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Possibility of Superconducting and Other Phases in Organic High Polymers of Polyacene Carbon Skeletons. II. Screened Electron-Electron Interaction —Method of Renormalization Group—

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The electron-electron interaction which is crucial in determining whether new phases will arise or not in polyacene is investigated by means of the renormalization group. This approach is valuable to effectively include, from the view-point of the group theory, the higher order diagrams not taken into account in the random phase approximation of the previous work. It is found that there is a range of coupling constants where the singlet superconducting phase without simultaneous CDW ordering can be expected.

In the previous papers,[1)] we have treated the electron-electron interactions in polyacene from the viewpoint of the random phase approximation. The system under consideration is, concretely speaking, composed of the one-dimensional polyacene skeleton (called spine) with suitable side chains. These are composed of, for instance, the dye molecules with several carbon atoms and several π-electrons.

The mechanism of phase change in our case is manipulated in terms of the highest valence band (v) and the lowest conduction band (c). The electron-electron interactions in these bands are treated to be screened as follows. We must consider two sources of screening. One is due to the excitation from the lower valence bands to the higher conduction bands inside the spine. The other is due to the excitation in the side chain. The former plays a role to reduce the long range Coulomb repulsion to a short range potential, while the latter produces attractive interaction in the spine. We assume that these two mechanisms of screening can be treated independently. In order to make the superconductivity advantageous, we attempt to optimize the side chain composition in the following manner. Replacing the carbon in the side chain by nitrogen, or replacing hydrogen by a suitable substituent group, we can make the transition amplitude between the highest occupied and lowest vacant orbitals as large as possible. This procedure leads possibly to the largest attractive interaction in the spine as expected.

Thus we might conclude that the superconducting phase be possible in this system, though an anxiety that other phases of CDW or SDW ordering overwhelm the superconducting phase remains.

As is mentioned above, the screening effect inside the spine is independent of that of the side chain, so that interference between them is disregarded. This last phenomenon seems to work unfavorably for the screening. One of the traditional approaches relies on the random phase approximation. It adopts only the ring diagrams, treating that various processes of scattering channels independently. In order to make up for these imperfections, we employ the method of renormalization group,[2,3)] as one of the exellent techniques to consider the interfering channels self consistently.

This method will be, in a considerably detail, explained in Appendix and expressed in a form suitable for the present problem. Here we outline the result, which is enough to proceed with the following analysis.

The Dyson equation is invariant under a multiple renormalization of Green's function and coupling parameter (see Eq. A.3). Due to this invariance a complicated scaling procedure leads to a concept of the invariant coupling satisfying a functional equation,

$$\tilde{g}_i(y, u, g) = \tilde{g}_i(y/t, u/t, \tilde{g}(t, u, g)), \tag{1}$$

where y and u are parameters with the dimension of energy, and g is the set of original couplings, $\{g_i\}$. In order to provide practical facilities, Eq. 1 is translated to a differential equation,

$$y\frac{\partial}{\partial y}\tilde{g}_i(y,u,g) = \frac{\partial}{\partial \xi}\tilde{g}_i(\xi, u/y, \tilde{g}(t, u, g))|_{\xi=1}. \tag{2}$$

To solve the above equation, we begin with estimating the right-hand side of Eq. 2 by means of the perturbation theory. Then, if $\tilde{g}_i$ is obtained as a solution of Eq. 2, it must satisfy the group theoretical condition of the renormalization group. We can convince that through this procedure the renormalized coupling parameters are improved better than in the simple random phase approximation. These in turn provide various response functions within the same renormalization scheme.

$$y\frac{\partial}{\partial y}\ln\Lambda(y,u,g) = \frac{\partial}{\partial \xi}\ln\Lambda(\xi, u/y, \tilde{g}(y,u,g))|_{\xi=1}\ , \tag{3}$$

where Λ is the external vertex.

Invariant Coupling, Application to the Case of Polyacene

Preliminarily, we observe the singular behaviour of the perturbation series in the case of polyacetylene and compare it with that of polyacene, which plays an important role in discussing the ground state of the systems. As is well known,[4,5] the terms in the perturbation series which become divergently large as the temperature is lowered are, in the case of polyacetylene:

$$\begin{aligned} &\text{I.} \quad g\ln(T/D),\ \{g\ln(T/D)\}^2,\ \cdots,\ \{g\ln(T/D)\}^n,\ \cdots,\\ &\text{II.} \quad g^2\ln(T/D),\ g\{g\ln(T/D)\}^2,\ \cdots,\\ &\text{III.} \quad g^3\ln(T/D),\ g^2\{g\ln(T/D)\}^2,\ \cdots,\\ &\cdots\cdots, \end{aligned} \tag{4}$$

where D is the band width of the conducting π-electrons. The series I is the most divergent terms, II and III, ⋯ being the next and further lower divergent terms. Similar behaviours of the perturbation series are well-known in another field of physics, e.g., in the case of the Kondo effect[6,7] and QED.[2] If we take into account only the most divergent series (I), the summation of series diverges at the mean-field critical temperature, T_c. If we do the next divergent series (II), the sum diverges only at the temperature of absolute zero.[5] This aspect is consistent with the theorem of absence of any phase change in a purely one-dimensional system at a finite temperature.

In the case of polyacene, however, the divergent series are not logarithmic but are classified as[1]

$$\begin{aligned} &\text{I.} \quad g(T/t)^{-1/2},\ \cdots,\ \{g(T/t)^{-1/2}\}^n,\ \cdots,\\ &\text{II.} \quad g^2(T/t)^{-1/2},\ \cdots,\ g\{g(T/t)^{-1/2}\}^n,\ \cdots,\\ &\cdots\cdots. \end{aligned} \tag{5}$$

The divergent character of this series are governed by the power law thus stronger than in the case of polyacetylene. The perturbation calculation based on the above classification becomes less accurate than the logarithmic problem. However, the renormalization group theory is still a convenient method to improve the perturbation method and obtain a qualitatively correct result.

It is noted that the most divergent series arises only in the correction of the vertex function, Γ. Zeroth order vertices are given by,[1]

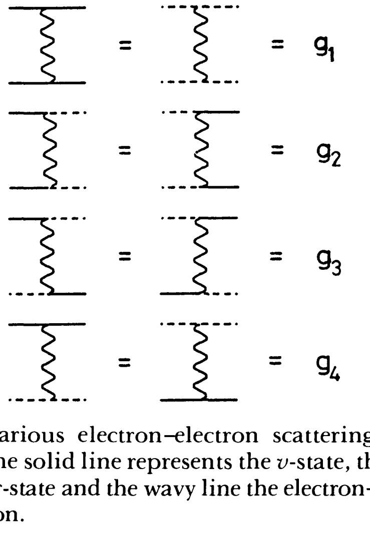

Fig. 1. Various electron–electron scattering amplitudes. The solid line represents the v-state, the dotted line the c-state and the wavy line the electron–electron interaction.

$$\begin{aligned} \Gamma^{(0)vvvv}_{\alpha\beta\gamma\delta} &= g_1(\delta_{\alpha\delta}\delta_{\beta\gamma}-\delta_{\alpha\gamma}\delta_{\beta\delta}),\\ \Gamma^{(0)vvcc}_{\alpha\beta\gamma\delta} &= g_2(\delta_{\alpha\delta}\delta_{\beta\gamma}-\delta_{\alpha\gamma}\delta_{\beta\delta}),\\ \Gamma^{(0)vcvc}_{\alpha\beta\gamma\delta} &= 2(g_3\delta_{\alpha\delta}\delta_{\beta\gamma}-g_4\delta_{\alpha\gamma}\delta_{\beta\delta}), \end{aligned} \tag{6}$$

where v and c denote valence and conduction bands lying closest to the Fermi surface, respectively. α—δ are spin indices. The electron-electron interactions g_1—g_4 are shown schematically in Fig. 1.

The complete vertex function, Γ is defined in terms of the two-particle Green's function as

$$\begin{aligned} G^{\text{II}}_{\alpha\beta\gamma\delta}&(x_1,\ x_2,\ x_3,\ x_4)\\ &= -<T\psi_\alpha(x_1)\psi_\beta(x_2)\psi^+_\gamma(x_3)\psi^+_\delta(x_4)S>_{conn}\\ &= G_{\alpha\gamma}(x_1,\ x_3)G_{\beta\delta}(x_2,\ x_4)-G_{\alpha\delta}(x_1,\ x_4)G_{\beta\gamma}(x_2,\ x_3)\\ &\quad+\int \mathrm{d}x_{1'}\text{—}\mathrm{d}x_{4'}\sum_{\alpha'\beta'\gamma'\delta'} G_{\alpha\alpha'}(x_1,\ x_{1'})G_{\beta\beta'}(x_2,\ x_{2'})\\ &\quad\times \Gamma_{\alpha'\beta'\gamma'\delta'}(x_{1'},\ x_{2'},\ x_{3'},\ x_{4'})G_{\gamma'\gamma}(x_{3'},\ x_3)G_{\delta'\delta}(x_{4'},\ x_4), \end{aligned} \tag{7}$$

where $G_{\alpha\alpha'}$ is the electron propagator and

$$G_{\alpha\alpha'} = \delta_{\alpha\alpha'}G. \tag{8}$$

As the lowest order correction, the renormalized Γ involves the contributions described by (a)—(j) in Fig. 2. Here we present in detail, as an example, a derivation of (a) type correction in Fig. 2: Consider the second order term in the expansion of S in Eq. 7, and take the constructions which give the diagram of Fig. 2(a). Then, we have

$$\begin{aligned} \delta G^{\text{II}}&(p_1,\ p_2,\ p_3,\ p_4)\\ &= -\frac{1}{2}\left(-\frac{1}{4}\right)^2\int \mathrm{d}t'\mathrm{d}t'\Gamma^{(0)vvvv}_{\alpha'\beta'\gamma'\delta'}\Gamma^{(0)vvvv}_{\alpha''\beta''\gamma''\delta''}\\ &\quad\times<Ta_{vp_1\alpha}(t_1)a_{vp_2\beta}(t_2)\\ &\quad\times a^+_{vp_1'\alpha'}(t')a^+_{vp_2'\beta'}(t')a_{vp_3'\gamma'}(t')a_{vp_4'\delta'}(t')\\ &\quad\times a^+_{vp_1''\alpha''}(t'')a^+_{vp_2''\beta''}(t'')a_{vp_3''\gamma''}(t'')a_{vp_4''\delta''}(t'')\\ &\quad\times a^+_{vp_3\gamma}(t_3)a^+_{vp_4\delta}(t_4)> \end{aligned} \tag{9}$$

$$\begin{aligned} &= \frac{1}{2}\int \mathrm{d}t'\mathrm{d}t''\Gamma^{(0)vvvv}_{\alpha\beta\gamma'\delta'}\Gamma^{(0)vvvv}_{\alpha'\beta'\gamma\delta}\delta_{\alpha'\gamma'}\delta_{\beta'\delta'}\\ &\quad\times G_{vq_1}(t'-t'')G_{vq_2}(t'-t'')\\ &\quad\times G_{vp_1}(t_1-t')G_{vp_2}(t_2-t')G_{vp_3}(t''-t_3)G_{vp_4}(t''-t_4). \end{aligned} \tag{9a}$$

In Eq. 9, the summation with respect to primed variables are implied. The unprimed momentum variables are subjected to the condition of the conservation. In order to get Eq. 9a four procedures (i)—(iv) are needed. (i) Two annihilation operators representing incoming lines are combined with the succeeding creation operators to yield propagators. (ii) The last four propagators yield propagators similarly. These four propagators expressed in the last line of Eq. 9a correspond to the external four lines in Fig. 2(a). (iii) The two propagators with momenta, q_1 and q_2 are constructed from the remaining four operators (The summation with respect to q_1 and q_2 is also omitted for simplicity.). (iv)

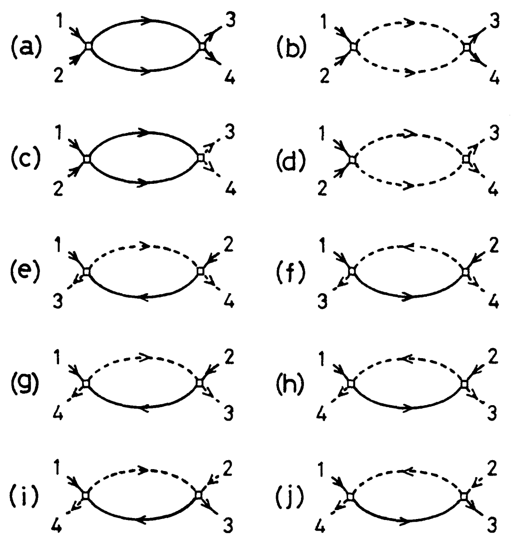

Fig. 2. Various second order corrections to Γ.

The equivalent terms are counted in following manner. The procedures (i)—(iii) are doubly possible, and further we can exchange wholly the singly primed terms for the doubly primed terms. These four procedures result in yielding sixteen equivalent terms. If we insert, in the integrand, $\delta(t_{2'}-t_{1'})$ together with an integration with respect to $t_{2'}$, we can arrange Eq. 9a in the form of Eq. 7, obtaining

$$\Gamma^{vvvv}_{\alpha\beta\gamma\delta}(a) = \frac{1}{2}T\sum G_v(q_1)G_v(q_2)\Gamma^{(0)vvvv}_{\alpha\beta\alpha'\beta'}\Gamma^{(0)vvvv}_{\alpha'\beta'\gamma\delta}$$
$$= -(\delta_{\alpha\delta}\delta_{\beta\gamma}-\delta_{\alpha\gamma}\delta_{\beta\delta})g_1{}^2\Pi^{vv} \tag{10a}$$

where, for example, q_1 denotes both frequency and momentum in short.

Other contributions denoted by Fig. 2 (b)—(j) are given in the following:

$$\Gamma^{vvvv}_{\alpha\beta\gamma\delta}(\mathrm{b}) = \frac{1}{2}T\sum G_c(q_1)G_c(q_2)\Gamma^{(0)vvcc}_{\alpha\beta\alpha'\beta'}\Gamma^{(0)ccvv}_{\alpha'\beta'\gamma\delta}$$
$$= -(\delta_{\alpha\delta}\delta_{\beta\gamma}-\delta_{\alpha\gamma}\delta_{\beta\delta})g_2{}^2\Pi^{vv}, \tag{10b}$$

$$\Gamma^{vvcc}_{\alpha\beta\gamma\delta}(\mathrm{c}) = \frac{1}{2}T\sum G_v(q_1)G_v(q_2)\Gamma^{(0)vvvv}_{\alpha\beta\alpha'\beta'}\Gamma^{(0)vvcc}_{\alpha'\beta'\gamma\delta}$$
$$= -(\delta_{\alpha\delta}\delta_{\beta\gamma}-\delta_{\alpha\gamma}\delta_{\beta\delta})g_1g_2\Pi^{vv}, \tag{10c}$$

$$\Gamma^{vvcc}_{\alpha\beta\gamma\delta}(\mathrm{d}) = \frac{1}{2}T\sum G_c(q_1)G_c(q_2)\Gamma^{(0)vvcc}_{\alpha\beta\alpha'\beta'}\Gamma^{(0)vvvv}_{\alpha'\beta'\gamma\delta}$$
$$= -(\delta_{\alpha\delta}\delta_{\beta\gamma}-\delta_{\alpha\gamma}\delta_{\beta\delta})g_1g_2\Pi^{vv}, \tag{10d}$$

$$\Gamma^{vvcc}_{\alpha\beta\gamma\delta}(\mathrm{e}) = \frac{1}{2}T\sum G_c(q_1)G_v(q_2)\Gamma^{(0)vvcc}_{\alpha\gamma'\gamma\beta'}\Gamma^{(0)vcvc}_{\beta\beta'\gamma'\delta}$$
$$= -\frac{1}{2}\{g_2g_3\delta_{\alpha\gamma}\delta_{\beta\delta}+g_2g_4(\delta_{\alpha\delta}\delta_{\beta\gamma}-\delta_{\alpha\gamma}\delta_{\beta\delta})\}\Pi^{vc}, \tag{10e}$$

$$\Gamma^{vvcc}_{\alpha\beta\gamma\delta}(\mathrm{f}) = \Gamma^{vvcc}_{\alpha\beta\gamma\delta}(\mathrm{e}), \tag{10f}$$

$$\Gamma^{vvcc}_{\alpha\beta\gamma\delta}(\mathrm{g}) = \frac{1}{2}T\sum G_c(q_1)G_v(q_2)\Gamma^{(0)vvcc}_{\alpha\gamma'\delta\beta'}\Gamma^{(0)vcvc}_{\beta\beta'\gamma'\gamma'}$$
$$= \frac{1}{2}\{g_2g_3\delta_{\alpha\delta}\delta_{\beta\gamma}-g_2g_4(\delta_{\alpha\delta}\delta_{\beta\gamma}-\delta_{\alpha\gamma}\delta_{\beta\delta})\}\Pi^{vc}, \tag{10g}$$

$$\Gamma^{vvcc}_{\alpha\beta\gamma\delta}(\mathrm{h}) = \Gamma^{vvcc}_{\alpha\beta\gamma\delta}(\mathrm{g}), \tag{10h}$$

$$\Gamma^{vcvc}_{\alpha\beta\gamma\delta}(\mathrm{i}) = T\sum G_v(q_1)G_c(q_2)\,\Gamma^{(0)vvcc}_{\alpha\beta'\alpha'\delta}\,\Gamma^{(0)vvcc}_{\alpha'\beta\gamma\beta'}$$
$$= g_2{}^2\delta_{\alpha\gamma}\delta_{\beta\delta}\Pi^{vc}, \tag{10i}$$

$$\Gamma^{vcvc}_{\alpha\beta\gamma\delta}(\mathrm{j}) = T\sum G_c(q_1)G_v(q_2)\,\Gamma^{(0)vcvc}_{\alpha\beta'\alpha'\delta}\,\Gamma^{(0)vcvc}_{\alpha'\beta\gamma\beta'}$$
$$= \{2g_3(g_3-g_4)\delta_{\alpha\delta}\delta_{\beta\gamma}+g_4{}^2\delta_{\alpha\gamma}\delta_{\beta\delta}\}\Pi^{vc}, \tag{10j}$$

It can be shown that Γ's given in the above equations depend not only on frequency and momentum of the external line but also on temperature in general. But if every momentum and frequency concerned are much smaller than temperature, Γ's are allowed to be functions only of temperature. We are concerned with this special case in the following analysis. Whence

$$\Pi^{vv} = -\Pi^{vc} \equiv L(T) \tag{11}$$

with

$$L(T) = \frac{Z}{2(tT)^{1/2}} - \frac{1}{2\pi t p_c}, \tag{12}$$

where

$$Z = \frac{1}{(2\pi)^{1/2}}\int_0^\infty \frac{dx}{x^{1/2}\cosh^2 x}. \tag{13}$$

In Eq. 12, p_c is the cut off momentum which is smaller than the Fermi momentum (namely $tp_c \fallingdotseq t$). If temperature is smaller than any of the other variables, T in Eqs. 11 and 12 must be understood as the largest of them. At $T \fallingdotseq t$, we can see

$$L(T) \fallingdotseq 0. \tag{14}$$

Contrariwise, we should in advance adjust p_c so that Eq. 14 is held. As the contribution from the region, $|p|>p_c$, is nonsingular, we can start with the initial coupling parameter g.

Thus we can express the coupling terms, corresponding to those in Eq. 6, as

$$\Gamma^{vvvv}_{\alpha\beta\gamma\delta} = g_1\Gamma_1(\delta_{\alpha\beta}\delta_{\beta\gamma}-\delta_{\alpha\gamma}\delta_{\beta\delta}),$$
$$\Gamma^{vvcc}_{\alpha\beta\gamma\delta} = g_2\Gamma_2(\delta_{\alpha\beta}\delta_{\beta\gamma}-\delta_{\alpha\gamma}\delta_{\beta\delta}),$$
$$\Gamma^{vcvc}_{\alpha\beta\gamma\delta} = g_3\Gamma_3\delta_{\alpha\delta}\delta_{\beta\gamma}-g_4\Gamma_4\delta_{\alpha\gamma}\delta_{\beta\delta}. \tag{15}$$

In Table 1, we have tabulated the contributions of Fig. 2(a)—(j).

For the sake of convenience, we express every g_i in unit of the transfer integral t:

$$g_i/t \to g_i. \tag{16}$$

Then we have

$$L(T) \to \frac{Z}{2}\sqrt{t/T} - \frac{1}{2\pi}\sqrt{t/D} \tag{17}$$

$L(T)$ vanishes at $T=t$ as required by Eq. 14. The condition leads to

$$D = t/(\pi Z)^2. \tag{18}$$

If we remember $D=tp_c{}^2$, the above requirement determines the cut-off parameter p_c. For the later conven-

Table 1. Coupling Terms Versus Diagrams

$g\Gamma$	Diagram	Contribution	Total
$g_1\Gamma_1$	(a)	$-g_1{}^2L(T)$	$-(g_1{}^2+g_2{}^2)L(T)$
	(b)	$-g_2{}^2L(T)$	
$g_2\Gamma_2$	(c)	$-g_1g_2L(T)$	$g_2(-2g_1-g_3+2g_4)L(T)$
	(d)	$-g_1g_2L(T)$	
	(e)	$-g_2(g_3-2g_4)L(T)$	
	(f)		
	(g)		
	(h)		
$g_3\Gamma_3$	(j)	$-2g_3(g_3-g_4)L(T)$	$-2g_3(g_3-g_4)L(T)$
$g_4\Gamma_4$	(i)	$g_2{}^2L(T)$	$(g_2{}^2+g_4{}^2)L(T)$
	(j)	$g_4{}^2L(T)$	

ience, it is better to introduce a parameter κ to rewrite Eq. 17 as

$$L(T) = \frac{1}{2\pi}\{\sqrt{t/(\kappa T)} - \sqrt{t/D}\}, \tag{19}$$

with

$$L(t)=0. \tag{20}$$

Now we try to get the invariant coupling $\tilde{g}_i$. As long as we work within the most divergent approximation, the Green's functions are not renormalized (d=1 in Eq. A.4). But the electron-electron interaction should be:

$$\tilde{g}_i = g_i\Gamma_i(y, u, g) \tag{21}$$

where, as mentioned in the previous section,

$$y=T/\lambda,\ u=t/\lambda. \tag{22}$$

As to g_1, consulting Table 1, we have

$$\tilde{g}_1 = g_1-(g_1{}^2+g_2{}^2)L(y, u, g) \tag{23}$$

with

$$L(y, u, g) = \frac{1}{2\pi}\{\sqrt{u/(\kappa y)} - \sqrt{u/u'}\}, \tag{24}$$

where

$$u'=D/\lambda. \tag{25}$$

Thus we have an explicit expression for the differential equation of the renormalization group, Eq. 2. Its right-hand side is

$$\begin{aligned}&\frac{\partial}{\partial\xi}\tilde{g}_1(\xi, u/y, \tilde{g}(y, u, g))\\ &= \frac{\partial}{\partial\xi}[\tilde{g}_1-(\tilde{g}_1^2+\tilde{g}_2^2)\frac{1}{2\pi}\{\sqrt{(u/y)/(\kappa\xi)} - \sqrt{u/u'}\}]|_{\xi=1}\\ &= \frac{1}{4\pi}\sqrt{u/(\kappa y)}\,(\tilde{g}_1^2+\tilde{g}_2^2).\end{aligned} \tag{26}$$

Then Eq. 2 becomes

$$y\frac{\partial}{\partial y}\tilde{g}_1 = \frac{1}{4\pi}\sqrt{u/(\kappa y)}\,(\tilde{g}_1^2+\tilde{g}_2^2). \tag{27}$$

Transforming the variable as

$$\frac{1}{2\pi}\sqrt{u/(\kappa y)} = x, \tag{28}$$

we can rewrite Eq. 27 as

$$\frac{\partial}{\partial x}\tilde{g}_1 = -(\tilde{g}_1^2+\tilde{g}_2^2). \tag{29}$$

Similar procedures are applicable to $\tilde{g}_2$—$\tilde{g}_4$ to lead to

$$\frac{\partial}{\partial x}\tilde{g}_2 = \tilde{g}_2(-2\tilde{g}_1-\tilde{g}_3+2\tilde{g}_4), \tag{30}$$

$$\frac{\partial}{\partial x}\tilde{g}_3 = -2\tilde{g}_3(\tilde{g}_3-\tilde{g}_4), \tag{31}$$

$$\frac{\partial}{\partial x}\tilde{g}_4 = \tilde{g}_2^2+\tilde{g}_4^2 \tag{32}$$

Instabily in Polyacene, Renormalization of the External Vertex

The external vertices in the case of polyacene are corrected, up to the first order of H_{int}, as[1]

$$\begin{aligned}&\Lambda_1=1+(-g_2-2g_3+g_4)L(T),\\ &\Lambda_2=1+(g_2+g_4)L(T),\\ &\Lambda_3=1-(g_1+g_2)L(T),\end{aligned} \tag{33}$$

where Λ_1 refers to CDW, Λ_2 to SDW, and Λ_3 to the singlet superconductivity (SS). If we use Eq. 33 for Λ_i of the right-hand side of Eq. 3, it follows that within the most divergent approximation

$$\Lambda_1(\xi, u/y, \tilde{g}(y, u, g))=1+(-\tilde{g}_2-2\tilde{g}_3+\tilde{g}_4)L(\xi, u/y), \tag{34}$$

and from Eq. 24

$$L(\xi, u/y) = \frac{1}{2\pi}\{\sqrt{u/(\kappa y)} - \sqrt{u/u'}\}. \tag{35}$$

Since we have set L as Eq. 14, it is seen that

$$L(1, u/y)=0, \tag{36}$$

or from Eq. 35

$$L(1, u/y) = \frac{1}{2\pi}\{\sqrt{u/(\kappa y)} - \sqrt{u/u'}\}. \tag{37}$$

Thus Eq. 3 becomes

$$y\frac{\partial}{\partial y}\ln\Lambda_1 = \frac{1}{4\pi}\sqrt{u/(\kappa y)}\,(\tilde{g}_2+2\tilde{g}_3-\tilde{g}_4). \tag{38}$$

Changing the variables as in Eq. 28, we get

$$\frac{\partial}{\partial x}\ln\Lambda_1 = -\tilde{g}_2-2\tilde{g}_3+\tilde{g}_4. \tag{39}$$

In a similar way, we have

$$\frac{\partial}{\partial x}\ln\Lambda_2 = \tilde{g}_2+\tilde{g}_4, \tag{40}$$

$$\frac{\partial}{\partial x}\ln\Lambda_3 = -\tilde{g}_1-\tilde{g}_2. \tag{41}$$

Relations obtained in Eqs. 29—32 and in Eqs. 39—41 are the same as those obtained by Kimura and Mishima[8] by means of the parquet diagram sum.

Finally we should like to add a few comments about approximations employed in the present treatment. The typical higher order corrections not taken into

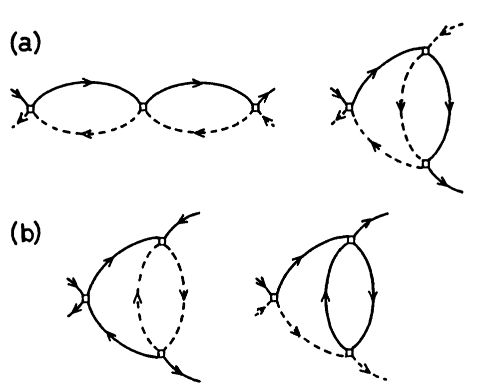

Fig. 3. Typical higher order corrections to Γ.

consideration can be expressed diagrammatically as shown in Figs. 3(a) and (b). The diagrams in Fig. 3(a) involve Π^{vc} twice (called overlap divergence), but those in Fig. 3(b) only once. Therefore, their contributions are proportional to $g^3L^2(T)$ in the former and are proportional to $g^3L(T)$ in the latter. If we use these diagrams to evaluate the right-hand side of Eq. 1, we obtain (with some constants, a and b)

$$\begin{aligned}\frac{\partial}{\partial\xi}\{\cdots + a\tilde{g}^3L^2(\xi, u/y, g) + b\tilde{g}^3L(\xi, u/y, g)\}|_{\xi=1} \\ = 2a\tilde{g}^3L(1, n/y, g)\frac{\partial}{\partial\xi}L(\xi, u/y, g)|_{\xi=1} \\ + b\tilde{g}^3\frac{\partial}{\partial\xi}L(\xi, u/y, g)|_{\xi=1}\,. \qquad (42)\end{aligned}$$

Here we use Eq. 36 to get

$$\text{Eq. 42} = b\tilde{g}^3\frac{\partial}{\partial\xi}L(\xi, u/y, g)|_{\xi=1}\,\cdot \qquad (43)$$

Namely, the terms of overlap divergence, g^nL^m ($m\geqq 2$) have no effect on the renormalization equation (Eq. 1). These have been implicitly taken into account when the elementary divergent term ($\propto L$) is input as an initial term.

Next, we examine the approximation arising from the condition that the cut-off parameter p_c is set so that the relation (36) is held. The polarization part is expressed more exactly as

$$\begin{aligned}\Pi^{vv} &= \int_{-\pi}^{\pi}\frac{dg}{2\pi}\,\frac{1}{2\varepsilon_q^v}\tanh\frac{\varepsilon_q^v}{2T} \\ &\equiv L(T) + L'(T)\,, \qquad (44)\end{aligned}$$

where

$$L(T) = \int_{-p_c}^{p_c}\frac{dq}{2\pi}\,\frac{1}{2\varepsilon_q^0}\tanh\frac{\varepsilon_q^0}{2T} \qquad (45)$$

with

$$\varepsilon_p^0(\doteqdot\varepsilon_p^v) = tp^2, \qquad (46)$$

and the residual part, L' is analyzed as

$$\begin{aligned}L'(T) &= \int_{-\pi}^{\pi}\frac{dq}{2\pi}\,\frac{1}{2\varepsilon_q^v}\tanh\frac{\varepsilon_q^v}{2T} - \int_{-p_c}^{p_c}\frac{dq}{2\pi}\,\frac{1}{2\varepsilon_q^0}\tanh\frac{\varepsilon_q^0}{2T} \\ &= \int_{-p_c}^{p_c}\frac{dq}{2\pi}\left(\frac{1}{2\varepsilon_q^v}\tanh\frac{\varepsilon_q^v}{2T} - \frac{1}{2\varepsilon_q^0}\tanh\frac{\varepsilon_q^0}{2T}\right) \\ &\quad + 2\int_{p_c}^{\pi}\frac{dq}{2\pi}\,\frac{1}{2\varepsilon_q^v}\tanh\frac{\varepsilon_q^v}{2T}\,. \qquad (47)\end{aligned}$$

We can see that from the above expression, L' is regular and a slowly varying function with respect to T. Therefore, since it might be possible for us to choose g, at the beginning, so as to include the effect from L', Π in Eq. 44 is well approximated only by $L(T)$.

Solutions of Renormalization Equation

Our basic equations to look for the low-temperature phases are Eqs. 29—32 for g_i's, and Eqs. 39—41 for A_i's.

First, we observe that the equations are invariant under the transformations

$$\tilde{g}_i\to\lambda\tilde{g}_i,\ x\to x/\lambda, \qquad (48)$$

where λ is an arbitrary constant.

The initial condition for $\tilde{g}_i$'s and A_i's is given at temperature $T=t$

$$\tilde{g}_i = g_i,\ \text{and}\ A_i = 1, \qquad (49)$$

according to Eq. 14. Because of the transformation property, Eq. 48, any solution for a given set of the values of g_i can be scaled into the solutions for another set of initial values λg_i.

We can obtain an analytic solution for Eqs. 29—32 only for the special case of $g_2=0$.

$$\begin{aligned}\tilde{g}_1 &= \frac{1}{x + g_1^{-1}}\,, \\ \tilde{g}_2 &= 0\,, \\ \tilde{g}_3 &= \frac{\tilde{g}_4^2}{2\tilde{g}_4 - Cg_4}\,, \\ \tilde{g}_4 &= \frac{-1}{x - g_4^{-1}}\,, \qquad (50)\end{aligned}$$

where

$$C = 2 - \frac{g_4}{g_3}\,. \qquad (51)$$

Substituting the above into Eqs. 39—41, we obtain

$$\begin{aligned}A_1 &= \frac{1}{Cg_3x + 1}\,, \\ A_2 &= \frac{-1}{g_4x - 1}\,, \\ A_3 &= \frac{1}{g_1x + 1}\,. \qquad (52)\end{aligned}$$

The phase diagrams corresponding to the case are shown in Figs. 4(a) and (b).

For the case of $g_2\neq 0$, the renormalization equations must be solved numerically. The resulting phase diagrams are shown in Figs. 4(c)—(i).

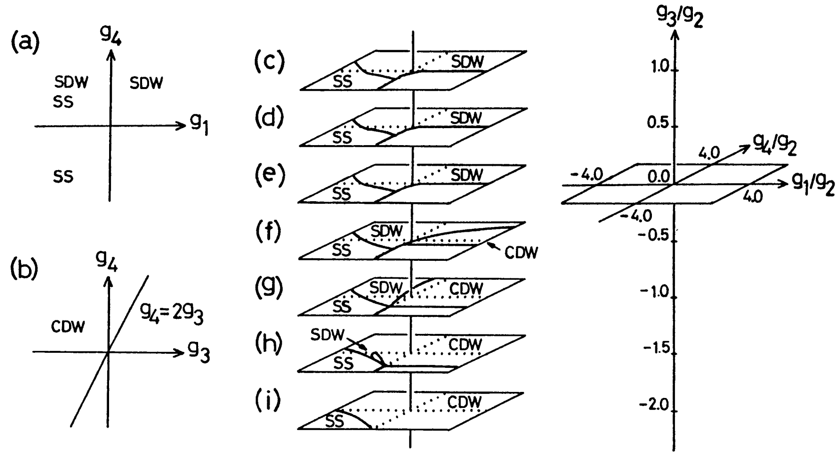

Fig. 4. Phase diagrams for various sets of g_j. (a) and (b): Those for the case of $g_2=0$. (c)—(i): Those for $g_2\neq 0$, and g_3/g_2 is 1.0, 0.5, 0.0, −0.5, −1.0, −1.5, and −2.0, respectively. The coordinate axis for them is shown on their right.

Conclusion

We have discussed the phase diagrams of the polyacene molecules in the framework of renormalization group theory within the most divergent approximation. Under this approximation the instability of the normal electronic state appears at a finite temperature.

Here, we must add some arguments for the justification of the present method. One may take a skeptical view about the validitiy of our results, considering that the renormalization group method is applicable only to a logarithmic singularity but not to a power low case. Indeed, the applications of this method thus far worked out have been fully successful for logarithmic problems.[2–5] However, we stress that the procedure to obtain the fundamental renormalization group equations is not grounded on or restricted within the logarithmic behaviour of the perturbation series, as reviewed in Appendix at some length. In the present problem, the singular terms in the perturbation series for the coupling constants are of the form

$$\tilde{g}=g+Ag^2L+Bg^3L^2+Cg^3L+\cdots, \tag{53}$$

where L is given by Eq. 19 and A, B, and C are constants. In our present analysis, we have taken only the second term of the right hand side of Eq. 53. The next order perturbation will give the third and fourth terms. The third B-term belongs to the most singular class, but does not contribute to the renormalization group equation due to the condition, Eq. 20. The effect has been included in the resultant solutions of that equation. Therefore, an overcounting of divergent diagrams does not occur. The situation is the same as in the logarithmic case. Thus the present results are justifiable within the most divergent approximation. A practical difficulty will arise to obtain the less divergent series, the C and further terms. As discussed in Ref. 1, the next divergent terms would lower the transition temperature to the absolute zero and shift the phase boundary to some extent. The correct estimation of these higher order terms is hard to manipulate because of the stronger singularity in the present problem than the logarithmic case.

The most divergent approximation gives correctly the behaviour of the dominant instabilities in the temperature region higher than the mean field transition temperatre. As for the phase diagram the present results are considered to be reliable at least qualitatively. In usual one-dimensional metals, it was found that superconductivity and CDW tend to appear simultaneously for the negative backward scattering. In the present case, however, the result shows that there is a wide range where nagative constants lead to only the superconductivity phase. In this respect the present system is expected to be more suitable to design for superconductivity.

In conclusion, the electron-electron interaction can lead to various type of ordered phases in the ground state. Such a variety of ordered phases has been observed in recent experiments about conducting organic materials such as TTF-TCNQ and BEDT-TTF where the states of superconductivity, CDW and SDW are mutually correlated and competing. Our result sheds some light on these phenomena. In this connection, we note the overlapping or adjacent appearance of superconducting and SDW states in our phase diagram, which has been discussed as the paramagnon effect in usual texts. By using the renormalization group method within g-ology, we can predict what kind of phase occurs for given interaction parameters. In the present paper, we have considered the interaction constants on the spine as parameters, which are influenced by various complex effects such as the screening by the σ-electron on the spine of polyacene and possibly, the interaction through the side-chain which may be synthesized with various

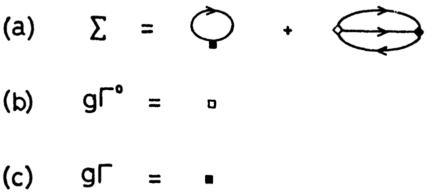

Fig. 5. Diagrammatic expressions for the self-energy and vertices. (a) Self-energy. (b) Bare vertex. (c) Full vertex.

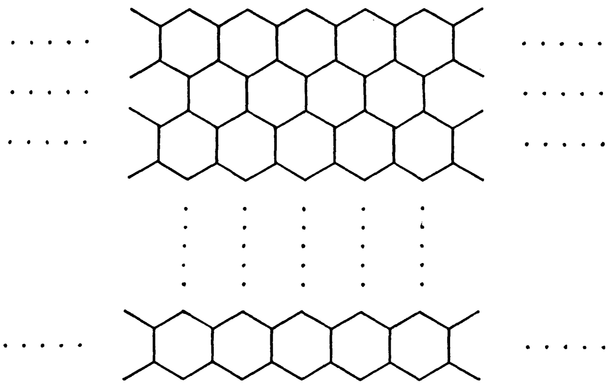

Fig. 6. Polyacene carbone skeleton.

designs. Therefore we can hope to get any phases in the ground state, if side-chains are suitably modified. The problem to analyze the effective interactions including a screening effect and an excitonic processes was discussed in our separate paper.[9]

As pointed earlier,[1,10] the π-electron energy spectrum is similar for polymers with a bridged array of an arbitrary number of polyacene skeletons (Fig. 6), i.e., the conduction- and valence bands are degenerate (or almost degenerate) at the points $k=\pm\pi$. The present theory applies equally to such a system. In the limit of an infinite number of such skeletons, however, the polymer tends to be system with a planar carbon lattice. Even in this two-dimensional lattice the degeneracy of two bands remains, but the one dimensional van Hove singularity as treated here disappears, so that $T^{-1/2}$ singularity will be weakened to the one of ln T. For the latter case many of the qualitative features of the present results remain unaltered. The detailed analysis will be reported elsewhere.

Appendix. Renormalization Group

In this appendix we reformulate the renormalization equations used in the text in a form suitable for the present analysis.[2,3] The Dyson equation for the Green's function G is written symbolically as

$$G=G^0+G^0\Sigma G, \qquad \text{(A. 1)}$$

which is a matrix notation, and G^0 is for one without interaction. The self-energy part, Σ is

$$\Sigma=g\Gamma G+g\Gamma^0 GGGg\Gamma, \qquad \text{(A. 2)}$$

and it can be expressed diagrammatically as shown in Fig. 5(a), where we extract the coupling g from the vertex part, say, the bare vertex, $g\Gamma^0$ and the full vertex, $g\Gamma$ corresponds to Figs. 5(b) and (c), respectively.

Relations (A. 1) and (A. 2) are invariant under the multiple renormalization such as

$$G \to \frac{1}{Z_1}G, \qquad G^0 \to \frac{1}{Z_1}G^0 ,$$

$$\Gamma_i \to \frac{1}{Z_{i,2}}\Gamma_i , \qquad \Gamma_i^0 \to \frac{1}{Z_{i,2}}\Gamma_i^0 ,$$

$$g_i \to Z_1{}^2 Z_{i,2} g_i , \qquad \text{(A.3)}$$

where the index i refers to the i-th element.

The Green's function G is formally written as

$$G(p) = \frac{d(p)}{\varepsilon - \varepsilon_p} , \qquad \text{(A.4)}$$

for which the transformation (A. 3) is interpreted in such manner,

$$d(T/\lambda_2,\ t/\lambda_2, g_{\lambda_2}) = \frac{1}{Z_1} d(T/\lambda_1, t/\lambda_1, g_{\lambda_1}) . \qquad \text{(A.5)}$$

Strictly speaking, G and Γ depend on quantities with the dimension of energy, i.e., on ε, ε_p, T (temperature) and t (transfer integral). However, we note explicitly only T and t.

We are allowed to set, without loss of generality, as

$$d(1,\ t/\lambda,\ g_\lambda)=1. \qquad \text{(A. 6)}$$

Then, putting $T=\lambda_2$ in Eq. A. 5, we get

$$Z_1=d(\lambda_2/\lambda_1,\ t/\lambda_1,\ g_{\lambda_1}), \qquad \text{(A. 7)}$$

and similarly

$$\Gamma_i(T/\lambda_2, t/\lambda_2, g_{\lambda_2}) = \frac{1}{Z_{i,2}}\Gamma_i(T/\lambda_1, t/\lambda_1, g_{\lambda_1}) . \qquad \text{(A.8)}$$

Putting $T=\lambda_2$ in Eq. A. 8, we obtain

$$Z_{i,2} = \frac{\Gamma_i(\lambda_2/\lambda_1, t/\lambda_1, g_{\lambda_1})}{\Gamma_i(1, t/\lambda_2, g_{\lambda_2})} . \qquad \text{(A.9)}$$

Relations (A. 7) and (A. 9) enable us to lead

$$g_{i,\lambda_2}= g_{i,\lambda_1} d^2(\lambda_2/\lambda_1, t/\lambda_1, g_{\lambda_1}) \ \frac{\Gamma_i(\lambda_2/\lambda_1, t/\lambda_1, g_{\lambda_1})}{\Gamma_i(1, t/\lambda_2, g_{\lambda_2})} . \qquad \text{(A.10)}$$

What we want to prove is invariant character of the right-hand side of Eq. A. 10 under a scale transformation.
To this end, inserting Eq. A. 7 into Eq. A. 5, and also Eq. A. 8 into Eq. A. 9, we obtain

$$d(T/\lambda_2,\ t/\lambda_2,\ g_{\lambda_2})= \frac{d(T/\lambda_1, t/\lambda_1, g_{\lambda_1})}{d(\lambda_2/\lambda_1, t/\lambda_1, g_{\lambda_1})} , \qquad \text{(A.11)}$$

$$\frac{\Gamma_i(T/\lambda_2, t/\lambda_2, g_{\lambda_2})}{\Gamma_i(1, t/\lambda_2, g_{\lambda_2})} = \frac{\Gamma_i(T/\lambda_1, t/\lambda_1, g_{\lambda_1})}{\Gamma_i(\lambda_2/\lambda_1, t/\lambda_1, g_{\lambda_1})} . \qquad \text{(A.12)}$$

Here we put

$$\Gamma_i(1,\ t/\lambda,\ g_\lambda)=1. \qquad \text{(A. 13)}$$

This assumption is not always necessary, but will be met in practical cases. From Eqs. A. 11 and A. 12, we obtain

$$\begin{aligned} &d^2(T/\lambda_2,\ t/\lambda_2,\ g_{\lambda_2})\ \Gamma_i(T/\lambda_2,\ t/\lambda_2,\ g_{\lambda_2}) \\ &\quad\times d^2(\lambda_2/\lambda_1,\ t/\lambda_1,\ g_{\lambda_1})\ \Gamma_i(\lambda_2/\lambda_1,\ t/\lambda_1,\ g_{\lambda_1}) g_{i,\lambda_1} \\ &\qquad = g_{i,\lambda_1} d^2(T/\lambda_1,\ t/\lambda_1,\ g_{\lambda_1}) \Gamma_i(T/\lambda_1,\ t/\lambda_1,\ g_{\lambda_1}). \end{aligned} \qquad \text{(A. 14)}$$

If we use Eq. A. 10 in the left-hand side of Eq. A. 14, we have

$$\begin{aligned} & g_{i,\lambda_2} d^2(T/\lambda_2, t/\lambda_2, g_{\lambda_2}) \Gamma_i(T/\lambda_2, t/\lambda_2, g_{\lambda_2}) \\ & \quad = g_{i,\lambda_1} d^2(T/\lambda_1, t/\lambda_1, g_{\lambda_1}) \Gamma_i(T/\lambda_1, t/\lambda_1, g_{\lambda_1}). \end{aligned} \tag{A. 15}$$

This relation is nothing but the invariant character which we have intended to show. We call the above quantity the *invariant coupling*:

$$\tilde{g}_i(T/\lambda, t/\lambda, g_\lambda) = d^2(T/\lambda, t/\lambda, g_\lambda) \Gamma_i(T/\lambda, t/\lambda, g_\lambda) g_{i,\lambda}. \tag{A. 16}$$

Now introducing new variables:

$$y = T/\lambda_1, \quad u = t/\lambda_1, \quad t = \lambda_2/\lambda_1, \tag{A. 17}$$

we get from Eq. A. 15,

$$\begin{aligned} \tilde{g}_i(y, u, g) & = d^2(y, u, g) \Gamma_i(y, u, g) g_i \\ & = d^2(y/t, u/t, g_{\lambda_2}) \Gamma_i(y/t, u/t, g_{\lambda_2}) g_{i,\lambda_2}, \end{aligned} \tag{A. 18}$$

where we put

$$g_{\lambda_1} = g. \tag{A. 19}$$

Since we can rewrite g_{i,λ_2} in Eq. A. 18, by the use of Eq. A. 10, as

$$\begin{aligned} g_{i,\lambda_2} & = g_i d^2(t, u, g) \Gamma_i(t, u, g) \\ & = \tilde{g}_i(t, u, g), \end{aligned} \tag{A. 20}$$

substituting this into Eq. A. 18, we can obtain

$$\begin{aligned} \tilde{g}_i(y, u, g) = {} & d^2(y/t, u/t, \tilde{g}(t, u, g)) \Gamma_i(y/t, u/t, \tilde{g}(t, u, g)) \\ & \times \tilde{g}_i(t, u, g). \end{aligned} \tag{A. 21}$$

Observing Eq. A. 16, we can rewrite the above as

$$\tilde{g}_i(y, u, g) = \tilde{g}_i(y/t, u/t, \tilde{g}_i(t, u, g)). \tag{A. 22}$$

This is a really beautiful functional equation.

In view of a practical use, a form of differential equation is preferable: Differentiating Eq. A. 22 with respect to y, followed by putting $t=y$, we obtain

$$y \frac{\partial}{\partial y} \tilde{g}_i(y, u, g) = \frac{\partial}{\partial \xi} \tilde{g}_i(\xi, u/y, \tilde{g}(y, u, g)) |_{\xi=1} \tag{A.23}$$

with the boundary condition, Eq. A. 19. In order to get $\tilde{g}_i$ through Eq. A. 23, we begin with calculating $\tilde{g}$ in the right-hand side by the perturbation method. Then solving the differential equation Eq. A. 23, we get $\tilde{g}_i$ being improved to be invariant under the operations of the renormalization group.

Another differential equation satisfying $\tilde{g}_i$ is obtained by differentiating Eq. A. 22 with respect to t, followed by putting $t=1$:

$$\left\{ y \frac{\partial}{\partial y} + u \frac{\partial}{\partial u} - \sum_j \frac{\partial \tilde{g}_j(t, u, g)}{\partial t} |_{t=1} \frac{\partial}{\partial g_j} \right\} \tilde{g}_i(y, u, g) = 0 . \tag{A.24}$$

Similar treatments are possible for d and Γ. From Eqs. A. 11, A. 12, and A. 13 we obtain

$$d(y, u, g) = d(y/t, u/t, \tilde{g}(t, u, g)) d(t, u, g) \tag{A. 25}$$

and

$$\Gamma_i d(y, u, g) = \Gamma_i(y/t, u/t, \tilde{g}(t, u, g)) \Gamma_i(t, u, g). \tag{A. 26}$$

If we differentiate logarithms of both side of Eq. A. 26 with respect to t, and then put $t=y$, the results are

$$y \frac{\partial}{\partial y} \ln d(y, u, g) = \frac{\partial}{\partial \xi} \ln d(\xi, u/y, \tilde{g}(y, u, g)) |_{\xi=1} \tag{A.27}$$

and

$$y \frac{\partial}{\partial y} \ln \Gamma_i(y, u, g) = \frac{\partial}{\partial \xi} \ln \Gamma_i(\xi, u/y, \tilde{g}(y, u, g)) |_{\xi=1} . \tag{A.28}$$

An entirely analogous analysis will be done for the external vertices. These will be transformed, together with ones in Eq. A. 3, as

$$\Lambda_i \rightarrow \frac{1}{Z_{i,3}} \Lambda_i \ , \tag{A.29}$$

which is interpreted as a scale transformation:

$$\Lambda_i(T/\lambda_2, t/\lambda_2, g_{\lambda_2}) = \frac{1}{Z_{i,3}} \Lambda_i(T/\lambda_1, t/\lambda_1, g_{\lambda_1}) . \tag{A.30}$$

In the same way as in Eq. A. 13, we assume

$$\Lambda_i(1, t/\lambda, g_\lambda) = 1. \tag{A. 31}$$

If we put $T=\lambda_2$ in Eq. A. 30, and use Eq. A. 31, it follows that

$$Z_{i,3} = \Lambda_i(\lambda_2/\lambda_1, t/\lambda_1, g_{\lambda_1}). \tag{A. 32}$$

Substituting this in Eq. A. 30, we obtain

$$\begin{aligned} & \Lambda_i(T/\lambda_1, t/\lambda_1, g_{\lambda_1}) \\ & \quad = \Lambda_i(T/\lambda_2, t/\lambda_2, g_{\lambda_2}) \Lambda_i(\lambda_2/\lambda_1, t/\lambda_1, g_{\lambda_1}). \end{aligned} \tag{A. 33}$$

By the use of Eqs. A. 17, A. 19, and A. 20, we can rewrite Eq. A. 33 as

$$\Lambda_i(y, u, g) = \Lambda_i(y/t, u/t, \tilde{g}(t, u, g)) \Lambda_i(t, u, g). \tag{A. 34}$$

If we differentiate this with respect to y and put $t=y$, we obtain the result similar to Eqs. A. 27 and A. 28,

$$y \frac{\partial}{\partial y} \ln \Lambda_i(y, u, g) = \frac{\partial}{\partial \xi} \ln \Lambda_i(\xi, u/y, \tilde{g}(y, u, g)) |_{\xi=1} . \tag{A.35}$$

We can easily realize the transformation characters given by Eqs. A. 3 and A. 29 by use of the perturbation expansions of the correponding quantities.

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