Model-independent sum rule analysis based on limited-range spectral data

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Abstract. Partial sum rules are widely used in physics to separate low- and high-energy degrees of freedom of complex dynamical systems. Their application, though, is challenged in practice by the always finite spectrometer bandwidth and is often performed using risky model-dependent extrapolations. We show that, given spectra of the real and imaginary parts of any causal frequency-dependent response function (for example, optical conductivity, magnetic susceptibility, acoustical impedance etc) in a limited range, the sum-rule integral from zero to a certain cutoff frequency inside this range can be safely derived using only the Kramers–Kronig dispersion relations without any extra model assumptions. This implies that experimental techniques providing both active and reactive response components independently, such as spectroscopic ellipsometry in optics, allow an extrapolation-independent determination of spectral weight 'hidden' below the lowest accessible frequency.

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Contents

1. Introduction

Global sum rules applied to response functions play a major role in physics as they quantitatively express fundamental conservation laws. Of interest are also *partial*, or *restricted* sum rules, where a properly chosen cutoff frequency separates low- and high-energy degrees of freedom of a physical system. For example, the low-frequency optical spectral weight [1]

$$W(\omega_c) = \int_0^{\omega_c} \sigma_1(\omega) \, d\omega \tag{1}$$

is a partial counterpart of the well known *f*-sum rule $\int_0^\infty \sigma_1(\omega) \, d\omega = \pi n e^2/(2m_e)$ for the optical conductivity $\sigma(\omega) = \sigma_1(\omega) + i\sigma_2(\omega)$, where n is the density of charges, e and m_e are the charge and the bare mass of an electron. In charge conducting systems, the integral up to a cutoff frequency ω_c somewhat larger than the free-carrier scattering rate but below the energies of transitions from occupied to empty bands is proportional to the number of carriers and the inverse band mass averaged over the Fermi surface. For example, in the simple Drude model, integrating out to 10 (20) times the scattering rate recovers 94% (97%) of the sum rule.

The effective mass can be strongly affected by electron correlations, especially in a case of narrow bandwidth. The dependence of $W(\omega_c)$ on temperature and other parameters, especially across a phase transition, is thus a valuable piece of information about the changes in the electronic system. The changes of $W(\omega_c)$ can be very large, as at the ferromagnetic–paramagnetic transition in colossal magneto-resistance manganites [2, 3], or rather small as at the superconducting transition in the high-T_c cuprates [4]–[7]. Even in the latter case, the subtle variations of the low-frequency spectral weight may potentially distinguish between physically different scenarios of superconductivity [8]. If a significant spectral overlap between the free charge and interband peaks is present, the intrepretation can be less obvious and requires direct theoretical calculation of the value of $W(\omega_c)$. Therefore it is worth using all means, experimental and computational, to improve the accuracy of $W(\omega_c)$ determined from the available spectra. Notably, the partial sum rules can be meaningfully applied not only to the optical spectra, but also in acoustical data, neutron scattering and other spectroscopic techniques.

Because of limitations on the bandwidth of any spectrometer, $\sigma_1(\omega)$ is not experimentally available down to zero frequency. The direct application of equation (1) assuming some low-frequency extrapolations of $\sigma_1(\omega)$ may lead to significant and uncontrollable error bars. This is most obvious for the optical conductivity of a superconductor, where the spectral weight of the condensate of the Cooper pairs is represented in $\sigma_1(\omega)$ by a δ-peak at zero-frequency. Here, the inductive component $\sigma_2(\omega)$ has to be used to estimate the condensate spectral weight [9, 10]. However, the common procedure used in this case still requires the extrapolation down to zero frequency.

Importantly, certain experimental techniques, such as spectroscopic ellipsometry, or simultaneous measurement of acoustical attenuation and the sound speed allow direct independent measurement of both components of the response function. The purpose of this paper is to show that the spectral weight $W(\omega_c)$, including a possible zero-frequency δ-peak, can be obtained model-independently, i.e. without any *a priori* assumptions about the low- and high-frequency spectral behaviour, if both $\sigma_1(\omega)$ and $\sigma_2(\omega)$ are measured in a *limited* frequency range $[\omega_{min}, \omega_{max}]$. We also present an efficient numerical algorithm optimized to reduce the output error bars in the case of the noisy data.

2. On the possibility of analytical continuation from a finite interval

The causality principle, i.e. the assumption that no response can precede the causing factor, puts constraints on the analytic behaviour of all physical response functions, such as the optical conductivity $\sigma(\omega) = \sigma_1(\omega) + i\sigma_2(\omega)$. In particular, these functions obey the Kramers–Kronig (KK) dispersion relations:

$$\sigma_1(\omega) = \frac{2}{\pi} \wp \int_0^\infty \frac{\omega' \sigma_2(\omega')\, d\omega'}{\omega'^2 - \omega^2}, \tag{2}$$

$$\sigma_2(\omega) = \frac{2\omega}{\pi} \wp \int_0^\infty \frac{\sigma_1(\omega')\, d\omega'}{\omega^2 - \omega'^2}, \tag{3}$$

where $\wp$ denotes the principal-value integral. Note that relations (2) and (3) are entirely model-independent since they only use the fact that the response function is analytical in the upper complex semiplane. One can say that the information about $\sigma_1(\omega)$ is encoded in $\sigma_2(\omega)$ and vice versa.

The determination of the partial sum-rule integral (1) is intimately related to a more general problem to restore the function $\sigma(\omega)$ itself outside the experimental range. It is well known [11] that a complex function $\sigma(\omega)$ analytical (holomorphic) in a certain domain D can be analytically continued from a subset Γ of the boundary of this domain into the whole domain, including the rest of the boundary. The specific form of such a continuation has been a subject of numerous studies since the late 1920s [12], which are summarized in [13]. In particular, the Carleman–Goluzin–Krylov formulae restore the function *exactly*[1] inside the analyticity domain from its

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[1] The exact conditions on $\sigma(\omega)$ for the validity of the Carleman–Goluzin–Krylov formula are given in [13]. For the present discussion it is important that all physical functions with the poles below the real axis would fit these requirements. In the case of the optical conductivity of a superconductor, which has a pole exactly at the real axis, one can shift the pole slightly down. This would only broaden the δ-peak by an arbitrary small amount but simultaneously provide the necessary condition.
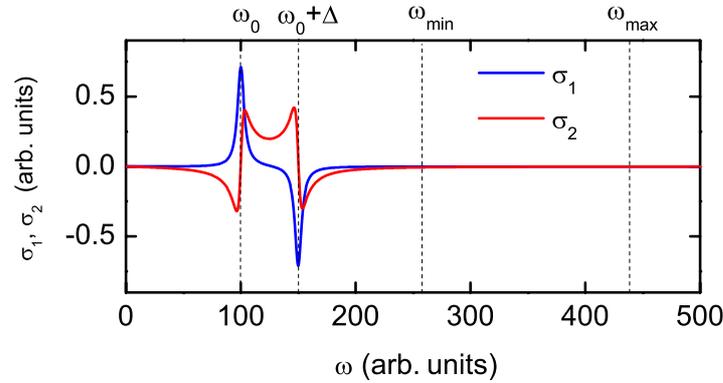
Figure 1. An example of $\sigma_1(\omega)$ and $\sigma_2(\omega)$ satisfying KK relations which are both almost zero at $[\omega_{min}, \omega_{max}]$ but show intense spectral features below ω_{min}. The 'unphysical' negative values of $\sigma_1(\omega)$ can be meaningful, for example, if $\sigma_1(\omega)$ is an addition to some background response function so that the result is positive.

values at Γ. They have the following general structure:

$$\sigma(\omega) = \lim_{n \to \infty} \int_\Gamma Q_n(\omega', \omega)\sigma(\omega')\,d\omega', \quad \omega \in D. \tag{4}$$

There are several possibilities to choose the kernel $Q_n(\omega', \omega)$. We point out just one option for the case $\Gamma = [\omega_{min}, \omega_{max}]$ [13]

$$Q_n(\omega', \omega) = \frac{(2\pi i)^{-1}}{\omega' - \omega} \left[\frac{(\omega' - \omega_{min})(\omega - \omega_{max})}{(\omega' - \omega_{max})(\omega - \omega_{min})} \right]^{ni/\pi}, \tag{5}$$

that illustrates the general property of these kernels: they oscillate as a function of both variables, with the frequency of oscillations increasing infinitely as n increases. Therefore the 'lim' operation cannot be applied directly to $Q_n(\omega', \omega)$ as it only exists for the whole integral (4). Using equations (4) and (5) one can, in principle, obtain the spectral weight

$$W(\omega_c) = \text{Re} \left\{ \lim_{n \to \infty} \int_{\omega_{min}}^{\omega_{max}} u_n(\omega', \omega_c)\sigma(\omega')\,d\omega' \right\}, \tag{6}$$

where $u_n(\omega', \omega_c) = \int_0^{\omega_c} Q_n(\omega', \omega)\,d\omega$.

In spite of the fact of its formal existence, the analytical continuation of a function from a finite interval appears to be a very ill-posed problem. For example, one can construct an analytical function, which is almost zero in the range $[\omega_{min}, \omega_{max}]$ but shows intense spectral structure below ω_{min} (figure 1). Let us consider $\sigma(\omega)$ to be a sum of two narrow Lorentzians: the first one with spectral weight A centred at ω_0 below ω_{min} and the second one with the opposite spectral weight $-A$ slightly displaced to $\omega_0 + \Delta$, still below ω_{min}. Normally, $\sigma_1(\omega)$ cannot be negative; however, in this example one can think of $\sigma_1(\omega)$ as an addition to some positive background response function, which makes the result always positive. A similar function would appear, in particular, if one takes a difference between two optical conductivities of the same sample at two different

temperatures in a case when the conductivity contains a single optical phonon peak which shifts as a function of temperature (assuming that the phonon spectral weight remains unchanged). The width of the peaks is assumed to be much less than Δ). The corresponding $\sigma_2(\omega)$ far from ω_0 would be approximately $(-4A\omega_0\omega\Delta/\pi)(\omega^2 - \omega_0^2)^{-2}$. By decreasing Δ, both $\sigma_1(\omega)$ and $\sigma_2(\omega)$ can be made vanishingly small in the range $[\omega_{min}, \omega_{max}]$. Obviously, the slightest noise on top of $\sigma(\omega)$ that would make it indistinguishable from zero prevents the extraction of the mentioned strong structures beyond the accessible range.

In the considered example, it was essential that the spectral weights of the two peaks exactly compensate each other in order to get the vanishing values of $\sigma_1(\omega)$ and $\sigma_2(\omega)$ at $[\omega_{min}, \omega_{max}]$. Otherwise one would get a detectable term $\sim 1/\omega$ in $\sigma_2(\omega)$ proportional to the total low-frequency spectral weight [14, 15]. This indicates that the 'hidden' spectral weight is much better determined by the limited-range data than the function $\sigma_1(\omega)$ itself. This is supported by the study of Aspnes [16], who examined the possibility to extrapolate an ellipsometrically measured dielectric function beyond the experimental range using the KK relations and found that the total spectral weights of a few broad spectral regions can be restored reasonably well while the high-resolution details of the spectra cannot be unambiguously determined. Some analytical treatments of the problem of the finite frequency range can be found in [17]–[19].

3. A practical algorithm for the noisy data

We are interested in an efficient and accurate numerical scheme to determine the sum-rule integral (1). It turns out that the straightforward application of the formulae (4) and (6) with strongly oscillating kernels to real data is not practical as it amplifies uncontrollably the experimental noise. In this case one has to look for different numerical algorithms.

The experimental spectra are collections of data points $\sigma_{1,j} \pm \delta\sigma_{1,j}$ and $\sigma_{2,j} \pm \delta\sigma_{2,j}$ on a mesh of frequencies ω_j ($j = 1, \ldots, N$). We assume that the spectral resolution is roughly the same as the distance between neighboring points. According to equation (6), $W(\omega_c)$ is a linear function of the real and imaginary parts of σ. We note that this directly follows from the fact that the KK relations are linear and is independent from the particular scheme of analytical continuation. Hence, it is logical to take the following formula for the calculations:

$$W(\omega_c) \approx \sum_{j=1}^{N} \left[u_{1,j}\sigma_{1,j} + u_{2,j}\sigma_{2,j} \right], \tag{7}$$

which is the most general linear relation between $W(\omega_c)$ and the measured values $\sigma_{1,j}$ and $\sigma_{2,j}$. The coefficients $u_{1,j}$ and $u_{2,j}$ that we call hereafter u-coefficients have to be chosen in such a way that formula (7) is approximately correct for any *arbitrarily* chosen response function. Since any causal response function can be represented as a linear superposition of narrow oscillator response functions $S_x(\omega) = S_{1x}(\omega) + iS_{2x}(\omega)$ centred at all frequencies x, one should optimize the u-coefficients in such a way that it gives a reasonably accurate answer when applied to $\sigma(\omega) = S_x(\omega)$ for *any* x. For $S_{1x}(\omega)$, one can take a narrow peaked function, for example a Gaussian, while $S_{2x}(\omega)$ should be the KK transform of $S_{1x}(\omega)$.

We introduce a function $D(x)$, which is the inaccuracy of the formula (7) when applied to $S_x(\omega)$

$$D(x) = \int_0^{\omega_c} S_{1x}(\omega)\, \mathrm{d}\omega - \sum_{j=1}^N \left[u_{1,j} S_{1x}(\omega_j) + u_{2,j} S_{2x}(\omega_j) \right].$$

The integrated inaccuracy can be defined as follows

$$D_{\mathrm{int}}^2 = \int_0^\infty D^2(x)\, \mathrm{d}x. \tag{8}$$

In order to make the formula (7) accurate for all x at the same time, one would need to minimize D_{int}^2 by varying the u-coefficients. If experimental noise is present, one should also take care that the error bar of the resulting spectral weight due to the noise

$$F^2 = \sum_{j=1}^N \left[u_{1,j}^2 (\delta\sigma_{1,j})^2 + u_{2,j}^2 (\delta\sigma_{2,j})^2 \right] \tag{9}$$

does not become too large. In general, D_{int}^2 and F^2 have to be minimized simultaneously. A more detailed description of this algorithm is given in the appendix 1.

We implemented this idea in a numerical code Devin[2], which takes a set of data points of $\sigma_1(\omega)$ and $\sigma_2(\omega)$ with error bars in a limited range $[\omega_{\min}, \omega_{\max}]$ and returns the estimated value and error bar of $W(\omega_c)$ for specified cutoff frequency ω_c. It is assumed that the real and imaginary parts of the response function are KK-consistent; otherwise output error bars are unpredictable. Note that the KK consistency of the limited-range data can be tested using exact bounds proposed in [18].

4. Random tests of the method

A series of Monte-Carlo tests were performed where the program answer based on limited-range spectral information can be compared with the exact value of $W(\omega_c)$, allowing one to scrutinize the model independence of the method. We generate a random KK-consistent function $\sigma(\omega)$ by adding up a random number of peaks of random spectral weights A_k, widths γ_k and centre frequencies $\omega_{0,k}$ distributed below, inside and above the range $[\omega_{\min}, \omega_{\max}]$. In particular, a sum of Lorentz peaks plus high-frequency background was taken[3]: $\sigma(\omega) = \sum_k (-2\mathrm{i}A_k\omega/\pi)(\omega_{0,k}^2 - \omega^2 - \mathrm{i}\gamma_k\omega)^{-1} - \mathrm{i}\epsilon_\infty\omega/(4\pi)$, where the number of peaks is changed between 1 and 50. The parameters were varied in the following limits: A_k—between 0 and 125, γ_k— between 0 and 3, $\omega_{0,k}$—between 0 and 5, ϵ_∞—between 0 and 5. The first oscillator was always a δ-function at zero frequency ($\omega_{0,1} = 0$, $\gamma_1 = 0$), imitating a condensate peak in superconductors. The 'experimental' data points sent to the program were generated with a step of 0.1 inside the range $[\omega_{\min}, \omega_{\max}]$ by convoluting the true functions with a Gaussian of width 0.1 to mimic the finite resolution and adding random noise with standard deviation of $\delta\sigma$. Each test series consisted of 30 independent generations of $\sigma(\omega)$ and a comparison of the true and calculated $W(\omega_c)$.

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[2] On-line robot version http://optics.unige.ch/Devin2 can be used for further tests.
[3] In these tests, ω and σ are taken in their respective (arbitrary) units; the unit of $W(\omega_c)$ is the product of the two.

The test results are summarized in figure 2. The series (a)–(c) demonstrate the sensitivity of the extracted spectral weight to the data noise. The experimental range [1, 4] and the cutoff $\omega_c = 1$ are the same, while $\delta\sigma$ varies from 0.5 to 10. One can see that for sufficiently small noise the program is able to provide quite accurate value of $W(\omega_c)$ for all 30 random inputs, which demonstrates that the method is indeed model-independent. On the other hand, relatively large error bars in series (b) and (c) show that the requirements to the signal-to-noise ratio for this particular set of data points are quite strict ($\sim$1%), although not unrealistic.

Series (a), (d) and (e) give a feeling of how the accuracy of this procedure depends on the width of experimental range at a constant noise amplitude. The range was consecutively narrowed from [1, 4] to [1, 2]. The range width appears to be a critical factor determining the method precision. The output error bars increase rapidly as we restrict the experimental range—much faster, in fact, than one would normally expect due to a simple decrease of the number of data points.

By comparing series (a), (f) and (g) one can see that the error bars increase dramatically if the cutoff ω_c is taken beyond the experimental range, both below ω_{min} or above ω_{max}. This is another indication that one can reliably determine the total 'hidden' spectral weight but not a part of it since the latter depends on the inaccessible spectral details of $\sigma_1(\omega)$.

5. Real-data example

In figure 3 the application of this program to real data is demonstrated. As an example, we calculate the sum-rule integral for the optical conductivity of a high-T_c superconducting compound $Bi_2Sr_2Ca_2Cu_3O_{10}$, based on data published in [20]. We use a set of data which spans the interval of wavenumbers $\omega/(2\pi c)$ between $100\,\text{cm}^{-1}$ and $20\,000\,\text{cm}^{-1}$. In figure 3(b) each point corresponds to a value of $W(\omega_c)$ calculated on the basis of input data from ω_{min} to $\omega_{max} = 20\,000\,\text{cm}^{-1}$ as a function of ω_{min}. The error bars are relatively small as long as ω_{min} is less than ω_c, but grow explosively as ω_{min} exceeds ω_c. In figure 3(c) each point corresponds to a value of $W(\omega_c)$ calculated on the base of input data from $\omega_{min} = 100\,\text{cm}^{-1}$ to ω_{max} as a function of ω_{max}. When ω_c is above the highest frequency point, the error bars again tend to diverge.

6. Discussion and conclusions

One should note that the involved algorithm that we used to extract the partial sum-rule integral $W(\omega_c)$ is not the only possibility to tackle this problem. Perhaps a more conventional and intuitive method is to fit the available spectra with a KK-consistent multi-parameter function, such as the Drude–Lorentz model or the variational function of [21]. A similar method of the KK integrals was used by Aspnes [16].

Interestingly, all fitting schemes where the model function is a linear superposition of the trial basis functions eventually reduce to the same type of linear formula (7), as demonstrated in the appendix 2. However, there is an important difference between the two approaches. In the method that we used in this paper, the u-coefficients are optimized in order to minimize the output error bars $\delta W(\omega_c)$, while in the fitting approach they are predetermined by the specific set of trial basis functions, which may not be always optimal. In this sense, our approach is more general and model-independent.
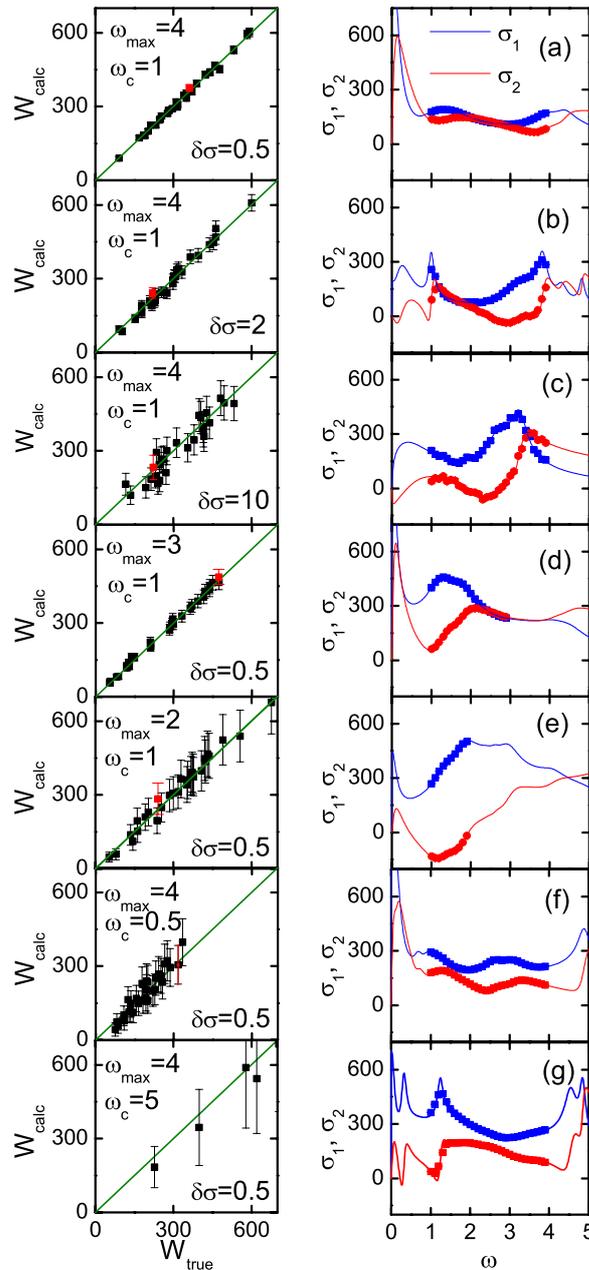
Figure 2. Series (a)–(g) of Monte-Carlo tests of the numerical algorithm that calculates the spectral weight $W(\omega_c)$ knowing only $\sigma_1(\omega)$ and $\sigma_2(\omega)$ in a limited range $(\omega_{min}, \omega_{max})$. Left panel: the correlation between the 'true' spectral weight $W_{true}(\omega_c)$ and the calculated one $W_{calc}(\omega_c)$; each point corresponds to one randomly generated KK consistent response function as described in the text. The error bars are as estimated by the program. Green lines refer to $W_{calc}(\omega_c) = W_{true}(\omega_c)$. Right panel: the curves $\sigma_{1,2}(\omega)$ corresponding to the point marked in red colour on the left panel. Solid lines are the 'true' functions, dots are the data points (with noise $\delta\sigma$ added and finite resolution applied) used as input. The values of ω_{max}, ω_c and $\delta\sigma$ corresponding to each series are given on the left panels ($\omega_{min} = 1$ in all series).
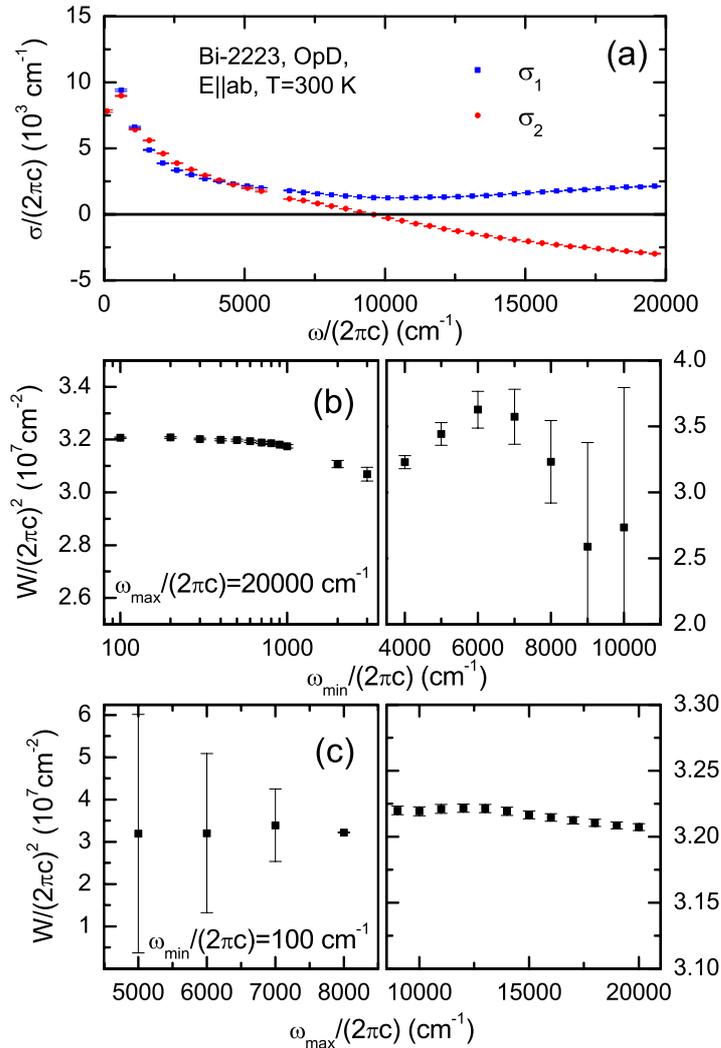
Figure 3. The application of the partial sum-rule analysis to optical conductivity (a) of optimally doped $Bi_2Sr_2Ca_2Cu_3O_{10}$ at room temperature for electric field parallel to CuO_2 planes [20]. All frequencies and conductivities are divided by $2\pi c$ in order to get the wavenumber units of cm^{-1}. Above $6000\,cm^{-1}$, $\sigma_1(\omega)$ and $\sigma_2(\omega)$ were measured directly by spectroscopic ellipsometry; below $6000\,cm^{-1}$ they were derived with error bars from simultaneous KK-constrained fit of reflectivity [21], measured down to $100\,cm^{-1}$ and the ellipsometric spectra. (b) The value of $W(\omega_c)$ calculated for $\omega_c = 8000\,cm^{-1}$ as a function of ω_{min} for $\omega_{max} = 20000\,cm^{-1}$. (c) The value of $W(\omega_c)$ for $\omega_c = 8000\,cm^{-1}$ as a function of ω_{max} for $\omega_{min} = 100\,cm^{-1}$. The error bars are indicative, as estimated by the program.

On the other hand, the data fitting approach can be straightforwardly applied also to experimental quantities that depend on $\sigma_1(\omega)$ and $\sigma_2(\omega)$ in a nonlinear way, for example, the optical reflectivity. Another advantage of the data fitting technique is that it can detect if $\sigma_1(\omega)$ and $\sigma_2(\omega)$ are KK inconsistent, for example, due to the systematic experimental uncertainties. Thus it is preferable to use both techniques in a combination.

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In summary, we have shown that the partial sum-rule analysis can be accurately performed on the basis of the real and imaginary parts of a response function, if the latter is experimentally available in a limited spectral range. In a sense, nature integrates for us $\sigma_1(\omega)$ beyond the accessible range and encodes information about this integral in $\sigma_2(\omega)$ inside the range where the experimental data is available. We have shown that it can be decoded using a simple linear formula (7) with optimally chosen u-coefficients. The determination is accurate only if the cutoff frequency lies inside the accessible interval. Even though the interval can be, formally speaking, arbitrarily small, the extraction of the sum-rule integral for a narrow interval would require much better data accuracy to obtain equivalent precision of $W(\omega_c)$ than for a broad one. We find, however, that the error bars are not uncontrollably large due to the notorious extrapolation uncertainty. They can be, at least in principle, made arbitrarily small by decreasing the experimental noise. This result is valid for all response functions satisfying the KK relations and thus applies to various domains of spectroscopy.

Acknowledgments

Appendix A. Optimization of the u-coefficients

Here, we describe a method that we use to optimize the u-coefficients in the approximate formula

$$W(\omega_c) \approx W_a = \sum_{\nu=1}^{2} \sum_{j=1}^{N} u_{\nu,j} \sigma_{\nu,j}. \tag{A.1}$$

The starting point is the spectral representation of the response function:

$$\sigma(\omega) = \wp \int_0^\infty \sigma_1(x) S(\omega, x) \, dx, \tag{A.2}$$

where $S(\omega, x) = \delta(\omega + x) + \delta(\omega - x) + (i/\pi)[(\omega - x)^{-1} + (\omega + x)^{-1}]$ is a response of an oscillator centred at frequency x (and at $-x$ to preserve the parity of the response functions). Put differently, any causal response function can be represented as a linear superposition of narrow oscillator functions. In reality, one has to convolute $S(\omega, x)$ with an apparatus function $A(\omega, \omega')$, for example, a Gaussian, which takes the experimental resolution into account: $\tilde{S}(\omega, x) = \int A(\omega, \omega') S(\omega', x) \, d\omega'$. The key idea of the method is based on the linearity of equation (A.1): in order to make this formula applicable to any $\sigma(\omega)$, one should optimize the u-coefficients in such a way that it gives a reasonably accurate answer when applied to $\sigma(\omega) = \tilde{S}(\omega, x)$ for *any x*.

To be quantitative, one can calculate a discrepancy function $D(x)$ for a given combination of the u-coefficients

$$D(x) = \tilde{W}_s(x) - \tilde{W}_{s,a}(x),$$

where

$$\tilde{W}_s(x) = \int_0^{\omega_c} \tilde{S}_1(\omega, x)\, \mathrm{d}\omega, \qquad \tilde{W}_{s,a}(x) = \sum_{\nu=1}^{2} \sum_{j=1}^{N} u_{\nu,j} \tilde{S}_\nu(\omega_j, x).$$

One can also define the discrepancy integrated over all x

$$D_{\text{int}}^2 = \int_0^\infty D^2(x)\, \mathrm{d}x. \tag{A.3}$$

In order to make the formula (A.1) accurate for all x simultaneously (assuming that it is possible!), one should minimize the integral discrepancy by varying the u-coefficients. This is easy since $D_{\text{int}}^2(\{u_{1,j}\}, \{u_{2,j}\})$ is a quadratic form

$$D_{\text{int}}^2 = \sum_{\nu,\mu=1}^{2} \sum_{i,j=1}^{N} A_{\nu\mu,ij} u_{\nu,i} u_{\mu,j} - 2 \sum_{\nu=1}^{2} \sum_{i=1}^{N} B_{\nu,i} u_{\nu,i} + C,$$

where the coefficients are given by the integrals over x:

$$
\begin{aligned}
A_{\nu\mu,ij} &= \int_0^\infty \tilde{S}_\nu(\omega_i, x) \tilde{S}_\mu(\omega_j, x)\, \mathrm{d}x, \\
B_{\nu,i} &= \int_0^\infty \tilde{S}_\nu(\omega_i, x) \tilde{W}_s(x)\, \mathrm{d}x, \\
C &= \int_0^\infty \tilde{W}_s^2(x)\, \mathrm{d}x.
\end{aligned}
\tag{A.4}
$$

The minimization of D_{int}^2 reduces to the linear system of equations:

$$\sum_{\mu=1}^{2} \sum_{j=1}^{N} A_{\nu\mu,ij} u_{\mu,j} = B_{\nu,i}.$$

In a case when the (frequency-dependent) spectral resolution $\delta(\omega)$ is given by a Gaussian

$$A(\omega, \omega') = \frac{1}{\sqrt{2\pi}\delta(\omega)} \exp\left[-\frac{(\omega-\omega')^2}{2\delta^2(\omega)}\right]$$

the above integrals can be taken analytically, which simplifies dramatically the calculations:

$$
\begin{aligned}
\tilde{S}_1(\omega, x) &= \frac{1}{\sqrt{2}\delta(\omega)} \left[g_1\left(\frac{\omega+x}{\sqrt{2}\delta(\omega)}\right) + g_1\left(\frac{\omega-x}{\sqrt{2}\delta(\omega)}\right) \right], \\
\tilde{S}_2(\omega, x) &= \frac{1}{\sqrt{2}\delta(\omega)} \left[g_2\left(\frac{\omega+x}{\sqrt{2}\delta(\omega)}\right) + g_2\left(\frac{\omega-x}{\sqrt{2}\delta(\omega)}\right) \right], \\
\tilde{W}_s(x) &= \frac{1}{2} \left[g_3\left(\frac{\omega_c+x}{\sqrt{2}\delta(\omega_c)}\right) + g_3\left(\frac{\omega_c-x}{\sqrt{2}\delta(\omega_c)}\right) \right],
\end{aligned}
$$

and

$$A_{11,ij} = \frac{1}{\delta_{ij}}\left[g_1\left(\frac{\omega_{ij}^+}{\delta_{ij}}\right) + g_1\left(\frac{\omega_{ij}^-}{\delta_{ij}}\right)\right], \quad A_{12,ij} = \frac{1}{\delta_{ij}}\left[g_2\left(\frac{\omega_{ij}^+}{\delta_{ij}}\right) - g_2\left(\frac{\omega_{ij}^-}{\delta_{ij}}\right)\right],$$

$$A_{21,ij} = \frac{1}{\delta_{ij}}\left[g_2\left(\frac{\omega_{ij}^+}{\delta_{ij}}\right) + g_2\left(\frac{\omega_{ij}^-}{\delta_{ij}}\right)\right], \quad A_{22,ij} = \frac{1}{\delta_{ij}}\left[-g_1\left(\frac{\omega_{ij}^+}{\delta_{ij}}\right) + g_1\left(\frac{\omega_{ij}^-}{\delta_{ij}}\right)\right].$$

$$B_{1,i} = g_3\left(\frac{\omega_{ic}^+}{\delta_{ic}}\right) - g_3\left(\frac{\omega_{ic}^-}{\delta_{ic}}\right), \quad B_{2,i} = g_4\left(\frac{\omega_{ic}^+}{\delta_{ic}}\right) - g_4\left(\frac{\omega_{ic}^-}{\delta_{ic}}\right), \quad C = \delta_c g_5\left(\frac{\omega_c}{\delta_c}\right),$$

where $\omega_{ij}^\pm = (\omega_i \pm \omega_j)/2$, $\delta_{ij}^2 = [\delta^2(\omega_i) + \delta^2(\omega_j)]/2$, $\omega_{ic}^\pm = (\omega_i \pm \omega_c)/2$, $\delta_{ic}^2 = [\delta^2(\omega_i) + \delta^2(\omega_c)]/2$ and $\delta_c = \delta(\omega_c)$. Here, we used auxiliary functions

$$g_1(x) = \pi^{-1/2}\exp(-x^2), \quad g_2(x) = \pi^{-1/2}\exp(-x^2)\mathrm{erfi}(x), \quad g_3(x) = \mathrm{erf}(x),$$

$$g_4(x) = 2\pi^{-1}x^2{}_2F_2(1, 1, 3/2, 1, -x^2), \quad g_5(x) = 2\pi^{-1/2}[\exp(-x^2) - 1] + 2x\,\mathrm{erf}(x),$$

where $\mathrm{erf}(x)$ is the error function, $\mathrm{erfi}(x) = \mathrm{erf}(\mathrm{i}x)/\mathrm{i}$ the imaginary error function and $_2F_2(\ldots, x)$ the hypergeometric function.

So far we ignored the experimental uncertainty of $\sigma_1(\omega)$ and $\sigma_2(\omega)$, which is another source of the output error bars. If we assume that it is just random noise with the standard deviations at each frequency given by $\delta\sigma_{1,j}$ and $\delta\sigma_{2,j}$ then the standard deviation of the output of equation (A.1) is:

$$F^2 = \sum_{\nu=1}^{2}\sum_{j=1}^{N} u_{\nu,j}^2(\delta\sigma_{\nu,j})^2. \tag{A.5}$$

Our experience shows that the optimization of D_{int}^2 alone may provide very inaccurate results for a noisy input. Instead, the minimization of a compound functional $D_{\mathrm{int}}^2 + wF^2$, where w is a weighting coefficient which is discussed later, works much better. From a numerical point of view, adding wF^2 enhances the diagonal elements of the matrix A:

$$A_{\nu\nu,ii} \rightarrow A_{\nu\nu,ii} + w(\delta\sigma_{\nu,i})^2$$

and makes it better conditioned. This addition prevents the u-coefficients from growing too much, therefore one can consider it as a *regularization* term.

The coefficient w describes the relative significance of the data noise compared to the inaccuracy of the linear equation (A.1). The subtlety is that the optimal value of w is determined by $W(\omega_c)$ and is thus not known *a priori*. A way out is to use a second optimization loop for w. As a criterion, it is logical to minimize the estimated total error bar $(\delta W)^2$, i.e. caused by both the formula uncertainty and the input noise.

A simple estimate that we use (which can be perhaps improved) is the following. For a given set of the u-coefficients, one can find W_a, F^2 and D_{int}^2. Since the two error sources are independent, one can approximately determine the range of possible values of the true spectral weight W by the inequality:

$$(W - W_a)^2 < F^2 + \kappa D_{\mathrm{int}}^2 W^2/\omega_c, \tag{A.6}$$

where κ is a number of the order 1–10. The goal of this parameter is to adjust the accuracy of the rough estimate (A.6). The variation of κ by one order of magnitude does not significantly affect
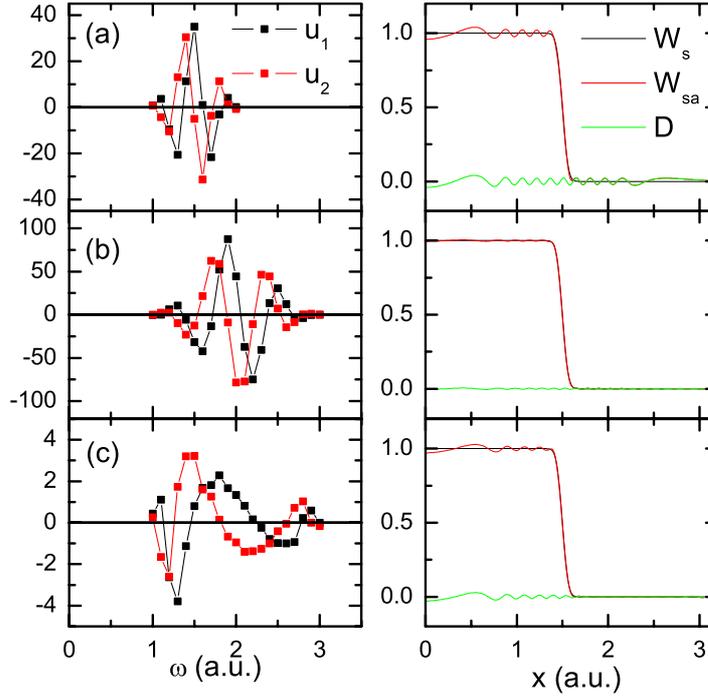
Figure A.1. The optimized u-coefficients (left panel) and the corresponding functions $\tilde{W}_s(x)$, $\tilde{W}_{s,a}(x)$ and $D(x) = \tilde{W}_s(x) - \tilde{W}_{s,a}(x)$ (right panel). Everywhere $\omega_c = 1.5$, $\omega_{min} = 1$, $\delta(\omega)$=0.1. (a) $\omega_{max} = 2$, no data noise; (b) $\omega_{max} = 3$, no data noise (c) $\omega_{max} = 3$, some data noise is added.

the value of W_0, although it does modify δW. We found that $\kappa = 5$ gives the best results in the numerical tests described in the main text. It is likely that more accurate estimates can remove an ambiguity here.

The inequality (A.6) can be resolved with respect to W

$$W_0 - \delta W < W < W_0 + \delta W, \tag{A.7}$$

where ($b = \kappa D_{int}^2/\omega_c$):

$$W_0 = \frac{W_a}{1 - b}, \quad \delta W = \frac{\sqrt{bW_a^2 + (1 - b)F^2}}{1 - b}.$$

After the numerical minimization of $(\delta W)^2$ as a function of w, the u-coefficients become dependent on $\sigma_{1,j}$ and $\sigma_{2,j}$. For example, in a case of a very large value of W, the relevant importance of the input error bars is small and the optimal u-coefficients tend to oscillate stronger than in a case of small W.

Figure A.1 shows some examples of the u-coefficients optimized as described above and the corresponding discrepancy function $D(x)$ for different sets of experimental frequencies and noise levels. Clearly, the spectral discrepancy function can be made quite small for all x by a proper optimization. The comparison between panels (a) and (b) tells that the discrepancy function is smaller if the range of experimental frequencies is broader. On the other hand, from panels (b) and (c) one concludes that taking error bars into account makes the u-coefficients much smaller, which results in a somewhat larger $D(x)$ but in a better overall accuracy $(\delta W)^2$ (not shown).

Appendix B. The equivalence of the least-square fit of $\sigma_1(\omega)$ and $\sigma_2(\omega)$ and the linear approximation formula

The most straightforward way to determine spectral weight is to fit experimental data with a model function

$$\sigma_{\text{mod}}(\omega) = \sum_{k=1}^{M} c_k \tilde{\sigma}_k(\omega). \tag{B.1}$$

This is a linear superposition of some basis functions $\tilde{\sigma}_k(\omega) = \tilde{\sigma}_{1,k}(\omega) + i\tilde{\sigma}_{2,k}(\omega)$, Lorentzians, for example, each of which satisfies the KK relations. Then one can estimate the partial sum-rule integral, using this model:

$$W(\omega_{\text{c}}) \approx \int_0^{\omega_{\text{c}}} \sigma_{1,\text{mod}}(\omega)\,\mathrm{d}\omega = \sum_{k=1}^{M} c_k \tilde{W}_k, \tag{B.2}$$

where $\tilde{W}_k = \int_0^{\omega_{\text{c}}} \tilde{\sigma}_{1,k}(\omega)\,\mathrm{d}\omega$.

Fitting the data points $\{\omega_j, \sigma_{\nu,j}, \delta\sigma_{\nu,j}\}$ ($\nu = 1, 2$, $j = 1 \ldots N$) with the model function (B.1) in the least-square sense means the minimization of

$$\chi^2 = \sum_{\nu=1}^{2} \sum_{j=1}^{N} \frac{1}{(\delta\sigma_{\nu,j})^2} \left[\sigma_{\nu,j} - \sum_{k=1}^{M} c_k \tilde{\sigma}_{\nu,k}(\omega_j) \right]^2$$

with respect to the coefficients c_k. This gives a linear system of equations

$$\sum_{k=1}^{M} a_{lk} c_k = b_l, \quad \text{or} \quad c_k = \sum_{l=1}^{M} (a^{-1})_{lk} b_l, \tag{B.3}$$

where

$$a_{lk} = \sum_{\nu=1}^{2} \sum_{j=1}^{N} \frac{\tilde{\sigma}_{\nu,l}(\omega_j)\tilde{\sigma}_{\nu,k}(\omega_j)}{(\delta\sigma_{\nu,j})^2}, \quad b_l = \sum_{\nu=1}^{2} \sum_{j=1}^{N} \frac{\tilde{\sigma}_{\nu,l}(\omega_j)\sigma_{\nu,j}}{(\delta\sigma_{\nu,j})^2}. \tag{B.4}$$

Substituting equation (B.3) and (B.4) into (B.2) we obtain, after some transformations, an expression identical to equation (A.1):

$$W(\omega_{\text{c}}) \approx \sum_{\nu=1}^{2} \sum_{j=1}^{N} u_{\nu,j} \sigma_{\nu,j} \tag{B.5}$$

with the u-coefficients independent of $\sigma_{\nu,j}$:

$$u_{\nu,j} = \frac{1}{(\delta\sigma_{\nu,j})^2} \sum_{l,k=1}^{M} (a^{-1})_{l,k} \tilde{\sigma}_{\nu,k}(\omega_j) \tilde{W}_l. \tag{B.6}$$

This implies that the strategy to obtain $W(\omega_{\text{c}})$ by fitting $\sigma_1(\omega)$ and $\sigma_2(\omega)$ is nothing else but the application of the linear formula (A.1) with specific u-coefficients determined by the basis of functions $\tilde{\sigma}_k(\omega)$.

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References

[1] Wooten F 1972 *Optical Properties of Solids* (New York: Academic)
[2] Okimoto Y *et al* 1995 *Phys. Rev. Lett.* **75** 109
[3] Millis A J 2001 *J. Electron Spectrosc. Relat. Phenom.* **114–116** 669
[4] Basov D N *et al* 1999 *Science* **283** 49
[5] Molegraaf H J A *et al* 2002 *Science* **295** 2239
[6] Santander-Syro A F *et al* 2003 *Europhys. Lett.* **62** 568
[7] Boris A V *et al* 2004 *Science* **304** 708
[8] Hirsch J E 1992 *Physica* C **199** 305
[9] Tinkham M 1956 *Phys. Rev.* **104** 845
[10] Dordevic S V *et al* 2002 *Phys. Rev.* B **65** 134511
[11] MacRobert T M 1958 *Functions of a Complex Variable* (London: MacMillan) p 122
[12] Carleman T 1926 *Les Fonctions Quasianalytiques* (Paris: Gauthier-Villars)
     Goluzin G M and Krylov V I 1933 *Mat. Sb.* **40** 144 (in Russian)
[13] Aizenberg L A 1993 *Carleman's Formulas in Complex Analysis* (Dordrecht: Kluwer)
[14] Bozovic I 1990 *Phys. Rev.* B **42** 1969
[15] Kuzmenko A B *et al* 2005 *Phys. Rev.* B **72** 144503
[16] Aspnes D E 1975 *Phys. Rev.* B **12** 4008
[17] Hulthen R 1982 *J. Opt. Soc. Am.* **72** 794
[18] Milton G W, Eyre D J and Mantese J V 1997 *Phys. Rev. Lett.* **79** 3062
[19] Dienstfrey A and Greengard L 2001 *Inverse Problems* **17** 1307
[20] Carbone F *et al* 2006 *Phys. Rev.* B **74** 024502
[21] Kuzmenko A B 2005 *Rev. Sci. Instrum.* **76** 083108