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Density of States in Aperiodic Solids

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Some fundamental questions concerning densities of states for dynamical systems in aperiodic solids are discussed by way of three examples: (1) Harmonic vibrations in a binary alloy, (2) Impurity scattering of electrons due to short range forces, (3) Virtual localized states near the Fermi level in a metal. The "Friedel sum rule" which connects the density of states in a disturbed system and that in an undisturbed one in terms of the sum of all scattering phase shifts is studied with each example to see how the latter quantities accumulate to produce an extensive nature inherent to that notion to be given to an infinite, thermodynamically stable system. (A kind of spatial fluctuation-dissipation theorem.) Requirements are deduced for the function, analytic as a function of the complex energy variable, whose boundary values on the real axis yield the density of states. It is based on Wigner's R-function which Wigner introduced in connection with nuclear scattering studies many years ago. The CPA theory—its approximation formula to compute the function (which we systematically derive here)—is re-examined from this point of view and is shown to meet such requirements.

Contents

§1. Introduction

Historically, the notion "density of states" was introduced in solid state physics first in connection with the specific heat problem by Debye,[1] who defined the eigenfrequency distribution of vibrations in a lattice as a function

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of the frequency variable ω, $\mathcal{N}(\omega)$, in such a way that the number of the eigen-modes fallen in the range between ω and $\omega+d\omega$ is equal to $\mathcal{N}(\omega)d\omega$, and thus succeeded in explaining the T^3-law of specific heats by means of the long wave-length acoustic approximation for the $\mathcal{N}(\omega)$. A similar introduction was made naturally also for electronic states in metals and semiconductors after the successful development of free-electron theory based on the Fermi statistics by Sommerfeld[2] and other prominent founders of solid states theory. Since then the notion has been used very widely and conveniently without inquiring its logical foundation, such an inquiry being nothing but a peda-gogical interest for the real knowledge about it in vast class of regular, periodic solids supplied from experiments and simulative calculations.[*]

The question "what is a density of states?" has to be (and has actually been) recognized as a real important problem, when aperiodic or disordered solids become interesting objects in solid state researches such as amorphous solids and liquid crystals. Here one meets with a general problem of finding formulas according to which the density of states can be computed. Such formulas quite valid for a dynamical system in periodic lattices we often write in a form of surface integration with respect to a wave-number vector variable k as

$$\mathcal{N}(\omega)=\frac{1}{(2\pi)^3}\int\frac{dS(k)}{|\operatorname{grad}_k\omega(k)|},\qquad(1\cdot1)$$

where $dS(k)$ means a surface element on a constant frequency surface, $\omega=\omega(k)$. (For electronic density of states the frequency variable ω will be re-placed by the energy variable E.) The existence of such surfaces entirely depends on the fact that any eigenmode of the dynamical system in the periodic lattice can be characterized by the wave number, called "dispersion relation". It is obvious that an attempt to apply the formula like $(1\cdot1)$ to aperiodic solids is obscured, because one does not know whether or not the wave-number characterization would be possible for dynamical systems in aperiodic solids. One would suppose that it is rather impossible.

The present writer conjectures that vast class of dynamical systems in aperiodic solids often referred to as "disordered systems" might still be charac-terized by the wave-number concept on the basis of which the formula (1-1) could be reconciled. A necessary alteration would be that the ordinary Brillouin-zone concept must be discarded and replaced by some other concepts to express adequately microscopic structures of the solid under consideration. To develop a convincing theory, however, mathematical obstacles are tre-

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[*] One important mathematical questioning about the basis of a distribution of the eigenfrequencies of sound waves in a continuum is whether its dependence upon the boundary shape of the continuum would become asymptotically negligible against its regular volume dependence (i.e., proportional to the system volume), which was investigated and answered by H. Weyl in 1912.[3]

mendous. The purpose of this article is to make a preliminary consideration before attempting such a theory. We discuss general matters about densities of states by taking the following three examples typical of aperiodic solids:

 (1) Harmonic vibrations in a binary alloy,
 (2) Impurity scattering of electrons due to short range forces,
 (3) Virtual localized states near the Fermi level in a metal.

Considerable investigations have already been published on these examples. Our chief object here is to reconsider them from a viewpoint of the so-called "Friedel sum rule" and its extension which aims to relate, shortly speaking, the density of states and scattering phase shifts, where a major effort will be placed on the question how the phase shift terms accumulate up to contribute to the extensive quantity of the density of states. If this question would be answered with a satisfactory mathematical representation, our starting problem of expressing the density of states in terms of the wave number integration should be resolved. This is based on an intuitive consideration that a wave propagating in a dispersive medium will change its wave number by suffering from continual scatterings receiving shifts of its phase.

 The scope of the present article is as follows: In §§2～4 the Friedel sum rule is discussed in its primitive form in accordance with the above three examples. In §5 the recently developed coherent potential approximation (CPA) is used to express the density of states in a generalized sense of the Friedel sum rule. An application of this scheme is carried out also to these examples. Section 6 is devoted to a special analysis to test the above-mentioned consideration, i.e., the analytic relationship between the wave number and the phase shift for the wave propagation in a dispersive medium with a model of one-dimensional Schrödinger waves. A reference is given in this section from those papers concerning the causality and dispersion relations by Wigner[4] and his successors which seem rarely quoted in the field of solid states but, in the writer's opinion, of great value for the theory of aperiodic solids. In the original scope it was intended to add several more sections to deal with a subject of Schrödinger waves in aperiodic fields as a prototype theory, which we hope to resume on other occasion.

§2.　Harmonic vibrations in a binary alloy[5]

 Consider a system of lattice vibration composed of atoms with a mass M situated in regular, periodic positions denoted by j, interacting with each other through a set of harmonic forces. For simplicity only one direction of polarization is taken into account. Replace n atoms in an arbitrary configuration denoted by $\{j\}$ out of the total N by different kinds of atoms with mass m. The Hamiltonian for this may be written in terms of the phonon operators constructed in the reference of the M-lattice basis (i.e., in terms of the eigen-

modes of a perfect lattice of the mass M-atoms with no isotopic defects). This is given by

$$H = \sum_j \frac{p_j^2}{2M} + \sum_{j,j'} \frac{k_{j-j'}}{2} x_j x_{j'} + \left(\frac{1}{2m} - \frac{1}{2M}\right) \sum_{(j)} p_j^2$$

$$= \sum_\nu \frac{\hbar\omega_\nu}{2}(a_\nu^* a_\nu + a_\nu a_\nu^*)$$

$$+ \frac{1}{4}\left(\frac{M}{m}-1\right)\hbar \sum_{(j)} (\sqrt{\omega_\mu} T_{j\mu})\sqrt{\omega_\nu} T_{j\nu}^*(a_\mu^* + a_\mu)(a_\nu^* + a_\nu) \qquad (2\cdot1)$$

where ω_ν is the eigenfrequency of the perfect M-lattice and $T_{j\nu}$ the matrix element of a unitary matrix of diagonalization connecting the j-th site to the ν-th eigenmode. An introduction of equation of motion to obtain true eigenmodes in the perturbed lattice, in a form of $A^* = \sum_\mu \sqrt{\omega_\mu}(U_\mu a_\mu^* + V_\mu a_\mu)$, leads us to a set of equations for the U's and V's as follows:

$$(\omega - \omega_\mu)U_\mu = (\omega + \omega_\mu)V_\mu$$

$$= \frac{1}{2}\left(\frac{M}{m}-1\right)\sum_{(j)} T_{j\mu} W_j, \qquad (2\cdot2a)$$

$$W_j = \sum_\nu T_{j\nu}^* \omega_\nu(U_\nu - V_\nu), \qquad (2\cdot2b)$$

$$\sum_\nu \omega_\nu(|U_\nu|^2 - |V_\nu|^2) = 1. \qquad (2\cdot2c)$$

Or, if the U's and V's are eliminated from $(2\cdot2b)$ by virtue of $(2\cdot2a)$, an $n \times n$ secular equation may be obtained for a vector W:

$$F(\omega)W = 0, \qquad (2\cdot3a)$$

that is, explicitly

$$\sum_{j'} F_{jj'}(\omega)W_{j'} = 0,$$

where

$$F_{jj'}(\omega) = \delta_{jj'} - \frac{M-m}{m}\frac{1}{N}\sum_\mu \frac{\omega_\mu^2}{\omega^2 - \omega_\mu^2} T_{j\mu} T_{j'\mu}^* \qquad (2\cdot3b)$$

is the (jj')-matrix elements of an $n \times n$ matrix $F(\omega)$. An alternate equivalent presentation of the secular equation may be obtained for a vector $U-V$ in the form

$$(\omega^2 - \omega_\mu^2)(U_\mu - V_\mu) = \left(\frac{M}{m}-1\right)\sum_\nu \rho_{(j)}(\mu-\nu)\omega_\mu\omega_\nu(U_\nu - V_\nu), \qquad (2\cdot3c)$$

where

$$\rho_{(j)}(\mu-\nu) = \sum_{(j)} T_{j\mu} T_{j\nu}^* = \frac{1}{N}\sum_{(j)} \exp\left\{i\frac{2\pi}{N}(\mu-\nu)j\right\} \qquad (2\cdot3d)$$

is the "density projector" defined in the particular configuration $\{j\}$.

We analyze a special case of one defect, $j=1$, in detail. The secular equation of the form (2·3a) is then

$$f(\omega)W_1 \equiv \left(1 - \frac{M-m}{m}\frac{1}{N}\sum_\nu \frac{\omega_\nu^2}{\omega^2-\omega_\nu^2}\right)\cdot\sum_\nu \omega_\nu T_{1\nu}(U_\nu - V_\nu) = 0.$$

Any eigenfrequency is obtainable either from $f(\omega)=0$ or $W_1=0$, where

$$f(\omega) = 1 - \frac{M-m}{m}\frac{1}{N}\sum_\nu \frac{\omega_\nu^2}{\omega^2-\omega_\nu^2}$$

$$= \frac{M}{m} - \left(\frac{M}{m}-1\right)\frac{1}{N}\sum_\nu \frac{\omega^2}{\omega^2-\omega_\nu^2}. \tag{2·4}$$

Every frequency Ω which satisfies $f(\Omega)=0$ is different from any ω_ν of the unperturbed lattice. On the other hand, the one from $W_1=0$ is possible only when Ω is equal to a particular ω_ν for which $U_\nu=1$ and all the rest of U's

$$\boxed{f_N(\omega) = 1 - \frac{M-m}{m}\frac{1}{N}\sum_{\nu>0}^{(N/2)}\frac{\sin^2\frac{\pi\nu}{N}}{\omega^2-\sin^2\frac{\pi\nu}{N}}}$$
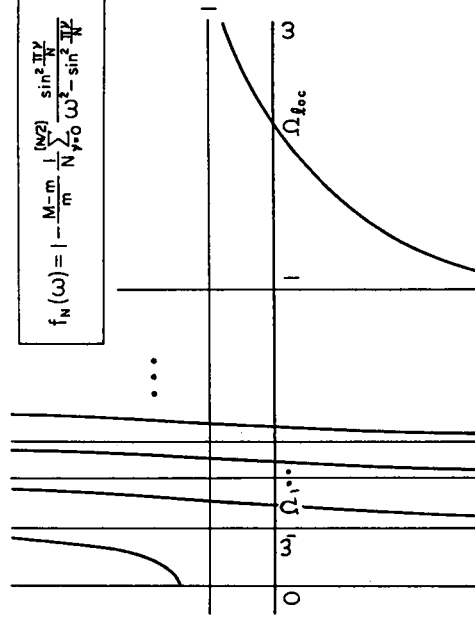

Fig. 1. The characteristic function $f_N(\omega)$ defined in (2·11) for a linear chain harmonic vibration composed of N atoms with one defect of mass $m < M$ (mass of major atoms).

and V's vanish, i.e., the eigenfrequency of the perturbed lattice is unshifted. (See Fig. 1.) In the former case, the normalization condition (2·2c) becomes

$$\left(\frac{M}{m}-1\right)^2 \frac{1}{N}\sum_\nu \frac{\omega\omega_\nu^2}{(\omega^2-\omega_\nu^2)^2}|W_1|^2 = 1,$$

from which

$$|W_1|^2 = \left(\left(\frac{M}{m}-1\right)^2 \frac{1}{N}\sum_\nu \frac{\omega\omega_\nu^2}{(\omega^2-\omega_\nu^2)^2}\right)_{\omega=\Omega}^{-1}$$

$$= \left(\frac{1}{2}\left(\frac{M}{m}-1\right)\cdot\frac{df}{d\omega}\right)_{\omega=\Omega}^{-1}.$$

Therefore, one gets a list of all the eigenmodes in the perturbed lattice:

$$\Omega\ ; f(\Omega) = 0 \quad U_\mu = \frac{1}{\Omega - \omega_\mu} \left(\frac{M - m}{2m} \frac{df}{d\omega}\right)^{1/2}_{\omega = \Omega},$$

$$V_\mu = \frac{1}{\Omega + \omega_\mu} \left(\frac{M - m}{2m} \frac{df}{d\omega}\right)^{1/2}_{\omega = \Omega},$$

$$\Omega\ ; (=\omega_\mu) \quad U_\nu = T_{1\mu}\delta_{\nu\mu}, \quad V_\nu = 0.$$ (2·5)

The density of states for such a finite system may be defined as follows:

$$\mathcal{N}_N(\omega) = \sum_\nu \{\delta(\omega - \Omega_\nu) + \delta(\omega + \Omega_\nu)\}$$

$$= \lim_{s \to 0} \frac{-1}{\pi} \mathrm{Im} \sum_\nu \frac{2\omega}{(\omega + is)^2 - \Omega_\nu^2}.$$ (2·6)

By means of the function $f(\omega)$ defined in (2·4) $\mathcal{N}_N(\omega)$ can be expressed: For the reason that (a) all the zeros of $f(\omega)$ cover all the eigenfrequencies of the perturbed lattice other than those unshifted from the unperturbed one, (b) any simple pole of $f(\omega)$ is identical with one of the ω_ν's, and (c) $f(\omega) \to 1$ as $\omega \to \infty$, we may write

$$f(\omega) = \frac{\prod_\nu (\omega^2 - \Omega_\nu^2)}{\prod_\nu (\omega^2 - \omega_\nu^2)}.$$ (2·7)

Taking the logarithm and differentiating, we get

$$\mathcal{N}_N(\omega) = \mathcal{N}_N^0(\omega) + \frac{-1}{\pi} \mathrm{Im} \left(\frac{f'(\omega + is)}{f(\omega + is)}\right)_{s \to 0}$$

$$= \mathcal{N}_N^0(\omega) + \frac{d}{d\omega} \frac{1}{\pi} \arctan\left(\frac{-\mathrm{Im} f(\omega + is)}{\mathrm{Re} f(\omega + is)}\right)_{s \to 0}.$$ (2·8)

This is a prototype formula which connects the density of states $\mathcal{N}_N(\omega)$ in a perturbed system with that in an unperturbed one, $\mathcal{N}_N^0(\omega)$, in terms of a characteristic function representing a phase shift. What we call "Friedel's sum rule" is a relation of integrals in the above formula:

$$\int_0^\omega (\mathcal{N}_N(\omega') - \mathcal{N}_N^0(\omega')) d\omega' = \frac{1}{\pi} \arctan\left(\frac{-\mathrm{Im} f(\omega + is)}{\mathrm{Re} f(\omega + is)}\right)_{s \to 0},$$ (2·9)

where $\mathrm{Im} f(0 + is)_{s \to 0} = 0$ is assumed in general and verified for the system treated presently.

The formulas (2·8) and (2·9) have been quoted frequently in literatures. The reason for still motivating our debate about them is their thermodynamic significance: Actually, these formulas are meaningful only when the system

is strictly finite, since the difference $\mathcal{H}_N(\omega) - \mathcal{H}_N^0(\omega)$ represented by a phase shift term is a fraction of order $1/N$ compared to $\mathcal{H}_N^0(\omega)$ itself. On the other hand, by the term "density of states" one tends to mean a thermodynamically stable quantity depending only on the bulk structure of the system for which the strict finiteness, in particular, a discreteness of the levels is often inconvenient.

In order to inquire the relations for a large system so as to keep the $1/N$ fraction without losing its proper meaning, let us consider a specific example which enables us to perform carefully the two kinds of limits, namely the limit of the system size infinity and the $s \to 0$ limit. Perhaps the simplest example at hand would be the nearest-neighbor coupled linear chain as an unperturbed system for which

$$\omega_\mu^2 = \sin^2\left(\frac{\pi\mu}{N}\right). \tag{2.10}$$

The characteristic function $f(\omega)$ in (2.4) for this example can be calculated to express in a compact form as follows:

$$f_N(\omega) = \frac{M}{m} - \left(\frac{M}{m} - 1\right) \frac{i\omega}{(1-\omega^2)^{1/2}} \frac{\{(1-\omega^2)^{1/2} + i\omega\}^{2N} + 1}{\{(1-\omega^2)^{1/2} + i\omega\}^{2N} - 1}$$

$$= \frac{M}{m} - \left(\frac{M}{m} - 1\right) \frac{\omega \cot(N \sin^{-1}\omega)}{(1-\omega^2)^{1/2}}. \tag{2.11}$$

(A derivation of this formula is outlined in the footnote.*) A schematic graph of the function $f_N(\omega)$ with a real ω is shown in Fig. 1. One could imagine how fantastic the graph would be when the integer N gets large.

To get a thermodynamically stable quantity it is convenient (and in fact a widely accepted process) to perform the limit $N \to \infty$ first and then the limit $s \to 0$. If this is done with $f_N(\omega)$, a very simple result turns out:

$$\lim_{s \to 0} \lim_{N \to \infty} f_N(\omega + is) = \frac{M}{m} - \left(\frac{M}{m} - 1\right) \frac{|\omega|}{\sqrt{\omega^2 - 1}}, \quad |\omega| > 1 \tag{2.12a}$$

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*) To perform the summation on the finite terms of $f_N(\omega)$ in (2.4) with the specific model of (2.10), it is convenient to invoke a handbook of mathematical formulas.[6] One finds

$$\prod_{\nu=1}^{n-1} (\sin^2 \frac{\pi\nu}{2n} - \sin^2\theta) = \frac{\sin 2n\theta}{2^{2(n-1)}\sin 2\theta},$$

$$\prod_{\nu=1}^{n} (\sin^2 \frac{\pi\nu}{2n+1} - \sin^2\theta) = \frac{\sin(2n+1)\theta}{2^{2n}\sin\theta}$$

which are valid for any θ and any positive integer n. Take the logarithms of both hand sides of the above equalities, differentiate with respect to θ, and set $\sin^2\theta = \omega^2$. After some algebra one gets

$$\sum_{\nu=0}^{[N/2]} \frac{2\omega}{\omega^2 - \sin^2\frac{\pi\nu}{N}} = \frac{1}{\sqrt{1-\omega^2}} N \cot(N \sin^{-1}\omega),$$

from which the expression (2.11) is derived. Note that the resulting secular equation, $f_N(\omega) = 0$, is precisely identical with that obtainable by means of the transfer matrix method.[7]

$$= \frac{M}{m} - \left(\frac{M}{m} - 1\right)\frac{i|\omega|}{\sqrt{1-\omega^2}}, \quad |\omega| < 1. \qquad (2\cdot12b)$$

In order to substitute these expressions into the relation (2·8) we must keep in mind several points. First of all, we are interested in the densities of states for large systems which may have definite values in the limit $N \to \infty$. Therefore, we redefine

$$N(\omega) \equiv \lim_{N\to\infty} \frac{1}{N} \mathfrak{N}_N(\omega), \qquad N^0(\omega) \equiv \lim_{N\to\infty} \frac{1}{N} \mathfrak{N}_N^0(\omega). \qquad (2\cdot13)$$

Second, we must be careful about the singularities of $\log f(\omega)$ which occur on the real ω-axis. These are $\omega^2 = 1$ and $\omega^2 = \Omega^2_{\mathrm{loc}} = M^2/(2M-m)m$ in case of $M > m$. It is a well-known fact that in case $M > m$ there exists one allowed mode at the frequency $\Omega_{\mathrm{loc}} > 1$ which corresponds to a localized mode associated with the m-defect.[5] Including this case, we now get the desired relation which is valid precisely in order of $1/N$. The result is written as

$$N(\omega) = N^0(\omega) - \frac{1}{N}\left\{\frac{d}{d\omega}\frac{1}{\pi}\arctan\left(\frac{M-m}{M}\frac{\omega}{\sqrt{1-\omega^2}}\right) + \frac{1}{2}\delta(\omega-1)\right\}$$
$$+ \frac{1}{N}\delta(\omega-\Omega_{\mathrm{loc}}). \qquad \begin{pmatrix}\text{The last term}\\\text{(Case } M > m \text{ only)}\end{pmatrix} \qquad (2\cdot14)$$

In Eq. (2·14) the *arctangent* is defined by its principal branch for $|\omega| < 1$ otherwise vanishes. It is then easy to see that this formula satisfies the following sum rule:

$$\int_{-\infty}^{\infty} N(\omega)d\omega = \int_{-\infty}^{\infty} N^0(\omega)d\omega = 1. \qquad (2\cdot15)$$

This is because, if $M < m$, the integral of the square bracket in (2·14) in the range ω from 0 to $+\infty$ vanishes, whereas if $M > m$ it exactly compensates the contribution from the localized mode. The occurrence of this mode is the consequence of an accumulation of all the small negative shifts of the frequencies in the quasi-continuum $0 < \omega < 1$, as can be seen from the identity:

$$\Omega^2_{\mathrm{loc}} + N \int_0^1 (N(\omega) - N^0(\omega))\omega^2 d\omega$$
$$= \left(\frac{M}{m} - 1\right)\int_0^1 N^0(\omega)\omega^2 d\omega = \frac{1}{2}\left(\frac{M}{m} - 1\right). \qquad (2\cdot16)$$

Note that this identity originates from an expansion of $f(\omega)$ in powers of ω^{-2} in the forms of both (2·4) and (2·7) and a comparison between each first term of order ω^{-2}. (The situation is similar to a sum rule for the plasma frequency in a Fermi gas.[8])

In an application of the formulas such as (2·14) to large systems it must be said unrealistic unless the presence of many defects is explicitly taken into

account, which may be one real motivation of theory of disordered systems.*) It is of course possible to extend formally the relation (2·8) to the n-defects problem: This is to replace the function $f(\omega)$ just by the determinant of the $n \times n$ matrix $\mathbf{F}(\omega)$ defined in (2·3b), namely,

$$\eta_N(\omega) = \eta_N^0(\omega) + \frac{d}{d\omega} \frac{-1}{\pi} \operatorname{Im} \log \det \mathbf{F}(\omega + is)_{s \to 0}. \qquad (2·17)$$

The difficulty lies in the fact that one does not really know a convincing method to get thermodynamically stable expressions for such quantities as those depending on the configurations of the defects.

§3. Impurity scattering of electrons due to short range forces

Our second example is the one which was first introduced by Lax and Phillips[10] for a study of the formation of an impurity band as a simplified model of random Kronig-Penny problems, and is expressed by the equation

$$\left[-\frac{d^2}{dx^2} - 2\kappa_0 \sum_{\{j\}} \delta(x - x_j) \right] \psi = E\psi. \qquad (3·1)$$

The problem will be seen to have a similarity in essence to the first example, but here it has a characteristic of dealing with a continuous spectrum from the beginning. Then, it is relevant to rewrite Eq. (3·1) in a form of scattering equation (the so-called Lippmann-Schwinger equation) as follows:

$$\psi_k^+(x) = \varphi_k(x) + \int_{-\infty}^{\infty} dx' \, G^+(xx'|k) V(x') \psi_k^+(x'), \qquad (3·2)$$

where

$$G^+(xx'|k) = \frac{1}{2\pi} \int_{-\infty}^{\infty} \frac{e^{ik_1(x-x')}}{k^2 - k_1^2 + is} dk_1 \qquad (3·3)$$

$$(0 < s \to 0)$$

is the (one-dimensional) free particle Green function, and the wave number k is introduced to satisfy $E = k^2$. We wish to illustrate here a mapping structure of this relation between the two complex planes of E and k (see Fig. 2). This is the basis of the analyticity problem in the scattering theory[11] and will be useful for later development of the present context, in particular, for a deeper understanding of the coherent potential approximation.

The wave number k is a two-valued function of E which we adopt the following convention:

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*) This point of view seems to have formed a background of I. M. Lifshitz's early works, as summarized in his review article.[9]

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$$E = k^2$$
$$(k = E^{1/2} = i (-E)^{1/2})$$
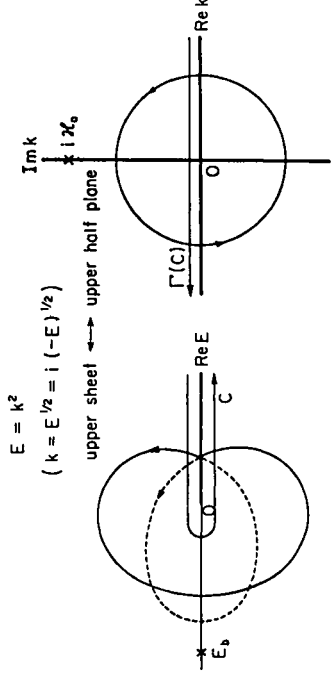
upper sheel $\longleftrightarrow$ upper half plane

Fig. 2. Physical and non-physical sheets of a complex E-plane which is mapped to a complex k-plane through $E = k^2$ in the theory of scattering.

$$k = E^{1/2} = i(-E)^{1/2},$$
$$(-E)^{1/2} = \sqrt{|E|}\, e^{i\frac{\theta}{2}} = \sqrt{|E|}\, e^{i\frac{\theta}{2} \mp i\frac{\pi}{2}} = \sqrt{|E|}\left(\pm \sin\frac{\theta}{2} \mp i\cos\frac{\theta}{2}\right), \qquad (3\cdot4)$$
$$(0 \le \theta (= \arg E) < 2\pi)$$

where the upper and the lower signs correspond to one and another sheet of the complex E-plane, called the physical sheet and the non-physical sheet, respectively, which totally represent the two-valued function $k(E)$. The physical sheet is characterized by the definition that a real, negative value of E corresponds to a positive $\mathrm{Im}\,k$, and that on the positive half of the real axis $\mathrm{Re}\,k(E+is)_{s\to0} = -\mathrm{Re}\,k(E-is)_{s\to0} \ge 0$ having a discontinuity. Similarly, the non-physical sheet is characterized by just vice versa. This is summarized in Table I. Here and in what follows we shall frequently use the notations such as $f(E+i0)$ and $f(E-i0)$, respectively, when the positive s tends to zero from the upper and the lower side of the real axis in the physical sheet.

Table I. Definition of the physical and non-physical sheets.

physical sheet	non-physical sheet
$\mathrm{Im}\,k = \mathrm{Re}\,\kappa = \mathrm{Re}(-E)^{1/2} \ge 0$	$\mathrm{Im}\,k = \mathrm{Re}\,\kappa = \mathrm{Re}(-E)^{1/2} < 0$
$\mathrm{Re}\,k(E+i0) \ge 0 \ (E=\text{real})$	$\mathrm{Re}\,k(E+i0) < 0$
$0 \le \arg E \le 2\pi$	$2\pi < \arg E < 4\pi$

Accordingly, the integration with respect to k_1 in the expression $(3\cdot3)$ may be performed without any sign ambiguity by means of contour integrations on the complex k_1-plane. For a given real value of k defined in the physical sheet, one has

$$\frac{1}{2\pi}\int_{-\infty}^{\infty}\frac{e^{ik_1(x-x')}}{k^2-k_1^2+i0}\,dk_1 = \frac{1}{2ik}e^{ik|x-x'|}. \qquad (3\cdot5)$$

This is because, if $x - x' > 0$, an integration along the contour composed of the real axis from $-R$ to R and a large semicircle of radius R in the upper-half plane gives a residue $(1/2ik)e^{ik(x-x')}$ at the pole $k_1 = \sqrt{k^2 + is}$ and, if $x - x' < 0$, another similar contour integration on the lower-half plane gives $(1/2ik)$ $\times e^{-ik(x-x')}$ at the other pole $k_1 = -\sqrt{k^2 + is}$, the integrals along the semicircles being to vanish as $R \to \infty$. However, the expression (3·5) may be generalized for any complex value of E, if one wishes, by an analytic continuation in accordance with (3·4) such that

$$\frac{1}{2ik}e^{ik|x-x'|} = -\frac{1}{2}(-E)^{-\frac{1}{2}}\exp\left\{-(-E)^{\frac{1}{2}}|x-x'|\right\}.$$

For convenience, let us introduce an imaginary wave number k defined by

$$\kappa = -ik = (-E)^{1/2}. \tag{3·6}$$

Then, the physical sheet is characterized by $\mathrm{Re}\,\kappa \geq 0$, and the expression

$$G^+(xx'|i\kappa) = \frac{-1}{2\kappa}e^{-\kappa|x-x'|} \tag{3·7}$$

shows that the Green kernel never grows up in this sheet. The integral equation (3·2) for the special form of $V(x) = -2\kappa_0 \sum_{(j)} \delta(x - x_j)$ now reduces to a discrete equation as follows:

$$\psi^+(x) = \varphi(x) + \frac{\kappa_0}{\kappa} \sum_{(j)} e^{-\kappa|x-x_{j'}|}\psi^+(x_{j'}), \tag{3·8}$$

and, in particular,

$$\psi^+(x_j) = \varphi(x_j) + \frac{\kappa_0}{\kappa} \sum_{(j)} e^{-\kappa|x_j - x_{j'}|}\psi^+(x_{j'}). \tag{3·8a}$$

The solution of the latter equation may be written as

$$\psi^+(x_j) = \sum_{(j')} F_{jj'}^{-1}\varphi(x_{j'}), \tag{3·9}$$

where $F_{jj'}^{-1}$ is the matrix element of the inverse of $\boldsymbol{F}$ defined by

$$F_{jj'} \equiv \delta_{jj'} - \frac{\kappa_0}{\kappa}e^{-\kappa|x_j - x_{j'}|}. \tag{3·9a}$$

As before, we shall be specialized for illustrative purpose to a single center scattering, the position of the center being fixed at an arbitrarily chosen point x_0. The solution for this may be given explicitly by virtue of (3·9) in the single center case, $\psi^+(x_0) = (1 - \kappa_0/\kappa)^{-1}\varphi(x_0)$, and the outgoing wave which corresponds to an incident plane wave $\varphi_k(x) = e^{ikx}$ is of the form

$$\psi_k^+(x) = \varphi_k(x) + A(x - x_0, k)\varphi_k(x_0)$$

$$= \varphi_k(x) + \frac{\kappa_0}{\kappa - \kappa_0} e^{-\kappa|x - x_0|}\varphi_k(x_0), \tag{3.10}$$

i.e.,

$$A(x, k) = \frac{\kappa_0}{\kappa - \kappa_0} e^{-\kappa|x|}, \tag{3.10a}$$

where k and κ are related through (3.6). It may be remarked that the scattering amplitude becomes singular at $\kappa = \kappa_0$, the corresponding energy being equal to $-\kappa_0^2 \equiv E_b$. This is interpreted as the formation of a bound state, which is possible only when $\kappa_0 > 0$, i.e., only when the amplitude has a (simple) pole on the physical sheet whose residue yields a normalizable eigenfunction:

$$\psi_b(x) = \text{const } e^{-\kappa_0|x - x_0|}. \tag{3.11}$$

Several important quantities in scattering theory such as the T matrix and the phase shift can be derived in a simple manner for the above single center problem. Using the expression

$$\psi_k^+ = \varphi_k + G_{\text{free}}^+ T\varphi_k \tag{3.12}$$

and assuming a form for the T; $T(x) = t\delta(x - x_0)$, we substitute the free electron Green kernel (3.7) into (3.12) to get

$$\psi_k^+(x) = \varphi_k(x) + \frac{-t}{2\kappa} e^{-\kappa|x - x_0|}\varphi_k(x_0),$$

and the comparison of this with (3.10) leads us to write

$$T(x) = \frac{-2\kappa_0}{1 - \kappa_0/\kappa} \delta(x - x_0). \tag{3.13}$$

This satisfies the well-known optical theorem

$$-2\mathrm{Im}(\varphi_k T\varphi_k) = 2\pi \sum_{k'} |(\varphi_k T\varphi_{k'})|^2 \delta(E - E_{k'}), \tag{3.14}$$

which may be seen presently from

$$2\mathrm{Im} \frac{2\kappa_0}{1 - \kappa_0/\kappa} = \frac{4\kappa_0^2}{|1 - \kappa_0/\kappa|^2} \mathrm{Im} \, 1/\kappa \tag{3.14'}$$

$$= \frac{4\kappa_0^2}{1 + \kappa_0^2/k^2} 1/k. \quad (E = \text{real} > 0) \tag{3.14''}$$

To introduce the phase shift associated with the above example of scattering we must analyze the scattering solution (3.10) more carefully. Suppose that the incident plane wave is set up sufficiently *right* to the center x_0 on the coordinate axis (see Fig. 3). Then, the $\varphi_k(x)$ should be of the form e^{-ikx}, for which the solution $\psi_k^+(x)$ in (3.10) may be written in accordance with (3.6) as follows:
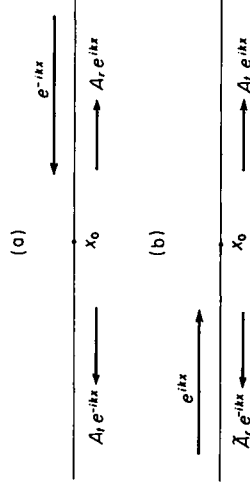
Fig. 3. A schematic presentaion of one-dimensional scattering by a center situated at x_0; (a) right (b) left incident plane waves.

$$\underset{x<x_0}{\psi_k^+(x)}=e^{-ikx}+A(k)e^{\kappa(x-x_0)}e^{-ikx_0}$$
$$=e^{-ikx}(1+A(k)),$$

$$\underset{x_0<x}{\qquad}e^{-ikx}+A(k)e^{-\kappa(x-x_0)}e^{-ikx_0}$$
$$=e^{-ikx}+e^{ikx}e^{ikx}A(k)e^{-2ikx_0}, \qquad (3\cdot15)$$

where

$$A(k)\equiv A(0,k)=\frac{\kappa_0}{\kappa-\kappa_0}$$
$$=\frac{-\kappa_0}{ik+\kappa_0}. \qquad (3\cdot15a)$$

Similarly, we may think of the scattering for another incident wave set up sufficiently *left* to the center x_0, i.e., $\varphi_k(x)=e^{ikx}$, for which we distinguish the solution by $\tilde{\psi}_k(x)$ from the previous $\psi_k(x)$ and write as follows:

$$\underset{x<x_0}{\tilde{\psi}_k^+(x)}=e^{ikx}+A(k)e^{\kappa(x-x_0)}e^{ikx_0}$$
$$=e^{ikx}+e^{-ikx}A(k)e^{2ikx_0},$$

$$\underset{x_0<x}{\qquad}e^{ikx}+A(k)e^{-\kappa(x-x_0)}e^{ikx_0}$$
$$=e^{ikx}(1+A(k)). \qquad (3\cdot15')$$

Clearly, Eq. (3·15) may be interpreted by the process that the right incident wave undergoes a transmission and a reflection whose relative amplitudes are given by

$$A_t(k)=1+A(k) \qquad (3\cdot16)$$

and

$$A_r(k)=A(k)e^{-2ikx_0}, \qquad (3\cdot17)$$

respectively. A similar interpretation holds also concerning Eq. (3·15') for the left incident wave with the amplitudes

$$\tilde{A}_t(k)=A_t(k)=1+A(k) \qquad (3\cdot16')$$

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$$\tilde{A}_r(k) = A(k)e^{2ikx_0}. \tag{3.17'}$$

For a real value of k these satisfy the conservation of the transition probability such that

$$|A_t|^2 + |A_r|^2 = |\tilde{A}_t|^2 + |\tilde{A}_r|^2 = 1, \tag{3.18}$$

as can be easily proved from (3.15a). In particular, the transmission amplitudes (3.16) and (3.16') which have the same expression for both directions of the incident waves yield the interpretation that each wave receives, through the transmission, a phase shift to an amount given by

$$\vartheta = \arg(1 + A(k)) = \operatorname{Im} \log \frac{1}{1 + \kappa_0/ik} \tag{3.19}$$

$$= \arctan \frac{\kappa_0}{k}. \qquad (E = \text{real} > 0) \tag{3.19'}$$

Since the quantity $A(k)$ is a single-valued (actually a rational) function of k, there is no problem about its analytic continuation to regard it as a function of E over the whole doubly connected E surface. As to the angular quantity $\vartheta(E)$, however, the problem is more complicated due to the many-valued character of the *logarithm* of the transmission amplitude arising, besides from the two-valuedness of $k(E) = E^{1/2}$, from poles as well as zeros of the amplitude, $1 + A(k)$.

We shall consider later the analytic aspect of these scattering quantities in one-dimensional scattering systems by setting the problem from a more general point of view. Here we only note that the branch of the arctangent in (3.19') may be understood such that the ϑ tends to zero as the wave number k tends to infinity along the real axis. The behavior of the $\vartheta(k)$ is then

$$\vartheta(0) = \frac{\pi}{2}, \quad \vartheta(k) \xrightarrow{k \to \infty} 0 \qquad \kappa_0 > 0 \quad \text{(attractive)} \tag{3.20}$$

$$= -\frac{\pi}{2}, \quad \vartheta(k) \xrightarrow{k \to \infty} 0 \qquad \kappa_0 < 0 \quad \text{(repulsive)}, \tag{3.20'}$$
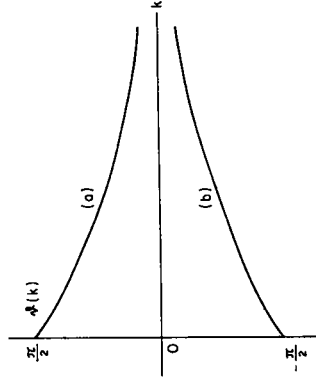
as shown in Fig. 4.

Now, the Friedel sum rule may be derived from the usual identity fulfilled between a true and a free Green kernel of the form

$$G^+ = G^+_{\text{free}} + G^+_{\text{free}} T G^+_{\text{free}}. \tag{3.21}$$

The diagonal part in the coordinate representation of this relation in the present problem is calculated as

Fig. 4. The phase shifts $\vartheta(k)$; (a) attractive (b) repulsive cases.

$$G^+(xx|i\kappa) = \frac{-1}{2\kappa} + \left(\frac{1}{2\kappa}\right)^2 \int_{-\infty}^{\infty} e^{-2\kappa|x-x'|} T(x')dx'$$

$$= \frac{-1}{2\kappa} + \left(\frac{1}{2\kappa}\right)^2 (-2\kappa_0) \frac{e^{-2\kappa|x-x_0|}}{1-\kappa_0/\kappa}. \tag{3·22}$$

To derive the relation it is necessary to assume here that the system is inside a long interval of the length L ($L\kappa \gg 1$) and to integrate both sides of the above equation, leading to

$$\frac{1}{L}\int_{-L/2}^{L/2} G^+(xx|i\kappa)dx = \frac{-1}{2\kappa} + \frac{1}{L}\frac{1-\kappa_0}{2\kappa^3}\frac{1}{1-\kappa_0/\kappa}$$

$$= \frac{-1}{2\kappa} + \frac{1}{L}\frac{1}{2\kappa}\frac{d}{d\kappa}\log(1-\kappa_0/\kappa)$$

$$= \frac{-1}{2\kappa} + \frac{1}{L}\frac{d}{dE}\log(1-\kappa_0/\kappa(E)). \tag{3·23}$$

Or, taking the minus of the imaginary parts defined in the physical sheet, we get

$$N(E) = N^0(E) - \frac{1}{\pi L}\frac{d}{dE}\mathrm{Im}\log(1-\kappa_0/\kappa(E+i0))$$

$$= N^0(E) + \frac{1}{\pi L}\frac{d}{dE}\vartheta(E) \tag{3·24}$$

and

$$\int_{-\infty}^{E}\{N(E') - N^0(E')\}dE' = \frac{1}{\pi L}\vartheta(E). \tag{3·24'}$$

Here, we have denoted the free electron density of states as $N^0(E)$, which is given by

$$N^0(E) = \frac{-1}{\pi}\mathrm{Im}\,G^+(xx|i\kappa)$$

$$= -\frac{1}{\pi}\mathrm{Im}\frac{1}{2\pi}\int_{-\infty}^{\infty}\frac{dk_1}{k^2-k_1^2+i0}, \tag{3·25}$$

$$= \mathrm{Im}\,1/2\pi\kappa(E+i0)$$

$$= 1/2\pi k. \quad (E=\text{real}>0) \tag{3·25'}$$

Note that the density of states $N(E)$ as well as $N^0(E)$ in this example is not normalizable in the whole range of E. However, the fact that the phase shift $\vartheta(E)$ satisfies the condition $\vartheta(E)\to 0$ as $E\to+\infty$ indicates that the number of available states is preserved precisely in order of $1/L$ when the perturbing potential is switched on into the unperturbed system. Note, also, that the difference between the attractive and repulsive cases in the phase shift

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ϑ at $k=0$ as indicated in (3.20) and (3.20') (also in Fig. 4) is caused from the presence of the one simple pole, $k=i\kappa_0$ ($\kappa_0>0$) located on the positive imaginary axis, a fact which shows that the number of "allowed" states is counted in the integrated density of states consistently just by one at the continuum edge $E=0$ for the attractive case.

In terms of $N^0(E)$ the optical theorem (3·14) may be re-expressed as

$$-\frac{1}{L}\mathrm{Im}(\varphi_k T\varphi_k)=\frac{\pi}{L}|(\varphi_k T\varphi_{-k})|^2 N^0(E) \quad (\equiv 1/\tau(E))$$

$$=\frac{1}{L}\frac{4\pi\kappa_0^2}{|1+\kappa_0/ik|^2}N^0(E), \qquad (3.26)$$

where the right-hand side represents the transition probability (reflection only) per unit time for an incident particle of wave number k, while the left-hand side the imaginary part of the energy shift of that particle, showing a way to calculate the decay rate (or, inverse of the life time) of a free state. This quantity, however, when considered for a scattering due to a single center, is vanishingly small in order of $1/L$. (This factor arises in (3·26) because of the normalization of the free state wave functions, which we have not respected in (3·14') but is certainly necessary for giving a physical significance to the quantity.) Thus we see again a necessity of extending the theory. Recently, Reading and Sigel[12] have made a rather detailed analysis of the many-center problem in the present example, and derived a density-of-states vs. phase-shift relation of the type (3·24). It is by this type of formulas that we can see how the many phase shift terms accumulate up to provide a substantial density of states and a thermodynamically significant life. We shall take up this question from a more analytic point of view in later sections.

§4. Virtual localized states near the Fermi level in a metal

Historically, the relation between a change of the "density" and a scattering phase shift was proposed first by Friedel[13] to investigate the charge displacement due to impurities dissolved in a metal. It was stimulated by extensive studies of localized magnetic states, as has been well summarized in a monograph written by Kondo.[14] Perhaps the most interesting question raised by the original Friedel's argument was a localization of the excess charge round the dissolved impurity atom arising from conduction-electron clouds to which a perfect screening effect may be attributed. An analogy of this argument to the spin polarization effect through coupling between conduction-electron spins and a local d-orbital spin leads one to ask if the excess spin polarization round the d-spin might also be localized. It may be said that a complete answer to this question has not yet been established up

to the present owing to a mathematical difficulty in dealing with the s-d Hamiltonian. Here we do not intend to concern ourselves with a large number of works to pursue the exact ground state of that Hamiltonian. Instead, we intend to investigate, by choosing more tractable models, the question of how an adequate meaning can be assigned to the word "localization". An interesting demonstration of the localization effect was made first by Anderson,[15] who considered a virtual state near the Fermi surface proposing a new interpretation of the mechanism in terms of what is called "compensation theorem". In another context Anderson considered the problem "absence of diffusion in disordered lattices",[16] which is regarded now as a more fundamental questioning in the subject of localized states in solids. Here we restate the compensation theorem associated with a virtual state in a continuous spectrum, and then study its nature of localization from a quantum diffusion point of view.

We begin by considering the *trace* of a Green operator (or, a resolvent) associated with a matrix Hamiltonian of the form

$$H = \begin{bmatrix} E_d & \cdots\cdots & V_{dκ} & \cdots \\ \vdots & & \vdots & \\ V_{κ'd} & \cdots & E_κ δ_{κ'κ} & \\ & & \ddots & \ddots \end{bmatrix},$$

(4·1)

where d and k denote the localized and propagating (or, conduction) states, respectively. (At this moment only one d-state present is assumed.) Since this is already partially diagonalized, non-vanishing matrix elements of H only appearing in the first row and column, the Green operator $G = (E-H)^{-1}$ of the form

$$G = \begin{bmatrix} G_{dd} & \cdots & G_{dκ} & \cdots \\ \vdots & & \vdots & \\ G_{κ'd} & \cdots & G_{κ'κ} & \\ & & & \ddots \end{bmatrix},$$

(4·2)

can be calculated explicitly by solving the operator equation $(E-H)G=1$, i.e., the following two sets of linear equations for all the elements of G:

$$(E-E_d)G_{dd} - \sum_{k'} V_{dk'}G_{k'd}=1, \quad -V_{k'd}G_{dd}+(E-E_{k'})G_{k'd}=0$$

(4·3a)

and

$$(E-E_d)G_{dκ} - \sum_{k'} V_{dk'}G_{k'κ}=0, \quad -V_{k'd}G_{dκ}+(E-E_{k'})G_{k'κ}=δ_{k'κ}.$$

(4·3b)

We eliminate the off-diagonal element $G_{k'd}$ in the first set, $G_{k'k}(k' \lessgtr k)$ and $G_{dκ}$ in the second set, to obtain equations for the diagonal elements G_{dd} and

G_{kk}. Thus from the first set of equations (4·3a) we get

$$G_{dd} \equiv G_d(E) = G_d^0(E) + G_d^0(E) \sum_{k'} |V_{dk'}|^2 G_{k'}^0(E) G_d(E), \qquad (4\cdot 4a)$$

$$G_{k'd} = G_{k'}^0(E) V_{k'd} G_d(E), \qquad (4\cdot 4b)$$

and from the second one (4·3b)

$$G_{kk} \equiv G_k(E) = G_k^0(E) V_{kd} G_{dk} + G_k^0(E) V_{kd} G_{dk}$$
$$= G_k^0(E) + G_k^0(E) |V_{kd}|^2 \frac{G_k(E)}{E - E_d - \sum_{k' \neq k} |V_{dk'}|^2/(E - E_{k'})}, \qquad (4\cdot 5a)$$

$$G_{k'k} = G_k^0, V_{k'd} G_{dk}, \quad (k' \neq k) \qquad (4\cdot 5b)$$

$$G_{dk} = \frac{V_{dk} G_k(E)}{E - E_d - \sum_{k' \neq k} |V_{dk'}|^2/(E - E_{k'})}, \qquad (4\cdot 5c)$$

where

$$G_d^0(E) = \frac{1}{E - E_d} \quad \text{and} \quad G_k^0(E) = \frac{1}{E - E_k} \qquad (4\cdot 5d)$$

are the elements of the unperturbed Green operator. Introducing a function defined by

$$f(E) = E - E_d - \sum_k \frac{|V_{dk}|^2}{E - E_k}, \qquad (4\cdot 6)$$

we can summarize the solutions simply as follows:

$$G_{dd}(= G_d(E)) = \frac{1}{f(E)}, \qquad (4\cdot 7a)$$

$$G_{k'k} = G_k^0(E) \delta_{kk'} + \frac{G_{k'}^0(E) V_{k'd} V_{dk} G_k^0(E)}{f(E)}. \qquad (4\cdot 7b)$$

In deducing the latter expression (4·7b) we have utilized the fact that for a real E the matrix $\mathbf{G}$ is hermitian thus $G_{dk} = G_{kd}^*$, so that the expression (4·4b) instead of (4·5c) may be substituted into the first line of Eq. (4·5a) or into (4·5b) to get the solution $G_{k'k}$. For the diagonal part G_{kk}, however, Eq. (4·5a) may be solved directly to get another expression

$$G_{kk}(= G_k(E)) = \frac{1}{E - E_k - |V_{kd}|^2 \{E - E_d - \sum_{k' \neq k} |V_{dk'}|^2/(E - E_{k'})\}^{-1}}$$
$$= \frac{1}{E - E_k - |V_{kd}|^2/f(E)}, \qquad (4\cdot 7c)$$

which together with the expression for $G_{dd}=1/f(E)$ forms a typical self-energy representation of the diagonal part of a Green operator. Noting that

$$|V_{kd}|^2 = O(1/N),$$ (4·8)

we can see that in this one-center problem the self-energy for the conduction states gives a correction to its energy only in order of $1/N$,*) whereas the self-energy for the d state a correction of finite magnitude in the limit $N\to\infty$.

Let us list up the densities of states for several species which are concerning presently.

(a) the perturbed d state: $\mathcal{N}_d(E) = \frac{-1}{\pi}\mathrm{Im}G_{dd}^+ = \frac{-1}{\pi}\mathrm{Im}\frac{1}{f(E+i0)},$

(b) the perturbed conduction states: $\mathcal{N}_c(E) = \frac{-1}{\pi}\mathrm{Im}\sum_k G_k(E+i0),$

(c) the total: $\mathcal{N}(E) = \mathcal{N}_c(E) + \mathcal{N}_d(E),$

(d) the unperturbed conduction states: $\mathcal{N}_{free}(E) = \frac{-1}{\pi}\mathrm{Im}\sum_k \frac{1}{E-E_k+i0}.$**)

A phase-shift relation is shown to be satisfied between (c) and (d):**)

$$\mathcal{N}(E) = \mathcal{N}_{free}(E) + \frac{d}{dE}\frac{-1}{\pi}\mathrm{Im}\log f(E+i0).$$ (4·9)

Anderson argued that, if the initially chosen d level is located in energy inside the free conduction-electron continuum near the Fermi surface, the density of states for the perturbed "d" electrons may be approximated to a Lorentizian form

$$\mathcal{N}_d(E) = \frac{1}{\pi}\frac{\Delta}{(E-E_d)^2+\Delta^2},$$ (4·10)

where the width parameter

$$\Delta = \pi\langle V^2\rangle_{av}\mathcal{N}_{free}(E_f)$$ (4·10a)

may be assumed constant independent of E. But this is equivalent to considering that the excess *total* density, i.e., its deviation from the free conduction-electron density is mostly incorporated into the expression (4·9), i.e., into the d-electron density, or equivalently

$$\int_{-\infty}^{E_f}\mathcal{N}_c(E)dE \simeq \int_{-\infty}^{E_f}\mathcal{N}_{free}(E)dE,$$ (4·11)

that is to say, the conduction-electron density is unchanged. This is because

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*) In the first expression of (4·7c) the sum over the conduction states k' avoids the term $k'=k$. This fact yield a difference of this self-energy expression from that given in the second expression, $|V_{kd}|^2/f(E)$, to an amount of $O(1/N^2)$ which may be ignored.
**) That the relation (4·8) holds exactly between the total density and the free conduction-electron density was noted first by Klein and Heeger[17] and subsequently by Langreth.[18]

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$$\int_{-\infty}^{E_f} \mathcal{N}_d(E)dE = \int_{-\infty}^{E_f} \frac{-1}{\pi} \mathrm{Im} \frac{1}{f(E+i0)} dE$$
$$\simeq \frac{1}{\pi} \int_{-\infty}^{E_f} \frac{dE}{(E-E_d)^2+\Delta^2}$$
$$= \frac{1}{\pi}\left(\arctan\frac{E_f-E_d}{\Delta} + \frac{\pi}{2}\right) = \frac{1}{\pi}\mathrm{arccot}\frac{E_d-E_f}{\Delta}, \quad (4\cdot12)$$

whereas from the relation $(4\cdot9)$

$$\Delta\rho \equiv \int_{-\infty}^{E_f}(\mathcal{N}(E)-\mathcal{N}_{\mathrm{free}}(E))dE$$
$$= \frac{1}{\pi}\arctan\left(\frac{\mathrm{Im}f(E+i0)}{-\mathrm{Re}f(E+i0)}\right)_{E=E_f}$$
$$= \frac{1}{\pi}\mathrm{arccot}\left(\frac{-\mathrm{Re}f(E+i0)}{\mathrm{Im}f(E+i0)}\right)_{E=E_f}$$
$$\simeq \frac{1}{\pi}\mathrm{arccot}\frac{E_d-E_f}{\Delta}. \quad (4\cdot13)$$

Note that the arccotangent in Eqs. $(4\cdot12)$ and $(4\cdot13)$ is defined by its principal branch, $0 < \mathrm{arccot} < \pi$, so that it yields a total excess density of just unity when its argument E_f varies from $-\infty$ to $+\infty$ (see Fig. 5).

Thus, for example, under the condition

$$\Delta \ll E_d - E_f, \quad (4\cdot14)$$

the excess density $(4\cdot13)$ may be

$$\Delta\rho \simeq \frac{1}{\pi}\frac{\Delta}{E_d-E_f}$$
$$= \mathcal{N}_{\mathrm{free}}(E_f)\frac{\langle V^2\rangle_{\mathrm{av}}}{E_d-E_f}, \quad (4\cdot15)$$

which yields an interpretation that the initially empty d level above the Fermi surface is now partially filled, after the interaction is switched on, to the amount given in the above. (Similarly, if the d level is below the E_f, the initially filled d level will be depleted to the same amount. These correspond physically to the processes of dissolving a d-level atom into the host metal.)

At the first sight of the expression for G_{kk} given by $(4\cdot7c)$ which indicates the self-energy for each conduction state to be

$$\Delta E_k = |V_{kd}|^2 f(E)$$
$$\simeq |V_{kd}|^2/(E_k - E_d), \quad (4\cdot16)$$

one might expect that such energy shifts accumulate up to yield an excess
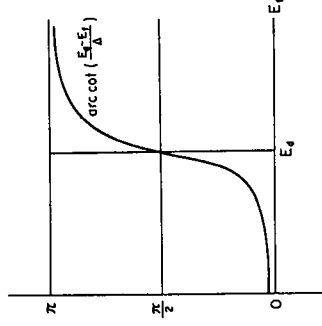

Fig. 5.   The phase shift for Anderson's virtual level formed in a free electron continuum.

density of the same magnitude as (4·15) to the conduction-electron density, $\int_{-\infty}^{E_f} \mathcal{N}_e(E)dE$. This is not the case indeed, and Anderson's demonstration of Eqs. (4·12) and (4·13) and hence of Eq. (4·11) shows clearly that the excess density contributes to the integral of $\mathcal{N}_d(E)$ instead of $\mathcal{N}_e(E)$. This is just what is meant by the "localization" of the excess conduction-electron density round the dissolved d-level atom. It should be stressed that in this interpretation the explicit setting of the d orbital is vital, because otherwise an appreciable excess density represented by the phase shift term must be assigned to the true conduction-electron density which has a spatially uniform component in order of magnitude $1/N$. By a perturbation-theoretic consideration, in fact, Anderson demonstrated also that a precise cancellation occurs between the two kinds of first-order density with the magnitude (4·15) arising from the energy shift of the conduction states and that from the *admixture* of their wave functions with the d orbital; hence the origin of the name "compensation theorem". Note that this latter admixture effect itself makes the "localized" nature of the d orbital obscured, which may be interpreted as the formation of a virtual (or resonance) state in the sense to be explained shortly.

In the above respect, therefore, one may still ask how it is possible to characterize a quantum state to be whether "localized" or not. This question is really a central one in the whole subjects of the theory of disordered systems. We must admit that we do not have a fully satisfactory answer to this question, although several plausible criterions have been proposed by Thouless.[19] Here, however, it is interesting to quote the approach of "quantum diffusion" recently pursued by Ishii,[20] the essence of which will be summarized as follows:

Consider a time evolution of a quantum system described by a Hamiltonian $\boldsymbol{H}$ which operates on a set of state vectors whose components are supposed to designate a discrete set of spatial positions (i.e., lattice sites) j, i.e.,

$$i\frac{d\boldsymbol{u}}{dt} = \boldsymbol{H}\boldsymbol{u} \qquad \left(i\frac{du_j}{dt} = \sum_{j'} H_{jj'} u_{j'}\right), \qquad (4\cdot17)$$

and take a particular solution $u_{jn}(t)$ which satisfies the initial condition

$$u_{jn}(t=0) = \delta_{jn}. \qquad (4\cdot18)$$

Then, the transition probability can be defined for the quantum transition from the site n to m during the time interval between $t=0$ to t:

$$P_{n\to m}(t) = |u_m u_n(t)|^2$$
$$= \mathrm{Tr}(\hat{\rho}_m e^{-itH}\hat{\rho}_n e^{itH}). \qquad (4\cdot19)$$

Here in the latter expression of the operator form the quantity $\hat{\rho}_n$ denotes the density matrix for the pure state (or, the projection operator, $\hat{\rho}_n^2 = \hat{\rho}_n$) localized at the site n. The question whether this state remains localized or not in

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the time evolution shall be tested, according to Ishii, by looking at the particular probability

$$P_{n\to n}(t) = \text{Tr}(\hat{\rho}_n e^{-itH}\hat{\rho}_n e^{itH}) \tag{4.19a}$$

for a long period $0 \leq t \leq \infty$, i.e., by distinguishing two cases such that

(I), $\overline{\lim_{t\to\infty}} P_{n\to n}(t) > 0$, (localized)

(II) $\overline{\lim_{t\to\infty}} P_{n\to n}(t) (= \lim_{t\to\infty} P_{n\to n}(t) = 0)$. (not localized)

In practice, the limit at t infinity of the time-dependent quantity may be replaced by an appropriate average to eliminate its fluctuating part. It is customary to put

$$\lim_{t\to\infty} P_{n\to n}(t) = \lim_{s\to 0} s \int_0^\infty e^{-st} P_{n\to n}(t) dt. \tag{4.20}$$

In fact, if the limit on the left hand really exists, it must be equal to the limit on the right hand whose existence is assured inasmuch as the time evolution obeys a linear equation of the type (4.7). Thus instead of (I) and (II)*) we may have

(I') $\lim_{s\to 0} s \int_0^\infty e^{-st} P_{n\to n}(t) dt > 0$, (localized)

(II') $\lim_{s\to 0} s \int_0^\infty e^{-st} P_{n\to n}(t) dt = 0$. (not localized)

The condition (I') for localization may be interpreted by saying that, if the probability of staying at site n, $P_{n\to n}(t)$, has its Laplace transform which contains δ-function type singularities at $s=0$, then the site n must be localized. Actually, for any finite system whose eigenvalue spectrum of the Hamiltonian is discrete so that the probability $P_{n\to n}(t)$ only has a discrete frequency spectrum, the condition always favors the localization. Therefore, a test whether a quantum state in solids be localized or not can be crucial only under the circumstance of taking the limit of the system volume infinite before the $s\to 0$ limit.

Now, let us apply the above criterion to the present example of Anderson's virtual state:

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*) A third form of the criterion actually adopted by Ishii as "weak absence" of diffusion is the following:

(I'') $\int_0^\infty P_{n\to n}(t) dt = \infty$, (localized)

(II'') $\int_0^\infty P_{n\to n}(t) dt < \infty$. (not localized)

The logical sequence of the three forms of the criterion is clearly

(I') $\Longrightarrow$ (I) $\Longrightarrow$ (I''),
(II') $\Longleftarrow$ (II) $\Longleftarrow$ (II'').

Thus the condition (I') may be looked as "strong absence" of diffusion.

$$\int_0^\infty e^{-st} P_{d\to d}(t)\,dt = \int_0^\infty e^{-st}\mathrm{Tr}\big(\hat{\rho}_d e^{-itH}\hat{\rho}_d e^{itH}\big)\,dt$$

$$= \frac{1}{2\pi}\int_C \mathrm{Tr}\Big(\hat{\rho}_d \frac{1}{E-\mathbf{H}+is}\hat{\rho}_d \frac{1}{E-\mathbf{H}}\Big)\,dE^{*)}$$

$$(|\mathrm{Im}\,E|<s)$$

$$= \frac{1}{2\pi}\int_{-\infty}^\infty \frac{1}{f(E+is)}\Big(\frac{1}{f(E-i0)} - \frac{1}{f(E+i0)}\Big)\,dE, \qquad (4\cdot21)$$

where $f(E)$ is given by (4·6). If the system is strictly finite, the function $f(E)$ is a rational function whose poles $\{E_k\}$ are all simple, located on the real axis, and have all negative residues. Let the total number of these poles be N and designate this assumption by f_N. Then, the function $f_N(E)$ has $N+1$ simple zeros denoted by $\{E_\nu\}$ $(\nu=0,1,2,\dots N)$ on the real axis and nowhere else. These are clearly the energy eigenvalues of the perturbed Hamiltonian. Near one of them, E_ν,

$$\frac{1}{f_N(E+is)}\Big(\frac{1}{f_N(E-i0)} - \frac{1}{f_N(E+i0)}\Big)$$

$$= \Big(\frac{df_N}{dE}\Big)^{-2}_{E=E_\nu}\frac{2\pi i\delta(E-E_\nu)}{E-E_\nu+is},$$ 　(4·22)

and the integration in (4·21) yields the form

$$\lim_{s\to0} s\int_0^\infty e^{-st} P_{d\to d}(t)\,dt = \sum_{\nu=0}^N \Big(\frac{df_N}{dE}\Big)^{-2}_{E=E_\nu}$$

$$= \sum_{\nu=0}^N \Big(1+\sum_k \frac{|V_{dk}|^2}{(E_\nu-E_k)^2}\Big)^{-2} > 0. \qquad (4\cdot23)$$

Note that in each term of the summation in the above the factor $(df_N/dE)^{-1}_{E=E_\nu}=1/\{1+\sum_k |V_{dk}|^2/(E_\nu-E_k)^2\}$ represents the square of the inner product between the vector u_d and the normalized eigenvector u_ν, as can be easily proved. If, on the other hand, the system is let to be infinite such that $N\to\infty$ and the free electron spectrum $\{E_k\}$ is replaced by a continuous spectrum which is assumed to have a known density of states $\mathcal{H}_{\mathrm{free}}(E)$, then

$$f(E+i0) = E-E_d - \mathrm{P}\int_{-\infty}^\infty \frac{|V_{dk}|^2}{E-E_k}\mathcal{H}_{\mathrm{free}}(E_k)\,dE_k$$

$$+ i\pi\langle|V_{dk}|\rangle^2 \mathcal{H}_{\mathrm{free}}(E), \qquad (4\cdot24)$$

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*) An exponential of a self-adjoint operator may be expressed by the so-called Dunford integral[21]

$$e^{itH} = \frac{1}{2\pi i}\int_{-\infty-is_0}^{\infty-is_0}\frac{e^{iEt}}{E-\mathbf{H}}\,dE, \quad t\geq0$$

$$= 0, \quad t<0$$

$$= \frac{1}{2\pi i}\int_C \frac{e^{iEt}}{E-\mathbf{H}}\,dE,$$

where the contour C encircles counterclockwise the spectrum of $\mathbf{H}$ on the real axis.

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and for any interval (E_1, E_2) of E where $\mathcal{N}_{\text{free}}(E_1) \neq 0$ and continuous the integral is bounded, i.e.,

$$\left| \int_{E_1}^{E_2} \frac{1}{f(E+is)} \text{Im} \frac{1}{f(E-i0)} dE \right| < \infty,$$

and so

$$\lim_{s \to 0} \frac{s}{2\pi} \int_{E_1}^{E_2} \frac{1}{f(E+is)} \left(\frac{1}{f(E-i0)} - \frac{1}{f(E+i0)} \right) dE = 0. \qquad (4 \cdot 25)$$

This implies the fact that a contribution to the integral in $(4 \cdot 21)$ from the (absolute) continuous part of the free-electron spectrum has no δ-function type singularity and hence is ineffective on the localization.

At such an interval of the real E-axis the function $f(E)$ now has a discontinuity on crossing the axis and its continuation necessitates a many-valued analytic function. To be important, the complex E-plane in which the rational function f_N is defined remains in the $N \to \infty$ limit to be a principal sheet where the limiting function $f(E)$ is still analytic and has no zero except on the real axis, but nothing can be said about the singularities and zeros on the other sheets to which the $f(E)$ is continued. Let this principal sheet be called "physical sheet" and all the others "non-physical sheets". It can be said that the energy E_d of the initial d level after dissolving into the metal will tend to a complex zero of the analytic function $f(E)$ which is located in the non-physical sheet and will make no contribution to the quantity given in the left hand of $(4 \cdot 23)$ as expressed in the right hand. This is the nature of the "virtual state": Its no contribution to the transition probability limit $(4 \cdot 20)$ may be attributed to the finiteness of its life time which comes from the imaginary part of the complex zero of the function $f(E)$ on the non-physical sheet. Therefore, we can summarize the present analysis as follows:

Anderson's virtual level is localized from the condition (I'), i.e., the (strong) absence of diffusion, only when the presence of an excess d-level atom forms a true bound state outside of the free-electron continuous spectrum in the metal, and, if this is the case,

$$\lim_{s \to 0} s \int_0^\infty e^{-st} P_{d \to d}(t) dt = |\langle \psi_b, \psi_d \rangle|^4 > 0, \qquad (4 \cdot 26)$$

where ψ_d and ψ_b represent the normalized d orbital and the normalized bound-state orbital, respectively.

Thus, it may be said that the word "localization" in terms of the quantum diffusion is actually not compatible with the originally intended meaning. A fully satisfactory assignment must be said to remain unsolved. However, since it is still attractive to pursue an understanding of the excess d-electron density given by $(4 \cdot 12)$ in terms of the transition probability concept, we

wish to give here a remark about how to associate the d-electron density in thermal equilibrium with the time-dependent transition probability. This is to demonstrate the way of the excess density formation in a time-dependent manner of the dissolving process of a foreign atom into a metal:

Let $P_{\alpha\to d}(t)$ be the quantum transition probability that a pure eigenstate α of the Hamiltonian before dissolving could be found at the time t in any state of the d-site being occupied, and average the $P_{\alpha\to d}(t)$ over the initial eigenstates with the usual canonical distribution, which is denoted by

$$\langle P_d(t)\rangle = \sum_\alpha W_\alpha P_{\alpha\to d}(t). \qquad (4\cdot27)$$

Then, the excess density $\Delta\rho$ in $(4\cdot13)$ can be identified by

$$\lim_{t\to\infty}\langle P_d(t)\rangle = \frac{1}{\pi}\int_{\text{cont}}\frac{1}{e^{\beta(E-\mu)}+1}\,\text{Im}\,\frac{-1}{f(E+i0)}\,dE$$

$$= \int_{E_{\min}}^{E_f}\frac{-1}{\pi}\,\text{Im}\,\frac{1}{f(E+i0)}\,dE \ (\text{at absolute zero}) = \Delta\rho, \qquad (4\cdot28)$$

where the contribution from the bound-state pole (if it exists) is excluded in the integration which is carried only over the continuous spectrum. The proof of this statement may be obtained by writing the right-hand side of $(4\cdot27)$ in the (second-quantized) operator form as

$$\text{Tr}(\hat{\rho}_d\hat{\rho}^0(t)) = \text{Tr}(\hat{\rho}_d e^{-it\mathcal{H}}e^{-\beta\mathcal{H}_0}e^{-it\mathcal{H}})$$

$$= \text{Tr}(\hat{\rho}_d e^{-it\mathcal{H}}e^{it\mathcal{H}_0}e^{-\beta\mathcal{H}_0}e^{-it\mathcal{H}_0}e^{it\mathcal{H}})$$

$$\xrightarrow{t\to\infty} \text{Tr}(\hat{\rho}_d W_+ e^{-\beta\mathcal{H}_0}W_+^\dagger), \qquad (4\cdot29)$$

where

$$W_+ = \lim_{t\to\infty} e^{-it\mathcal{H}}e^{it\mathcal{H}_0} \qquad (4\cdot29a)$$

is the scattering wave operator[22] which satisfies the "intertwining property"

$$W_+ e^{-\beta\mathcal{H}_0} = e^{-\beta\mathcal{H}}W_+, \qquad (4\cdot30)$$

and also the well-known identity

$$W_+ W_+^\dagger = 1 - \hat{\rho}_b. \qquad (4\cdot31)$$

§5. Density-of-states formulas by the coherent potential method

5.1 *The single-site approximation*

We proceed to considering the problem of how to treat the phase shift term in the Friedel sum relation taken up in §2.4 in such a way that it may be expressed, by any approximation, as a nontrivial, thermodynamically meaning-

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ful quantity. There have been considerable studies aiming at such expressions along the line of calculating the *trace* of the Green operators associated with a chosen model of disordered systems. In most of such theories the Green operator is expanded in power series of a disordered part of the Hamiltonian and then averaged over a physically plausible variety of systems having similar Hamiltonians. This is called "ensemble average", a keynote of securing the thermodynamical stability of the expression in this kind of approach. Here we follow Yonezawa's approach to random lattice problems[23] in its first order approximation (single-site approximation) to find such formulas. It has appeared that the approximation is equivalent to the coherent potential theory.[24]

By an extensive graphical analysis of perturbation series applied to a system of lattice composed of N sites in which $N-n$ are occupied by A-atoms and the rest n by B-atoms (i.e., a binary alloy), Yonezawa arrived at a self-consistent relationship between an ensemble averaged Green operator G and its self-energy part S as follows:

$$G(E)_{kk'} = \frac{\delta_{kk'}}{E - E_k - S_k(E)} \equiv G_k(E)\delta_{kk'}, \qquad (5\cdot1a)$$

$$S_k(E) = N \sum_{s=1}^{\infty} Q_s(c)\{\underbrace{V \cdot GV \cdot GV \cdots GV}_{s-1}\}_{kk}, \qquad (5\cdot1b)$$

where V represents a perturbation potential caused by a replacement of a single B-atom in the perfect A-lattice. Thus, the above presentation of $G(E)$ and $S(E)$ has the reference basis of the perfect A-lattice, but there should be no *a priori* reason to choose this reference and so the resulting self-consistent solutions must not depend on any particular reference. In other words, they should satisfy the host-defect or A-B dual symmetry. This was in fact one chief motivation in the Yonezawa-Matsubara paper,[25] where a detailed analysis was made to study a mathematical structure of the ensemble average of products of the density projectors ρ defined in (2·3d) with an emphasis of taking into account the "volume exclusion effects" (i.e., to eliminate over-counting of more than two defects to occupy the same site) to insure the sym-metry. Another important point related closely to this emphasis is that one must select carefully terms in the perturbation series according to each degree of the approximation prescribed from graphs: Otherwise, a "spurious" singularity arises in the expression for the self-energy part.[23] Thus, the originally introduced polynomials $P_s(c)$ for the s-th cumulant of the average of the ρ's have been replaced by $Q_s(c)$ in (5·1b), where

$$Q_s(c) = \sum_{m=1}^{s} (-1)^{m-1} \frac{(s+m-2)!}{m!(s-m)!(m-1)!} c^m \qquad (5\cdot2)$$

is a polynomial of order s of the concentration of the B-atoms, defined by

$$c = \frac{n}{N}. \tag{5.3}$$

The set of polynomials $\{Q_s(c)\}$ is characterized by a generating function of the form

$$I(z, c) = \sum_{s=1}^{\infty} Q_s(c) z^{s-1} \tag{5.4}$$

$$= \frac{1}{2z} \{z - 1 + [(1-z)^2 + 4cz]^{1/2}\} \tag{5.4a}$$

with

$$I(0, c) = Q_1(c) = c, \tag{5.4b}$$

which satisfies the identity

$$I(z, c) + I(-z, 1-c) = 1. \tag{5.5}$$

Therefore, if we define a self-energy operator $S(E)$ by extending the expression (3.1b) to inclusion of off-diagonal elements thus

$$S(E) = NV \sum_{s=1}^{\infty} Q_s(c) (GV)^{s-1}, \tag{5.6}$$

then,

$$S_k(E) = S(E)_{kk} = N \{ V I(GV, c) \}_{kk}$$
$$= N V_{kk} - N \{ V \cdot I(-GV, 1-c) \}_{kk}. \tag{5.7}$$

This indicates that the averaged Green operator is invariant under the symmetry transformation

$$E_k \rightarrow \bar{E}_k = E_k + V_{kk}, \quad V \rightarrow \bar{V} = -V, \quad c \rightarrow \bar{c} = 1 - c, \tag{5.8}$$

which is the mentioned dual symmetry.

The self-energy operator $S(E)$ may be related to the usual T matrix in scattering theory in the extreme limit $c \rightarrow 0$ or $c \rightarrow 1$: From the expansion of $I(z, c)$ with respect either to c or to $1-c$, we have

$$S(E) = NcV(1 - GV)^{-1}, \qquad c \rightarrow 0 \tag{5.9a}$$

$$= NV + N(1-c)(-V)(1 + GV)^{-1}, \quad c \rightarrow 1 \tag{5.9b}$$

respectively. The expression (5.9a) shows that the self-energy in the extremely low concentration of B-atom is just a sum of the T matrix of each independent scattering due to a single perturbation potential V acting from B-atoms, and (5.9b) just in the opposite limit situation. Therefore, Eq. (5.6) would provide a reasonable interpolation for $0 \leq c \leq 1$. In general cases, as Yonezawa shows by means of graphs, the $S(E)$ may be written as

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$$S(E) = NcV(1-GV\zeta)^{-1} \equiv NcV\eta,$$

and ζ is related to η in another way: $V\zeta = V(1-c\eta)$. If we introduce a parameter σ in place of $c\eta$, which appears more convenient in the operator relation

$$S(E) = NV \cdot \sigma,$$

therefore, σ is related with itself through GV by

$$\sigma (= I(GV, c)) = \frac{c}{1-GV(1-\sigma)}, \tag{5.10}$$

or, conversely,

$$GV = -\frac{c}{\sigma} - \frac{1-c}{\sigma-1}. \tag{5.11}$$

Another way of putting this equation to connect with the original CPA formulation[24] that the *effective T* matrix vanishes on the average is the following:

$$\frac{(1-c)(-\sigma)}{1-GV\cdot(-\sigma)} + \frac{c(1-\sigma)}{1-GV\cdot(1-\sigma)} = 0. \tag{5.11'}$$

Note that the generating function (5.4a) with $z = GV$ is nothing but one portion of the explicit solutions of Eq. (5.11) satisfying the condition (5.4b).

Equation (5.11) or (5.11') is the fundamental setting in the single-site approximation theory which has the following implications:
(a) The self-energy of the Green operator contains only a single-site potential;
(b) It satisfies the dual symmetry, namely $\bar{G}\bar{V} = GV$ with $\bar{V} = -V$, $\bar{\sigma} = 1-\sigma$, $\bar{c} = 1-c$ and $\bar{G} = G$;
(c) GV as interpreted as a function of the parameter σ has no singularity other than $\sigma = 0$ or $\sigma = 1$ where it has a simple pole—a necessary and sufficient singularity from the single-site occupation point of view.[*]

5.2 Construction of the formulas

The requirement of self-consistency between the (ensemble averaged) Green operator and its self-energy implied in Eqs. (5.1a) and (5.1b) is solvable explicitly, when the single-site potential V is a "separable" form; $V_{kk'} = N^{-1}\sqrt{v_k}\sqrt{v_{k'}}$ (thus applicable to a δ-potential model or same kinds of approximations, and to a mass-defects disorder problem of vibrations, etc.). In such cases one can take advantage of a lemma, saying that for any function F of the operator GV,

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[*] For this statement to receive a better understanding one must resort a representation of the pertinent quantity as a function of the complex variable σ. See §7.

$$\{V \cdot F(GV)\}_{kk'} = V_{kk'} F(z), \tag{5.12a}$$

where

$$z = \frac{1}{N} \sum_k v_k G_k(E). \tag{5.12b}$$

The proof of this is easy, by considering polynomials and hence any convergent power series. The simplest one is

$$(V \cdot GV)_{kk'} = \frac{1}{N} \sqrt{v_k} \left(\frac{1}{N} \sum_k v_k G_k(E) \right) \sqrt{v_{k'}} = V_{kk'} z, \tag{5.13}$$

and similar matrix products apply repeatedly to any order. Thus, for example,

$$(V \cdot \sigma)_{kk'} = \{V \cdot I(GV, c)\}_{kk'} = V_{kk'} I(z, c). \tag{5.14}$$

Applying the same rule to the expression (5.11), we also have

$$(V \cdot GV)_{kk'} = V_{kk'} \cdot \left(-\frac{c}{\sigma(z)} - \frac{1-c}{\sigma(z)-1} \right). \tag{5.15}$$

On comparing this with (5.13), we get one relation between z and σ:

$$z = -\frac{c}{\sigma} - \frac{1-c}{\sigma-1}. \tag{5.16}$$

Another relation may be obtained by substituting the form of $G_k(E)$ given by (5.1a) into (5.12b), and by noting that (5.16) is the inverse relation of (5.4a, b), that is

$$z = \frac{1}{N} \sum_k \frac{V_k}{E - E_k - v_k\sigma}. \tag{5.17}$$

Therefore, the problem reduces to a self-consistency determination of the c-number parameter σ from Eqs. (5.16) and (5.17). In the following, we discuss a simple example of constant matrix elements, $V_{kk'} = v/N$, for illustrative purpose. This example corresponds to a tight-binding energy band or Frenkel exciton in a mixed crystal.[26]

If $v_k = v$ (independent of k) in (5.17), the density of states is simply proportional to $-\text{Im} z(E+i0)$. Define, therefore, the quantity $z_A(E)$ for the $\sigma = 0$ limit (the perfect A-lattice) as

$$z_A(E) = \frac{v}{N} \sum_k \frac{1}{E - E_k}. \tag{5.18}$$

Then, the quantity z for an arbitrary σ is given simply by a shift of the variable E in $z_A(E)$,

$$z = z_A(E - v\sigma). \tag{5.19}$$

Or, denoting the inverse function of z_A by ϕ_A, we may have

$$E = \phi_A(z) + v\sigma. \tag{5.19'}$$

Equations (5.16) and (5.19') may be considered as a representation of the z vs. E relation through an analytic parameter σ: A complete determination of z as a function of E is to be given by inserting $\sigma(E)$ thus solved into the expression (5.19); $z_A(E - v\sigma(E))$. To get a density-of-states vs. phase-shift relation let us introduce a subsidiary energy variable u: $E - v\sigma(E) \equiv u$, or

$$E = u + v\sigma. \tag{5.19''}$$

Then,

$$dE = du + v d\sigma, \tag{5.19'''}$$

and we may write

$$z(E)dE = z_A(u)du + \left(-\frac{c}{\sigma} - \frac{1-c}{\sigma - 1}\right)v d\sigma, \tag{5.20}$$

where we have used the two expressions (5.19) and (5.16) for z in the first and second parts, respectively, of the right-hand side. Or, noting that $z(E)$ and $z_A(E)$ are v/N times the *traces* of the Green operators, Tr $G(E)$ and Tr $G_A(E)$, respectively, we may rewrite (5.20) also as follows:

$$\mathrm{Tr}\,G(E)dE = \mathrm{Tr}\,G_A(u)du + N\left(-\frac{c}{\sigma} - \frac{1-c}{\sigma - 1}\right)d\sigma. \tag{5.20'}$$

We assume that $z(E)$ and $z\{u(E)\} \to 0$ as $E \to -\infty$ to which corresponds the value $\sigma = c$ in (5.16). Then, upon integrating both sides of (5.20') from $E = -\infty$ to E along a straight line located just above the real axis,

$$\int_{-\infty}^{E} \mathrm{Tr}\,G(E')dE' = \int_{-\infty}^{E - v\sigma(E)} \mathrm{Tr}\,G_A(E')dE' + N \int_{c}^{\sigma(E)} \left(-\frac{c}{\sigma} - \frac{1-c}{\sigma - 1}\right)d\sigma$$

$$= \int_{-\infty}^{E - v\sigma(E)} \mathrm{Tr}\,G_A(E')dE' + Nc\log\frac{c}{\sigma(E)} + N(1-c)\log\frac{1-c}{1-\sigma(E)}. \tag{5.21}$$

This is the first form of our aimed formula. It is seen to satisfy the dual symmetry, because $G_B(E) = G_A(E - v)$ and a shift of the variable of integration of the Tr $G_A(E)$ assures

$$\int_{-\infty}^{E - v\sigma(E)} \mathrm{Tr}\,G_A(E')dE' = \int_{-\infty}^{E - \bar{v}\bar{\sigma}(E)} \mathrm{Tr}\,G_B(E')dE'. \tag{5.22}$$

This symmetry leads to a more convenient representation by introducing the *virtual crystal*, defined by

$$G_{\text{virtual}}(E) = G_A(E - cv) = G_B(E + (1-c)v)$$
$$= G_B(E - \bar{c}v). \tag{5.23}$$

The G_{virtual} $(= G_{\text{vir}})$ is invariant under the symmetry transformation (5.8), and thus, in place of (5.21), our formula is now

$$\int_{-\infty}^{E} \text{Tr}\, G(E')\, dE' = \int_{-\infty}^{E+cv-v\sigma(E)} \text{Tr}\, G_{\text{vir}}(E')\, dE'$$
$$+ Nc\log\frac{c}{\sigma(E)} + N(1-c)\log\frac{1-c}{1-\sigma(E)}. \tag{5.24}$$

This is supplemented by the parameter σ vs. E relation which we repeat here:

$$E = \phi(z) + v\sigma - cv, \tag{5.25a}$$

$$z = -\frac{c}{\sigma} + \frac{1-c}{1-\sigma}, \quad (\sigma = I(z, c)) \tag{5.25b}$$

where ϕ is the inverse function of the sum over the virtual crystal defined such that

$$u = \phi(z) \rightleftarrows z = \frac{V}{N}\text{Tr}\, G_{\text{vir}}(u). \tag{5.25c}$$

For practical purposes the formula (5.24) can be put in another representation. This is to normalize the upper bound of the integration of $\text{Tr}\, G_{\text{vir}}(E')$ up to the given energy E, and to make an approximation of expanding a fraction of the integral to lowest order in such a way that

$$\int_{-\infty}^{E+cv-c\sigma(E)} \text{Tr}\, G_{\text{vir}}(E')\, dE' = \int_{-\infty}^{E} + \int_{E}^{E+cv-v\sigma(E)} \text{Tr}\, G_{\text{vir}}(E')\, dE'$$
$$\simeq \int_{-\infty}^{E} + (c-\sigma(E))v\,\text{Tr}\, G_{\text{vir}}(E+cv-v\sigma(E))$$
$$= \int_{-\infty}^{E} + N(c-\sigma(E))z(E). \tag{5.26}$$

The approximation in the above may be allowed, if the $\text{Tr}\, G_{\text{vir}}(E)$ is a smooth function of E (generally not assured depending on the range of E). Accordingly, we have

$$\int_{-\infty}^{E} \{\text{Tr}\, G(E') - \text{Tr}\, G_{\text{vir}}(E')\}\, dE'$$
$$= N\{(c-\sigma(E))z(E) + c\log\frac{c}{\sigma(E)} + (1-c)\log\frac{1-c}{1-\sigma(E)}\}. \tag{5.27}$$

But, from the previous manipulations (5.16)~(5.21), the above logarithmic terms are equal to the integral

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and therefore by means of an integration by parts and with a use of the power series expansion (5·4)

$$\int_c^{\sigma(E)} \left(-\frac{c}{\sigma} - \frac{1-c}{\sigma-1} \right) d\sigma = \int_c^{\sigma(E)} z d\sigma,$$

$$\frac{1}{N} \times \text{Eq.}(5\cdot27) = (c - \sigma(E)) z(E) + \int_c^{\sigma(E)} z d\sigma$$

$$= -\int_0^{z(E)} \sigma dz = -\int_0^{z(E)} I(z, c) dz$$

$$= -\sum_{s=1}^{\infty} \frac{Q_s(c)}{s} \{z(E)\}^s. \qquad (5\cdot28)$$

Noting that, for the separable potential case, any function F of the operator GV has its *trace* simply given by $\text{Tr}\, F(GV) = F(\text{Tr}\, GV) = F(z)$, we get a simple result of rewriting the formula as follows:

$$\int_{-\infty}^E \{\text{Tr}\, G(E') - \text{Tr}\, G_{\text{vir}}(E')\} dE' = -N \sum_{s=1}^{\infty} \frac{Q_s(c)}{s} \text{Tr}\, \{G(E) \cdot V\}^s$$

$$= N \text{Tr} \{(cV - V\sigma(E)) G(E)\}$$

$$+ Nc\, \text{Tr} \log \frac{c}{\sigma(E)} + N(1-c)\, \text{Tr} \log \frac{1-c}{1-\sigma(E)}. \qquad (5\cdot29)$$

We consider this formula as a general formula of connecting the trace of the Green operators between a perturbed and an unperturbed (virtual lattice) binary alloy in the single-site approximation by means of the self-energy parameter $\sigma(E)$, which may not necessarily be restricted to the constant matrix-element potential.*) We note that the integrated density-of-states relation is obtained from (5·29) by multiplying a factor $1/N\pi$, going to the limit $N \to \infty$ thereby keeping the concentration factor c=constant, and then by taking the imaginary part defined on the physical sheet.   (The meaning of the "physical sheet" for the present use will be discussed in §7.)   The result is now of the form

$$\rho(E) - \rho_{\text{vir}}(E) \equiv \int_{-\infty}^E \{N(E') - N_{\text{vir}}(E')\} dE'$$

$$= \frac{-1}{\pi} \text{Im}\, \text{Tr}((cV - V\sigma(E+i0)) G(E+i0)$$

$$+ \frac{c}{\pi} \text{Tr} \arg \sigma(E+i0) + \frac{1-c}{\pi} \text{Tr} \arg(1 - \sigma(E+i0)). \qquad (5\cdot30)$$

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*) Because of its simplicity in form we have tried to give a justification of its wider applicability not restricted to the constant matrix-element case, or even not to the "separable" matrix-element cases, by graphical analyses, but not succeeded.

It should be an interesting question to inquire the physical significance of the *real part* of the relation (5·29) instead of the imaginary part, which will be taken up in a later discussion.

5.3 *Application to the three examples*

Let us specialize our prototype formulas derived so far to the three examples in §2.4 to get a convenient form for each case.

(1) Harmonic vibrations in a binary alloy

The formulation in the preceding subsection may be applied, if the following changes of notations in §2 (in particular the presentation of the secular equation (2·3 c)) are made:

$$E = \omega^2, \quad E_k = \omega_k^2, \qquad \begin{pmatrix} \text{The matrix index is} \\ \text{changed from } \mu \text{ to } k. \end{pmatrix} \tag{5·31a}$$

$$V_{kk'} = \frac{1}{N}\left(\frac{M}{m} - 1\right)\omega_k \omega_{k'}, \quad V_{kk} = \frac{1}{N}\left(\frac{M}{m} - 1\right)E_k, \tag{5·31b}$$

$$S_{kk'} = N(V \cdot \sigma)_{kk'} = \left(\frac{M}{m} - 1\right)\omega_k \omega_{k'} \sigma, \tag{5·31c}$$

$$E_k + S_k = E_k\left(1 + \left(\frac{M}{m} - 1\right)\sigma\right), \tag{5·31d}$$

$$z(E) = \left(\frac{M}{m} - 1\right)\frac{1}{N}\sum \frac{E_k}{E - (E_k + S_k)}. \tag{5·31e}$$

It is convenient here to introduce a parameter μ to replace σ such that

$$E_k + S_k = \frac{M}{\mu}E_k \rightleftarrows \sigma = \frac{m}{M - m}\left(\frac{M}{\mu} - 1\right). \tag{5·32}$$

Since the starting basis is a perfect lattice with mass M (the M-lattice) for which $\omega_k^2\ (=E_k)$ is proportional to $1/M$, the above representation of the energy spectrum has the meaning of a lattice vibration of the same lattice structure with M being replaced by μ. In terms of μ, then, the z vs. σ relation (3·16) becomes now

$$z = \left(\frac{M}{m} - 1\right)\left(\frac{c\mu}{\mu - M} + \frac{(1-c)\mu}{\mu - m}\frac{m}{M}\right).$$

On the other hand, from (3·31) and (3·32)

$$\frac{M}{\mu}\frac{m}{M - m}z = \frac{1}{N}\sum \frac{E_k + S_k}{E - (E_k + S_k)} = -1 + \frac{1}{N}\sum \frac{E}{E - (E_k + S_k)},$$

so the fundamental z vs. σ relation is replaced by the following Z vs. μ relation

where

$$Z = \frac{c\mu}{\mu - M} + \frac{(1-c)\mu}{\mu - m} = \frac{\mu(\mu - \mu_0)}{(\mu - M)(\mu - m)},$$ (5·33a)

$$Z = \frac{1}{N}\sum_{k} \frac{E}{E - (E_k + S_k)} = \frac{E}{N}\operatorname{Tr}\boldsymbol{G}_M(E).$$ (5·33b)

In (5·33 a) μ_0 is given by

$$\mu_0 = cm + (1-c)M,$$ (5·34)

which is the mean mass, indicating that this is an adequate constant with a meaning of mass that characterizes the virtual lattice in the present problem. If this is used, (5·33 b) is rewritten as

$$Z = \frac{1}{N}\sum_{k} \frac{\mu E}{E - ME_k} \left(= \frac{\mu E}{\mu_0}\frac{1}{N}\operatorname{Tr}\boldsymbol{G}_{\mu_0}\!\left(\frac{\mu}{\mu_0}E\right)\right).$$ (5·35)

A system of constitutive equations for the present single-site problem is, therefore,

$$E = \frac{\mu_0}{\mu}\phi(z), \quad \left(\begin{array}{l}\phi\text{ is the inverse}\\\text{function of }Z(E).\end{array}\right)$$ (5·36a)

$$Z = \frac{\mu(\mu - \mu_0)}{(\mu - M)(\mu - m)}.$$ (5·36b)

Also, the relation between the trace of the Green operators for the μ- and μ_0-lattices is given, from (3·35), by

$$\operatorname{Tr}\boldsymbol{G}_\mu(E) = \frac{N}{E}z(E) = \frac{\mu}{\mu_0}\operatorname{Tr}\boldsymbol{G}_{\mu_0}\!\left(\frac{\mu}{\mu_0}E\right),$$ (5·37)

from which

$$\operatorname{Tr}\boldsymbol{G}(E)dE = \operatorname{Tr}\boldsymbol{G}_{\mu_0}(u)du - N\left(\frac{c}{\mu - M} + \frac{1-c}{\mu - m}\right)d\mu,$$ (5·38)

where the subsidiary energy variable u is defined presently by

$$u = \frac{\mu}{\mu_0}E \quad \text{or} \quad u = \phi(Z) \quad (\text{from }(5·36a, \text{ b})).$$ (5·39)

We note that the value of μ at the virtual-lattice mass μ_0 corresponds in the present problem to $E = 0$, which can be seen from Eqs. (5·36 a,b) and (5·35). Thus, by integrating both sides of the differential relation (5·38) from $E = 0$ to E, we get the aimed formulas;

$$\int_0^\omega \text{Tr}\,\mathbf{G}(\omega')2\omega'd\omega'\left(=\int_0^E \text{Tr}\,\mathbf{G}_\mu(E')dE'\right)$$

$$=\int_0^{\omega\mu/\mu_0}\text{Tr}\,\mathbf{G}_{\text{vir}}(\omega')2\omega'd\omega'+Nc\log\left(\frac{\mu_0-M}{\mu-M}\right)+N(1-c)\log\left(\frac{\mu_0-m}{\mu-m}\right)$$

$$\simeq\int_0^\omega \text{Tr}\,\mathbf{G}_{\text{vir}}(\omega')2\omega'd\omega'+\omega^2(\text{Tr}\,\mathbf{G}(\omega)-\text{Tr}\,\mathbf{G}_{\text{vir}}(\omega))$$

$$+Nc\log\left(\frac{\mu_0-M}{\mu-M}\right)+N(1-c)\log\left(\frac{\mu_0-m}{\mu-m}\right),\qquad(5\cdot40)$$

$$\int_0^\omega\{N(\omega')-N_{\text{vir}}(\omega')\}d\omega'$$

$$\simeq\frac{\omega}{2}\{N(\omega)-N_{\text{vir}}(\omega)\}$$

$$+\frac{c}{\pi}\arg(\mu(\omega+i0)-M)+\frac{1-c}{\pi}\arg(\mu(\omega+i0)-m).\qquad(5\cdot41)$$

The self-consistent treatment along the foregoing line for the lattice vibration was proposed first by Davies and Langer,[27] and later studied numerically by Taylor[28] and Nakamura and Yonezawa.[29] For a purpose of specialized interests we present here an explicit form of the set of Eqs. (5·36 a,b) applied to the example of a nearest-neighbor coupled linear chain discussed in §2, for which the inverse function $\phi(Z)$ may be given in terms of an elementary function. The frequency spectrum of this system with the mean mass μ_0 (i.e., of the virtual lattice) is given by

$$E_k(=\omega_k^2)=\frac{1}{\mu_0}\sin^2\left(\frac{kd}{2}\right).$$

$$(k=\frac{\pi}{d}\times\text{integer up to }N)\qquad(5\cdot42)$$

Accordingly, the function $Z(E)$ defined in (5·35) is calculated in the limit $N\to\infty$, as

$$Z=w\{w(w-1)\}^{-1/2}=\left(\frac{w}{w-1}\right)^{1/2},\qquad(5\cdot43a)$$

where

$$w=\frac{\mu}{\mu_0}E.\qquad(5\cdot43b)$$

Therefore,

$$w=\phi(Z)=\frac{Z^2}{Z^2-1}.\qquad(5\cdot43c)$$

Equations (5·36 a,b) are found to be of the forms

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$$E = \frac{\mu_0 \mu (\mu - \mu_0)^2}{2\bar{\mu}_0 (\mu - \mu_1)(\mu - \mu_2)(\mu - \mu_3)}, \tag{5.44a}$$

$$Z = \frac{\mu(\mu - \mu_0)}{(\mu - M)(\mu - m)}, \tag{5.44b}$$

in which the constant mean mass μ_0 is given in (5.34) and all the others $\bar{\mu}_0$ μ_1, μ_2, and μ_8 in some way.
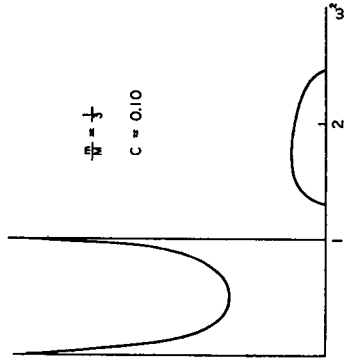

Fig. 6. The frequency spectrum of a linear chain of binary alloy calculated by the CPA method after Taylor[28] (schematic).

Equation (5.44 a) is a cubic equation for the "mass" variable μ, a complex root of which yields, when inserted into Eq. (5.44 b), a direct solution for the density of states (actually the frequency spectrum) of the CPA lattice vibration of a linear-chain binary alloy. Figure 6 shows a numerical result of such density-of-states curves after Taylor.[28] It would be an interesting exercise to grasp how such curves come out by considering the mapping structure between the energy variable $E(=\omega^2)$ and the function Z represented on the complex μ-plane. Actually, there exists a nontrivial conceptual difference in Taylor's result from the present one. These matters are taken up separately in the Appendix.

(2) Impurity scattering of (one-dimensional) electrons due to short range forces

This is essentially the limiting case $c \to 0$ of the illustrative example, $v_k = v$ (independent of k), given in Eqs. (5.16)~(5.30), inasmuch as the free electron spectrum extends to $E \to +\infty$ as $|k| \to +\infty$, which corresponds to an infinitely large Brillouin zone. In the limit $c \to 0$, the parameter constitutive equations (5.25 a) and (5.25 b) are replaced by

$$E = \phi_A(z) + v\sigma,$$

$$\sigma = I(z, c \to 0) = c \sum_{s=1}^{\infty} z^{s-1} \ (Q_s(c) = c \text{ in } (5.2)) \tag{5.45a}$$

$$= \frac{c}{1-z}, \tag{5.45b}$$

where the A-lattice basis has been chosen rather than the virtual lattice for obvious reason. Accordingly, the expressions (5.29) and (5.30) become

$$\int_{-\infty}^{E} \{ \mathrm{Tr}\, G(E') - \mathrm{Tr}\, G_A(E') \} dE' = -Nc \sum_{s=1}^{\infty} \frac{1}{s} \mathrm{Tr}\, \{ G(E) \cdot V \}^s$$

$$= Nc\, \mathrm{Tr}\, \log(1 - G(E) \cdot V)$$

$$= Nc\, \log(1 - z(E)) \tag{5.46}$$

and

$$\rho(E) - \rho_A(E) = -\frac{c}{\pi} \arg(1 - z(E+i0)).$$ (5·46′)

To apply these formulas to a system of free electrons moving under the action of randomly distributed δ-potentials (expressed in Eq. (3·1)), the trace operation is considered as limited inside a long interval L, being divided by L, and then L is made to infinity. The concentration factor c is accordingly redefined as

$$c = \lim_{L \to \infty, n \to \infty} \frac{n}{L}.$$ (5·47)

Since $\mathrm{Tr}\,G_{\mathrm{free}}(E)$ is given by $-1/2\kappa(E) = -1/2(-E)^{1/2}$, the parameter relations (5·45 a) and (5·45 b) are summarized by a single equation of the form

$$E = -\frac{\kappa_0^2}{z^2} - \frac{2c\kappa_0}{1-z}, \qquad (v = -2\kappa_0)$$ (5·48)

or

$$E z^3 - (E + 2c\kappa_0) z^2 + \kappa_0^2 z - \kappa_0^2 = 0.$$ (5·48′)

This cubic equation as a result of the self-consistent determination of the Tr G for the model (3·1) was first treated by Klauder[30] and then applied in a modified form to three dimensional case by Yonezawa.[31] Also, several physical applications have been made to study impurity banding effects in semiconductor physics.[32]~[34] In particular, the present author examined a detailed analytic structure of the function $z(E)$ which maps the complex E-plane into the complex z-plane through Eq. (5·48) or (5·48′), thus establishing several consistency aspects in the approximation, e.g., a partial sum rule of the density of states associated with the impurity band.[32]

In the early stage of the above studies it was a principal subject to find out a best approximate expression for the self-energy part in the $G_k(E)$. From the CPA point of view this question is now answered by taking one of the roots of the cubic equation (5·48′), $z(E)$, which satisfies

$$-\mathrm{Im}\,v z(E+i0) = \mathrm{Im}\,2\kappa_0 z(E+i0) \geq 0$$ (5·49)

and by substituting it into the $G_k(E)$ thus

$$G_k(E) = \frac{1}{E - k^2 - NV\sigma(E)}$$

$$= \frac{1}{E - k^2 + 2c\kappa_0/(1-z(E))}.$$ (5·50)

This provides a life of the free-particle state denoted by $1/\tau_k(E)$ as follows:

$$\frac{1}{\tau_k(E)} = -NV \operatorname{Im} \sigma(E) \quad (k\text{-independent})$$

$$= 2c\kappa_0 \operatorname{Im} z(E+i0)/|1-z(E+i0)|^2.$$

If we now remind ourselves of the self-consistent technique in determining the Tr G implied in (5·45 a, b) (see also (5·18) and (5·19) which are the origin of the technique), we observe that

$$z(E) = -\frac{2\kappa_0}{L} \sum_k G_k(E) = 2\kappa_0 \cdot \frac{-1}{2\pi} \int_{-\infty}^{\infty} G_k(E) dk, \tag{5·51}$$

i.e.,

$$\operatorname{Im} z(E+i0) = 2\kappa_0 \pi N(E), \tag{5·51'}$$

so that

$$\frac{1}{\tau(E)} = \frac{4\pi c\kappa_0^2}{|1-z(E+i0)|^2} N(E). \tag{5·52}$$

This form assumes a complete parallelism to the infinitesimal probability in the expression (3·26) but now with a thermodynamically significant meaning through the function $z(E)$, its imaginary part yielding the self-consistent density of states $N(E)$, and also the concentration factor c. The parallelism is shown to be perfect, if we rewrite the sum over the $G_k(E)$ in such a way that

$$-\frac{1}{L} \sum_k G_k(E) = -\frac{1}{L} \sum_k G_k(E - v\sigma(E))$$

$$= \frac{-1}{2\pi} \int_{-\infty}^{\infty} \frac{dk}{E - k^2 + 2\kappa_0/(1-z(E))}$$

$$= \frac{1}{2\kappa(E)}, \tag{5·51''}$$

where the so defined function $\kappa(E)$ is related to the $z(E)$ as

$$z(E) = \kappa_0/\kappa(E), \tag{5·51'''}$$

and so

$$\frac{1}{\tau(E)} = \frac{4\pi c\kappa_0^2}{|1-\kappa_0/\kappa(E+i0)|^2} N(E). \tag{5·52'}$$

It is clear that the usual Born approximation is a consequence of this formalism valid when $|\kappa| \gg |\kappa_0|$ and $N(E) \simeq N^0(E)$, and therefore

$$\frac{1}{\tau(E)_{\text{Born}}} = 4\pi c\kappa_0^2 N^0(E) \quad (=\pi c v^2 N^0(E)). \tag{5·53}$$

The Friedel sum rule (5·46) is now rewritten as

$$\int_{-\infty}^{E} \{\mathrm{Tr}\mathbf{G}(E') - \mathrm{Tr}\mathbf{G}^0(E')\}\,dE' = c\log(1 - \kappa_0/\kappa(E)), \qquad (5\!\cdot\!54)$$

which is again parallel to the result (3·23): Only the significant modification here is the concentration factor c multiplied to the logarithmic term. It will be seen later that the logarithmic term in the above relation can be interpreted in fact as a scattering phase shift, in a sense averaged, of the scattering due to many centers. Another point to note is that the $\kappa(E)$ here is not a simple function $(-E)^{1/2} \equiv \kappa^0(E)$ but satisfies the self-consistent relation (5·48) via (5·51′′′), i.e.,

$$E = -\kappa^2 - \frac{2c\kappa_0\kappa}{\kappa - \kappa_0}, \qquad (5\!\cdot\!55)$$

which may be looked as a "dispersion relation" in the CPA disordered electron system.[35] The use of this $\kappa(E)$ instead of the free-electron $\kappa^0(E)$ in the logarithmic term yields a better approximation than the form $\log(1 - \kappa_0/\kappa^0(E))$ for a discussion of the impurity band formation, because it gives a finite band width. In another respect it is a rather poor approximation, in particular, for the actual limit $c \to 0$, where the predicted width is too large. In the free-electron continuum, i.e., when E is positive and large, the difference between $\log(1 - \kappa_0/\kappa(E))$ and $\log(1 - \kappa_0/\kappa^0(E))$ is insignificant.
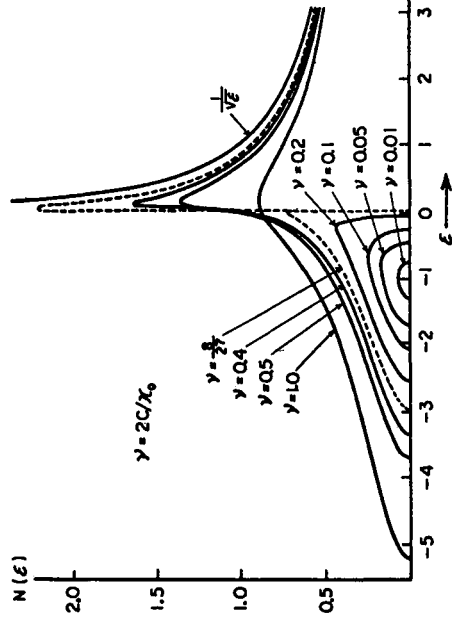
Fig. 7. The CPA density of states of a one-dimensional free electrons perturbed by uniformly distributed δ potentials (after Shiba, Kanda, Hasegawa and Fukuyama[34]).

Some examples of the calculated density of states according to the formulas (5·51′) and (5·48′) are shown in Fig. 7. The integrated density of states of the same model was compared with the free-electron square-root shape by Klauder as quoted in Halperin's paper,[36] which can be viewed from the present stand-point just to illustrate the Friedel relation (5·46′).

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(3) Virtual localized states near the Fermi level in a metal

The problem of a virtual d-level atom dissolved in a metal in §4 will now be retreated from the CPA point of view by considering the following matrix equation:

$$\left[\begin{array}{c|c} (E-E_d)\delta_{j'j} & -V_{j'k} \\ \hline -V_{k'j} & (E-E_{k'})\delta_{k'k} \end{array}\right]\left[\begin{array}{c|c} G^{(d)}_{j'j} & G_{j'k} \\ \hline G_{k'j} & G^{(s)}_{k'k} \end{array}\right]=1. \tag{5.56}$$

In each of these matrices the upper left and the lower right blocks correspond to the d- and s-electronic states, respectively, where the indices j and k designate the lattice sites and the wave number, respectively. Thus we are dealing with a tight-binding electron system in an A-B alloy composed of A-atoms with an s orbital and B-atoms with the same s and another d orbital. The s-d mixing matrix element V_{jk} may assume the form

$$V_{jk}=\frac{v}{\sqrt{N}}e^{ik\cdot j} \tag{5.57}$$

with a k-independent parameter v. Eliminating the s-d off-diagonal part of the G-matrix in a similar manner as in §4, we have

$$(E-E_d)G^{(d)}_{j'j}-\sum_{(j'')}\frac{1}{N}\sum_{k}\frac{v^2e^{ik\cdot(j'-j'')}}{E-E_k}G^{(d)}_{j''j}=\delta_{j'j}, \tag{5.58a}$$

$$(E-E_{k'})G^{(s)}_{k'k}-\sum_{k''}\frac{v^2}{E-E_{k'}}\rho_{(j)}(k''-k')G^{(s)}_{k''k}=\delta_{k'k}, \tag{5.58b}$$

where $\rho_{(j)}(k''-k)$, the density projector, is the same as in (2.3 d).

A conventional argument to get a simple, uncorrelated form of $G^{(d)}$ is just to ignore the off-diagonal part in the sum over $\{j''\}$ in Eq. (5.58 a), leading to a result

$$G^{(d)}_{j'j}=\delta_{j'j}G_d(E), \tag{5.59}$$

where $G_d(E)$ is given by (4.7 a). This is of course unsatisfactory and is subject to an examination whether its validity could be deduced or not, in the dilute limit of the d atoms, from a more general stand point. For this purpose let us perform a Fourier-transform of Eq. (5.58 a):

$$G^{(d)}_{k'k}=\frac{1}{N}\sum_{j'j}e^{i(k'\cdot j'-k\cdot j)}G^{(d)}_{j'j}. \tag{5.60}$$

Making use of the density projector, we can write the equation for $G^{(d)}_{k'k}$ in a form

$$(E-E_d-\frac{v^2}{E-E_{k'}})G^{(d)}_{k'k}+\sum_{k''}\frac{v^2}{E-E_{k''}}\rho_{(j)}(k''-k')G^{(d)}_{k''k}=\delta_{k'k}, \tag{5.58'}$$

where $\{\bar{j}\}$ represents the *dual* configuration of $\{j\}$, i.e., all of those sites unoccupied by the d atoms. It is then possible to apply the CPA formulation both to the $G^{(s)}$ and $G^{(d)}$ matrices by imposing the respective self-consistency conditions (Prescription by Eqs. (5·16) and (5·17)) between their average and the self-energy: We have the k-diagonal representations for the ensemble-averaged $G^{(s,d)}$ in terms of the self-energy parameters σ and $\tilde{\sigma}$ in the form

$$G_k^{(s)}(E) = \frac{1}{E - E_k - \sigma v^2/(E - E_d)}, \tag{5·61a}$$

$$G^{(d)}(E) = \frac{1}{E - E_d - v^2/(E - E_k) + \tilde{\sigma} v^2/(E - E_k)}, \tag{5·61b}$$

where the σ and $\tilde{\sigma}$ are to be determined from a respective set of equations of the type (5·16) and (5·17).

Let us denote the concentration of the d-level atom (B-atom) by $c = n_d/N$ (the number of the B-atoms divided by the total lattice sites), and analyze the two limiting situations, $c \to 0$ and $c \to 1$, in terms of the s-band density-of-states function $z_0(E)$ defined by

$$z_0(E) \equiv \frac{1}{N} \sum_k \frac{1}{E - E_k}. \tag{5·62}$$

Case $c \to 0$ limit

The self-consistent equations (5·16) and (5·17) for the $G_k^{(s)}$ can be written as

$$z = \frac{v^2}{E - E_d} z_0 \left(E - \frac{v^2 \sigma}{E - E_d} \right) = -\frac{c}{\sigma} - \frac{1 - c}{\sigma - 1}, \tag{5·63a}$$

where, from (5·45 b), $\sigma = c/(1 - z)$ to first order in c. Similarly, for the $G_k^{(d)}$

$$\tilde{z} = \frac{-v^2}{E - E_d} z_0 \left(E - \frac{v^2}{E - E_d} (1 - \tilde{\sigma}) \right) = -\frac{1 - c}{\tilde{\sigma}} - \frac{c}{\tilde{\sigma} - 1}, \tag{5·63b}$$

$$\tilde{\sigma} = 1 - \frac{c}{1 + \tilde{z}} \quad \text{to first order in } c.$$

Thus,

$$\frac{1}{N} \sum_k G_k^{(s)}(E) = z_0(E) - c v^2 \frac{d z_0(E)}{dE} \bigg/ (E - E_d - v^2 z_0(E)), \tag{5·64a}$$

$$\frac{1}{N} \sum_k G_k^{(d)}(E) = \frac{1 - c}{E - E_d} + \frac{c}{E - E_d - v^2 z_0(E)}. \tag{5·64b}$$

A word should be given to the result of (5·64 b). The second term on the right

is what we have expected from the conventional argument omitting the off-diagonal part, $j'' \neq j$, in the sum in (5·58 a). It expresses the density-of-states function for the dissolved d atoms in the dilute limit which is precisely equal to c times the $G_d(E)$ in (4·7 a) calculated in the single d-atom treatment. What meaning, then, is to be assigned to the first term? It may be interpreted as the *rest of free d atoms* prepared but not dissolved in the metal. By this interpretation the quantity $N \times (z_0(E) + 1/(E - E_d))$ represents the trace of the Green operator at the initial state, namely, the density-of-states function for the system composed of the s-band lattice plus additional N free d atoms, which is denoted by $\mathrm{Tr}\,\mathbf{G}^0(E)$. Accordingly, Eqs. (5·64 a,b) may be summarized by

$$\mathrm{Tr}\,\mathbf{G}(E) = \mathrm{Tr}\,\mathbf{G}^0(E)$$
$$+ Nc \left\{ \frac{\left(1 - v^2 \dfrac{dz_0(E)}{dE}\right) \Big/ (E - E_d - v^2 z_0(E))}{-\dfrac{1}{E - E_d}} \right\}. \qquad (5\cdot65)$$

Another interesting point of the present study is the "detailed balance" relation to be satisfied by the inverse life times for the two species denoted by $1/\tau_s(E)$ and $1/\tau_d(E)$. Recall the expressions for the $G^{(s)}(E)$ and for the *solute part* of $(1/N)\mathrm{Tr}\mathbf{G}^{(d)}(E)$ to first order in c:

$$G_k^{(s)}(E) = \frac{1}{E - E_k - cv^2/(E - E_d - v^2 z_0(E))}, \qquad (5\cdot66a)$$

$$\frac{1}{N} \sum_k G_k^{(d)}(E) \bigg|_{\text{solute}} = \frac{c}{E - E_d - v^2 z_0(E)}. \qquad (5\cdot66b)$$

Thus the self-energy for the former is proportional to the latter and also vice versa, so the relation may be expressed as

$$\frac{N_s(E)}{\tau_s(E)} = \frac{N_d(E)}{\tau_d(E)}, \qquad (5\cdot67)$$

where the densities of states for the two species are defined here by

$$N_s(E) = \frac{-1}{\pi}\mathrm{Im}\,z_0(E) \qquad (5\cdot68a)$$

and

$$N_d(E) = \frac{-1}{\pi}\mathrm{Im}\,\frac{c}{E - E_d - v^2 z_0(E)}. \qquad (5\cdot68b)$$

Case $c \to 1$ limit

In the actual limit $c = 1$ we have $\sigma = 1$ and $\tilde{\sigma} = 0$, and so

$$G_k^{(s)}(E) = \frac{1}{E - E_k - v^2/(E - E_d)}, \quad G_k^{(d)}(E) = \frac{1}{E - E_d - v^2/(E - E_k)}.$$

Therefore, the sum $\sum_k (G_k^{(s)} + G_k^{(d)})_{c=1}$ yields the density-of-states function for the perfect s-d tight-binding lattice with two bands, $E_\pm(k)$, obtainable as the roots of the secular equation,

$$E^2 - (E_d + E_k)E + E_d E_k - v^2 = 0:$$

$$\sum_k (G_k^{(s)} + G_k^{(d)})_{c=1} = \sum_k \left(\frac{1}{E - E_+(k)} + \frac{1}{E - E_-(k)} \right). \qquad (5\cdot69)$$

In terms of the function $z_0(E)$ this is given by

$$= N z_0 \left(E - \frac{v^2}{E - E_d} \right) + \frac{N}{E - E_d} \left\{ 1 + \frac{v^2}{E - E_d} z_0 \left(E - \frac{v^2}{E - E_d} \right) \right\}. \qquad (5\cdot69')$$

More precisely to first order in $1-c$, we find

$$\frac{1}{N} \sum_k G_k^{(s)}(E) = z_0 + (1-c)v^2 \frac{dz_0}{dE} \Big/ (E - E_d + v^2 z_0), \qquad (5\cdot70a)$$

$$\frac{1}{N} \sum_k G_k^{(d)}(E) = \frac{1}{E - E_d} \left(1 + \frac{v^2 z_0}{E - E_d} \right)$$

$$+ (1-c) \frac{v^4}{(E - E_d)^2} \frac{dz_0}{dE} \Big/ (E - E_d + v^2 z_0)$$

$$- \frac{1-c}{E - E_d} + \frac{1-c}{E - E_d + v^2 z_0}, \qquad (5\cdot70b)$$

where the argument of the function z_0 in the above is assumed to take $E - v^2/(E - E_d)$ without exception. Defining, therefore

$$z_1(E) \equiv z_0(E - v^2/(E - E_d)), \qquad (5\cdot71)$$

and denoting the left-hand side of Eq. (5·69) as $\text{Tr } G^0(E)$, we have in parallel to (5·65)

$$\text{Tr } G(E) = \text{Tr } G^0(E)$$

$$+ N(1-c) \times \left\{ \frac{1}{E - E_d} \times \left\{ \left(1 + v^2 \frac{dz_1(E)}{dE} \right) \Big/ (E - E_d - v^2 z_1(E)) \right\} \right\}. \qquad (5\cdot72)$$

It may be noted that the three contributions to the $\text{Tr } G^{(d)}(E)$ given in (5·70 b) in the order of $1-c$, viz. 2nd, 3rd and 4th terms on the right are interpreted,

respectively, as arising from one of the self-energy correction to the perfect s-d band, the *free defects* of d atoms outside the metal, and the dissolved defects of d atoms. Thus assigning a meaning of the density-of-states function of the dissolved defects to the last term, $1 - c/(E - E_d + v^2 z_1(E))$, we see again that a detailed balance relation holds in the same manner as in (5·67) but here with replacing the function $z_0(E)$ by $-z_1(E)$.

We conclude this section by rewriting the derived relations (5·65) and (5·72) in the familiar Friedel sum form as follows:

$$\frac{1}{N} \int_{-\infty}^{E} \{\mathrm{Tr}\, \boldsymbol{G}(E') - \mathrm{Tr}\, \boldsymbol{G}^0(E')\}\, dE'$$

$$= c \log\left(1 - \frac{v^2}{E - E_d} z_0(E)\right), \quad c \to 0 \tag{5·73a}$$

$$= (1 - c) \log\left(1 + \frac{v^2}{E - E_d} z_1(E)\right). \quad c \to 1 \tag{5·73b}$$

The present study complements the recent work by Sasada and Hasegawa[37] which deals with the bottle-neck problem of an electron spin resonance of localized magnetic moments in dilute alloys where a theoretical foundation had to be necessitated for the meaning of the s- and d-spin polarization as well as for the detailed balance relation between the two s-d relaxation constants.

§6.　A general treatment of one-dimensional transmission problems

All the preceding studies have suggested a possibility that the integrated density of states of a thermodynamic system in (aperiodic) solids is expressible in terms of the imaginary part of a certain logarithmic function which may be interpreted as the total sum of phase shifts of every scattering of the dynamical species occurring in the system. This idea should be disciplined seriously so that it may achieve a mathematically firm foundation. The present section will be devoted to one such discipline by treating a general scattering problem in one dimension, namely, the problem of transmission and reflection of a Schrödinger particle through a finite interval of an arbitrary potential barrier. Reading and Sigel's recent treatment[12] of the random δ-potential problem as mentioned in the end of §3 can be included into the present study, provided the distribution of the potential centers is such that they are confined in the interval of length L, called the scattering region, outside of which the particle is assumed to move freely. We present here a result of our analysis of this problem, from which one can get a better understanding of the CPA formula discussed in §5.

Table II. Boundary-value problem of the scattering for a one-dimensional Schrödinger particle.

$V(x)=0$ $x=a$	scattering region $V(x)\neq0$ $x=0$	$V(x)=0$ $x=b$
$A_t(k)e^{-ikx}$	$\longrightarrow$ $\psi_k^+(x)$ $\longrightarrow$	$e^{-ikx}+A_r(k)e^{ikx}$
$e^{ikx}+\tilde{A}_r(k)e^{-ikx}$	$\longrightarrow$ $\tilde{\psi}_k^+(x)$ $\longrightarrow$	$\tilde{A}_t(k)e^{ikx}$
$A_t(-k)e^{ikx}$	$\longrightarrow$ $\psi_k^-(x)$ $\longrightarrow$	$e^{ikx}+A_r(-k)e^{-ikx}$
$e^{-ikx}+\tilde{A}_r(-k)e^{ikx}$	$\longleftarrow$ $\tilde{\psi}_k^-(x)$ $\longrightarrow$	$\tilde{A}_t(-k)e^{-ikx}$

Setting up two incident plane waves with a wave number k and considering the corresponding reflected and transmitted components of the waves are essentially the same as in §3, which are summarized in Table II. There, besides the usual outgoing solutions $(\psi^+, \tilde{\psi}^+)$ a pair of incoming solutions $(\psi^-, \tilde{\psi}^-)$ are listed which may be obtained just by inverting the sign of k in the former expressions. The reflection and the transmission coefficients can be determined as a result of the Schrödinger boundary-value problem in Table II for each wave which obeys a second-order, linear, homogeneous differential equation of the type (3·1).

It is well-known that any two such solutions ψ_1 and ψ_2 satisfy a conservation of current, i.e.,

$$W(\psi_1, \psi_2)\equiv\psi_1\psi_2'-\psi_1'\psi_2=\text{const.} \tag{6·1}$$

For example, a substitution of the expressions for ψ_k^+ and $\tilde{\psi}_k^+$ into $W(\psi_k^+,\tilde{\psi}_k^+)$ at the points a and b which are chosen outside the scattering region sufficiently left and right, respectively, leads us to a relation $A_t(k)=\tilde{A}_t(k)$. There are six such relations, thus, as a consequence of the current conservation, which may be summarized by

$$\begin{pmatrix} A_t(k) & A_r(k) \\ \tilde{A}_r(k) & \tilde{A}_t(k) \end{pmatrix}\cdot\begin{pmatrix} A_t(-k) & \tilde{A}_r(-k) \\ A_r(-k) & \tilde{A}_t(-k) \end{pmatrix}=\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}, \tag{6·2}$$

$$\tilde{A}_t(k)=A_t(k). \tag{6·3}$$

The 2×2 matrix in the above has a meaning of the S-matrix in this scattering problem, since

$$\begin{pmatrix} A_t(k) & A_r(k) \\ \tilde{A}_r(k) & \tilde{A}_t(k) \end{pmatrix}=\begin{pmatrix} (\psi_k^-\psi_k^+) & (\psi_k^-\tilde{\psi}_k^+) \\ (\tilde{\psi}_k^-\psi_k^+) & (\tilde{\psi}_k^-\tilde{\psi}_k^+) \end{pmatrix}$$

$$\equiv S(k), \tag{6·4}$$

where the inner products $(\psi_k^- \psi_k^+)$ etc. are calculated in the outside of the scattering region. Since the incoming and outgoing solutions are time-reversal conjugate to each other, every matrix element of the S satisfies

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$$\{A_{t,\,r}(k^{*})\}^{*}=A_{t,\,r}(-k), \tag{6.5}$$

thus together with (6·2) and (6·3)

$$\{S(k^{*})\}^{*}=S(-k), \tag{6.6}$$

$$S(k)\cdot{}^{t}S(-k)=1 \quad ({}^{t}S \text{ denotes the transpose of } S), \tag{6.7}$$

leading to the fundamental fact that the S is unitary when $k=$real, a summarized statement of the probability conservation (3·18).

A consideration of the analyticity of S-matrix as a function of k as well as E developed in early days by Wigner,[4] Schützer and Tiomno,[38] van Kampen[39] and Toll[40] provides a guiding principle to the present study.*) Our main program is to find a representation of the $S(k)$ in terms of analytically simpler functions. For this purpose let us consider a pair of solutions, $\alpha(x, E)$ and $\beta(x, E)$, of the second-order differential equation which satisfy the initial values at $x=0$ such that

$$\alpha(0, E)=1, \qquad\qquad \beta(0, E)=0, \tag{6.8a}$$

$$\alpha'(0, E)=\left(\frac{d\alpha}{dx}\right)_{x=0}=0, \quad \beta'(0, E)=1. \tag{6.8b}$$

The continuation of each linear combination of these two solutions for the ψ^{+} and $\tilde{\psi}^{+}$, its magnitude and the derivative (or, equivalently, the logarithmic derivative) at $x=a$ and $x=b$, to those of the plane waves indicated in Table II leads us to get an expression for $A_{r}(k)$ and $\tilde{A}_{r}(k)$, and then from the conservation relation (6·2) and (6·3)

$$A_{t}(k)A_{t}(-k)=1-A_{r}(k)A_{r}(-k)=1-\tilde{A}_{r}(k)\tilde{A}_{r}(-k), \tag{6.9}$$

$$\frac{A_{t}(k)}{A_{t}(-k)}=-\frac{A_{r}(k)}{\tilde{A}_{r}(-k)}=\det S(k), \tag{6.10}$$

yielding an expression for $A_{t}(k)$ and the determinant of $S(k)$. The results are expressed in terms of four functions, $A(E)$, $B(E)$, $C(E)$, $D(E)$, and also of the wave number $k(=E^{1/2})$ as follows:

$$A_{r}(k)=-\frac{C+Bk^{2}+(A-D)ik}{C-Bk^{2}-(A+D)ik}e^{-2ikb}, \tag{6.11a}$$

$$\tilde{A}_{r}(k)=-\frac{C+Bk^{2}-(A-D)ik}{C-Bk^{2}-(A+D)ik}e^{2ika}, \tag{6.11b}$$

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*) Recently, a good review about the causality and dispersion relations has been published by Nussenzveig.[47]

$$A_t(k) = -\frac{2ik}{C - Bk^2 - (A+D)ik} e^{-ik(b-a)}, \tag{6·11c}$$

$$\det S(k) = A_t^2(k) - A_r(k)\tilde{A}_r(k)$$

$$= -\frac{C - Bk^2 + (A+D)ik}{C - Bk^2 - (A+D)ik} e^{-2ik(b-a)}, \tag{6·11d}$$

where by means of the solutions α and β

$$\begin{pmatrix} A(E) & B(E) \\ C(E) & D(E) \end{pmatrix}$$

$$= \begin{pmatrix} \alpha(b)\beta'(a) - \beta(b)\alpha'(a) & -\alpha(b)\beta(a) + \beta(b)\alpha(a) \\ \alpha'(b)\beta'(a) - \beta'(b)\alpha'(a) & -\alpha'(b)\beta(a) + \beta'(b)\alpha(a) \end{pmatrix}$$

$$= \begin{pmatrix} \alpha(b,E) & \beta(b,E) \\ \alpha'(b,E) & \beta'(b,E) \end{pmatrix} \begin{pmatrix} \beta'(a,E) & -\beta(a,E) \\ -\alpha'(a,E) & \alpha(a,E) \end{pmatrix}. \tag{6·12}$$

Note that this is also equal to the matrix

$$= \begin{pmatrix} \alpha_a(b,E) & \beta_a(b,E) \\ \alpha_a'(b,E) & \beta_a'(b,E) \end{pmatrix} \tag{6·12'}$$

by means of the solutions $\alpha_a(x,E)$ and $\beta_a(x,E)$ satisfying

$$\alpha_a(a,E) = 1, \quad \beta_a(a,E) = 0, \tag{6·13a}$$

$$\alpha_a'(a,E) = 0, \quad \beta_a'(a,E) = 1. \tag{6·13b}$$

Note also that every matrix appearing in (6·12) and (6·12') has its derterminant unity due to the current conservation associated with the α and β.

An important fact about these functions is, according to the theory of ordinary differential equation,[41] that each of $\alpha(x, E)$, $\alpha'(x, E)$, $\alpha''(x, E), \ldots$ and hence of $A(E), B(E), \cdots$ is an *entire function* of E, i.e., one-valued, holomorphic (regular) everywhere in the finite E-plane so that its Taylor series expansion has an infinite convergence radius. Furthermore, it can be shown that any zero point of these functions is simple and is restricted to locate on the real axis. Thus a ratio of any two such functions is meromorphic everywhere in the finite E-plane, whose zeros and poles are all simple and located on the real axis. Wigner[4] investigated a special class of such functions which he named "R-functions": An R-function, $R(E)$, is a one-valued analytic function of E which is meromorphic everywhere in the finite E-plane and satisfies the condition

$$\text{Im } R(E) \gtrless 0 \text{ according to } \text{Im } E \gtrless 0. \tag{6·14}$$

It is then possible to deduce some elementary properties of the $R(E)$ such that

(a) $\{R(E^*)\}^* = R(E)$, and it assumes real values only on the real axis,

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(b)　its zeros as well as poles are all simple and located on the real axis,

(c)　its derivative is real positive at every regular point of the real axis,

(d)　it yields an absolutely convergent Mittag-Leffler series

$$R(E)=\alpha E+\beta+\sum \left(\frac{\gamma_\mu^2}{E_\mu-E} - \frac{\gamma_\mu^2}{E_\mu} \right) \tag{6.14'}$$

with real constants, $\alpha \,(\geq 0)$, β, γ's and E_μ's.

Its profile is just like as illustrated in Fig. 1. Its best example we have met is the function $f(E)$ defined in (4.6) under the assumption of the discreteness of E_k. Examples of R-functions here are $a'(a, E)/a(a, E)$, $a(b, E)/a'(b, E)$, $A(E)/C(E)$, $B(E)/D(E)$ and so on (see the footnote related to Eq. (6.19)).

It is now possible to state the analytic structure of our formulas (6.11 a~d). They are all one-valued analytic function of k, meromorphic everywhere in the finite k-plane, the poles of which are identified with all the zeros of the common denominator, an entire function of k denoted by

$$f(k) \equiv C(k^2)-B(k^2)k^2-(A(k^2)+D(k^2))ik, \tag{6.15}$$

whose locations are either

(I)　on the imaginary axis (all simple), or

(II)　inside of the lower half plane situated symmetrically with respect to the imaginary axis (see Fig. 6).

Thus, all the S-matrix elements and hence $\det S(k)$ are holomorphic in the upper half of the k-plane except at the simple poles indicated in (I). In particular, the function $\det S(k)$ yields a product expansion of the form

$$\det S(k) = -\frac{f(-k)}{f(k)} e^{-2ik(b-a)}$$

$$= -e^{-2ik \cdot l} \prod_\nu \frac{k+i\kappa_\nu}{k-i\kappa_\nu} \cdot \prod_\nu \frac{(k+K_\nu)(k-K_\nu^*)}{(k-K_\nu)(k+K_\nu^*)}, \tag{6.16}$$

$$0<l\leq b-a, \tag{6.16a}$$

where $i\kappa_\nu$'s and K_μ's $(\mathrm{Re} K_\mu>0, \mathrm{Im} K_\mu<0)$ are the stated zeros of $f(k)$ in (I) and (II), respectively. (The physical meaning of these zeros are the bound states for (I) and the so-called "resonance states" for (II). Anderson's "virtual level" discussed in §4 is a typical example for the latter.)

The fact that the $f(k)$ defined by (6.15) has no zero (besides its regularity) in the upper-half k-plane with possible exceptions of the bound-state zeros on the $+i$ axis can be deduced from the theory of boundary-value problems in second-order linear differential equation: It says that there exists one and unique linear combination of $\alpha(x)$ and $\beta(x)$ which continues to $\psi_k(x)$ at $x \to -\infty$, or to $\tilde{\psi}_k(x)$ at $x \to +\infty$, their amplitudes decaying exponentially to each direction, when the wave number k lies in the upper-half plane. Physically, it is a

consequence of the *causality*, namely the fact that no scattered wave arises before an incident wave present. Hence, the scattering amplitudes A_t, A_r and $\tilde{A}_r$ are all regular functions of k in that region, or equivalently, of the energy E in the physical sheet. Under the circumstance, if we rewrite

$$\det S(k) = -e^{-2ik(b-a)}\frac{1+ikR(E)}{1-ikR(E)}, \tag{6.17}$$

then

$$R(E) = \frac{A(E)+D(E)}{C(E)-B(E)E} \tag{6.18}$$

must necessarily be a Wigner's R-function, as was proved by van Kampen.[39]

For our starting purpose of the Friedel sum rule, the theory of second-order linear differential equations provides a useful formula:[*]

$$\frac{1}{W(\psi_k^+, \tilde{\psi}_k^+)} \int_a^b \psi_k^+(x)\tilde{\psi}_k^+(x)dx$$

$$= \frac{\dfrac{d}{dE}(C(E)-B(E)E)-ik\dfrac{d}{dE}(A(E)+D(E))}{f(E)}, \tag{6.19}$$

where, to be added, the left-hand side represents the *trace* of the Green operator associated with the boundary-value problem under consideration, i.e., $\int_a^b G^+$ $(x \cdot x|k)dx \equiv \mathrm{Tr}\, G^+(E)$. Using Eqs. (6.11 c), (6.15) and (6.18) and noting that $k = E^{1/2}$, we can rewrite (6.19) as

$$\mathrm{Tr}\, G^+(E) = -\frac{d}{dE}\log\{e^{ik(b-a)}A_t(k)\}$$

$$+ \frac{1}{1-ikR(E)}\frac{1}{k}\frac{dk}{dE}. \tag{6.20}$$

---

[*] For any two solutions ψ_1 and ψ_2 of the differential equations

$$-\psi_1'' + V(x)\psi_1 = E_1\psi_1, \qquad -\psi_2'' + V(x)\psi_2 = E_2\psi_2,$$

the following identity holds:

$$(E_1-E_2)\int_a^b \psi_1(x)\psi_2(x)dx = W(\psi_1, \psi_2)_b - W(\psi_1, \psi_2)_a.$$

Letting $E_1 \to E_2 = E$, one has

$$\int_a^b \psi_1(x)\psi_2(x)dx = W\left(\frac{\partial\psi_1}{\partial E}, \psi_2\right)_b - W\left(\frac{\partial\psi_1}{\partial E}, \psi_2\right)_a.$$

A use of this identity together with the imposed boundary conditions will lead one to the formula (6.19). Also, setting $E_2^* = E_1 = E$ and choosing the initial values at a such that $\psi_1 = 1$, $\psi_1' = 0$, one has

$$\mathrm{Im}\, E \int_a^b |\psi_1(x)|^2 dx = |\psi_1'(b)|^2 \mathrm{Im}\left(\frac{\psi_1}{\psi_1'}\right)_{x=b}.$$

This shows that $\psi_1(b)/\psi_1'(b)$ $(a<b)$ is an R-function.

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The second term on the right may be interpreted to exhibit a boundary effect viz. a term arising from the boundary conditions for $(\psi^+, \bar\psi^+)$ at a and b which vary depending on the energy E. The phase shift associated with this scattering may be introduced by means of the transmission coefficient $A_t(k)$ for the physical reason that it connects the incident and transmitted components of the wave as discussed in the example of §3. Here let us write

$$A_t(k) = e^{i\vartheta(k)}, \tag{6.21}$$

$\vartheta(k)$ being a complex function of the complex variable k which satisfies

$$\{\vartheta(k^*)\}^* = -\vartheta(-k). \tag{6.22}$$

Consequently, the integral of the both-hand sides of (6.20), divided by the interval $b-a=L$ is now of the form

$$\frac{1}{L}\int^E \mathrm{Tr}\, G^+(E')dE' = -ik - \frac{i}{L}\vartheta(k)$$
$$+ [\text{boundary term}], \tag{6.23}$$

where

$$[\text{boundary term}] = \frac{1}{L}\int^{k(E)}\int \frac{1}{1-ikR(k^2)}\frac{dk}{k}, \tag{6.23a}$$

and the lower limit of the integration is unspecified for the moment. The $\vartheta(k)$ thus defined has a complexity of many-valuedness owing besides to the poles to possible zeros of the analytic function $A_t(k)$. To be important, however, the representation (6.11 c) shows clearly that only the zero of this function is the origin $k=0$, a fact which characterizes it from the others in (6.11). Thus, the possible singularities of the function $\log A_t(k) = i\vartheta(k)$ are those poles defined in (I), (II) and the zero at $k=0$. Note that in the Friedel relation (6.23) the right-hand side is free from the logarithmic singularity at $k=0$, because the boundary term compensates such a singularity arising from the $\vartheta(k)$ near $k=0$. Another important characteristic of the $A_t(k)$ is that

$$A_t(k) \xrightarrow{|k|\to\infty} 1 \quad 0 < \arg k < \pi, \tag{6.24}$$

which may be verified from the free-particle asymptotic form of the matrix in (6.12') for $|E|\to\infty$ in the physical sheet. Thus the $\vartheta(k)$ may be regarded as a one-valued analytic function inside of the contour Γ indicated in Fig. 8, where

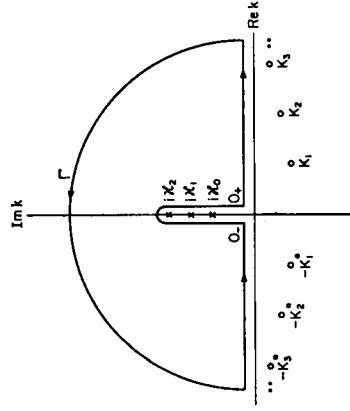$$\vartheta(k) \xrightarrow{|k|\to\infty} 0 \quad 0 < \arg k < \pi. \tag{6.24'}$$

Fig. 8. Poles of the transmission coefficients $A_t(k)$ in the complex k-plane for a general one-dimensional scattering. The cross on the positive imaginary axis and the circles in the lower half plane are (I) bound-state simple poles and (II) resonance poles, respectively. There is another set of simple poles (which are not indicated in this figure) located on the negative imaginary axis whose reflection images with respect to the real k-axis intervene, one by one, the bound-state poles of (I). See the footnote after Eq. (6·27′).

On the other hand, if the total number of the bound-states zeros is denoted by n,

$$\mathrm{Re}\,\vartheta(0)(=\frac{1}{2}(\vartheta(0+)-\vartheta(0-))=(n-\frac{1}{2})\pi. \qquad (6\cdot25)$$

This relation, known as Levinson's theorem[42] which states that the phase shift at $k=0$ is an indicator of the total number of the bound states localized in the scattering region, can be easily deduced by considering the contour integration along Γ of the function $(d/dk)A_t(k)/A_t(k)$. The appearance of a half-integer $-1/2$ is due to the special situation for this one-dimensional scattering problem and is related to the fact that

$$A_t(k=0)=0 \quad \text{and} \quad \det S(k=0)=-1. \qquad (6\cdot26)$$

To specify the lower bound of the integrations in the relation $(6\cdot23)$ let us take the imaginary part of its both sides. The boundary term $(6\cdot23\ \mathrm{a})$ then becomes

$$\frac{1}{L}\int^{k(E)}\frac{R\,dk}{1+k^2R^2}$$

which is free from the logarithmic singularity near $k=0$. We can use Levinson's theorem $(6\cdot25)$ to specify the lower bound in such a way that the integrated density of states at $E=0$ shall be equal to the number of the bound states n, thus

$$\int_{-\infty}^{E}\frac{-1}{L}\mathrm{Im}\,\mathrm{Tr}\,G^+(E')dE'=k(E)+\frac{1}{L}\,\mathrm{Re}\,\vartheta\{k(E)\}$$
$$+\frac{1}{L}\left(\frac{\pi}{2}-\int_0^{k(E)}\frac{R\,dk}{1+k^2R^2}\right). \qquad (E\geq0)$$

For a large system $(L\to\infty)$ the third term on the right which represents the boundary effect may be ignored compared to the other two, and so

$$\int_{-\infty}^{E}\frac{-1}{L}\mathrm{Im}\,\mathrm{Tr}\,G^+(E')dE'=k(E)+\frac{1}{L}\,\mathrm{Re}\,\vartheta\{k(E)\} \qquad (6\cdot27)$$

$$(k(E)=\sqrt{E}>0)$$

$$= k(E)\left(1-\frac{\ell}{L}\right)$$

$$+\frac{1}{L}\sum_{\nu=1}^{n-1}\left(\arctan\frac{\kappa_\nu}{k(E)}+\arctan\frac{|\tilde{\kappa}_\nu|}{k(E)}\right)+\frac{1}{L}\arctan\frac{\kappa_0}{k(E)}$$

$$+\frac{1}{L}\sum_{\nu=1}^{\infty}\left(\arctan\frac{\operatorname{Im}K_\nu}{k(E)+\operatorname{Re}K_\nu}+\arctan\frac{\operatorname{Im}K_\nu}{k(E)-\operatorname{Re}K_\nu}\right). \quad (6\cdot27')$$

The second expression of the series of arctangents in the above can be obtained from the product expansion $(6\cdot16)^*$ and by using the relation

$$\det S(k)=\frac{A_t(k)}{A_t(-k)}=\exp\{i(\vartheta(k)-\vartheta(-k))\}$$
$$=\exp\{2i\operatorname{Re}\vartheta(k)\}. \quad (k=\text{real}) \qquad (6\cdot28)$$

In view of the current conservation the transmission coefficient $A_t(k)$ satisfies $|A_t(k)|\leqq1$ on the real k-axis, which implies the inequality

$$\operatorname{Im}\vartheta(k)\geqq0. \quad (k=\text{real}) \qquad (6\cdot29)$$

We now wish to add another point of discussion concerning the important physical role played by the imaginary part of the phase-shift function $\vartheta(k)$. This inequality, which is a property associated with the real part of the Tr $G(E)$ instead of its imaginary part (see $(6\cdot23)$), may be considered to represent an effect of dissipation of the momentum of the Schrödinger particle in the course of the scattering. This is because the attenuating character of the transmitted component of the wave can be attributed to the consequence of a number of reflections that the particle undergoes virtually inside of the scattering region. Toll[40] made a similar argument concerning a general response function $A(\omega)$, as a function of the frequency ω, in which he considered the inequality $|A(\omega)|\leqq1$ as a dissipation of the energy and called it an "absorption". The present argument is quite parallel to Toll with replacement of the frequency ω by the wave number k as the variable of description. The quantity $(1/L)$ $\operatorname{Im}\vartheta(k)$ in fact may be considered to give an imaginary-part correction to the wave number $k(E)$ in the Friedel relation $(6\cdot27)$. Therefore, if this relation extended to include the imaginary part is converted to an E vs. k

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*) The poles of the analytic function $A_t(k)$ on the imaginary axis as classified in (I), the bound-state zeros of $f(k)$, have a twin structure such that to each bound-state pole $i\kappa_\nu$ ($\nu=1,2,\cdots n-1$) on the $+i$ axis there corresponds another pole $i\tilde{\kappa}_\nu$ ($\tilde{\kappa}_\nu<0$) on the $-i$ axis except one denoted by κ_0 so that the total number of these simple poles, (I), is $2n-1$. It is possible to arrange them in such a way that

$$\kappa_0<|\tilde{\kappa}_1|<\kappa_1<|\tilde{\kappa}_2|<\cdots<|\tilde{\kappa}_{n-1}|<\kappa_{n-1}.$$

Consequently, the poles and zeros of the function $\det S(k)=A_t(k)/A_t(-k)$ on the imaginary axis are situated just alternatingly (see van Kampen[39]). Every arctangent in the series $(6\cdot27')$ takes its principal value and conforms to Levinson's theorem $(6\cdot25)$.

relation, it would provide a correction to the dispersion of energy, i.e., the self-energy, of the free-particle state and, in particular, its inverse life time.

Let us denote the quantity $(1/L) \operatorname{Tr} \boldsymbol{G}(E)$ by $z(E)$ and write the differential form of the Friedel relation as

$$z(E) = \frac{1}{L} \operatorname{Tr} \boldsymbol{G}(E)$$

$$= z_0(E) + \frac{1}{L} z_1(E), \tag{6·30}$$

where

$$z_0(E) = \frac{-1}{2}(-E)^{-1/2} \tag{6·30a}$$

does not depend on L and

$$z_1(E) = -i\frac{d}{dE}\vartheta\{k(E)\}, \tag{6·30b}$$

if the boundary term is neglected. Let us consider the factor $1/L$ as a perturbation parameter and find the converted form of the Friedel relation (6·30) up to first order in $1/L$ such that

$$E = E_0(z) + \frac{1}{L} E_1(z). \tag{6·31}$$

Or, by substituting into the above z the free-particle z vs. k relation

$$z = \frac{1}{2ik},$$

we find the answer as follows:

$$E = k^2 + \frac{2k^2}{L}\frac{d\vartheta(k)}{dk}. \tag{6·32}$$

Thus we can summarize the physical roles of the real and imaginary parts of $(d/dk)\vartheta$ by writing

density of states

$$N(E) = N^0(E) + \frac{1}{\pi L}\left(\frac{1}{2k}\operatorname{Re}\frac{d}{dk}\vartheta\right)_{k=\sqrt{E}}, \tag{6·33}$$

inverse life time

$$\frac{1}{\tau(E)} = \frac{2E}{L}\operatorname{Im}\left(-\frac{d}{dk}\vartheta\right)_{k=\sqrt{E}}. \tag{6·34}$$

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In terms of the bound- and resonance-states poles $i\kappa_\nu$, $i\tilde{\kappa}_\nu$ and K_ν, we have also

$$\mathrm{Re}\left(\frac{d}{dk}\vartheta\right) = -\sum_{\nu=0}^{n-1}\frac{\kappa_\nu}{k^2+\kappa_\nu^2} - \sum_{\nu=1}^{n-1}\frac{|\kappa_\nu|}{k^2+\tilde{\kappa}_\nu^2}$$

$$+\sum_{\nu=1}^{\infty}\frac{2(k^2+|K_\nu|^2)(-\mathrm{Im}\,K_\nu)}{(k^2-\mathrm{Re}\,K_\nu^2)^2+(\mathrm{Im}\,K_\nu^2)^2} - \vartheta, \qquad (6\cdot33')$$

$$-\mathrm{Im}\left(\frac{d}{dk}\vartheta\right) = \sum_{\nu=0}^{n-1}\frac{k}{k^2+\kappa_\nu^2} + \sum_{\nu=1}^{n-1}\frac{k}{k^2+\tilde{\kappa}_\nu^2} + \frac{1}{k}$$

$$+\sum_{\nu=1}^{\infty}\frac{2k(\mathrm{Re}\,k_\nu^2-k^2)}{(k^2-\mathrm{Re}\,K_\nu^2)^2+(\mathrm{Im}\,K_\nu^2)^2}, \qquad (6\cdot34')$$

where the convergence of the infinite series is assured equivalent to the convergence of the infinite product (6.16).

The analysis we have carried out so far in this section is still not sufficient for a satisfactory answer to the starting question about the thermodynamical stability of the density of states. For example, it is still not clear how insignificant the derived quantity in (6.33') would be regarding the choice of the boundaries a and b. To inquire this problem it is necessary to impose some further restrictions on the nature of the potential inside of the scattering region, which links up with the fundamental question, namely "what is disordered system?" Loosely speaking, the required condition is a "uniformity" of the system expressed in some way by the nature of the potential function inside of the scattering region. That is to say, what one expects is this: If the potential function is of such a nature that its variation in the scattering region is sufficiently uniform, then, the boundary variation of the formulas (6.33'), (6.34') would be insensitive so that the series on the right-hands are always nearly proportional to the distance $b-a=L$ for every choice of the points a and b. We shall formulate this consideration in a later publication[*] by means of a more powerful mathematical tool. Here we quote again the important paper by Wigner[4] enlightening this problem, in which he gave the concept of "uniform R-functions". An R-function $R(E)$ of the form (6.14') is called uniform, if the following conditions are fulfilled:

(a) its linear term vanishes, i.e., $\alpha=0$,

(b) it has a *pole density* denoted by ρ such that in any interval of length $L\rangle$ $L(\epsilon)$ (to be determined for an arbitrary small ϵ) the number of poles E_μ is equal, within an error proportional to ϵ, to ρL, and

(c) it has a *definite strength* denoted by s such that the sum of the residues, $\sum\gamma_\mu^2$, within the above interval, is equal to sL.

An important fact about this definition is that these characteristics are in-

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[*] A preliminary report has been given by H. Hasegawa and A. Kishimoto.[43]

variant under linear fractional transformations of the $R(E)$ which produces a family of analytic functions, as corresponding to the boundary variations if interpreted in the present transmission problem. Thus the boundary-insensitive phase-shift function $\vartheta(k)$ could be deduced essentially from this family of analytic functions.

In conclusion, it may be remarked that the present analysis indicates clearly, in the above-mentioned situation of the uniformity of the system, how the phase shift ϑ divided by the scattering length L will tend to the (complex) wave number correction in the thermodynamic limit $L\to\infty$ of the system, as may be seen from the expression (6·23).

§7. Summary and remarks

For a dynamical system with a finite number of scattering centers the Friedel sum rule we have considered may be expressed in the form

$$\int_{-\infty}^{E}\mathrm{Tr}\,\boldsymbol{G}(E')dE'=\int_{-\infty}^{E}\mathrm{Tr}\,\boldsymbol{G}_0(E')dE'+\log\det\boldsymbol{F}(E).$$

Here $\boldsymbol{F}(E)$ is an $n\times n$ matrix defined as a function of the energy variable E in a complex plane, and satisfies

(a) single-valued, analytic and regular (spanning an n-dimensional vector space, or $\det\boldsymbol{F}(E)\not\equiv 0$) everywhere there except on the real axis,

(b) $\det\boldsymbol{F}^*(E^*)=\det\boldsymbol{F}(E)$, (the principle of reflection)

(c) Im $\det\boldsymbol{F}(E)<0$ for Im$E>0$,

(d) $\lim\limits_{E\to\infty}\det\boldsymbol{F}(E)=1$ for $0<\arg E<2\pi$,

(e) possible zeros of the $\det\boldsymbol{F}(E)$ on the real axis are simple and finite in number.

For the three examples taken up in §2.4 the matrix $\boldsymbol{F}$ is given explicitly as follows:

(1) Harmonic vibrations in a binary alloy

$$F(E)_{jj'}=\delta_{jj'}-\frac{M-m}{m}\frac{1}{N}\sum_{\mu=1}^{N}\frac{E_{\mu}}{E-E_{\mu}}e^{i(j-j')\mu}, \tag{7·1}$$

(2) Impurity scattering of electrons due to short range forces

$$F(E)_{jj'}=\delta_{jj'}-\frac{\kappa_0}{\kappa(E)}\exp\{-\kappa(E)|x_j-x_{j'}|\}, \tag{7·2}$$

$$\kappa(E)=(-E)^{1/2},$$

(3) Virtual localized states near the Fermi level

$$F(E)_{jj'}=\delta_{jj'}-\frac{1}{E-E_d}\frac{1}{N}\sum_{k=1}^{N}\frac{v^2}{E-E_k}e^{i(x_j-x_{j'})k}. \tag{7·3}$$

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The analytic function $\det F(E)$ of the properties (a)~(d) is specific in physics, characterizable as a one-sided Laplace transform of a time response function, and may be called a "causal function". If, further, it satisfies another property

(e') meromorphic everywhere in the finite E-plane,

then the minus sign of it is just a Wigner's R-function, as exemplified by the above (1) and (3). (These are actually rational R-functions with a finite number of poles.) In the example (2) the function $-\det F(E)$ is not an R-function because of the double-valuedness of the function $\kappa(E)=(-E)^{1/2}$ which arises from the background continuous spectrum for the assumed infinite system.

It is really one most difficult point in constructing the theory of density of states that we must consider infinite systems, in other words, take the so-called "thermodynamic limit" of the R-functions associated with each finite system. Thus it is quite intrinsic to consider ensemble of system, only on which a thermodynamically meaningful density of states may be defined. In this limit, generally, the series of the R-functions may not tend to a definite limit, and, if it does, the limiting function represents an analytic function of a more general nature, i.e., a causal function. The problem to pursue the spectrum of a "disordered system" can then be fixed firmly from the set of all the singular points as well as the zeros of that function.

A zero point of an R-function characteristic to a finite system before taking the thermodynamic limit is restricted to locate only on the real axis and represents an "allowed" state of the system. On going to the limiting infinite system, a zero point of the resulting causal function can never be predicted to locate on the real axis only, but a possibility arises that there occurs its zeros off from the real E-axis which in general correspond to the so called "resonance states". However, to be the most important conclusion in the present investigation, we can assert that there should remain a complex E-plane preserved in the limiting process, on which a function element of the resulting function may be single-valued, analytic, and with no zeros except at the points of a closed set on the real axis, i.e., the spectrum. Possible zeros and singularities other than the spectrum off from the real axis must belong to some other E-planes. This means that for a complete representation of the causal function more than one sheet are necessary which constitute the totality of a Riemann surface; the one composed of a principal sheet with the stated causal nature and all the rests, which we have called the physical and the non-physical sheets, respectively.

The coherent potential approximation (CPA) is a handy approximation (but of rather narrow applicabilities) to compute the thermodynamic limit, yielding an analytic function which fulfills the above-discussed requirement. The totality of the analytic function, called the density-of-states function, $z(E)$, can be seen just by the parameter representation given for the simple binary-alloy problem by Eqs. (5·25a,b,c), i.e.,

$$E = \phi(z) + (c-\sigma)v, \tag{7.4}$$

$$z = -\frac{c}{\sigma} - \frac{1-c}{\sigma-1}, \tag{7.5}$$

$$u = \phi(z) \rightleftarrows z = \frac{v}{N} \operatorname{Tr} \boldsymbol{G}_{\mathrm{vir}}(u)$$
$$\equiv z_0(u). \tag{7.6}$$

Here the set of these equations implies that a functional relation between z and E may be established through a parameter σ as in Eqs. (7.4) and (7.5), wheres $\phi(z)$ is obtainable from the inverse function of the known density-of-states function $z_0(u)$ given in Eq. (7.6). It is then possible to discuss all the analytic structures of the CPA density-of-states function $z(E)$ on the σ-plane translated from the entire E-surface, where the physical sheet will be mapped into a generally multiply-connected region of the σ-plane. This is schematically shown in Fig. 9. It can be seen that the contours which encircle this region (Γ_0 and Γ_1 in Fig. 9) are the maps of the boundary lines on the real E-axis
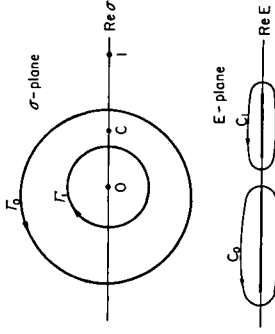
Fig. 9. A mapping between the complex E-plane and the complex σ-plane by which the physical sheet is mapped into the doubly-connected region encircled by the two closed contours Γ_0 and Γ_1. The sum rules in (7.7) can be derived by transforming the contour integrations along the respective boundary contours C_0 and C_1 of the physical sheet of the E-plane onto those on the σ-plane, i.e., along Γ_0 and Γ_1, respectively. Note that the contour integrals of the function $z_0\{u(\sigma)\}$, the density-of-states function for the associated virtual lattice, yield 0 and 1 along Γ_1 and Γ_0, respectively, for the reason of the presence of the simple pole $\sigma = c$ (which corresponds to $E = \infty$) outside of Γ_1 and inside of Γ_0.

where the CPA density of states is non-vanishing. Also, it is a general expectation that these contours avoid the possible singularities $\sigma = 0$ and $\sigma = 1$, excluding them from the physical region, which establishes the analyticity of the $z(E)$ in the physical sheet. (Only the possible singular point of the $z\{E(\sigma)\}$ in this region is the simple pole at $\sigma = c$ corresponding to $E = \infty$, where $z \cdot dE/d\sigma$ has the residue 1.) Under this circumstance, we now have the fundamental sum rule by means of the CPA, namely

$$\frac{1}{2\pi i} \int_{C_0} z(E)dE = 1-c, \quad \frac{1}{2\pi i} \int_{C_1} z(E)dE = c. \tag{7.7}$$

These relations imply, of course, that the total band may be split into two subbands separated by a finite gap, each component having an integral of the total density of states proportional to the respective density (concentration) of atoms in the A-B alloy. In case that the band is not split, the physical

region of the σ-plane is singly-connected, for which only the following total sum rule holds

$$\frac{1}{2\pi i}\int_{C(=C_0+C_1)} z(E)dE=1. \tag{7.8}$$

Or, in terms of the density of states $N(E)$ in any case

$$\int_{-\infty}^{\infty} N(E)dE=1. \tag{7.8'}$$

Similarly, on the basis of the analyticity in the physical region of the σ-plane, the CPA Green function satisfies

$$\frac{1}{2\pi i}\int_C G_k(E)dE=\frac{1}{2\pi i}\int_C \frac{dE}{E-E_k-v\sigma(E)}$$
$$=\int_{-\infty}^{\infty} \frac{-1}{\pi}\operatorname{Im} G_k(E)dE=1. \tag{7.9}$$

It is not a difficult task to make similar sum rules for every examples (1)~(3) presented in §5.

For one-dimensional systems, the determinantal function on the right-hand side of the Friedel relation can be interpreted in terms of the transmission coefficient, as discussed in §6, that is

$$A_t(E)=\frac{1}{\det F(E)}. \tag{7.10}$$

This relation has been pointed out also by Reading and Sigel.[12] By this analogy we can set for the CPA binary alloy also

$$A_t(E)=\left(\frac{\sigma(E)}{c}\right)^c\left(\frac{1-\sigma(E)}{1-c}\right)^{1-c}\exp\int_{E-v\sigma(E)}^{E} z_0(E')dE', \tag{7.11}$$

which represents the probability of an incident wave to transmit in a unit length of the binary-alloy medium. For this to be the case, however, the following inequality should be proved:

$$|A_t(E)|\leq 1 \left(\begin{array}{l} E=\text{real and}\\ \text{belongs to the continuous spectrum} \end{array}\right). \tag{7.12}$$

We have not succeeded to give a general proof of this inequality in (7.11) from the general CPA construction. As discussed in §6, it is related to the real part of the trace of the Green operator instead of the imaginary part, and reflects a dissipation of the wave propagation. Therefore, it is interesting to remark a possibility to introduce a concept of *entropy* in the theory of disordered systems by considering $\log |A_t|$ which may represent in a sense a

degree of disorderedness of the system. It is a matter of without saying to point out the close relation of this consideration to the problem of "exponential growth" discussed by Borland,[44] Halpern,[36] Minami and Hori[45] Matsuda and Ishii[46] and possibly other investigators in this field of researches.

Appendix

—Details of the CPA analytic consideration of the frequency spectrum in a linear-chain binary alloy—

We wish to present here an illustration convenient how to get the frequency distribution curve in Fig. 6 from the CPA formulas, i.e., from Eq. (5·37)

$$\frac{1}{N}\text{Tr}\,\boldsymbol{G}(E) = \frac{1}{E}Z(E), \quad E = \omega^2, \tag{A·1}$$

together with Eqs. (5·44a, b). The latter equations represent a functional relation between Z and E via the "mass" variable μ, rewritten here as follows:

$$E = \frac{\mu_0 \mu (\mu - \mu_0)^2}{2\bar{\mu}_0 (\mu - \mu_1)(\mu - \mu_2)(\mu - \mu_3)}, \tag{A·2}$$

$$Z = \frac{\mu(\mu - \mu_0)}{(\mu - M)(\mu - m)}, \tag{A·3}$$

where the several mass constants μ_0, $\bar{\mu}_0$ and μ_i ($i=1$, 2, 3) are some combinations of the starting masses M and m ($m < M$) of the constituent atoms whose concentrations are $1-c$ and c, respectively, such that

$$\mu_0 = cm + (1-c)M, \quad \text{(the virtual-lattice mass)} \tag{A·4a}$$

$$\bar{\mu}_0 = cM + (1-c)m, \tag{A·4b}$$

$$\mu_1 = \frac{Mm}{cM + (1-c)m}, \tag{A·4c}$$

$$\mu_2, \mu_3 : \mu_2 + \mu_3 = \frac{1}{2}(M + m + \mu_0), \quad \mu_2 \cdot \mu_3 = \frac{Mm}{2}. \tag{A·4d}$$

It can be shown that in the possible range of the concentration factor $0 < c < 1$ the six mass constants are in the following order (μ_2 is assumed to take the smaller one of the two roots in (A·4d)):

$$\mu_2 < m < \mu_1 < \mu_0 < \mu_3 < M. \tag{A·5}$$

Then, by rewriting Eq. (A·2) in the form

$$E/E_0 = 1 + \frac{\alpha_1}{\mu - \mu_1} + \frac{\alpha_2}{\mu - \mu_2} + \frac{\alpha_3}{\mu - \mu_3}, \tag{A·2'}$$
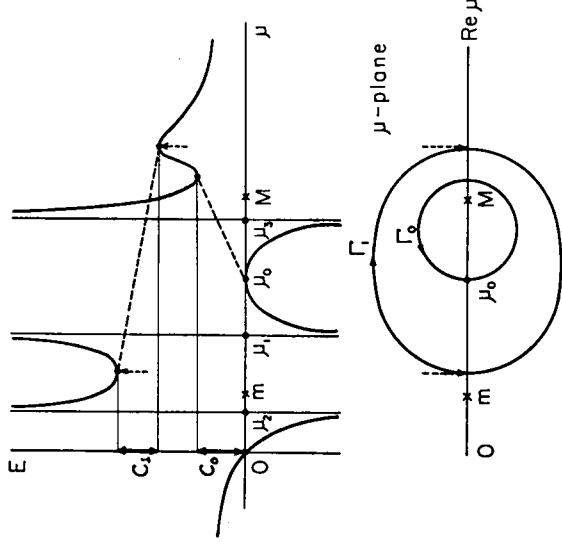
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Fig. 10. A mapping between the complex E-plane and the μ-plane similar to Fig. 9 through Eq. (A·2) or (A·2′), showing the way how the real E-axis is mapped onto several curves in the μ-plane, i. e., the real μ-axis and the closed contours Γ_0 and Γ_1. Note that the order and the orientation of the contours Γ_0 and Γ_1 are just opposite to the situation in Fig. 9 for the reason of the definition of the variable μ which is, apart from a constant factor, reciprocal to σ (see Eq. (5·32)).

$$E_0 = \frac{\mu_0}{2\bar{\mu}_0}, \qquad \alpha_1 < 0, \quad \alpha_2, \, \alpha_3 > 0, \qquad (A\cdot2'a)$$

we can draw a projection of the E vs. μ mapping relation on the plane consisting of the real E vs. real μ axes. This is shown in Fig. 10. Since this is purely an algebraic mapping, the possible singular points of the function $E(\mu)$ and hence the branch points of the inverse $\mu(E)$ can be located easily. For any given complex value of E there exist three complex roots of μ except at such a branch point. In particular, for a real value of E the three roots of $\mu(E)$ are all real in several restricted intervals of the real E-axis, and in all others one root out of the three is real, the rest two being complex conjugate to each other. Clearly, a branch point of the above-stated nature occurs at a boundary of the two intervals of the different types.

In the situation of Fig. 10, possible two intervals where a pair of the roots are complex may occur, as indicated by the two broken lines, which correspond to two possible subbands of the frequency spectrum. Accordingly, one may grasp a gross feature of the conformal mapping of the complex E-plane onto the μ-plane through the analytic function $\mu(E)$, the inverse of the rational function given in (A·2), by drawing the contours which cor-

respond to the real E-axis. This is indicated in the lower part of Fig. 10, where the two contours Γ_0 and Γ_1 correspond to the respective intervals C_0 and C_1 on the real E-axis of the allowed subbands. The analytic properties of the density-of-states function—existence of the physical sheet in which the function is holomorphic except at the two points $E=0$, and ∞—as well as the fundamental CPA sum rules discussed in a general manner in §7 can be explicitly demonstrated in the present example by recalling the differential formula (5·38), i.e.,

$$\frac{1}{N}\operatorname{Tr}\boldsymbol{G}(E)dE = Z(E)\frac{dE}{E}$$

$$= \frac{1}{N}\operatorname{Tr}\boldsymbol{G}\mu_0(u)du - \left(\frac{c}{\mu-M}+\frac{1-c}{\mu-m}\right)d\mu, \qquad (A\cdot6)$$

where

$$u = \frac{\mu}{\mu_0}E(\mu) = \frac{\mu^2(\mu-\mu_0)^2}{2\bar{\mu}_0(\mu-\mu_1)(\mu-\mu_2)(\mu-\mu_3)}. \qquad (A\cdot7)$$

Also, we add another differential formula for the Green function as follows:

$$\boldsymbol{G}_k(E)dE = \frac{du}{u-\dfrac{M}{\mu_0}E_k} - \frac{u(\mu)}{u(\mu)-\dfrac{M}{\mu_0}E_k}\frac{d\mu}{\mu}. \qquad (A\cdot8)$$

From a careful study of these expressions the stated analyticity can be established. Note that the zero of the denominator in the right-hand side of (A·8) occurs outside of the physical region (the ring encircled by Γ_0 and Γ_1) in the μ-plane, indicating that it yields a kind of virtual level. Note also that (A·7) gives another mapping from u- to μ-planes by which the real u-axis is mapped onto the real μ-axis plus a certain closed contour, the latter corresponding to the allowed range C_0^* of the virtual-lattice spectrum on the real u-axis. If we consider its inverse map from μ- to u-planes through (A·7), then, the contour Γ_0 is mapped onto a closed contour which encircles C_0^* but the other one Γ_1 onto another which does not encircles C_0^*. From this consideration it is possible to see the following integration formulas:

$$\frac{1}{2\pi i}\int_{\Gamma_0}\frac{1}{N}\operatorname{Tr}\boldsymbol{G}_{\mu_0}\{u(\mu)\}\frac{du}{d\mu}d\mu = 1, \qquad (A\cdot9)$$

$$\frac{1}{2\pi i}\int_{\Gamma_1}\frac{1}{N}\operatorname{Tr}\boldsymbol{G}_{\mu_0}\{u(\mu)\}\frac{du}{d\mu}d\mu = 0. \qquad (A\cdot10)$$

Consequently, we have

$$\frac{1}{2\pi i}\int_{\Gamma_0}\frac{1}{N}\operatorname{Tr}\boldsymbol{G}\{E(\mu)\}\frac{dE}{d\mu}d\mu = 1-c, \qquad (A\cdot11)$$

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which are the desired sum rules. Another sum rule about the Green function (A·8) can be derived in a similar manner.

Taylor, dealing with the same problem with a similar parametric representation, derived different sum rules compared to (A·11), (A·12).[28] An examination shows that what he calculates is the Green function associated with the time correlation function of the atomic displacements u and $u(t)$, thus physically the polarizability of the binary alloy which is different from the frequency spectrum in the usual meaning. In terms of the present mass variable μ his spectral function is obtainable just by dividing our Z-function by μ, and, with a similar analyticity consideration, the sum rules (A·11) and (A·12) are modified to read $(1-c)/M$, and c/m, respectively on the right-hand sides. This clarifies a puzzling feature which Yonezawa and the present writer met when started to investigate the analytic problem of the CPA theory.

$$\frac{1}{2\pi i} \int_{\Gamma_1} \frac{1}{N} \operatorname{Tr} \boldsymbol{G}\{E(\mu)\} \frac{dE}{d\mu} \, d\mu = c, \qquad (A\cdot12)$$

Acknowledgement

References

1) P. Debye, Ann. Phys. Lpz. (4) **39** (1912), 789.
2) A. Sommerfeld, Z. Phys. **47** (1928), 1.
3) H. Weyl, Math. Ann. **71** (1912), 441.
4) E. P. Wigner, Ann. Math. **53** (1951), 36.
5) A. A. Maradudin, E. W. Montroll and G. H. Weiss, *Solid State Physics Suppl.* **3**, ed. by F. Seitz and D. Turnbull (Academic Press, N.Y., 1963).
6) Moriguchi et al., *Sūgaku Kōshiki* II, Iwanami Zensho 229, p. 188.
7) J. Hori and T. Asahi, Prog. Theor. Phys. **17** (1957), 523.
8) K. Sawada, K. A. Brueckner, N. Fukuda and R. Brout, Phys. Rev. **108** (1957), 507. See also R. Brout and P. Curruthers, *Lectures on the Many-Electron Problems* (N.Y. Interscience Pub., 1963).
9) I. M. Lifshitz, Soviet Phys.–Uspekhi **7** (1965), 549.
10) M. Lax and J. C. Phillips, Phys. Rev. **110** (1958), 41.
11) L. D. Landau and E. M. Lifshitz, *Quantum Mechanics*, Sec. 128, 2nd ed. (Pergamon Press, 1958).
12) J. F. Reading and J. L. Sigel, Phys. Rev. B**5** (1972), 556.
13) J. Friedel, Phil. Mag. **43** (1952), 153. See also Supple VII, Ser. X, Del Nuovo Cim. (1958), 287.
14) J. Kondo, *Solid State Physics*, ed. by F. Seitz and D. Turnbull (Academic Press, N.Y.), Vol. **23** (1969), p. 183.
15) P. W. Anderson, Phys. Rev. **124** (1961), 41.
16) P. W. Anderson, Phys. Rev. **109** (1958), 1492.
17) A. P. Klein and A. J. Heeger, Phys. Rev. **144** (1966), 458.
18) D. C. Langreth, Phys. Rev. **150** (1966), 516.

19) D. J. Thouless, *Amorphous and Liquid Semiconductors*, ed. by M. H. Cohen and G. Lucovsky (North-Holland Pub. Co., Amsterdam, 1972), p. 461.

20) K. Ishii, this issue:

21) T. Kato, *Perturbation theory for linear operators* (Springer-Verlag Berlin-Heidelberg-New York, 1966), p. 487.

22) J. M. Jauch, Helv. Phys. Acta **31** (1958), 127.
    See also T. Kato in Ref. 21) Chap. X.

23) F. Yonezawa, Prog. Theor. Phys. **40** (1968), 734.

24) B. Velický, S. Kirkpatrick and H. Eherenreich, Phys. Rev. **175** (1968), 747.

25) F. Yonezawa and T. Matsubara, Prog. Theor. Phys. **35** (1966), 357.

26) Y. Onodera and Y. Toyozawa, J. Phys. Soc. Japan **24** (1968), 341.

27) R. W. Davies and J. S. Langer, Phys. Rev. **131** (1963), 163.

28) D. W. Taylor, Phys. Rev. **156** (1967), 1017.

29) M. Nakamura and F. Yonezawa, Prog. Theor. Phys. **47** (1972), 1194.

30) R. Klauder, Ann. der Phys. **14** (1961), 43.

31) F. Yonezawa, Prog. Theor. Phys. **31** (1963), 357.

32) H. Hasegawa and M. Nakamura, J. Phys. Soc. Japan **26** (1969), 1362.

33) M. Saitoh, H. Fukuyama, Y. Uemura and H. Shiba, J. Phys. Soc. Japan **27** (1969), 26.

34) H. Shiba, K. Kanda, H. Hasegawa and H. Fukuyama, J. Phys. Soc. Japan **30** (1971), 972.

35) H. Hasegawa, F. Yonezawa and M. Nakamura, J. Non-crystalline Solids **8–10** (1972), 166.

36) B. I. Halperin, Adv. Chem. Phys. **13** (1967), 123.

37) T. Sasada and H. Hasegawa, Prog. Theor. Phys. **45** (1971), 1072.

38) W. Schützer and J. Tiomno, Phys. Rev. **83** (1951), 249.

39) N. G. van Kampen, Phys. Rev. **89** (1953), 1072; **91** (1953), 1267.

40) J. S. Toll, Phys. Rev. **104** (1956), 1760.

41) K. Yosida, *Sekibun-hōteishiki-ron*, Chap. 1, Iwanami Zensho, p. 117.

42) N. Levinson, Kgl. Danske Vid. Sels. Mat-fys. **25** (1949), No. 9.
    See also, P. Swan, Proc. Roy. Soc. **A228** (1955), 10.

43) H. Hasegawa and A. Kishimoto, Tech. Report ISSP, Ser. B No. 15 (1973), 105.

44) R. E. Borland, Proc. Roy. Soc. **A274** (1963), 529.

45) S. Minami and J. Hori, Prog. Theor. Phys. Suppl. No. 45 (1970), 87.

46) H. Matsuda and K. Ishii, Prog. Theor. Phys. Suppl. No. 45 (1970), 56.

47) H. M. Nussenzveig, "Causality and Dispersion Relations Mathematics" in *Science and Engineering* Vol. 95 (Academic Press, N. Y. and London, 1972).

48) H. Hasegawa and F. Yonezawa, J. Phys. Soc. Japan **26**, Suppl (1969), 74.