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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.

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

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

$$X = \frac{1}{2^{\frac{1}{3}}}\, x = \frac{1}{2^{\frac{1}{3}}}\frac{\Theta}{T}, \qquad x = \frac{\Theta}{T}.$$

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.

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

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 $\boldsymbol{c}_0, \boldsymbol{c}_2, \boldsymbol{c}_4, \boldsymbol{c}_6, \cdots$ converge monotonously to the final values, while the odd ones $\boldsymbol{c}_1, \boldsymbol{c}_3, \boldsymbol{c}_5, \boldsymbol{c}_7, \cdots$ 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-

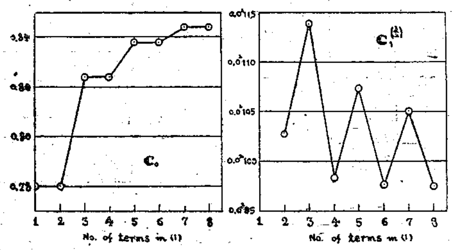

Fig. 1. Convergence of $\boldsymbol{c}_0$ and $\boldsymbol{c}_1$ for $T/\Theta=0.5$ as functions of the number of terms in (1).

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^{-6}	10^{-9}
0.1	10^{-1}	10^{-4}	10^{-3}	10^{-6}	10^{-5}	10^{-8}	10^{-7}	10^{-11}

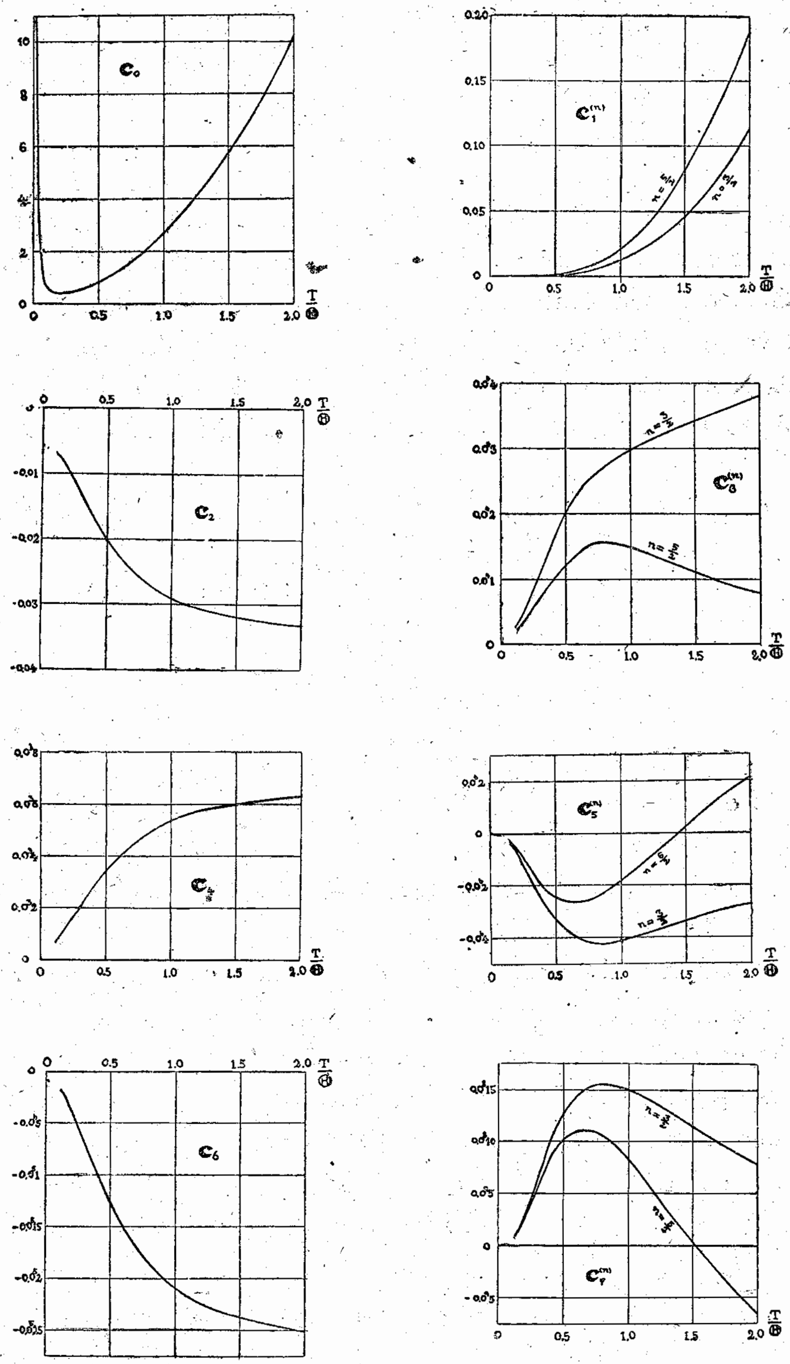

Fig. 2. $c_0, \cdots c_7$ as functions of the temperature T/Θ.

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

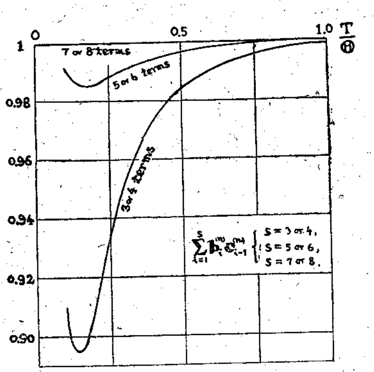

Fig. 3. Relative values of the variational expression (2) in three approximations as functions of the temperature.

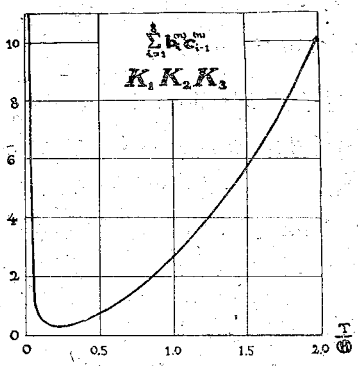

Fig. 4. Variational expression (2) as well as principal quantities K_1, K_2 and K_3 in the approximation of 7 or 8 terms as functions of the temperature.

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 b_i and c_i, represents at the same time that of K_1, K_2 and K_3,

$$b_1^{(m)}c_0^{(n)} + b_2^{(m)}c_1^{(n)} + \cdots\cdots = K_{m+n-2} \qquad m,\, n = \frac{3}{2} \text{ or } \frac{5}{2}, \tag{6}$$

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

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

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

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

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

$I_0=(1-e^{-z})^{-1}[z]$,
$I_1=(1-e^{-z})^{-1}[-(1/2)z^2]$,
$I_2=(1-e^{-z})^{-1}[4a_1z+(1/3)z^3]$,
$I_3=(1-e^{-z})^{-1}[-6a_1z^2-(1/4)z^4]$,
$I_4=(1-e^{-z})^{-1}[8a_3z+8a_1z^3+(1/5)z^5]$,
$I_5=(1-e^{-z})^{-1}[-20a_3z^2-10a_1z^4-(1/6)z^6]$,
$I_6=(1-e^{-z})^{-1}[12a_5z+40a_3z^3+12a_1z^5$
$\quad +(1/7)z^7]$,
$I_7=(1-e^{-z})^{-1}[-42a_5z^2-70a_3z^4-14a_1z^6$
$\quad -(1/8)z^8]$,
$I_8=(1-e^{-z})^{-1}[16a_7z+112a_5z^3+112a_3z^5$
$\quad +16a_1z^7+(1/9)z^9]$,
$I_9=(1-e^{-z})^{-1}[-72a_7z^2-252a_5z^4-168a_3z^6$
$\quad -18a_1z^8-(1/10)z^{10}]$,
$I_{10}=(1-e^{-z})^{-1}[20a_9z+240a_7z^3+504a_5z^5$
$\quad +240a_3z^7+20a_1z^9+(1/11)z^{11}]$,
$I_{11}=(1-e^{-z})^{-1}[-110a_9z^2-660a_7z^4-924a_5z^6$
$\quad -330a_3z^8-22a_1z^{10}-(1/12)z^{12}]$,
$I_{12}=(1-e^{-z})^{-1}[24a_{11}z+440a_9z^3+1584a_7z^5$
$\quad +1584a_5z^7+440a_3z^9+24a_1z^{11}+(1/13)z^{13}]$,
$I_{13}=(1-e^{-z})^{-1}[-156a_{11}z^2-1430a_9z^4$
$\quad -3432a_7z^6-2574a_5z^8-572a_3z^{10}-26a_1z^{12}$
$\quad -(1/14)z^{14}]$,
$I_{14}=(1-e^{-z})^{-1}[28a_{13}z+728a_{11}z^3+4004a_9z^5$
$\quad +6864a_7z^7+4004a_5z^9+728a_3z^{11}+28a_1z^{13}$
$\quad +(1/15)z^{15}]$,
$I_{15}=(1-e^{-z})^{-1}[-210a_{13}z^2-2730a_{11}z^4$
$\quad -10010a_9z^6-12870a_7z^8-6006a_5z^{10}$
$\quad -910a_3z^{12}-30a_1z^{14}-(1/16)z^{16}]$,
$I_{16}=(1-e^{-z})^{-1}[32a_{15}z+1120a_{13}z^3+8736a_{11}z^5$
$\quad +22880a_9z^7+22880a_7z^9+8736a_5z^{11}$
$\quad +1120a_3z^{13}+32a_1z^{15}+(1/17)z^{17}]$.

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

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

$J_5(\infty) = 1.244313\cdot10^2$, $J_7(\infty) = 5.082080\cdot10^3$, $J_9(\infty) = 3.63\,088\cdot10^5$,
$J_{11}(\infty) = 3.993653\cdot10^7$, $J_{13}(\infty) = 6.227785\cdot10^9$, $J_{15}(\infty) = 1.307714\cdot10^{12}$,
$J_{17}(\infty) = 3.556901\cdot10^{14}$, $J_{19}(\infty) = 1.216453\cdot10^{17}$, $J_{21}(\infty) = 5.109093\cdot10^{19}$.

$a_{11} = J_5,$

$a_{12} = (1/2)J_5,$

$a_{13} = 4a_1J_5+(1/3)J_7,$

$a_{14} = 6a_1J_5+(1/4)J_7,$

$a_{15} = 8a_3J_5+8a_1J_7+(1/5)J_9,$

$a_{16} = 20a_3J_5+10a_1J_7+(1/6)J_9,$

$a_{17} = 12a_5J_5+40a_3J_7+12a_1J_9+(1/7)J_{11},$

$a_{18} = 42a_5J_5+70a_3J_7+14a_1J_9+(1/8)J_{11},$

$a_{19} = 16a_7J_5+112a_5J_7+112a_3J_9+16a_1J_{11} + (1/9)J_{13},$

$a_{22} = 4a_1J_5-(1/6)J_7,$

$a_{23} = 14a_1J_5+(5/12)J_7,$

$a_{24} = 8a_3J_5+2a_1J_7-(1/20)J_9,$

$a_{25} = 52a_3J_5+22a_1J_7+(3/10)J_9,$

$a_{26} = 12a_5J_5+20a_3J_7+2a_1J_9-(1/42)J_{11},$

$a_{27} = 114a_5J_5+170a_3J_7+30a_1J_9 + (13/56)J_{11},$

$a_{28} = 16a_7J_5+70a_5J_7+42a_3J_9+2a_1J_{11} - (1/72)J_{13},$

$a_{29} = 200a_7J_5+644a_5J_7+392a_3J_9+38a_1J_{11} + (17/90)J_{13},$

$a_{33} = 8a_3J_5+(1/30)J_9,$

$a_{34} = 68a_3J_5+24a_1J_7+(17/60)J_9,$

$a_{35} = 12a_5J_5+8a_3J_7+(1/105)J_{11},$

$a_{36} = 162a_5J_5+210a_3J_7+32a_1J_9 + (37/168)J_{11},$

$a_{37} = 16a_7J_5+40a_5J_7+12a_3J_9+(1/252)J_{13},$

$a_{38} = 296a_7J_5+854a_5J_7+462a_3J_9+40a_1J_{11} + (13/72)J_{13},$

$a_{39} = 20a_9J_5+112a_7J_7+112a_5J_9+16a_3J_{11} + (1/495)J_{15},$

$a_{44} = 12a_5J_5+4a_3J_7-(1/140)J_{11},$

$a_{45} = 186a_5J_5+222a_3J_7+32a_1J_9 + (187/840)J_{11},$

$a_{46} = 16a_7J_5+22a_5J_7+2a_3J_9-(1/504)J_{13},$

$a_{47} = 360a_7J_5+954a_5J_7+478a_3J_7+40a_1J_{11} + (51/280)J_{13},$

$a_{48} = 20a_9J_5+72a_7J_7+42a_5J_9+2a_3J_{11} - (1/1320)J_{15},$

$a_{49} = 590a_9J_5+2804a_7J_7+3080a_5J_9 + 878a_3J_{11}+48a_1J_{13}+(183/1188)J_{15},$

$a_{55} = 16a_7J_5+16a_5J_7+(1/630)J_{13},$

$a_{56} = 392a_7J_5+992a_5J_7+480a_3J_9+40a_1J_{11} + (687/3780)J_{13},$

$a_{57} = 20a_9J_5+48a_7J_7+12a_5J_9+(1/2310)J_{15},$

$a_{58} = 670a_9J_5+3012a_7J_7+3150a_5J_9 + 880a_3J_{11}+48a_1J_{13}+(203/1320)J_{15},$

$a_{59} = 24a_{11}J_5+120a_9J_7+112a_7J_9+16a_5J_{11} + (1/6435)J_{17},$

$a_{66} = 20a_9J_5+40a_7J_7+4a_5J_9-(1/2772)J_{15},$

$a_{67} = 710a_9J_5+3100a_7J_7+3166a_5J_9 + 880a_3J_{11}+48a_1J_{13}+(853/5544)J_{15},$

$a_{68} = 24a_{11}J_5+90a_9J_7+44a_7J_9+2a_5J_{11} - (1/10296)J_{17},$

$a_{69} = 1116a_{11}J_5+7630a_9J_7+13640a_7J_9 + 8006a_5J_{11}+1456a_3J_{13}+56a_1J_{15} + (12013/90090)J_{17},$

$a_{77} = 24a_{11}J_5+80a_9J_7+24a_7J_9 + (1/12012)J_{17},$

$a_{78} = 1164a_{11}J_5+7800a_9J_7+13708a_7J_9 + 8008a_5J_{11}+1456a_3J_{13}+56a_1J_{15} + (48047/360360)J_{17},$

$a_{79} = 28a_{13}J_5+152a_{11}J_7+124a_9J_9+16a_7J_{11} + (1/45045)J_{19},$

$$\begin{aligned}
a_{88} &= 28a_{13}J_5+140a_{11}J_7+84a_9J_9+4a_7J_{11} \\
&\quad -(1/51480)J_{19}, \\
a_{89} &= 1778a_{13}J_5+16954a_{11}J_7+45654a_9J_9 \\
&\quad +45758a_7J_{11}+17472a_5J_{13} \\
&\quad +2240a_3J_{15}+64a_1J_{17} \\
&\quad +(12113/102960)J_{21}, \\
a_{99} &= 32a_{15}J_5+224a_{13}J_7+224a_{11}J_9 \\
&\quad +32a_9J_{11}+(1/218790)J_{21}.
\end{aligned}$$

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

$$\begin{aligned}
b_{22} &= J_5, \\
b_{24} &= 12a_1J_5+(1/2)J_7, \\
b_{26} &= 40a_3J_5+20a_1J_7+(1/3)J_9, \\
b_{28} &= 84a_5J_5+140a_3J_7+28a_1J_9+(1/4)J_{11},
\end{aligned}$$

$$\begin{aligned}
b_{33} &= 16a_1J_5+(1/3)J_7, \\
b_{35} &= 64a_3J_5+24a_1J_7+(4/15)J_9, \\
b_{37} &= 144a_5J_5+200a_3J_7+32a_1J_9+(3/14)J_{11}, \\
b_{39} &= 256a_7J_5+784a_5J_7+448a_3J_9+40a_1J_{11} \\
&\quad +(8/45)J_{13},
\end{aligned}$$

$$\begin{aligned}
b_{44} &= 72a_3J_5+24a_1J_7+(3/10)J_9, \\
b_{46} &= 180a_5J_5+220a_3J_7+32a_1J_9 \\
&\quad +(19/84)J_{11}, \\
b_{48} &= 336a_7J_5+924a_5J_7+476a_3J_9+40a_1J_{11} \\
&\quad +(11/60)J_{13},
\end{aligned}$$

$$\begin{aligned}
b_{55} &= 192a_5J_5+224a_3J_7+32a_1J_9 \\
&\quad +(23/105)J_{11}, \\
b_{57} &= 384a_7J_5+984a_5J_7+480a_3J_9+40a_1J_{11} \\
&\quad +(19/105)J_{13}, \\
b_{59} &= 640a_9J_5+2944a_7J_7+3136a_5J_9 \\
&\quad +880a_3J_{11}+48a_1J_{13}+(76/495)J_{15},
\end{aligned}$$

$$\begin{aligned}
b_{66} &= 400a_7J_5+1000a_5J_7+480a_3J_9 \\
&\quad +40a_1J_{11}+(23/126)J_{13}, \\
b_{68} &= 700a_9J_5+3080a_7J_7+3164a_5J_9 \\
&\quad +880a_3J_{11}+48a_1J_{13}+(61/396)J_{15},
\end{aligned}$$

$$\begin{aligned}
b_{77} &= 720a_9J_5+3120a_7J_7+3168a_5J_9 \\
&\quad +880a_3J_{11}+48a_1J_{13}+(71/462)J_{15}, \\
b_{79} &= 1152a_{11}J_5+7760a_9J_7+13696a_7J_9 \\
&\quad +8008a_5J_{11}+1456a_3J_{13}+56a_1J_{15} \\
&\quad +(6004/45045)J_{17},
\end{aligned}$$

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

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

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