ \pm 1,\ \pm 2;\quad \Sigma a_{jk} = 1 \end{cases} . \qquad (38)$$

The inequalities which fix the conditions for the realization of each of the possible cases give a region in the configuration space of the $x_j$, and its relative volume determines the probability of such a case. Therefore the probability density for the quantity s is a sum of terms, one for each of the possible cases (38) (with s determined by one, two, or a larger number of neighbors). The resulting rapidly converging series is a sum of positive functions:

$$P(s) = \sum P_n(s), \qquad P_n(s) > 0, \qquad \int P(s)\, ds = 1, \quad (39)$$

and neither the expressions (38) themselves, nor the inequalities which determine the possibility of realizing them, nor the volumes in x space which give the probabilities contain any small parameters or depend on the limiting case of small concentrations. The decrease of the terms $P_n(s)$ in the series (39) is due to the rapid decrease of the relative volumes in x space in which the successive cases are realized. For example, as is shown in the Appendix, in the one-dimensional case the $P_n(s)$ fall off as 1/n! Therefore to good accuracy one can use only the first few terms of this series.

The inequalities in Eq. (38) define respective volumes $\omega_1(x_{12})$, $\omega_2(x_{12}, x_{23}, x_{31})$, . . . which do not contain any other impurity centers besides those on which the values of the levels s depend. The probability of such an event is $e^{-\omega}$. Therefore the probabilities $P_1(s)$, $P_2(s)$, . . . are given by the respective equations

$$P_1(s) = \frac{d}{ds} \int\limits_{x<s} e^{-\omega_1(x)}\, d\mathbf{x} \qquad (x_{12} = x);$$

$$P_2(s) = \frac{1}{2}\frac{d}{ds} \iint\limits_{\substack{x_{12} < x_{23},\ x_{31} \\ x_{23}+x_{31}-x_{12} < s}} \frac{1}{2} e^{-\omega_2(x_{12},\ x_{23},\ x_{31})}\, d\mathbf{x} d\mathbf{x}'$$

$$(x_{13} = x, \quad x_{12} = |\,\mathbf{x} - \mathbf{x}'\,|,\ x_{23} = x'). \qquad (40)$$

The first term $P_1(s)$, which corresponds to the equation $2s = 2x_{12}$, i.e., gives two levels with different signs of $\eta$, arises, as has already been said, when there are no other impurity centers in the spheres of radius $x_{12}$ described around each of the points $x_1$, $x_2$ (see Fig. 5). The volume $\omega_1(x_{12})$ occupied by these intersecting spheres is given by

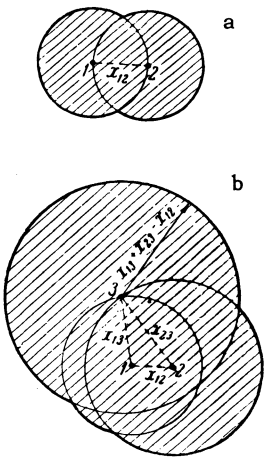

FIG. 5. a – The volume $\omega_1(x_{12})$; b – the volume $\omega_2(x_{12}, x_{23}, x_{31})$.

$$\omega_1(x_{12}) = \frac{9}{4}\pi x_{12}^3 \qquad (x_{12} = s).$$

Therefore the desired probability $P_1(s)$ is [by Eq. (40)]

$$P_1(s) = e^{-9\pi s^3/4}\, 4\pi s^2.$$

The most natural variable is the volume

$$\Omega = \frac{4}{3}\pi s^3 = \frac{4\pi}{3}\frac{c}{\alpha^3}\ln^3\left|\frac{\lambda c^{1/3}}{\varepsilon}\right| .$$

In terms of this variable the distribution $\rho(\Omega)\, d\Omega$ can be written in the form

$$\rho(\Omega) = \sum \rho_n(\Omega), \qquad (41)$$

$$\rho_n(\Omega) > 0, \qquad p(\varepsilon) = \rho(\Omega)\, d\Omega/d\varepsilon;$$

$$\rho_1(\Omega) = e^{-27\Omega/16}. \qquad (42)$$

We note that according to Eq. (42) the first term $P_1(s)$ in the series (39), or the corresponding term $\rho_1(\Omega)$ in the series (41), already gives almost $^2/_3$ of the whole integrated density $[\int \rho_1(\Omega)\, d\Omega = {}^{16}/_{27}]$. On the other hand, since for $\Omega \to 0$ the probability is simply equal to the volume $d\Omega$, i.e., $\rho(0) = 1$, all of the other terms go to zero for $\Omega \to 0$. Finally, for large $\Omega$ ($s \gg 1$) the main contribution comes from configurations in which the nearest neighbor is at the distance $x = s/2$ and the others are at arbitrary distances from each other outside the sphere of radius s/2. This gives $\rho(\Omega)\,|_{\Omega \gg 1} \sim e^{-\Omega/8}$.

The entire sum (39), and also the sum (41), can be divided into two parts:

$$P(s) = P^{\mathrm{I}}(s) + P^{\mathrm{II}}(s) \qquad (\rho = \rho^{\mathrm{I}} + \rho^{\mathrm{II}}).$$

The first term $P^{\mathrm{I}}(s)$ corresponds to the contributions from those $P_n(s)$ which come from solutions of the equation (I) and correspond to states collectivized among several centers and having energies $\eta = \pm|\eta|$. The contribution of these terms to the spectral density $p(\epsilon)$ is symmetric around the point $\epsilon = 0$. A particular one of these terms is $P_1(s)$, which we have already calculated. The second part $P^{II}(s)$ comes from terms $P_n(s)$ which correspond to solutions of Eq. (II), i.e., to states localized near one of the impurity centers. These terms correspond to energies of definite sign and give an asymmetric contribution to the spectral density. Thus the spectral density for $\epsilon > 0$ is given by the expression $P_+(s) = P^I(s)/2 + P_+^{II}(s)$, and for $\epsilon < 0$ it is given by the expression $P_-(s) = P^I(s)/2 - P_-^{II}(s)$.

For $\epsilon = 0$, i.e., $s \to \infty$, $P_+(s)$ and $P_-(s)$ go to zero, i.e., in the pure quantum case the distribution $p(\epsilon)$ has a dip at $\epsilon = 0$, and the maximum of $p(\epsilon)$ in the neighborhood of $\epsilon = 0$ is split (cf. Fig. 2, b).

As can be seen from this analysis, states collectivized among all of the impurity centers, i.e., "smeared out" over the entire volume of the crystal, as happens in periodic structures, have zero probability.

The whole picture of concentration broadening in the quantum case which is constructed above relates to the ground level $\epsilon = 0$. As for the supplementary discrete levels $\epsilon_k \neq 0$ which arise from nearby impurity atoms (cf. Sec. 1, article 2), their "quantum" concentration broadening is determined by trivial formulas of the type of Eqs. (8) and (9), which take into account only the nearest neighbor at distance $r \sim \bar{r}$. This is due to the fact that there is no resonance situation for any level other than $\epsilon = 0$—the potential level of the individual center does not coincide with the total potential of the nearby impurity centers that produce the supplementary level.

The results of this last section are for the case of the wave limit, and are scarcely to be found in actual systems. From this analysis of the situation and of the systematics of the states one can, however, get an idea of the nature of impurity quantum states in disordered systems. The examination of concrete systems, and also of the consequences to which this sort of systematics of the states leads in kinetic phenomena, must be the subject of a separate paper.

## APPENDIX

### CONCENTRATION BROADENING OF A LEVEL IN THE ONE-DIMENSIONAL CASE

The theory of concentration broadening is simplest in the one-dimensional case. The initial equation can be written in the form

$$\psi''(y) + E\psi(y) = -\lambda \sum \psi(y_i)\,\delta(y - y_i).$$

In the case of one perturbing center the local level $E_0$ is $E_0 = -\lambda^2/4$. Choosing the new distance scale $x = cy$ and the energy scale $\eta = (E_0 - E)/c = \epsilon/c$, we get

$$\frac{d^2\psi}{dx^2} - (t^2 + \eta)\,\psi + 2t \sum_i \psi(x_i)\,\delta(x - x_i) = 0,$$

$$t = \frac{\lambda}{2c} \gg 1.$$

Just as before, we can bring the equation for the energy eigenvalues $\eta$ into the form

$$D(\eta) = \begin{vmatrix} \cdots & \cdots & \cdots & \cdots & \cdots \\ \cdots & \eta & e^{-tx_{01}} & e^{-tx_{02}} & \cdots \\ \cdots & e^{-tx_{01}} & \eta & e^{-tx_{12}} & \cdots \\ \cdots & e^{-tx_{02}} & e^{-tx_{12}} & \eta & \cdots \\ \cdots & \cdots & \cdots & \cdots & \cdots \end{vmatrix} = 0.$$

If we renumber the points $x_i$ in increasing order so that

$$y_i = x_{i+1} - x_i > 0,$$

we have

$$x_{j,\,j+k} = |x_{j+k} - x_j| = \sum_{n=1}^{k} y_{j+n}.$$

In this case the outlines $\Gamma^{(p)}$ of polygons with p vertices reduce to doubled segments $x_{i,i+p-1}$:

$$l(\Gamma^{(p)}) = 2(y_i + \ldots + y_{i+p-1}).$$

It is easy to see that the minimum quantity $L_m = \min \mathcal{L}_m$ can involve only segments connecting a pair of points or a set of three neighboring points: $l^{(2)} = y_i$, $l^{(3)} = y_i + y_{i+1}$. Furthermore the sum $L_m = \Sigma l^{(2)} + \Sigma l^{(3)}$ contains segments $l^{(2)}$, $l^{(3)}$ which do not involve common points; i.e., for $y_p$ and $y_q$ appearing in different $l^{(i)}$ we have $|p - q| > 1$.

If as before we introduce the quantity $s = -\ln|\eta|/t$, the systematics of the levels is much simpler than in the three-dimensional case. Collectivized levels $\eta_{1,2} = \pm|\eta|$ occur in cases for which

$$s = \begin{cases} y_0 & (y_1,\ y_{-1} > y_0) \\ y_1 + y_{-1} - y_0 & (y_{-2} > y_{-1} > y_0 < y_1 < y_2,\ y_{-1} < y_0 + y_1). \\ \cdots\cdots & \cdots\cdots\cdots\cdots \end{cases} \tag{I}$$

The nonresonance levels are determined by the formulas

$$s = \begin{cases} 2y_1 & (y_{-1} > y_0 + y_1, \quad y_1 > y_0, \quad y_2 > 2y_1) \\ 2(y_2 - y_1) & (y_{-1} > y_0 + y_1, \quad y_0 < y_1 < y_2 < y_3) \\ \cdots & \cdots\cdots\cdots\cdots \end{cases} \tag{II}$$

and the equivalent expressions obtained by replacing $y_n$ by $y_{-n}$.

The probability $P_1^{\mathrm{I}}$, which is the contribution from the resonance levels $s = y_0$ given by (I), is

$$P_1(s)\,ds = 2e^{-3s}\,ds.$$

Its integrated contribution is

$$\int_0^\infty P_1(s)\,ds = \frac{2}{3}$$

The probability $P_1^{\mathrm{II}}$, which is the contribution of the nonresonance levels $s = 2y_1$, subject to the inequalities (II), is readily verified to be

$$P_2(s) = \frac{1}{2}(e^{-2s} - e^{-3s}).$$

Its integrated contribution is $1/12$.

As a simple calculation shows, the integrated contribution from the terms determined by a chain of inequalities of the type $y_0 < y_1 < y_2 < \ldots < y_n$ falls off as $1/n!$ For large $s$ the overwhelmingly most probable case is that in which the nearest neighbor of the given impurity center is a distance $s/2$ from it, and all of the others are separated from each other by arbitrary distances $\sim 1$. The probability of this is $\sim e^{-s}$.

Coming back from the logarithmic quantity $s = -2c\lambda^{-1}\ln|\eta|$ to the energy $\eta$, we get

$$p_1(\eta) = P_1(s)\frac{ds}{d\eta} = \frac{4c}{\lambda}\eta^{6c/\lambda-1}.$$

For $|\eta| \to 0$ (i.e., $s \to \infty$) we have $P(s) \sim e^{-s}$,

$$p(\eta) \sim \frac{c}{\lambda}|\eta|^{2c/\lambda-1} \qquad (\eta < 0).$$

Thus, in contrast with the three-dimensional case, for which $p(\eta)|_{\eta\to 0} \to 0$, the spectral density $p(\eta)$ has an integrable singularity at the point $\eta = 0$. The fractional number of levels in the interval $(0, \eta)$ is

$$W(\eta) = \int_0^\eta p(\eta)\,d\eta \sim \eta^{2c/\lambda}.$$

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