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On the Convergence of the Kroll Method

By

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Solving directly Kroll's set of equations, the nature of the solution of Bloch's integral equation has been investigated. It is a slowly varying and nearly even function, as it was assumed. By means of the results, the degree of accuracy of the solution in polynom has been tested by the degree of convergence of the variational expression of Bloch's integral equation towards the extremum. The polynom of 7 or 8 terms seems to be a practically sufficient approximation.

To solve Bloch's integral equation, Kroll[1] has transformed it into an infinite set of equations which enables the solution to be found in a power series systematically to any desired accuracy. In practice, however, it is impossible to solve an infinite set of equations, so that we have to take necessarily only a finite number of equations, that means to replace the power series by a polynom. Then its degree of accuracy is to be questioned. Recently one of us (K.U.)[2] has transformed Bloch's integral equation into a variational form which is expressed by means of the polynom in s terms for $c^{(n)}(\eta)$

$$c^{(n)}(\eta) = c_0^{(n)} + c_1^{(n)}\eta + c_2^{(n)}\eta^2 + \cdots\cdots + c_{s-1}^{(n)}\eta^{s-1} \qquad (1)$$

in a very simple form as a function of s

$$b_1^{(n)}c_0^{(n)} + b_2^{(n)}c_1^{(n)} + \cdots\cdots + b_s^{(n)}c_{s-1}^{(n)} = \text{extremum}, \qquad (2)$$

provided that $c_0^{(n)}$, $c_1^{(n)}$ $\cdots\cdots$ are the roots of Kroll's set of equations. This enables the questioned degree of accuracy of the polynom to be determined by seeing how closer this variational expression (2) does converge towards the maximum as the number of terms in the polynom s increases. This procedure provides at the same time

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a method to test the convergence of the power series (1) or the validity of the Kroll method.

In order to evaluate the variational expression (2), it is primarily necessary to determine the values of c_0, c_1, ... by solving numerically for every temperature Kroll's set of equations, which is put in the case of monovalent metals for the convenience of computation into the following form, where only the ratio θ/ζ appears as the material constant of the individual metal.

$$\sum_{j=1}^{s} \boldsymbol{F}_{ij}(x)\, c_{j-1}^{(n)} = \boldsymbol{b}_i^{(n)} \qquad i = 1, 2 \cdots\cdots s,\ n = \frac{3}{2}, \frac{5}{2}, \tag{3}$$

where
$$\boldsymbol{F}_{ij}(x) = \boldsymbol{b}_{ij}(x) + \frac{1}{X^2}\boldsymbol{a}_{ij}(x), \qquad \frac{kT}{\zeta}\boldsymbol{a}_{ij}(x),$$
$$i+j = \text{even} \qquad\qquad i+j = \text{odd}$$
$$X = \frac{1}{2^{\frac{1}{3}}}x = \frac{1}{2^{\frac{1}{3}}}\frac{\theta}{T}, \qquad x = \frac{\theta}{T}.$$

i	1	2	3	4	5	6	7	8	9
$\boldsymbol{b}_i^{(\frac{3}{2})}$:		$\frac{1}{2}\pi^2\frac{kT}{\zeta}$,		$\frac{7}{10}\pi^4\frac{kT}{\zeta}$,		$\frac{31}{14}\pi^6\frac{kT}{\zeta}$,		$\frac{127}{10}\pi^8\frac{kT}{\zeta}$,	
	1,		$\frac{1}{3}\pi^2$,		$\frac{7}{15}\pi^4$,		$\frac{31}{21}\pi^6$,		$\frac{127}{15}\pi^8$.
$\boldsymbol{b}_i^{(\frac{5}{2})}$:		$\frac{5}{6}\pi^2\frac{kT}{\zeta}$,		$\frac{7}{6}\pi^4\frac{kT}{\zeta}$,		$\frac{155}{42}\pi^6\frac{kT}{\zeta}$,		$\frac{127}{6}\pi^8\frac{kT}{\zeta}$,	

These values follow from the neglection of $(kT/\zeta)^2$, which is at most of the order of 10^{-5} in the temperature range lower than 2θ, though there remain some more considerations for the second order phenomena.

$$\boldsymbol{a}_{ij}(x) \equiv \int_0^x \frac{z^4 dz}{e^z - 1}\int_{-\infty}^{+\infty} \frac{(\eta+z)^{i-1}\eta^{j-1}}{(1+e^{\eta})(1+e^{-\eta-z})}\, d\eta \qquad i+j=\text{even},$$
$$\equiv \int_0^x \frac{z^2 dz}{e^z - 1}\int_{-\infty}^{+\infty} \frac{2\eta^{i+j-1} - (\eta+z)^i\eta^{j-1} - (\eta+z)^{i-1}\eta^j}{(1+e^{\eta})(1+e^{-\eta-z})}\, d\eta \qquad i+j=\text{odd},$$
$$\boldsymbol{b}_{ij}(x) \equiv 2\int_0^x \frac{z^2 dz}{e^z - 1}\int_{-\infty}^{+\infty} \frac{\eta^{i+j-2} - (\eta+z)^{i-1}\eta^{j-1}}{(1+e^{\eta})(1+e^{-\eta-z})}\, d\eta. \tag{4}$$

These integrals can be expressed by the radiation integrals $J_n(x)$, as tabulated in the appendix. Our quantities in Gothic letters are related to the corresponding ones used by Kroll or in reference (2) in the following manner.

$$\left.\begin{aligned} a_{ij} &= \begin{cases} (k\Theta)^2(2D)^{-1}a_{ij} & i+j=\text{even}, \\ a_{ij} & i+j=\text{odd}, \end{cases} \\ b_{ij} &= (2\zeta)^{-1}b_{ij}, \\ b_i^{(n)} &= \zeta^{-n}b_i^{(n)}, \\ c_i^{(n)} &= \zeta^{-n+1}c_i^{(n)}. \end{aligned}\right\} \quad (5)$$

We have solved the set of equations (3) for every number of terms from $s=1$ to $s=8$ in the temperature range $T/\Theta=0.1\sim 2$. The even coefficients $c_0, c_2, c_4, c_6, \cdots$ converge monotonously to the final values, while the odd ones $c_1, c_3, c_5, c_7, \cdots$ oscillatorily, as the number of terms s increases. Fig. 1 shows this situation for $T/\Theta=0.5$ as an example. The temperature dependence of these coef-

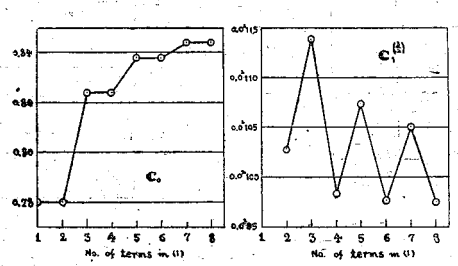

Fig. 1. Convergence of c_0 and c_1 for $T/\Theta=0.5$ as functions of the number of terms in (1).

ficients are traced in Fig. 2. At lower temperatures than the Debye temperature, the odd coefficients are markedly smaller compared to the even ones, as seen from the orders of magnitude given in TABLE I, so that the function $c^{(n)}(\eta)$ is nearly even, as Bloch[3] has ever assumed. Due to the exceptionally large value of c_0 the function $c^{(n)}(\eta)$ is a slowly varying function, as it was also supposed. At the limit $T\to 0$, however, all the odd coefficients increase infinitely as T^{-1}, whereas the even ones tend to the finite limiting values, except c_0 increases strongly infinitely as T^{-2}.

TABLE I. *Orders of magnitude of the coefficients of the power series* (1) *at several temperatures.*

T/Θ	c_0	c_1	c_2	c_3	c_4	c_5	c_6	c_7
2	10	10^{-1}	10^{-2}	10^{-5}	10^{-4}	10^{-7}	10^{-6}	10^{-9}
1	1	10^{-2}	10^{-2}	10^{-5}	10^{-4}	10^{-7}	10^{-6}	10^{-9}
0.5	1	10^{-3}	10^{-2}	10^{-5}	10^{-4}	10^{-7}	10^{-8}	10^{-9}
0.1	10^{-1}	10^{-4}	10^{-3}	10^{-6}	10^{-5}	10^{-8}	10^{-7}	10^{-11}

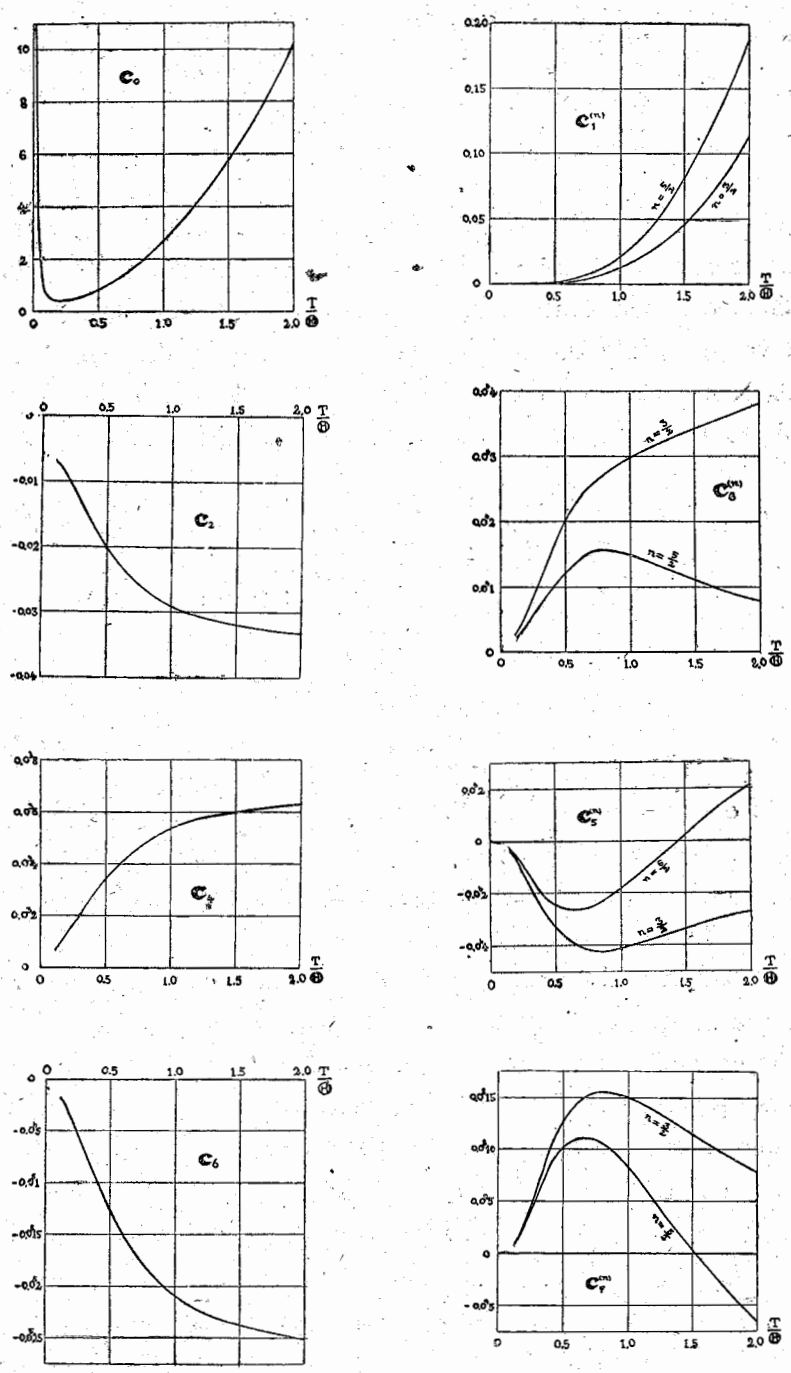

Fig. 2. $c_0, \cdots c_7$ as functions of the temperature T/Θ.

Now we can evaluate the variational expression (2) in every number of terms at every temperature. Fig. 3 shows the relative values of the variational experssion (2) in 3 or 4 terms and in 5

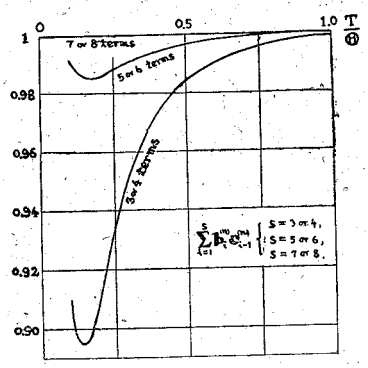

Fig. 3. Relative values of the variational expression (2) in three approximations as functions of the temperature.

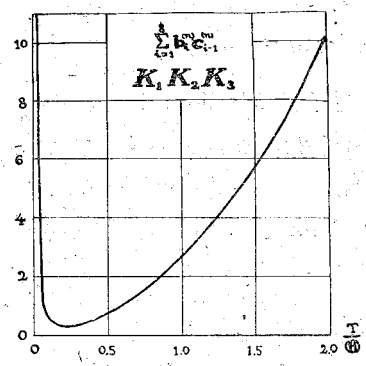

Fig. 4. Variational expression (2) as well as principal quantities K_1, K_2 and K_3 in the approximation of 7 or 8 terms as functions of the temperature.

or 6 terms at every temperature with respect to the value of (2) in 7 or 8 terms. That the curves of these three approximations diverge from each other at intermediate temperatures markedly larger than at lower and higher temperatures, indicates that the convergence of the Kroll method is relatively poor at intermediate temperatures. Since the discrepancy between the approximations in 5 or 6 terms and the one in 7 or 8 terms is at most 1%, the polynom of 7 or 8 terms, i.e. the substitution of 7 or 8 equations for the infinite set of equations, should be an approximation with the practically sufficient accuracy.

Because the variational expression (2) is for $n = 3/2$ and $5/2$ respectively equivalent to the principal quantities K_1 and K_3, and the difference between K_1, K_2 and K_3 is too small to be shown in the figure, the temperature dependence of the variational expression (2), given in Fig. 4 by means of the obtained values of $\boldsymbol{b}_i$ and $\boldsymbol{c}_i$, represents at the same time that of $\boldsymbol{K}_1$, $\boldsymbol{K}_2$ and $\boldsymbol{K}_3$,

$$\boldsymbol{b}_1^{(m)}\boldsymbol{c}_0^{(n)} + \boldsymbol{b}_2^{(m)}\boldsymbol{c}_1^{(n)} + \cdots\cdots\cdots = \boldsymbol{K}_{m+n-2} \qquad m, n = \frac{3}{2} \text{ or } \frac{5}{2}, \qquad (6)$$

which determine several quantities in the conduction theory, e.g.

directly the electrical conductivity, and by their difference of the order (kT/ζ) the thermal conductivity, the thermoelectric power, the Thomson coefficient etc. as functions of the temperature. These practical applications of the obtained results will be given in the continued article.

In conclusion, we wish express our sincere thanks to Dr. Kroll who has stimulated us while his stay in Sapporo as the visiting lecturer. The financial supports of The Department of Education and The Hattori-Hôkôkai are gratefully acknowledged.

Appendix

$$a_m \equiv \int_0^\infty \frac{\eta^m}{1+e^\eta}\, d\eta = \left(1-\frac{1}{2^m}\right) m!\, \zeta(m+1)\,,$$

$$\zeta(m) \equiv 1+\frac{1}{2^m}+\frac{1}{3^m}+\frac{1}{4^m}+\cdots\cdots\,,$$

$a_1=(1/12)\pi^2$, $a_3=(7/120)\pi^4$, $a_5=(31/252)\pi^6$, $a_7=(127/240)\pi^8$, $a_9=(511/132)\pi^{10}$, $a_{11}=(1414477/32760)\pi^{12}$, $a_{13}=(8192/12)\pi^{14}$, $a_{15}=(118518239/8160)\pi^{16}$.

$$I_n \equiv \int_{-\infty}^{\infty} \frac{\eta^n}{(1+e^\eta)(1+e^{-\eta-z})}\, d\eta \begin{array}{l} = \dfrac{1}{1-e^{-z}}\left[\displaystyle\int_0^\infty \frac{(\eta+z)^n-(\eta-z)^n}{1+e^\eta}\, d\eta + \frac{z^{n+1}}{n+1}\right] \quad n=\text{even}, \\ = \dfrac{1}{1-e^{-z}}\left[\displaystyle\int_0^\infty \frac{2\eta^n-(\eta+z)^n-(\eta-z)^n}{1+e^\eta}\, d\eta - \frac{z^{n+1}}{n+1}\right] n=\text{odd}, \end{array}$$

$I_0=(1-e^{-z})^{-1}[z]$,

$I_1=(1-e^{-z})^{-1}[-(1/2)z^2]$,

$I_2=(1-e^{-z})^{-1}[4a_1z+(1/3)z^3]$,

$I_3=(1-e^{-z})^{-1}[-6a_1z^2-(1/4)z^4]$,

$I_4=(1-e^{-z})^{-1}[8a_3z+8a_1z^3+(1/5)z^5]$,

$I_5=(1-e^{-z})^{-1}[-20a_3z^2-10a_1z^4-(1/6)z^6]$,

$I_6=(1-e^{-z})^{-1}[12a_5z+40a_3z^3+12a_1z^5+(1/7)z^7]$,

$I_7=(1-e^{-z})^{-1}[-42a_5z^2-70a_3z^4-14a_1z^6-(1/8)z^8]$,

$I_8=(1-e^{-z})^{-1}[16a_7z+112a_5z^3+112a_3z^5+16a_1z^7+(1/9)z^9]$,

$I_9=(1-e^{-z})^{-1}[-72a_7z^2-252a_5z^4-168a_3z^6-18a_1z^8-(1/10)z^{10}]$,

$I_{10}=(1-e^{-z})^{-1}[20a_9z+240a_7z^3+504a_5z^5+240a_3z^7+20a_1z^9+(1/11)z^{11}]$,

$I_{11}=(1-e^{-z})^{-1}[-110a_9z^2-660a_7z^4-924a_5z^6-330a_3z^8-22a_1z^{10}-(1/12)z^{12}]$,

$I_{12}=(1-e^{-z})^{-1}[24a_{11}z+440a_9z^3+1584a_7z^5+1584a_5z^7+440a_3z^9+24a_1z^{11}+(1/13)z^{13}]$,

$I_{13}=(1-e^{-z})^{-1}[-156a_{11}z^2-1430a_9z^4-3432a_7z^6-2574a_5z^8-572a_3z^{10}-26a_1z^{12}-(1/14)z^{14}]$,

$I_{14}=(1-e^{-z})^{-1}[28a_{13}z+728a_{11}z^3+4004a_9z^5+6864a_7z^7+4004a_5z^9+728a_3z^{11}+28a_1z^{13}+(1/15)z^{15}]$,

$I_{15}=(1-e^{-z})^{-1}[-210a_{13}z^2-2730a_{11}z^4-10010a_9z^6-12870a_7z^8-6006a_5z^{10}-910a_3z^{12}-30a_1z^{14}-(1/16)z^{16}]$,

$I_{16}=(1-e^{-z})^{-1}[32a_{15}z+1120a_{13}z^3+8736a_{11}z^5+22880a_9z^7+22880a_7z^9+8736a_5z^{11}+1120a_3z^{13}+32a_1z^{15}+(1/17)z^{17}]$.

$$J_n(x) \equiv \int_0^x \frac{z^n}{(e^z-1)(1-e^{-z})}\,dz, \qquad x \equiv \frac{\Theta}{T},$$

$$J_n(\infty) = n!\ \zeta(n),$$

$$J_5(\infty) = 1.244313\cdot 10^2, \quad J_7(\infty) = 5\,082080\cdot 10^3, \quad J_9(\infty) = 3.63\,088\cdot 10^5,$$
$$J_{11}(\infty) = 3.993653\cdot 10^7, \quad J_{13}(\infty) = 6.227785\cdot 10^9, \quad J_{15}(\infty) = 1.307714\cdot 10^{12},$$
$$J_{17}(\infty) = 3.556901\cdot 10^{14}, \quad J_{19}(\infty) = 1.216453\cdot 10^{17}, \quad J_{21}(\infty) = 5.109093\cdot 10^{19}.$$

$$a_{11} = J_5,$$
$$a_{12} = (1/2)\,J_5,$$
$$a_{13} = 4a_1 J_5 + (1/3)J_7,$$
$$a_{14} = 6a_1 J_5 + (1/4)J_7,$$
$$a_{15} = 8a_3 J_5 + 8a_1 J_7 + (1/5)J_9,$$
$$a_{16} = 20a_3 J_5 + 10a_1 J_7 + (1/6)\,J_9,$$
$$a_{17} = 12a_5 J_5 + 40a_3 J_7 + 12a_1 J_9 + (1/7)J_{11},$$
$$a_{18} = 42a_5 J_5 + 70a_3 J_7 + 14a_1 J_9 + (1/8)\,J_{11},$$
$$a_{19} = 16a_7 J_5 + 112a_5 J_7 + 112a_3 J_9 + 16a_1 J_{11} + (1/9)J_{13},$$

$$a_{22} = 4a_1 J_5 - (1/6)J_7,$$
$$a_{23} = 14a_1 J_5 + (5/12)\,J_7,$$
$$a_{24} = 8a_3 J_5 + 2a_1 J_7 - (1/20)J_9,$$
$$a_{25} = 52a_3 J_5 + 22a_1 J_7 + (3/10)J_9,$$
$$a_{26} = 12a_5 J_5 + 20a_3 J_7 + 2a_1 J_9 - (1/42)J_{11},$$
$$a_{27} = 114a_5 J_5 + 170a_3 J_7 + 30a_1 J_9 + (13/56)J_{11},$$
$$a_{28} = 16a_7 J_5 + 70a_5 J_7 + 42a_3 J_9 + 2a_1 J_{11} - (1/72)J_{13},$$
$$a_{29} = 200a_7 J_5 + 644a_5 J_7 + 392a_3 J_9 + 38a_1 J_{11} + (17/90)J_{13},$$

$$a_{33} = 8a_3 J_5 + (1/30)J_9,$$
$$a_{34} = 68a_3 J_5 + 24a_1 J_7 + (17/60)J_9,$$
$$a_{35} = 12a_5 J_5 + 8a_3 J_7 + (1/105)J_{11},$$
$$a_{36} = 162a_5 J_5 + 210a_3 J_7 + 32a_1 J_9 + (37/168)J_{11},$$
$$a_{37} = 16a_7 J_5 + 40a_5 J_7 + 12a_3 J_9 + (1/252)J_{13},$$
$$a_{38} = 296a_7 J_5 + 854a_5 J_7 + 462a_3 J_9 + 40a_1 J_{11} + (13/72)J_{13},$$
$$a_{39} = 20a_9 J_5 + 112a_7 J_7 + 112a_5 J_9 + 16a_3 J_{11} + (1/495)J_{15},$$

$$a_{44} = 12a_5 J_5 + 4a_3 J_7 - (1/140)J_{11},$$

$$a_{45} = 186a_5 J_5 + 222a_3 J_7 + 32a_1 J_9 + (187/840)J_{11},$$
$$a_{46} = 16a_7 J_5 + 22a_5 J_7 + 2a_3 J_9 - (1/504)J_{13},$$
$$a_{47} = 360a_7 J_5 + 954a_5 J_7 + 478a_3 J_7 + 40a_1 J_{11} + (51/280)J_{13},$$
$$a_{48} = 20a_9 J_5 + 72a_7 J_7 + 42a_5 J_9 + 2a_3 J_{11} - (1/1320)J_{15},$$
$$a_{49} = 590a_9 J_5 + 2804a_7 J_7 + 3080a_5 J_9 + 878a_3 J_{11} + 48a_1 J_{13} + (183/1188)J_{15},$$

$$a_{55} = 16a_7 J_5 + 16a_5 J_7 + (1/630)J_{13},$$
$$a_{56} = 392a_7 J_5 + 992a_5 J_7 + 480a_3 J_9 + 40a_1 J_{11} + (687/3780)J_{13},$$
$$a_{57} = 20a_9 J_5 + 48a_7 J_7 + 12a_5 J_9 + (1/2310)J_{15},$$
$$a_{58} = 670a_9 J_5 + 3012a_7 J_7 + 3150a_5 J_9 + 880a_3 J_{11} + 48a_1 J_{13} + (203/1320)J_{15},$$
$$a_{59} = 24a_{11} J_5 + 120a_9 J_7 + 112a_7 J_9 + 16a_5 J_{11} + (1/6435)J_{17},$$

$$a_{66} = 20a_9 J_5 + 40a_7 J_7 + 4a_5 J_9 - (1/2772)J_{15},$$
$$a_{67} = 710a_9 J_5 + 3100a_7 J_7 + 3166a_5 J_9 + 880a_3 J_{11} + 48a_1 J_{13} + (853/5544)J_{15},$$
$$a_{68} = 24a_{11} J_5 + 90a_9 J_7 + 44a_7 J_9 + 2a_5 J_{11} - (1/10296)J_{17},$$
$$a_{69} = 1116a_{11} J_5 + 7630a_9 J_7 + 13640a_7 J_9 + 8006a_5 J_{11} + 1456a_3 J_{13} + 56a_1 J_{15} + (12013/90090)J_{17},$$

$$a_{77} = 24a_{11} J_5 + 80a_9 J_7 + 24a_7 J_9 + (1/12012)J_{17},$$
$$a_{78} = 1164a_{11} J_5 + 7800a_9 J_7 + 13708a_7 J_9 + 8008a_5 J_{11} + 1456a_3 J_{13} + 56a_1 J_{15} + (48047/360360)J_{17},$$
$$a_{79} = 28a_{13} J_5 + 152a_{11} J_7 + 124a_9 J_9 + 16a_7 J_{11} + (1/45045)J_{19},$$

$$a_{88} = 28a_{13}J_5+140a_{11}J_7+84a_9J_9+4a_7J_{11} -(1/51480)J_{19},$$

$$a_{89} = 1778a_{13}J_5+16954a_{11}J_7+45654a_9J_9 +45758a_7J_{11}+17472a_5J_{13} +2240a_3J_{15}+64a_1J_{17} +(12113/102960)J_{21},$$

$$a_{99} = 32a_{15}J_5+224a_{13}J_7+224a_{11}J_9 +32a_9J_{11}+(1/218790)J_{21}.$$

$$b_{11} = b_{13} = b_{15} = b_{17} = b_{19} = \cdots = 0,$$

$$b_{22} = J_5,$$

$$b_{24} = 12a_1J_5+(1/2)J_7,$$

$$b_{26} = 40a_3J_5+20a_1J_7+(1/3)J_9,$$

$$b_{28} = 84a_5J_5+140a_3J_7+28a_1J_9+(1/4)J_{11},$$

$$b_{33} = 16a_1J_5+(1/3)J_7,$$

$$b_{35} = 64a_3J_5+24a_1J_7+(4/15)J_9,$$

$$b_{37} = 144a_5J_5+200a_3J_7+32a_1J_9+(3/14)J_{11},$$

$$b_{39} = 256a_7J_5+784a_5J_7+448a_3J_9+40a_1J_{11} +(8/45)J_{13},$$

$$b_{44} = 72a_3J_5+24a_1J_7+(3/10)J_9,$$

$$b_{46} = 180a_5J_5+220a_3J_7+32a_1J_9 +(19/84)J_{11},$$

$$b_{48} = 336a_7J_5+924a_5J_7+476a_3J_9+40a_1J_{11} +(11/60)J_{13},$$

$$b_{55} = 192a_5J_5+224a_3J_7+32a_1J_9 +(23/105)J_{11},$$

$$b_{57} = 384a_7J_5+984a_5J_7+480a_3J_9+40a_1J_{11} +(19/105)J_{13},$$

$$b_{59} = 640a_9J_5+2944a_7J_7+3136a_5J_9 +880a_3J_{11}+48a_1J_{13}+(76/495)J_{15},$$

$$b_{66} = 400a_7J_5+1000a_5J_7+480a_3J_9 +40a_1J_{11}+(23/126)J_{13},$$

$$b_{68} = 700a_9J_5+3080a_7J_7+3164a_5J_9 +880a_3J_{11}+48a_1J_{13}+(61/396)J_{15},$$

$$b_{77} = 720a_9J_5+3120a_7J_7+3168a_5J_9 +880a_3J_{11}+48a_1J_{13}+(71/462)J_{15},$$

$$b_{79} = 1152a_{11}J_5+7760a_9J_7+13696a_7J_9 +8008a_5J_{11}+1456a_3J_{13}+56a_1J_{15} +(6004/45045)J_{17},$$

$$b_{88} = 1176a_{11}J_5+7840a_9J_7+13720a_7J_9 +8008a_5J_{11}+1456a_3J_{13}+56a_1J_{15} +(3433/25740)J_{17},$$

$$b_{99} = 1792a_{13}J_5+17024a_{11}J_7+45696a_9J_9 +45760a_7J_{11}+17472a_5J_{13} +2240a_3J_{15}+64a_1J_{17} +(12869/109395)J_{19}.$$

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