On the Singularities at the Metal-Insulator Transitions. I
—The Coherent Potential Approximation in the 50-50 Binary Alloys—

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Generally, the ground state energy of a many-electron system may have some singularities as a function of the coupling constant. Such a singularity is sometimes associated with a metal-insulator transition. The only case known is the discontinuity of the second derivative at the Brinkman-Rice transition which is derived in the Hubbard model by the Gutzwiller approximation. The critical exponent in this case is 2. In this paper, the value 7/2 is analytically derived for the critical exponent of the metal-insulator transition lead by CPA, where the level separation of two components of the binary alloy plays the role of the coupling constant. The sign of the additional term to the energy of the metallic phase turns out to be positive in this model while it is negative in the Gutzwiller approximation.

§ 1. Introduction

No investigations have ever been done on the singularities at the metal-insulator transitions of any type. Exceptionally, a little is known on what derived in the ground state of the half-filled Hubbard model of a single band by the Gutzwiler approximation.1 Brinkman and Rice2 pointed out that a transition from a metal to an insulator takes place as the disappearance of the doubly occupied atoms by the electrons with the opposite spins in this treatment.

When the total ground state energy density $\varepsilon$ is expressed as a function of the coupling constant $U$ of the interelectronic repulsion, it vanishes quadratically at a critical value $U_c$ as

$$\varepsilon(U) = \begin{cases} -\frac{(U_c-U)^2}{8U_c}, & U \leq U_c, \\ 0, & U > U_c, \end{cases} \quad (1.1)$$

in this approximation. Plainly, the disappearance of the doubly occupied atoms at a finite coupling constant is not plausible and this result may be a confession of the roughness of this approximation.3 Brinkman and Rice4 pointed out that this approximation leads unphysically to a negative value of the component density of states when applied to an independent particle problem in a disordered system. These defects have surely some connection with each other. It, however, is not the present subject to discuss the incompleteness of this method, which is very useful and worth improving.

Anyway, the singularity in this case is the discontinuity in the second deriva-
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The aim of this series of papers is to investigate the singularity at some metal-insulator transitions which have been commonly accepted. For example, the coherent potential approximation (CPA) for the independent particle states in binary alloys may be regarded as settled and leads to a metal-insulator transition. The density of states which is derived by CPA has no gap if the level separation of two components is comparatively small and has a gap if the separation is larger. Roughly speaking, the system is an insulator if the chemical potential of the electrons lies among a gap and otherwise it is a metal. More rigorously, one who likes to distinguish a metal from an insulator should examine whether the wave functions at the chemical potential are extended or localized. However, the total ground state energy density seems to have some singularity at a critical value of the level separation where a gap begins to appear, apart from the rigorous criterion of a metal and an insulator.

In this paper, an analysis is made on the singularity of the total ground state energy density which is derived by CPA as a function of the level separation of two components in the fifty-fifty binary alloys.

§ 2. The model

We are concerned with a 50%-binary alloy described by a single-particle Hamiltonian in a tight-binding model,

$$H = \sum_i \sum_j |i\rangle V_{ij} \langle j|,$$

where the basis $|i\rangle$ is the atomic orbital at the site $i$. The sites arrange on a regular lattice. The diagonal parts $V_{ii}$ of the matrix $V$ are assumed to be random,

$$V_{ii} = \pm \delta w/2$$

according as the species of the atom at the site $i$ is $A$ or $B$. The off-diagonal parts of $V_{ij}$ are not random. A bare density of the states is assumed to complete the model as

$$\rho^{\text{b}}(z) = \begin{cases} (2/\pi \delta w)^{\frac{1}{2}} \sqrt{w^2 - z^2}, & |z| \leq w, \\ 0, & |z| > w, \end{cases}$$

instead of specifying an explicit form of $V_{ij}$. Equation (2.3) corresponds to the spectral density of the reference problem in which all the diagonal parts of $V$ are zero and the off-diagonal parts are in common with the original $V$. 
If the coherent potential approximation (CPA) is applied to this model, the averaged site-diagonal Green's function

\[ F(z) = N^{-1} \langle \text{Tr} (z-H)^{-1} \rangle = \langle i | \langle (z-H)^{-1} | i \rangle \]  

is a root of a cubic equation

\[ \frac{1}{16} F^3 - \frac{1}{2} z F^2 + \left[ \frac{z^2}{4} - \frac{1}{4} (\delta^2 - 1) \right] F - z = 0, \]  

where \( \delta = \langle V_{ii} \rangle = 0 \) has been substituted into Eq. (4.32) of Velicky et al. because the concentration has been already assumed to be 50%. The density of states \( \rho(z) \) is proportional to the imaginary part of \( F \),

\[ \rho(z) = \pi^{-1} \text{Im} F(z-i0), \]  

whose normalization is

\[ \int_{-\infty}^{\infty} \rho(z) dz = 1. \]  

The electron density \( n \) and the total ground state energy density \( \varepsilon \) are given by

\[ n = \int_{-\infty}^{\infty} \rho(z) dz \]  

and

\[ \varepsilon = \int_{-\infty}^{\infty} z \rho(z) dz, \]  

respectively.

§ 3. Analysis of Eq. (2.5)

Being cubic, the basic equation (2.5) can be solved analytically as is well known. It, however, seems difficult to carry out the integration in Eqs. (2.8) and (2.9) non-numerically. If we are more interested in its singularity at the metal-insulator transition than in the value of the energy itself, we can sift it out analytically.

It has been known that the density of states of this system consists of a single band for \( \delta < 1 \) and of two bands for \( \delta \geq 1 \). This critical value \( \delta = 1 \) is the only singularity in the system. A parameter

\[ \kappa = \delta - 1 \]  

is introduced in order to describe the nature of the singularity. A macroscopic state of the system is specified by two parameters; the one is \( \kappa \) and the other is the electron density \( n \). It is only in the cases \( n = 1/2 \) and \( \kappa > 0 \) that the elec-
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Electrons fill up just the lower band of the two and the system is an insulator. The insulating region is shown in Fig. 1 where \( \nu \) is defined as

\[
\nu = n - 1/2.
\]

Equation (2.8) leads to

\[
\mu = 0 \quad \text{for } \nu = 0
\]

because of the symmetry of the problem. It is the problem concerning the behaviour of \( \varepsilon \) of Eq. (2.9) for \( \mu = 0 \) as a function of \( \kappa \) what is brought forward at the beginning of this paper.

The basic equation (2.5) is cast into the standard form of a cubic equation

\[
\phi^3 + 3\rho \phi + q = 0,
\]

\[
\phi = F - \frac{8}{3} z,
\]

\[
p = -\frac{4}{9} (4\pi^2 + 3\varepsilon),
\]

\[
q = \frac{16}{27} z \{8\varepsilon^3 - 9(3 + 2\kappa)\},
\]

It is convenient to introduce the real part and the imaginary part of \( \phi \):

\[
x = \text{Re } \phi = \text{Re } F - \frac{8}{3} z,
\]

\[
y = \text{Im } \phi = \text{Im } F = \pi \rho.
\]

All the coefficients \( p \) and \( q \) are real for real \( z \). Therefore Eq. (3.4) is transformed into a coupled equation for \( x \) and \( y \),

\[
x^3 - 3xy^2 + 3px + q = 0,
\]

\[
y(3x^2 - y^2 + 3\rho) = 0
\]

for \( y \neq 0 \), \( x \) is easily eliminated by

\[
x = 3q / (8y^3 - 6\rho)
\]

and the equation reduces to a cubic equation for \( y^2 \)

\[
4(y^2 - 3\rho)^2 (4y^2 - 3\rho)^3 - 27q^2 = 0.
\]
The substitution of Eqs. (3.6) and (3.7) to this reveals that this is quadratic in \( z^2 \) and it is easier to solve on \( z^2 \) for a given \( y^2 \) than the inverse problem. The explicit form of the equation for \( z^2 \) is

\[
16(4+y^2+4\kappa)z^4 - \{36(3+4\kappa) - 8(y^2+4\kappa)(y^2-\kappa)\}z^2
+ (y^2+4\kappa)(y^2+\kappa)^2 = 0. \tag{3.13}
\]

Among two roots of \( z^2 \), we are interested in the one with smaller absolute value which changes its sign at \( \kappa = 0 \). The asymptotic behaviour of this root is given by

\[
z^2 = (y^2+4\kappa)(y^2+\kappa)^{1/108}. \tag{3.14}
\]

This expression is valid irrespective of the sign of \( \kappa \). The expressions for \( y^2 \) or \( y \) are too complicated to see the interrelation between the various cases,

\[
\begin{align*}
\gamma^2 &= -4\kappa + 12\kappa^2 z^2, \\
y &= 2\sqrt{-\kappa + 3(\kappa - 1)z^2}, \\
y^2 &= 3(4z^2)^{1/3}, \\
y &= \sqrt{3}(2z)^{1/3}, \\
y^2 &= 12\kappa^{-1}(z^2 - \kappa^2/3) \\
y &= 2\sqrt{3}\kappa^{-1}(z^2 - \kappa^2/3)^{1/3} \\
&= 2(12/\kappa)^{1/3}(|z| - \sqrt{\kappa^2/3})^{1/3} \\
y &= 0 \quad \text{for } z^2 > \kappa^2/3, \\
y &= 0 \quad \text{otherwise},
\end{align*}
\tag{3.15}
\]

A remarkable advantage of the expression (3.14) is found in the next section.

§ 4. The derivation of the critical exponent

It was shown in the last section that \( z^2 \) is expressed compactly in terms of \( \gamma^2 \) but the expression of \( y^2 \) in terms of \( z^2 \) is very complicated.

Let us transform the integrals, Eqs. (2.8) and (2.9) by using the inverse function. This transformation can be regarded as a partial integration. For a given value of \( \mu \), it is easily seen that

\[
y(\mu) = n(\mu) - \frac{1}{2} = \int_{\mu}^{\nu} \rho(z)dz = \frac{1}{\pi} \int_{0}^{\nu} \eta(z)dz
= \frac{1}{\pi} \left\{ \mu \eta(\mu) - \int_{\mu}^{\nu} \zeta(y)dy \right\}, \tag{4.1}
\]

where the functions \( \eta(z) \) and \( \zeta(y) \), which are the inverse functions with each other, are introduced so as to avoid the confusion. The function \( \eta \) is \( y \) as a function of \( z \) and the function \( \zeta \) is \( z \) as a function of \( y \). Explicitly, the function \( \zeta(y) \) is given by
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\[ \zeta(y) = (y^2 + \kappa) \sqrt{(y^2 + 4\kappa)/108} \]  

(4·2)

from Eq. (3·14) for positive values of \( z \). The integration of \( \zeta(y) \) can be carried out indefinitely as

\[ \int \zeta(y) \, dy = y(y^2 + 4\kappa)^{1/2}/\sqrt{1728}. \]  

(4·3)

Then Eq. (4·1) is expressed in terms of \( y = \tilde{\gamma}(\mu) \):

\[ v = \frac{1}{\pi} \left[ y(y^2 + \kappa) \sqrt{(y^2 + 4\kappa)/108} - y(y^2 + 4\kappa)^{1/2}/\sqrt{1728} \right] \]

\[ = \frac{1}{8\sqrt{3}\pi} \frac{1}{\mu} \frac{1}{\kappa} y^2 \sqrt{y^2 + 4\kappa}, \]  

(4·4)

where the relations \( \mu \eta(\mu) = \gamma(\gamma) \) and \( \eta(0) = 2\sqrt{-\kappa \theta(-\kappa)} \) are used.

Quite similarly, the integration (2·9) is transformed into

\[ \lambda(\mu) = \varepsilon(\mu) - \varepsilon(0) = \int_0^\infty \gamma \rho(z) \, dz = \frac{1}{\pi} \int_0^\infty \gamma \gamma(z) \, dz \]

\[ = \frac{1}{\pi} \left[ \frac{1}{2} \mu \eta(\mu) - \frac{1}{2} \int_{y=0}^{y_{0}} (\zeta(y))^2 \, dy \right]. \]  

(4·5)

The integration in the second term of Eq. (4·5) is carried out as

\[ \int_{y=0}^{y_{0}} (\zeta(y))^2 \, dy = \frac{1}{108} \left[ \frac{1}{7} y^7 + \frac{6}{5} \kappa y^5 + 3\kappa y^4 + 4\kappa y^3 \right]_{y_{0}}^{y_{0}} = \frac{1}{1780} (5y^7 + 42\kappa y^5 + 105\kappa y^4 + 140\kappa y^3) - 2\pi\lambda_0, \]  

(4·6)

where the last term comes from the lower bound of the integration and is explicitly given by

\[ \lambda_0 = -2(-\kappa)\theta(-\kappa)/(105\pi). \]  

(4·7)

Then Eq. (4·5) reduces to

\[ \lambda = \lambda_0 + \lambda_0, \]  

(4·8)

\[ \lambda = (5y^7 + 28\kappa y^5 + 33\kappa y^4)/(1260\pi). \]  

(4·9)

The relation between \( \lambda \) and \( \nu \) is mediated by \( \gamma \) in Eqs. (4·4) and (4·8) while by \( \mu \) in Eqs. (2·8) and (2·9). Only the second term is singular in \( \kappa \) in Eq. (4·8) when \( \nu \neq 0 \).

Let us trace back to the origin of this singularity. Always \( \lambda = 0 \) for \( \nu = 0 \).

For a while \( \nu \) is kept at a non-zero constant value. It follows from Eq. (4·4) that \( \gamma \) is regular in \( \kappa \). Therefore \( \lambda(\nu \neq 0) \) is regular in \( \kappa \) and then \( \lambda(\nu \neq 0) \) has
no other singularities than in \( \lambda_0 \). This singularity in \( \lambda_0 \) is independent of \( \nu \). It is proved below that \( \varepsilon(\nu \neq 0) \) is regular in \( \kappa \). Then the singularity in \( \lambda(\nu) \) should be attributed to \( \varepsilon(0) \) since \( \lambda(\mu) \) was defined in Eq. (4.5) and \( \lambda(\nu) \) is defined as \( \lambda(\mu) \) for \( \mu(\nu) \).

The proof of the regularity of \( \varepsilon(\nu \neq 0) \) in \( \kappa \) is as follows. The density of state is not zero only when \( 4p^3 + q^2 > 0 \) as derived by the standard method for a cubic equation. As a function of \( \nu \), \( \gamma(z, \kappa) \) is regular in the regions where \( \nu \neq 0 \) since \( p \) and \( q \) are both regular in \( z \). Only at the band edges where \( 4p^3 + q^2 = 0 \), \( \gamma \) is singular in \( z \). However, \( \gamma \) can be well approximated by \( A(\kappa) \sqrt{z - z_0(\kappa)} \) in the vicinity of the bottom \( z_0(\kappa) \) of the band with the regular functions \( A(\kappa) \) and \( z_0(\kappa) \). The partial differentiation of Eq. (3.12) with respect to \( \kappa \) reveals that \( \gamma(z, \kappa) \) is singular in \( \kappa \) also only at the band edges. For infinitesimal values of \( \nu \), \( \varepsilon(\mu) \) is regular in \( \kappa \) and this regularity continues in the whole range of \( \nu < 0 \) because of the regularity of \( \gamma \) in the concerned range. The symmetry of the band ensures that \( \varepsilon(\nu) = \varepsilon(-\nu) \). Thus the regularity of \( \varepsilon(\nu \neq 0) \) in \( \kappa \) is proved.*

It is concluded that the critical exponent in the total electronic energy as a function of the level separation is \( 7/2 \) and the sign of the additional singular term to the metallic side is positive in the metal-insulator transition appearing in CPA of the fifty-fifty binary alloys.

§ 5. Further examinations

The singular part of \( \varepsilon \) as a function of \( \nu \) and \( \kappa \) is extracted in \( \lambda_i \) which can be regarded as obtained from \( \varepsilon \) by the subtraction of the unknown regular part. The behaviour of \( \lambda_i \) is schematically illustrated in Fig. 2. For \( \kappa < 0 \), \( \lambda_i \) has the \( U \)-type minimum or the quadratic minimum at \( \nu = 0 \). This is characteristic of the metallic states or the existence of a Fermi surface. For the critical case \( \kappa = 0 \), \( \lambda_i \sim \nu^{7/4} \). For \( \kappa > 0 \), \( \lambda_i \) starts linearly in \( |\nu| \) from the \( V \)-type minimum at \( \nu = 0 \), since the density of states has a gap and the chemical potential is discontinuous in \( \nu \). The conclusion of the last section is that \( \lambda_i = -\lambda_0 \) along the line of \( \nu = 0 \) and that \( \lambda_i \) has an additional positive term only in \( \kappa < 0 \).

Imagine a sheet of paper which has a crease of semi-infinite length along

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* It is easy to extend this proof for the cases of other concentrations than 50\%.
the positive part of the $\kappa$ axis. The surface in Fig. 2 can be likened to this. Such a conversion in the type of the minimum, from $U$-type to $V$-type, is rather general in some categories of the metal-insulator transitions. Some hidden interrelations between the metal and the insulator back to back with each other may be exposed from more general viewpoint, if some proper variables are found and the unphysical sheets, associating with the roots of Eq. (4-4) for the pure imaginary values of $\nu$ come to light. It is an interesting future problem.

It should be pointed out that the additional term $-\lambda_0$ to the energy in the metallic region $\kappa<0$ is positive while the corresponding term is negative in the Brinkman-Rice transition (1-1). This sign is another interesting future problem.

§ 6. Summary and remarks

It will afford a better understanding to summarize the logical structure of drawing the results since several unconventional ideas are taken in it.

In the beginning, we know that $\varepsilon(\kappa, \nu)$ has a singularity as a function of $\kappa$ only in the case $\nu=0$ if $\nu$ is kept constant. In order to get the analytical expression of $\varepsilon$, the quantity $\varepsilon \rho(\nu)$ must be analytically integrable by any means, where $\rho(\nu)$ is the density of states at the energy $\nu$. It, however, is not always necessary if we are satisfied with only the singular part. Then we investigate the difference $\lambda(\nu) = \varepsilon(\nu \neq 0) - \varepsilon(\nu = 0)$ instead of the direct study of $\varepsilon$. Only the detailed knowledge on small $\nu$ region is enough for this purpose.

One should throw away the prejudice that the density of states $\rho(\nu)$ is the function of $\nu$ and not the inverse $\nu(\rho)$. The inverse picture prevents from missing the interconnection between $\kappa<0$ and $\kappa>0$, and removes the difficulty in carrying out the integration. It turns out that $\lambda$ for $\nu \neq 0$ has a singularity which is irrespective of $\nu$. This singularity is finally attributed to that of $\varepsilon(\nu = 0)$ because no other singularities can arise. We sift out only the singular part of $\varepsilon$, leaving the regular part unknown.

A comment is given on the position of the present model. The place of the metal-insulator transitions has not been settled yet in the phase transitions in general. For example, what is the order parameter of a metal-insulator transition especially in a finite temperature? Are the definitions of metals and insulators absolute or relative, in other words, intrinsic or extrinsic? Note that a gas and a liquid can be distinguished only along the coexistence curve in the $p$-$T$ plane.

There are a variety of metal-insulator transitions. They are conventionally classified into the Wilson-type, the Mott-type, and the Anderson-type from the viewpoint of the mechanism. The metal-insulator transitions of these types are thought to take place in the models with only the electronic degrees of freedom. Most of the metal-insulator transitions actually observed are of first order and some cooperations of other degrees of freedom such as the lattice system seems essential. One may think that the models of only electrons is unrealistically too simple.
The metal-insulator transition of first order can be rather easily derived without asking what is the essential mechanism in the electronic system. The first order transitions, however, may have a critical point and the conceptual distinction of metals and insulators is necessary above the critical temperature. If they are defined intrinsically, some transition should remain in the supercritical region. If extrinsically, not. The models with only electrons are important at least in this sense.

The band splitting as in the present model is the most familiar, the most primitive and the most ideal picture of the metal-insulator transition. The method of the inverse function in this paper will serve a further development of this picture, providing interconnection of two states.

In order to understand the Mott transition, one must go beyond the single particle scheme. However, the alloy analogy introduced by Hubbard supplies a convenient view and a tool which connects the electron correlation problem and the alloy problem. Hubbard's approximation in the correlation problem is a sister of CPA. The singularity in the metal-insulator transition in the Hubbard model will be examined on the basis of the present result in a forthcoming paper. This is more closely connected with the reality than the present model.

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References