Electromagnetic response of superconductors and optical sum rule.

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Abstract

The interrelation between the condensation energy and the optical sum rules has been investigated. It has been shown that the so called 'partial' sum rule violation is related mainly to a temperature dependence of the relaxation rate rather than to the appearance of superconductivity itself. Moreover, we demonstrate that the experimental data on the temperature dependence of the optical sum rule can be explained rather well by an account of strong electron-phonon interaction.

Many recently published works are concerned with the origin of the condensation energy of the superconducting state, a possible violation of so-called 'optical sum rules', and the relation between these phenomena. These papers include both theoretical investigations\textsuperscript{1–6} of these problems and experimental attempts\textsuperscript{7–10} to observe a violation of the optical sum rule. Usually, the possibility of such violation is related to the change of the kinetic energy of metals under superconducting transition. If this statement would be correct, than the violation of the optical sum rule should be most clear seen in the Bardeen-Cooper-Schrieffer\textsuperscript{12}(BCS) type superconductors. It has been proved exactly by Bogolyubov\textsuperscript{11} that the original model does not contain any potential energy. It is easy to see considering the
original $BCS$ Hamiltonian

$$H_{BCS} = \sum_{k,s} \varepsilon_k a_{k,s}^+ a_{k,s} + \sum_{k,k'} V_{kk'} a_{k\uparrow}^+ a_{-k' \downarrow}^+ a_{-k' \downarrow} a_{k \uparrow}. \quad (1)$$

N. Bogolyubov has proven that for the normal state

$$\left\langle N \left| \sum_{k,k'} V_{kk'} a_{k\uparrow}^+ a_{-k' \downarrow}^+ a_{-k' \downarrow} a_{k \uparrow} \right| N \right\rangle \propto 1/\Omega, \quad (2)$$

where $\Omega$ is the system volume. It means that in the thermodynamic limit

$$\langle N | V_{BCS} | N \rangle \equiv 0. \quad (3)$$

The $BCS$ Hamiltonian can be exactly diagonalized in the superconducting state using the Bogolyubov-Valatin transformation

$$\gamma_{k\uparrow} = u_k a_{k\uparrow} - v_{-k} a_{-k\downarrow}^+, \quad (4)$$

$$\gamma_{-k\downarrow}^+ = u_k a_{-k\downarrow}^+ + v_{k} a_{k\uparrow}$$

It leads to

$$H_{BCS} = \sum_{k,s} E_k \gamma_{k,s}^+ \gamma_{k,s} \quad (5)$$

where

$$E_k = \pm \sqrt{\varepsilon_k^2 + \Delta^2}, \quad (6)$$

which is a Hamiltonian of noninteracting but superconducting quasiparticles. The condensation energy arises from the decreasing of the ground state eigenvalue of the expression (5) due to an appearance of a gap $\Delta$. The same is true for any mechanisms of superconductivity. The decrease of a properly defined one-quasiparticle energy due to the appearance of the gap on a Fermi level is the main contribution to the condensation energy. This phenomenon has a certain feature is common to a metal-insulator transition, where the band structure contribution to the total energy decreases also due to the appearance of the gap on the Fermi level. The example of the BCS model shows that the division of the total energy into kinetic...
and potential parts is not a trivial problem even for weakly interacting quasiparticles. This division becomes even worse defined in systems with strongly interacting electrons. The study of the optical sum rule and its change below the superconducting transition should be based, from our point of view, on calculations of the conductivity itself and a detailed analysis of this function and its dependence on temperature and frequency.

The optical sum rule can be written in general form as

\[ \int_0^\infty d\omega \sigma_1(\omega) = \frac{\omega_{pl}^2}{8} = \frac{\pi ne^2}{2m} \]  

where \( \sigma_1(\omega) \) is the real part of the dynamical conductivity, \( n \) is the total electron density and \( m \) is the bare electron mass. The function \( \sigma_1(\omega) \) has a zero frequency \( \delta \)-function peak in the superconducting state due to the dissipationless (rigid) response of the superconducting condensate. The amplitude of this peak \( A \) can be expressed in terms of an corresponding penetration depth \( \lambda_L \)

\[ A = \frac{c^2}{8\lambda_L^2}, \]  

where \( c \) is the velocity of light. The existence of this \( \delta \)-function contribution to \( \sigma_1(\omega) \) in the superconducting state leads to the so-called Ferrel-Glover-Tinkham sum rule

\[ \int_0^\infty d\omega \left[ \sigma_1^N(\omega) - \sigma_1^S(\omega) \right] = \frac{c^2}{8\lambda_L^2}, \]  

where \( \sigma_1^{N,S}(\omega) \) is the conductivity in the normal and superconducting states, correspondingly. In such general form this sum rule can never be violated for any superconductors possessing ideal diamagnetic response with a finite penetration depth \( \lambda_L \). The real measurement of the dynamical conductivity can never be made up to infinite frequency. They are restricted in practice to some finite value \( \omega_c \). As it is well known, the sum rule (9) is totally satisfied in conventional superconductors when the integration is performed up to \( \omega_c \approx (4 - 6) \Delta \) where \( \Delta \) is the superconducting gap. This value of \( \omega_c \) is of the order of the characteristic phonon energies. The statements about the sum rules violation, which has
been made in the experimental papers\textsuperscript{3, 4, 7–10}, mean that the value $\omega_c$ in high-$T_c$ superconductors is much larger than in conventional ones. The maximum value $\omega_c$ in high-$T_c$ systems, if they were also conventional, should be $\simeq 0.1 eV$ because they have a magnitude of the gap $\Delta \approx 20 meV$. It has been shown in\textsuperscript{3, 4} that for the interlayer conductivity the optical sum rules are not saturated at least in underdoped regime for $\omega_c \simeq 0.1 eV$. Even more intriguing results have been obtained recently in the paper\textsuperscript{8, 10} where the violation sum rules have been observed up to very high energies $\omega_c \simeq 2 eV$. The main goal of the present paper is to show that the observed violation of the optical sum rules at least for $\omega_c > 0.1 eV$ is not related explicitly to any mechanism of superconductivity. This violation is the direct consequence of a high value of the electron relaxation rate $\Gamma (\omega, T)$, critical temperature $T_c$ and $\Delta$ themselves.

Let us consider the for the future discussion important the so-called restricted or 'partial' optical sum rule. Usually it is used in the form

$$\int_0^{\omega_c} d\omega \sigma_1 (\omega) = \frac{\pi ne^2}{2m_b}.$$  

Here $1/m_b$ is the an effective inverse electron band mass, which is defined as

$$\frac{n}{m_b} = \frac{2}{\Omega} \sum_k \frac{\partial^2 \varepsilon_k}{\partial k_x^2} n_k,$$  

where $n_k$ is an electron distribution function. For a Hamiltonian with nearest neighbor hopping $1/m_b$ can be presented in terms of a average of the one band kinetic energy\textsuperscript{4}

$$\frac{n}{m_b} = \frac{a_x^2}{\Omega} \langle -T_{kin} \rangle,$$  

$$T_{kin} = - \sum_i t_{i,i+a_x} a_i^+ a_{i+a_x}.$$  

Here $a_x$ is the lattice spacing in $x$ - direction and $t_{i,i+a_x}$ is the nearest neighbor hopping integral. Usually it is believed that the high energy cut off frequency $\omega_c$ should be chosen of the order of the corresponding band plasma frequency $\bar{\omega}_{pl} = \sqrt{4\pi e^2 n/m_b}$ and is much smaller than the energies of interband transitions. This partial sum rule can be easily proved
for noninteracting band electrons including the *interband* transitions in the expression for the conductivity

\[ \sigma_{\text{inter}}^{1}(\omega) = \frac{2\pi e^2}{\Omega m^2} \sum_{k,j} n_k \frac{|\langle kj | \nabla_x | k \rangle|^2}{\varepsilon_{kj} - \varepsilon_k} \delta (\varepsilon_{kj} - \varepsilon_k - \omega). \tag{14} \]

Here the summation is over all empty high energy bands with an electron dispersion \( \varepsilon_{kj} \). The minimum of the value \( \varepsilon_{kj} - \varepsilon_k = E_g \) is the energy of the interband transitions. Now, using \( \omega_c < E_g \) we can easily prove the sum rules (10) and (12) which give the well known identity for the electron inverse effective mass

\[ \frac{n}{m_b} = \frac{n}{m} - \frac{2}{\Omega m^2} \sum_{k,j} n_k \frac{|\langle kj | \nabla_x | k \rangle|^2}{\varepsilon_{kj} - \varepsilon_k}. \tag{15} \]

However it is not the case for interacting electrons. This fact can be easily understood using the model of electrons interacting with impurities. The *intraband* contribution to the optical conductivity can be written in this case in form of the usual Drude expression for \( \sigma_1(\omega) \)

\[ \sigma_1(\omega) = \frac{\tilde{\omega}_p^2}{4\pi} \frac{\Gamma}{\omega^2 + \Gamma^2}, \tag{16} \]

where \( \Gamma/2 \) is the relaxation rate due to impurity scattering. One can derive the well known result for the partial optical sum rule

\[ \int_0^{\omega_c} d\omega \sigma_1(\omega) = \frac{\tilde{\omega}_p^2}{8} \left( 1 - \frac{2\Gamma}{\pi \omega_c} \right). \tag{17} \]

This example shows that the *intraband* sum rules (10) and (12) can be satisfied in the presence of the interaction only in the limit \( \omega_c \to \infty \). It is also true for any interactions other than impurity scattering including, for example, the electron-phonon interaction. Moreover, this violation of the optical sum rules can not be obtained from the calculation of the kinetic energy change from Eq. (12) as it was made in the Refs.\(^{15}\). As it follows from Eq. (17) the optical sum rules violation depends on the high energy cutoff \( \omega_c \) but this parameter is certainly absent in the expression for the kinetic energy.

The *interband* transitions will also be changed due to electron interactions. We can rewrite Eq. (14) for the impurity scattering model in the simplest approximation as
\[ \sigma^\text{inter}_1(\omega) = \frac{2\pi e^2}{\Omega m^2} \sum_{\mathbf{k},j} n_{\mathbf{k}} \frac{|\langle k j | \nabla_x | k \rangle|^2 \Gamma}{(\varepsilon_{kj} - \varepsilon_k - \omega)^2 + \Gamma^2}. \]  

The general sum rule (7) is certainly satisfied in this model for any value of the relaxation rate \( \Gamma \) but it is not true for the partial sum rule as we have discussed above. Further, as it follows from Eq. (18), the interband contribution to the conductivity becomes now spread out over all intervals of energies including very low \( \omega \). It means that we can not even divide experimental data into intraband contributions and interband ones. All these effects are small as \( \Gamma/\omega_c \) and \( \Gamma/E_g \). However, if we shall take into account that the relaxation rate in high-\( T_c \) compounds can reach values \( \Gamma \approx 100 \text{meV} \) we see immediately that these effects can be very important even in the normal state.

As the discussion given above confirms, there is no other way to understand the behavior of the partial sum rules than to calculate the conductivity itself as a function of frequency, temperature, doping etc. It can be obtained by a calculation of a current-current correlation function. We would like to emphasize here that expression for the current-current correlation function does not contain, at least in the absence of the vertex corrections, any explicit information about the mechanism of superconductivity. All implicit information about the mechanism is contained in the one-particle Green’s function which can be written as

\[ \hat{G}^{-1}(\mathbf{k}, \omega) = \omega Z(\mathbf{k}, \omega) \hat{1} - \varepsilon_{\mathbf{k}} \hat{\tau}_3 - Z(\mathbf{k}, \omega) \Delta(\mathbf{k}, \omega) \hat{\tau}_1. \]  

Here \( Z(\mathbf{k}, \omega) \) is a renormalization function, \( \Delta(\mathbf{k}, \omega) \) is the superconducting order parameter, and \( \hat{\tau}_i \) are Pauli matrices. These functions should be calculated in turn from the general equations for the Green’s function of electrons. Such equations have been derived by Eliashberg\(^\text{16}\) for conventional superconductors with the electron-phonon pairing mechanism and, for example, in Refs.\(^\text{17}\) for \( d \)-wave superconductivity. The expression for \( \sigma^S(\omega) \) can be written for \( \omega \gg 2\Delta \) in the form

\[ \frac{\sigma^S(\omega)}{\sigma^N_1(\omega)} = \frac{2}{\omega} \int_{\Delta}^{\omega/2} d\omega' \left\{ \Re \frac{\omega - \omega'}{\sqrt{(\omega - \omega')^2 - \Delta^2 (\omega - \omega')}} \Re \frac{\omega'}{\sqrt{\omega'^2 - \Delta^2 (\omega')}} - \Re \frac{\Delta (\omega - \omega')}{\sqrt{(\omega - \omega')^2 - \Delta^2 (\omega - \omega')}} \Re \frac{\Delta (\omega')}{\sqrt{\omega'^2 - \Delta^2 (\omega')}} \right\}. \]
The expression on the right hand side of the Eq. (20) is nothing else than the BCS type coherency factors. The Eq. (20) have been derived\textsuperscript{18,19} for the conventional superconductors and was used recently\textsuperscript{9} to discuss the problem of the influence of the superconducting gap on the optical spectra at $\omega_c \simeq 1.2eV$. In spite of that this expression has been derived in the framework of the usual $s$–wave superconductivity, it has with a slight modification much wider areas of applications. One can, for example, include the angular dependence of the gap for anisotropic superconductors and perform the integration over the angle. It is easy to show using Eq. (20), that for $\omega \gg 2\Delta$ we have
\begin{equation}
\sigma_1^S (\omega) = \sigma_1^N (\omega) \left( 1 - \alpha \frac{\Delta^2}{\omega^2} \right).
\end{equation}

Here the numerical coefficient $\alpha$ is of the order of unity and it is included to take into account the possible averaging of the angular dependence of the gap function. The same estimation for the dynamical conductivity of a superconducting state at $\omega \gg \Delta$ can be obtained from the equations derived in Ref.\textsuperscript{17}. Eq. (21) shows that the direct contribution of the superconducting gap to the dynamical conductivity and, therefore, to the optical sum rules has the same smallness for any mechanism of superconductivity, that is $(\Delta/\omega)^2$. This smallness is, certainly, different for conventional superconductors and high-$T_c$ ones because the gap in the later is one order larger.

Eqs. (14), (18) for the interband contribution can also be generalized for the superconducting case and it can be shown that their difference from the normal state is of the order of $(\Delta/\omega)^2$. We shall not consider the behavior of the optical sum rules in the superconducting state further in this paper because the real mechanism of superconductivity in high-$T_c$ systems is unknown. The investigation of the optical sum rules for the normal state will be of our main interest in the rest part of this paper. The detailed experimental study of this problem has been done by D. van der Marel and coworkers.\textsuperscript{8} They have measured the conductivity in a wide frequency range and temperature intervals and than two optical sum rules have been calculated. One of them was the low energy sum rule $A_L$
where $\lambda_{ab}$ is the penetration depth in the $CuO$ plane and the other one is the high energy sum rule $A_h$

$$A_L = 8 \int_{0^+}^{1.25eV} d\omega \sigma_1(\omega) + \frac{e^2}{\lambda_{ab}^2(T)} \quad (22)$$

$$A_h = 8 \int_{1.25eV}^{2.5eV} d\omega \sigma_1(\omega). \quad (23)$$

A few very prominent features in the behavior of both $A_L$ and $A_h$ have been found in this work. First, $A_L$ and $A_h$ are temperature dependent in the superconducting state as well as in the normal one. Second, this dependence, at least, in the normal state is well described by a quadratic function of $T$. In addition, the low energy part depends on the high-energy cutoff frequency $\omega_c$, if we consider the cases $\omega_c = 1.25eV$ and $\omega_c = 2.5eV$.

We are coming now to the consideration of details in the high energy part of the optical sum rule $A_h$. Preliminary we shall neglect the direct contributions of the superconducting gap to the value of $A_h$ because the ratio $\Delta^2/\omega^2$ for the considered values of frequencies is very small $\approx 2 \cdot 10^{-4}$. The main problem in the calculation of the normal state conductivity is to establish the origin of the electron relaxation in high-$T_c$ systems. This problem along with the problem of the origin of superconductivity itself has been disputed during the last 15 years. It was shown (see for details\(^2\)) that the main source of the relaxation processes in the normal state of high-$T_c$ superconductors is the strong electron-phonon interaction. Recently, it has been additionally demonstrated through examination of the frequency and temperature dependence of the optical reflectivity in the $YBCO$ system\(^2\) that this interaction leads to a strong temperature dependence of the conductivity up to very high frequencies. The experimental verification of the existence of strong electron-phonon interaction in high-$T_c$ superconductors has been also obtained in ARPES measurements\(^2\) as an effect of an electron mass renormalization. There is some discussion\(^2\) about the possibility, that the electron mass renormalization observed in Ref.\(^2\) and the corresponding change of the relaxation rate can be explained by the interaction with the so-called 'magnetic resonance peak'. This
possibility, however, is unlikely\textsuperscript{24,25}, at least, for the normal state. As is well known, in the normal state the conductivity $\sigma^N(\omega,T)$ in a presence of the strong electron-phonon interaction can be written in the form\textsuperscript{20,21}

$$\sigma^N(\omega,T) = \frac{\omega^2_{pl}}{4\pi} \frac{1}{-i\omega m^*(\omega,T) + \Gamma(\omega,T)}, \quad (24)$$

where $m^*(\omega,T)$ is the frequency dependent optical mass and $\Gamma(\omega,T)$ is the optical relaxation rate. The readers can find the precise expressions for both these functions in terms of the Eliashberg function in Refs.\textsuperscript{20,21} and we shall not reproduce them here. Eq. (24) for high values of frequencies ($\omega \gg \{\omega_{ph},\Gamma\}$) can be rewritten for the real part of the conductivity in the form

$$\sigma_1^N(\omega,T) \approx \frac{\omega^2_{pl}}{4\pi} \frac{\Gamma(T)}{\omega^2}, \quad (25)$$

where $\Gamma(T)$ is independent on frequency\textsuperscript{20,21}

$$\Gamma(T) = 2\pi \int_0^\infty d\Omega \alpha^2_{tr}(\Omega) F(\Omega) \coth \frac{\Omega}{2T}. \quad (26)$$

Here $\alpha^2_{tr}(\Omega) F(\Omega)$ is the transport Eliashberg function. It is easy to show by using Eq. (26), that

$$\Gamma(T = 0) = \lambda_{tr}\pi \langle \omega \rangle, \quad (27)$$

where

$$\lambda_{tr} = 2 \int_0^\infty d\Omega \frac{\alpha^2_{tr}(\Omega) F(\Omega)}{\Omega} \quad (28)$$

is the transport constant of EPI, and $\langle \omega \rangle$ is the average phonon frequency. At considerably high temperatures, on the other hand, $\Gamma(T)$ can be written as

$$\Gamma(T) \approx 2\lambda_{tr}\pi T. \quad (29)$$

Eqs. (27) and (29) show that the relaxation rate can increase considerably with increasing of temperature. It will lead, to some increase of the high frequency part of the optical sum rule, which can be written in the form
\[ A_h = 8 \int_{\omega_1}^{2\omega_1} d\omega \sigma_1(\omega) = \frac{\omega_{pl}^2 \Gamma(T)}{\omega_1}, \]  
(30)

where \( \omega_1 = 1.25eV \). Using Eqs.(25) and (26) we can easily calculate this value. There are two independent fitting parameters in this procedure: the plasma frequency \( \omega_{pl} \) and the coupling constant \( \lambda_{tr} \). We have chosen the value \( \lambda_{tr} \lesssim \lambda \approx 1.5 \) in accordance with APRES data\(^2\). The value of the intraband plasma frequency is also unknown, but it is bounded from above by the value of the low part of the sum rule obtained in Ref.\(^8\), that is

\[ \omega_{pl} \lesssim 2eV. \]  
(31)

For the numerical calculations we have employed the Eliashberg function from our preceding papers\(^2,1\) and use the general expression for the conductivity (24), rather than approximate Eq.(25). We carried out our calculations for two slightly different Eliashberg functions shown in the inset in Fig.1, having the same value of \( \lambda_{tr} \). The difference between these spectra is related to the different coupling of electrons with a soft phonon \( \omega_{ph} \approx 20meV \) and harder ones. The temperature dependence of \( A_h \) is shown in Fig.1 at \( 0 \lesssim T \lesssim 200K \). We have used as in Ref.\(^8\) the \( T^2 \) scale for the temperature to demonstrate the near perfect quadratic dependence \( A_h \) on \( T \). The overall agreement of our results with the experimental data is reasonably well. The same is true concerning the experimentally observed difference

\[ A_h (T = 200K) - A_h (T = 0K) \approx 0.08 (eV)^2. \]  
(32)

It can also be seen from Fig.1, that \( A_h \) has a temperature dependence also at \( T < T_c \), where \( T_c \) is the critical temperature of the superconducting transition ( \( T_c = 88K \) for the considered case). We would also like to emphasize that there is a little different behavior of these curves at low temperatures. The value \( A_h \) decreases with decreasing of temperature for a softer spectrum even faster for low temperature than \( T^2 \) as it has for high \( T \). In contrast, \( A_h \) has a more weaker temperature dependence at low \( T \) for more harder spectrum. The difference \( A_h (T = 200K) - A_h (T = 0K) \) for the spectrum with soft low frequency phonons is larger
then for the harder one. We did not take into account in our calculations the influence of
the superconductivity on $A_h$. It is small from our point of view but it can exist. It is clear
from the above consideration that it is very difficult to separate using experimental data
this specific superconducting contribution from the total change of $A_h$ connected with the
change of the relaxation rate.

The general behavior of the low energy sum rule $A_L (T)$ (not shown in Fig.1) is also
reproduced rather well in our approach, at least for the normal state. There is only one
contradiction related to the total amplitude of the change of the value $A_L (T)$. It is clear
from the above consideration that the following equality should be satisfied in the normal
state

$$A_L (T = 200) - A_L (T = 100) = A_h (T = 200) - A_h (T = 100)$$

$$+ A'_h (T = 200) - A'_h (T = 100),$$

(33)

where

$$A'_h = 8 \int_{2.5eV}^{\infty} d\omega \sigma_1 (\omega).$$

(34)

It is easy to see that

$$A'_h = A_h.$$  

(35)

It means that the total change of the low energy sum rule $A_L (T)$ should be twice larger
than the change of $A_h (T)$. Measurements give rather the value 1.5 instead of two. We
do not know the exact origin of this contradiction. It is possible that it is related to the
temperature dependence of the interband transitions which have not been included into
our calculations. Indeed, we have obtained as the value of the intraband contribution to
$A_h \approx 0.21 (eV^2)$ at $T = 200K$. It is much smaller than the experimentally measured $A_h$
$\approx 1.8 (eV)^2$. The difference between these two values comes from the interband transitions.
It is difficult to say anything definite at this time about the temperature dependence of the
interband transitions and we will continue our activity in this direction. Now we would like
to emphasize that it not easy to find any other mechanism of the relaxation besides the electron-phonon one which can lead to a temperature dependence of the relaxation rate at so high frequencies. Many of them, including, for example, the marginal Fermi liquid\textsuperscript{27}, do not give any temperature dependence at $T \ll \omega$.

We can not calculate and compare with the experiment the sum rules in the underdoped regime due to the existence of a pseudogap phenomenon because its origin is also unknown. We can, however, claim that it is very likely that the discussed effect will be also exist in the underdoped case. This statement is based on observations obtained both by optical measurements\textsuperscript{28} and as well as ARPES\textsuperscript{23}, that the relaxation rate increases with decreasing the doping level. This also is confirmed by result obtained in Ref.\textsuperscript{10} on the sum rules violation.

In summary, we have shown that there are no new energy scales defining the influence of the superconductivity on the intraband contribution to the optical sum rules, besides the superconducting energy gap itself. This is true for any mechanism of the superconductivity because the expression for $\sigma_1(\omega, T)$ at high frequencies does not include any explicit information about such mechanisms. The experimentally observed violation of the sum rule is mainly related to the properties of the normal state of high-$T_c$ superconductors and it is ruled mainly by the frequency and temperature dependence of the relaxation rate. We also have shown that the experimental data obtained in the Ref.\textsuperscript{11} can be explained very reasonably in the framework of the usual model with strong electron-phonon interaction. The consideration of the sum rules for the interplanar conductivity where the coherent transport is absent in the normal state requires a more serious approach and the knowledge of the mechanism blocking this transport. We should also know more details about the pseudogap phenomenon and its interplay with superconductivity in order to make more conclusive statements about the sum rule behavior in the underdoped regime.

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I. FIGURE CAPTION.

Fig. 1 $A_h$ (see text) as a function of $T^2$ for two different spectral functions as shown in the inset.
\( \alpha^2(\omega)F(\omega) \)

- **A**
- **B**

- spectrum A
- spectrum B

- \( \alpha = 2 \text{ eV} \)
- \( \lambda = 1.5; \gamma_{imp} = 12.5 \text{ meV} \)