CHOICE OF PSEUDOPOTENTIAL AND ELECTRORESISTANCE OF SIMPLE DISORDERED METALS

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An expression is investigated for inverse relaxation time for electroconductivity in the simple disordered metals within a framework of a kinetic equation method and a perturbation theory by the powers of a pseudopotential of electron–ion interaction. Numerical calculation of the third-order term by a pseudopotential for inverse relaxation time of 25 simple disordered metals is carried out. Three different model local pseudopotentials are used. Strong relation of the results of calculation between the choice of a model pseudopotential and concrete values of the pseudopotential parameters is found out for all metals. Selection criterions for the model pseudopotentials are formulated.

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1. Introduction

The most important factor, influencing a numerical value of the kinetic coefficients, describing electron transport phenomena in the simple disordered metals, is the higher order terms of perturbation theory on an electron–ion interaction in expansion of the appropriate inverse relaxation times. Complex solution of the specified problem requires a solution of the large number of more special tasks.

The first of them derives the expressions for the higher order terms of perturbation theory on an electron–ion interaction. Numerous inconsistent attempts of promoting in this direction were undertaken for a long time [1–13] and have not reduced in emerging a conventional expression even for a third-order term. Coinciding results are not present among the outcomes of various authors.

The second unsolved task is calculation of influence of a choice of an electron–ion pseudopotential on a magnitude of a third-order contribution in the various kinetic coefficients.

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The third task is calculation of influence of the approximations, used for electron gas, on the results of the numerical calculations.

The fourth — influence on the calculations of the approximations, used for the multiparticle structure factors of an ion subsystem. Nowadays, researches are absent on the last three items.

In the present paper we want to put a beginning of a systematic study of all formulated above problems. We shall consider only a third-order term of a pseudopotential in expansion for the inverse relaxation time for the electroconductivity process. Numerical calculations will be carried out for majority of the simple disordered metals. Influence on its results of a choice of the model local pseudopotential and concrete values of adjusting parameters will be investigated, too. The criterions, describing a fitness of the various model local pseudopotentials for the considered numerical calculations, also will be formulated.

The third-order term, obtained by a kinetic equation method [2, 12, 14], most simple from the point of view of deriving algorithm and numerical calculations, will be put on a basis of reviewing. Its important feature is that a majority of results of other authors after simplifications also can be reduced to in such aspect. In a consequence, it is supposed to investigate the other more complicated approaches.

2. Electroresistance

For the simple disordered metals the almost free electron model is applicable and electroresistance R is determined by the well-known Drude formula [1–5]:

$$R = \frac{m}{ne^2}\tau^{-1}. \tag{1}$$

Here n is density of the conductivity electrons, m, e are mass and charge of an electron, τ is relaxation time for the electroconductivity process. In the most common case the inverse relaxation time can be presented as the following series:

$$\tau^{-1} = \sum_{n=2}^{\infty} \tau_n^{-1}. \tag{2}$$

Within the framework of the kinetic equation method [2, 12, 14] and in the random phase approximation for an electron subsystem, and in the local model pseudopotential approximation the common term of this expansion has the form

$$\tau_n^{-1} = \frac{N}{V^n} \sum_{\boldsymbol{q}_1,\ldots,\boldsymbol{q}_n} W(\boldsymbol{q}_1)\ldots W(\boldsymbol{q}_{n-2}) S(\boldsymbol{q}_1,\ldots,\boldsymbol{q}_n)\Gamma(\boldsymbol{q}_1,\ldots\boldsymbol{q}_n). \tag{3}$$

Here

$$S(\boldsymbol{q}_1,\ldots,\boldsymbol{q}_n) = N^{-1}\langle\rho(\boldsymbol{q}_1)\ldots\rho(\boldsymbol{q}_n)\rangle \tag{4}$$

is n-particle structure factor of an ion subsystem, N is amount of the ions in a system, angular brackets designate an average with a help of a density matrix, containing Hamiltonian of an ion subsystem,

$$\rho(\boldsymbol{q}) = \sum_n \exp(-\mathrm{i}\boldsymbol{q}\boldsymbol{R}_n) \tag{5}$$

is the Fourier component of an ion density operator, $\boldsymbol{R}_n$ is radius-vector of the n-th ion, $W(\boldsymbol{q})$ is screening form factor of a local model electron–ion pseudopotential, $\Gamma(\boldsymbol{q}_1,\ldots,\boldsymbol{q}_n)$ is electron multipole for an electroconductivity process.

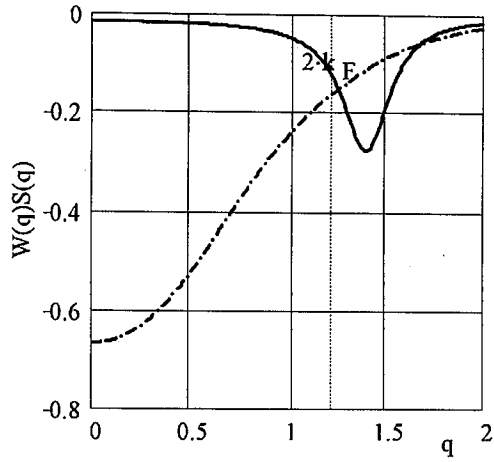

Fig. 1. $W(q)$ is the screening form factor of the Krasko–Gurskii pseudopotential for gold (dashed curve) divided by the Fermi energy; $W(q)S(q)$ is a product of this form factor on the two-particle structure factor (continuous curve). Vertical dotted line corresponds to the Fermi wave vector.

Expansion in a perturbation theory series is carried out by the dimensionless parameter $W(q)/\varepsilon_{\mathrm{F}}$, where ε_{F} is the Fermi energy. Graph of the Krasko–Gurskii pseudopotential form factor for gold is demonstrated in Fig. 1, as an example. Here the dashed vertical line corresponds to the value of the Fermi wave vector. As can be seen, this parameter is not small for all values of the wave vector. In the same Fig. 1 a graph of a product of this form factor on a two-particle static structure factor of an ion subsystem (the continuous curve) is reproduced. Such product already is small in the whole range of the wave vector values ($W(q)S(q)/\varepsilon_{\mathrm{F}} \ll 1$). Only this fact that in any order of perturbation theory on pseudopotential its form factor enters in a combination with appropriate structure factor of an ion subsystem as weight factor, allows to consider a pseudopotential as a small parameter for the majority of simple disordered metals.

3. Third-order contribution to electroresistance

Second-order contribution to inverse relaxation time of the simple disordered metals for the electroconductivity process is investigated enough (see for example [15]). For this reason we shall review the higher-order terms. The third-order contribution on a pseudopotential has the form

$$\tau_3^{-1} = \frac{N}{V^3} \sum_{q_1,\ldots,q_3} W(q_1)W(q_2)W(q_3)S(q_1,q_2,q_3)\Gamma(q_1,q_2,q_3). \tag{6}$$

For a noninteracting electron gas the electron three-pole, obtained by a kinetic equation method, has the form

$$\Gamma(k_1-k_2,k_2-k_3,k_3-k_1) = \frac{\hbar z\pi}{3mk_{\mathrm{B}}TN}(k_1-k_2)^2\, n(k_1)\,[1-n(k_1)]\,\frac{\delta(\varepsilon_{k_2}-\varepsilon_{k_1})}{\varepsilon_{k_2}-\varepsilon_{k_3}}, \tag{7}$$

where T is absolute temperature, k_B is the Boltzmann constant, ε_k is free electron energy, $n(k)$ is the Fermi–Dirac distribution function.

In this case for a third-order contribution is possible to obtain the following expression:

$$\tau_3^{-1} = \frac{\hbar\pi}{3mk_BTzV^3} \sum_{k_1,k_2,k_3} (k_1 - k_2)^2 W(k_1 - k_2) W(k_2 - k_3) W(k_3 - k_1)$$

$$\times S(k_1 - k_2, k_2 - k_3, k_3 - k_1) n(k_1)[1 - n(k_1)] \frac{\delta(\varepsilon_{k_2} - \varepsilon_{k_1})}{\varepsilon_{k_2} - \varepsilon_{k_3}}, \tag{8}$$

where z is metal valency.

4. Numerical calculations

Numerical calculations of a third-order contribution were carried out with the use of three different model local pseudopotentials, namely the Ashcroft pseudopotential

$$W_0(q) = -\frac{4\pi z}{q^2}\cos(qr), \tag{9}$$

a local form of the Xeine–Abarenkov pseudopotential,

$$W_0(q) = \frac{4\pi z}{q^2}\left[(1+a)\cos(qr) - a\frac{\sin(qr)}{qr}\right]\exp\left(-0.03\frac{q^4}{16k_F}\right), \tag{10}$$

and the Krasko–Gurskii pseudopotential

$$W_0(q) = \frac{4\pi z}{q^2}\frac{(2a-1)(qr)^2 - 1}{[(qr)^2+1]^2}. \tag{11}$$

Detailed discussion of these form factors can be found in [16, 17]. Here r and a are adjusting parameters, r is effective radius of an ion, a is depth of a potential hole created by an ion.

For effective dielectric permeability of a cooperating electron gas in the random phase approximation we used an expression

$$\varepsilon(q) = 1 + [\nu(q) + u(q)] n \pi_0(q). \tag{12}$$

Here $\nu(q)$ is the Fourier component of the Coulomb potential of an electron–electron interaction. Exchange interaction and correlations of the electrons were taken into account in a local field approximation with the help of the potential

$$u(q) = -\frac{2\pi}{q^2 + \lambda k_F^2}, \tag{13}$$

where λ is taken equal to 2 for all metals. Polarising operator of a noninteracting electron gas has a traditional form

$$\pi_0(q) = \frac{3}{k_F^2}\left(\frac{1}{2} + \frac{4k_F^2 - q^2}{8k_Fq}\ln\left|\frac{2k_F + q}{2k_F - q}\right|\right).$$

As a two-particle static structure factor of an ion subsystem an exact solution for the rigid sphere model of Percuss–Yevic equation [18] was used. Density packing parameter $\eta = 0.45$ is considered identical for all metals.

TABLE

Input data for numerical accounts.

Met.	Z	k_F [a.u.]	R_{exp} [$\mu\Omega$ cm]	Met.	Z	k_F [a.u.]	R_{exp} [$\mu\Omega$ cm]
Li	1	0.5752	25.0	Si	4	0.9838	71
Na	1	0.4742	9.61	Ge	4	0.9298	73
K	1	0.3820	13.45	Sn	4	0.8537	48
Rb	1	0.3564	22.89	Pb	4	0.8171	95
Cs	1	0.3320	39.47	Sb	5	0.8898	113.5
Mg	2	0.7018	27.4	Bi	5	0.8090	128
Ca	2	0.5650	33.0	Zn	2	0.8090	37.4
Sr	2	0.5232	84.8	Cd	2	0.7217	34.7
Ba	2	0.5037	306	Hg	2	0.7060	91
Al	3	0.8863	24.2	Cu	1	0.6937	21.1
Ga	3	0.8861	25.8	Ag	1	0.6116	17.2
In	3	0.7860	33.1	Au	1	0.6145	31.3
Tl	3	0.7807	73.1				

All data, used for calculations of the electroresistance of 25 simple disordered metals, namely valency, Fermi wave vector and experimental value of an electroresistance, are reproduced in Table. All of them are taken at the melting temperature of metals.

One parameter r of the Krasko–Gurskii and Xeine–Abarenkov pseudopotentials was chosen arbitrarily. For determination of the second parameter a (for the Ashcroft pseudopotential this one is unique) the Ziman formula, i.e. the second-order term in an appropriate expansion of an inverse relaxation time, was used. Such approach to a choice of the pseudopotential parameters is chosen because we are interested only in a relative magnitude of a third-order term by a comparison with a second-order one. Thus, it is possible to exclude from consideration all remaining reasons of a divergence between the experimental data and the results of calculations, based on Ziman formula.

For all considered model pseudopotentials there are at least two values of a pseudopotential parameter a, which for the experimental values of electroresistance equal the values determined with the help of Ziman formula (see, for example, Fig. 2 for the Krasko–Gurskii pseudopotential).

Thus, a magnitude of a third-order correction essentially depends on what values of the pseudopotential parameters are used in the calculations. This distinction is especially essential for the Ashcroft pseudopotential (see Fig. 3). It is less essential for the Xeine–Abarenkov pseudopotential and, at last, it is least essential for the Krasko–Gurskii pseudopotential (see Fig. 4). In the latter case an absolute value of a correction almost does not vary. For a smaller value of a parameter a a third-order correction is always positive, for greater — is always negative. For

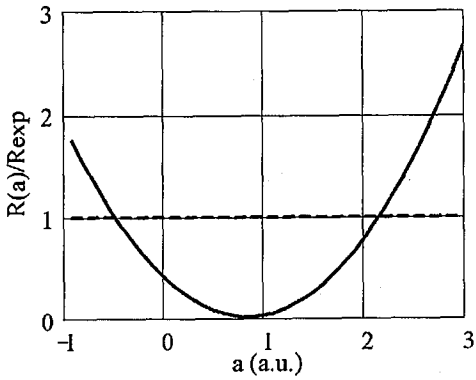

Fig. 2. Electroresistance of the liquid gold calculated on the basis of the Ziman formula with the use of the Krasko–Gurskii pseudopotential and divided by experimental value, as a function of the adjusting parameter a.

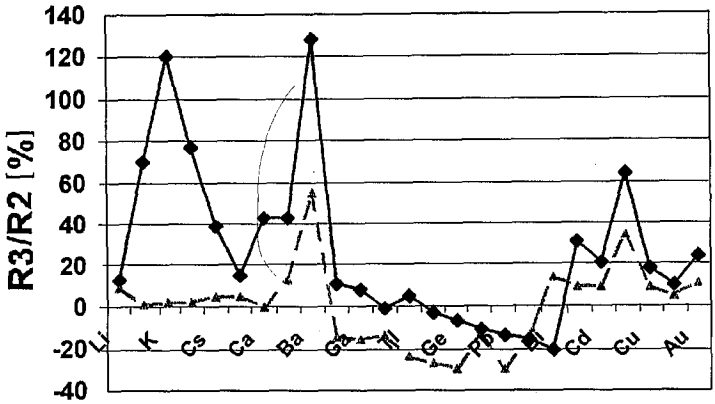

Fig. 3. Relative magnitude of a third-order correction (in %), calculated with the use of the Ashcroft pseudopotential for two different values of the adjusting parameter r ($r = \sigma/4$ for the lower curve and $r = \sigma/2$ and $r = \sigma/4$ for the upper curve).

the Ashcroft (Xeine–Abarenkov) pseudopotential (see Fig. 3) it is negative for a greater value and can be both positive and negative for a smaller value of a parameter r (a).

Among the results of other authors we meet equally frequently both positive and negative values of a third-order correction. The problem about what sign of a third-order correction should be for different metals was not considered. From our point of view a third-order correction should be always positive, as it takes into account an additional scattering of the conductivity electrons on the ion density fluctuations, circumscribed by a three-particle correlation function.

In this connection, it is possible to formulate the first criterion for a choice of a model pseudopotential in a form: that model pseudopotential is better, which for bigger numbers of the metals ensures a positiveness of a third-order correction to an electroresistance. Let us notice that from the three considered model pseu-

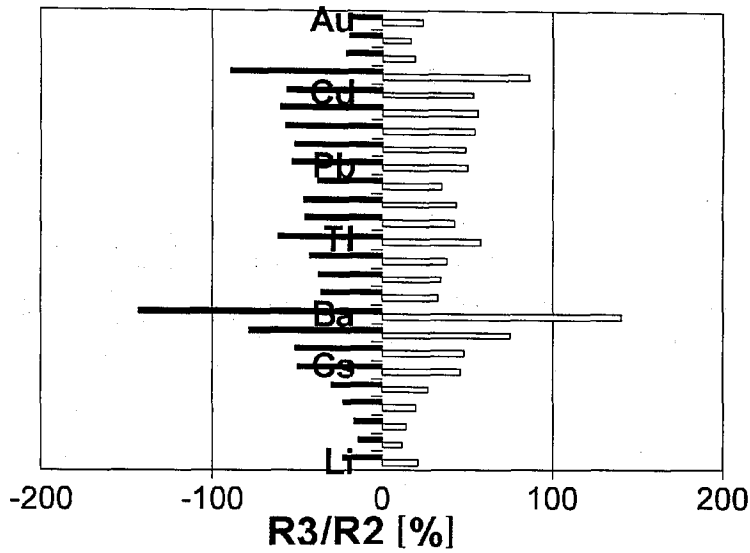

Fig. 4. Relative magnitude of a third-order correction (in %), calculated with the use of the Krasko–Gurskii pseudopotential for two different values of the adjusting parameter a ($r = \sigma/4$).

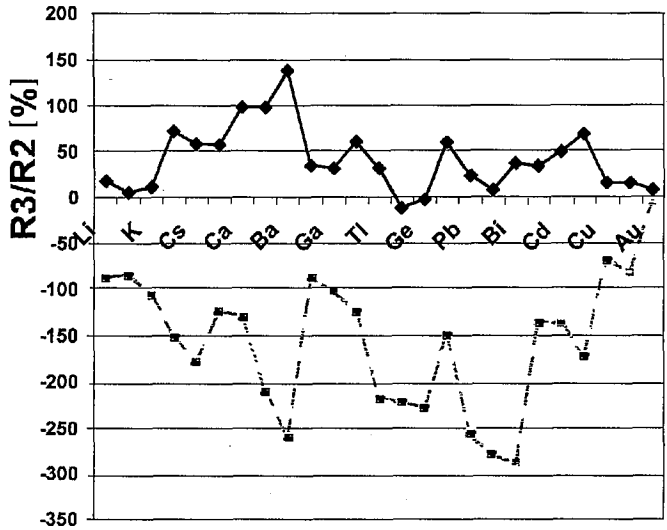

Fig. 5. Relative magnitude of a third-order correction (in %), calculated with the use of the Xeine–Abarenkov pseudopotential for two different values of the adjusting parameter $r = \sigma/4$ (lower curve) and $r = \sigma/2$ (upper curve).

dopotentials only the Krasko–Gurskii one for a definite set of the parameter values ensures a positiveness of a third-order correction for all considered metals.

We investigated also a problem of arbitrariness in a choice of a parameter r for the two-parameter model Xeine–Abarenkov and Krasko–Gurskii pseudopoten-

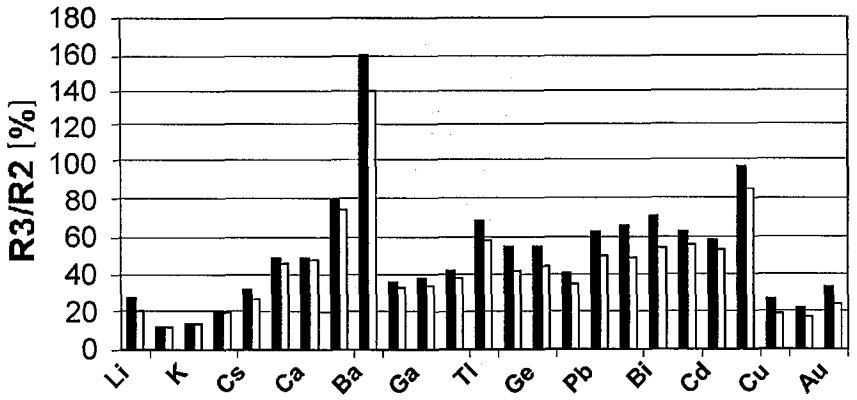

Fig. 6. Relative magnitude of a third-order correction (in %), calculated with the use of the Krasko–Gurskii pseudopotential for two different values of the adjusting parameter $r = \sigma/4$ (dark rectangle) and $r = \sigma/2$ (bright rectangle).

tials. With this purpose the magnitude of a third-order correction was calculated with the use of the two different values of parameter r. In one case (see Figs. 5 and 6) the value $r = \sigma/4$ was used. Here σ is a rigid sphere diameter appearing in an exact solution of Percuss–Yevik equation. The value $r = \sigma/2$ was used in other case (see Figs. 5 and 6). Different choice of considered parameter of the Xeine–Abarenkov pseudopotential has resulted in an essentially different magnitude of a third-order correction (see Fig. 5). For the Krasko–Gurskii pseudopotential (see Fig. 6) the magnitude of correction practically does not depend on a choice of this parameter.

In this connection, the second criterion for a choice of a model pseudopotential can be formulated in this way: that model pseudopotential is better, which ensures the least association of a third-order correction with a concrete choice of the adjusting parameter values. The Krasko–Gurskii pseudopotential in the best way satisfies the second criterion, too.

The numerical calculations, carried out by us, allow to draw such conclusion: a choice of a model local pseudopotential essentially influences the magnitude of a third-order correction and this one is enough large for all considered simple disordered metals. The same conclusion follows from the numerical calculations of other authors. Really, in the paper [8] a third-order correction for Na is greater than 100%, for Zn is 20%, for Al is greater than 100%. In the papers [4, 5] a correction for Zn is greater than 100%. In the paper [11] the corrections for one and two-valence simple metals are from 5% to 40%.

Appendix
Calculated formula for a third-order contribution

Let us show that the integration multiplicity in the third-order contribution can be essentially reduced. For that goal we shall decompose the integrand to a triple series with the use of the Legendre polynomials

$$(\boldsymbol{k}_1-\boldsymbol{k}_2)^2 W(\boldsymbol{k}_1-\boldsymbol{k}_2)W(\boldsymbol{k}_2-\boldsymbol{k}_3)W(\boldsymbol{k}_3-\boldsymbol{k}_1)S(\boldsymbol{k}_1-\boldsymbol{k}_2,\boldsymbol{k}_2-\boldsymbol{k}_3,\boldsymbol{k}_3-\boldsymbol{k}_1)$$

$$=\sum_{n,m,l} F_{nml}(k_1,k_2,k_3)P_n(\cos\theta_{12})P_m(\cos\theta_{23})P_l(\cos\theta_{31}). \tag{A.1}$$

The following designations here are introduced:

$$P_n[\cos(\boldsymbol{k}_i\wedge\boldsymbol{k}_j)]=P_n(\cos\theta_{ij}), \tag{A.2}$$

$$F_{nml}(k_1,k_2,k_3)=\frac{2n+1}{2}\frac{2m+1}{2}\frac{2l+1}{2}\int_0^\pi \mathrm{d}\theta_{12}\sin\theta_{12}P_n(\cos\theta_{12})$$

$$\times\int_0^\pi \mathrm{d}\theta_{23}\sin\theta_{23}P_m(\cos\theta_{23})\int_0^\pi \mathrm{d}\theta_{31}\sin\theta_{31}P_l(\cos\theta_{31})(\boldsymbol{k}_1-\boldsymbol{k}_2)^2$$

$$\times W(\boldsymbol{k}_1-\boldsymbol{k}_2)W(\boldsymbol{k}_2-\boldsymbol{k}_3)W(\boldsymbol{k}_3-\boldsymbol{k}_1)S(\boldsymbol{k}_1-\boldsymbol{k}_2,\boldsymbol{k}_2-\boldsymbol{k}_3,\boldsymbol{k}_3-\boldsymbol{k}_1). \tag{A.3}$$

After integration of this expansion the expression for the third-order contribution has the form

$$\tau_3^{-1}=\frac{m^2}{24\pi^5 z\hbar^5 k_\mathrm{F}^2}\sum_n(2n+1)\int_0^\infty \mathrm{d}k\frac{k^2}{k_\mathrm{F}^2-k^2}F_{nnn}(k_\mathrm{F},k_\mathrm{F},k) \tag{A.4}$$

and contains one integration and one summation. With the use of the next uncoupling of a three-particle structure factor

$$S(\boldsymbol{q}_1,\boldsymbol{q}_2,\boldsymbol{q}_3)=S(\boldsymbol{q}_1)S(\boldsymbol{q}_2)S(\boldsymbol{q}_3) \tag{A.5}$$

we can represent the function $F_{nnn}(k_\mathrm{F},k_\mathrm{F},k)$ with the help of the following combination of the single integrals:

$$F_{nnn}(k_\mathrm{F},k_\mathrm{F},k)=A_n(k_\mathrm{F},k)B_n(k_\mathrm{F})^2. \tag{A.6}$$

Here

$$A_n(k_\mathrm{F})=\int_0^{2k_\mathrm{F}}\frac{W_0(q)}{\varepsilon(q)}S(q)P_n\left(\frac{2k_\mathrm{F}^2-q^2}{2k_\mathrm{F}^2}\right)q^3\mathrm{d}q, \tag{A.7}$$

$$B_n(k_\mathrm{F},k)=\int_{|k-k_\mathrm{F}|}^{k+k_\mathrm{F}}\frac{W_0(q)}{\varepsilon(q)}S(q)P_n\left(\frac{k^2+k_\mathrm{F}^2-q^2}{2kk_\mathrm{F}}\right)q\mathrm{d}q, \tag{A.8}$$

where $P_n(x)$ is the n-th order Legendre polynomial.

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