

Tuning sum rules with window functions for optical constant evaluation

Luis V. Rodríguez-de Marcos¹, José A. Méndez, Juan I. Larruquert²

GOLD-Instituto de Óptica-Consejo Superior de Investigaciones Científicas

Serrano 144, 28006 Madrid, Spain

1: lv.rodriguez@io.cfmac.csic.es

2: j.larruquert@csic.es

Abstract: Sum rules are a valuable tool to evaluate the global accuracy of a set of optical constants. A procedure to spectrally tune sum rules is presented. It enables enhancing the weight of a desired spectral range within the sum-rule integral. The procedure consists in multiplying the complex refractive index with an adapted function, which is named window function. Window functions are constructed through integration of Lorentz oscillators. The asymptotic decay of these window functions enables the derivation of a multiplicity of sum rules akin to the inertial sum rule, along with one modified version of f -sum rule. This multiplicity of sum rules combined with the selection of a photon energy range provides a double way to tune the spectral contribution within the sum rule. Window functions were applied to reported data of SrF₂ and Al films in order to check data accuracy in each specific spectral range. The use of window functions shows that the optical constants of SrF₂ are consistent in a broad spectrum; regarding Al, some spectral ranges present a lower consistency. Hence window functions are seen a helpful tool to evaluate the local accuracy of optical constants.

Keywords: 78.20.-e Optical properties of bulk materials and thin films; 78.20.Ci Optical constants; Optical materials; Extreme Ultraviolet; Vacuum Ultraviolet, vacuum; Soft x-rays.

References and links

1. M. Altarelli, D. L. Dexter, H. M. Nussenzveig, and D. Y. Smith, "Superconvergence and Sum Rules for the Optical Constants", *Phys. Rev. B* **6**, 4502-4509 (1972).
2. A. Villani and A. H. Zimerman, "Generalized f -sum rules for the optical constants", *Phys. Lett.* **44A**, 295-297 (1973)
3. M. Altarelli, D. Y. Smith, "Superconvergence and sum rules for the optical constants: Physical meaning, comparison with experiment, and generalization", *Phys. Rev. B* **9**, 1290-1298 (1974).
4. F. W. King, "Sum rules for the optical constants", *J. Math. Phys.* **17**, 1509-1514 (1976).
5. D. Y. Smith, "Dispersion theory, sum rules, and their application to the analysis of optical data", in *Handbook of optical constants of solids*, ed. E. D. Palik (Academic Press, San Diego, 1985, 1998), Chap. 3.
6. Y.-C. Liu, S. Okubo, "Tests of new π -N superconvergent dispersion relations", *Phys. Rev. Lett.* **19**, 190-192 (1967).
7. A. Villani and A. H. Zimerman, "Superconvergent sum rules for the optical constants", *Phys. Rev. B* **8**, 3914-3916 (1973).
8. G. Bimonte, "Generalized Kramers-Kronig transform for Casimir effect computations", *Phys. Rev. A* **81**, 062501 (2010).
9. G. Bimonte, "Making precise predictions of the Casimir force between metallic plates via a weighted Kramers-Kronig transform", *Phys. Rev. A* **83**, 042109 (2011).
10. V. Lucarini, J. J. Saarinen, K. -E. Peiponen, E. M. Vartiainen, *Kramers-Kronig relations in optical materials research* (Springer Series in optical sciences, Springer, 2005).
11. M. Altarelli and D. Y. Smith, "Superconvergence and sum rules for the optical constants: Physical meaning, comparison with experiment, and generalization", *Phys. Rev. B* **9**, 1290-1298 (1974).
12. E. Shiles, T. Sasaki, M. Inokuti, and D. Y. Smith, "Self-consistency and sum-rule tests in the Kramers-Kronig analysis of optical data: applications to aluminium," *Phys. Rev. B* **22**, 1612-1628 (1980).
13. L. Rodríguez-de Marcos, J. I. Larruquert, J. A. Aznárez, M. Fernandez-Perea, R. Soufli, J. A. Méndez, S. L. Baker, E. M. Gullikson, "Optical constants of SrF₂ thin films in the 25-780-eV spectral range", *J. Appl. Phys.* **113**, 143501 (2013).
14. W. Kaiser, W. G. Spitzer, R. H. Kaiser, and L. E. Howarth, "Infrared Properties of CaF₂, SrF₂, and BaF₂," *Phys. Rev.* **127**, 1950-1954 (1962).
15. D. R. Bosomworth, "Far-Infrared Optical Properties of CaF₂, SrF₂, BaF₂, and CdF₂", *Phys. Rev.* **157**, 709-715 (1967).
16. J. Frandon, B. Lahaye, and F. Pradal, "Spectra of Electronic Excitations in CaF₂, SrF₂, and BaF₂ in the 8 to 150 eV Range", *Phys. Status Solidi B* **53**, 565-575 (1972).
17. L. Rodríguez-de Marcos, J. I. Larruquert, J. A. Aznárez, M. Vidal-Dasilva, S. García-Cortés, J. A. Méndez, L. Poletto, F. Frassetto, A. M. Malvezzi, D. Bajoni, A. Giglia, N. Mahne, S. Nannarone, "Transmittance and optical constants of Sr films in the 6-1,220 eV spectral range", *J. Appl. Phys.* **111**, 113533 (2012).
18. B. L. Henke, E. M. Gullikson, and J. C. Davis, *At. Data Nucl. Data Tables* **54**, 181 (1993).
19. http://henke.lbl.gov/optical_constants/
20. C. T. Chantler, K. Olsen, R. A. Dragoset, J. Chang, A. R. Kishore, S. A. Kotochigova, and D. S. Zucker, "X-ray form factor, attenuation and scattering tables," *J. Phys. Chem. Ref. Data* **29**, 597-1048 (2000); C. T. Chantler, "Theoretical Form Factor,

1. Introduction

The optical constants of a material, n and k , can be determined through different methods, which, obviously, always involve some inaccuracy. n and k are not independent since they are connected through Kramers-Krönig (KK) dispersion relations. This property is useful to obtain one of the optical constants out of the other, which must be known in the whole electromagnetic spectrum. However, measurements are always limited to a finite spectrum. Hence, KK analysis involves some sort of data extrapolation and/or of the use of models to extend the available optical constant data outside the measured range.

Procedures to validate the accuracy of the optical constants calculated with KK analysis are necessary. A common procedure is the use of the so-called sum rules. Sum rules are based on straightforward assumptions on the large-energy limit of the optical constants, which give rise to known integrated values of the optical constants in the whole spectrum¹. These sum rules are useful to evaluate the global accuracy of optical constants. Since these sum rules involve integration in the whole spectrum, it would be useful to derive sum rules that are tuned in a specific spectral range in order to check the consistency mainly of that range.

In addition to the common set of two sum rules, which are usually referred to as f - and inertial sum rules, more rules can be obtained based on fundamental assumptions on the optical constants. The optical constants of materials are described by a complex function that has an analytical continuation in the upper complex half-plane; this function must have a specific parity and asymptotical behaviour, which are the requirements for the validity of KK analysis. These properties enable obtaining new functions also satisfying KK relations by combining the optical constant function with itself or with other analytic functions, as long as parity and asymptotic behaviour are preserved. This procedure has been used for the generation of sum rules involving powers of $[N(\omega)-1]$ combined with powers of $\omega^{2,3,4}$, where $N(\omega) \equiv n+ik$ stands for the complex refractive index and ω stands for the frequency; such functions may result in the acceleration of sum-rule convergence for large ω ⁵. Other functions have been also used in KK analysis and in the generation of new sum rules^{4,6,7}. Such functions, that are incorporated as factors in KK analysis and sum-rule generation, will be named window functions when they are used for the purpose of giving more weight to a desired spectral band^{8,9}. Hence King⁴ proposed highly damped sum rule relations in order to reduce the weight of spectral ranges lacking accurate measurements, in a target coincident with this research, although he did not display the benefits of the new sum rules for this purpose. Research on KK analysis and sum rules has been summarized in the literature^{5,10}.

The present research proposes a method to develop window functions enhancing the desired range over the spectrum, which is applied to generate sum rules that involve more weight of the selected spectral range. For instance, by adjusting the window function to the spectral range of a set of experimental data, the contribution of extrapolations to sum rules can be minimized, and hence the accuracy of the specific spectral range can be better determined. The window function is introduced in Section 2, which gives rise to the development of adapted generalized KK relations and sum rules. Section 3 applies the new sum rules to reported sets of optical constant of SrF₂ and Al thin films, which enables the evaluation of its accuracy in selected spectral ranges. By scanning the spectrum with tuned window functions, the ranges with uncertain optical constants are highlighted.

2. The use of window functions in KK analysis and sum rules

2.1 Development of window functions

Basic assumptions on linearity and causality in the response of a medium to an electromagnetic excitation result in that the optical constants of the medium can be described by a complex function of real variable, $N(E)=n(E)+ik(E)$ (from now on, energy $E=\hbar\omega$ instead of frequency, ω , will be used), which satisfies the properties given below. All the following analysis could be similarly derived for the optical properties of a material described by its dielectric constant $\varepsilon(E)=\varepsilon_1(E)+i\varepsilon_2(E)$. As a result from causality, the continuation of that function to a complex function of complex variable must be analytic in the upper half-plane. The function must have an asymptotic decrease for large energy modulus $|E|$ faster than $1/|E|$. Finally, the function must satisfy parity conditions, which, at the real axis, its real and imaginary parts must be even and odd, respectively.

The above are the conditions for a function to satisfy KK relations, which for $N(E)$ they are expressed as:

$$n(E) - 1 = \frac{2}{\pi} P \int_0^{\infty} \frac{E' k(E')}{E'^2 - E^2} dE' \quad (1a)$$

$$k(E) = -\frac{2E}{\pi} P \int_0^{\infty} \frac{[n(E') - 1]}{E'^2 - E^2} dE' \quad (1b)$$

where P stands for the Cauchy principal value.

The above conditions can still be satisfied if we multiply $N(E)-1$ by a function $F(E)$ that does not destroy any of the above properties: it has the correct parity, it is analytic, and it keeps a fast enough asymptotic decay. Hence the product function also satisfies KK relations:

$$\text{Re}\{F(E)[N(E) - 1]\} = \frac{2}{\pi} P \int_0^{\infty} \frac{E' \text{Im}\{F(E')[N(E') - 1]\}}{E'^2 - E^2} dE' \quad (2a)$$

$$\text{Im}\{F(E)[N(E) - 1]\} = -\frac{2E}{\pi} P \int_0^{\infty} \frac{\text{Re}\{F(E')[N(E') - 1]\}}{E'^2 - E^2} dE' \quad (2b)$$

Here, $F(E)$ will be developed to have filtering properties outside a desired spectral range and will be called window function.

In a typical practical case, spectral data for a material will be available only within a limited spectral range; let E_1 and E_2 be the limits of that range, with $E_1 < E_2$. In order to turn KK relations of the product function less dependent on data outside the measured spectrum, the window function would be ideally selected to take larger values in the target spectrum and to strongly decrease in the out-of-band, which can be partly obtained. Let us construct an approximate to that target function.

A first approach to a window function is a Lorentz oscillator:

$$O(E; E_0, c) = \frac{-E_0}{(E^2 - E_0^2) + icE}, \quad (3)$$

where i is the imaginary unit, E_0 stands for the central energy of the oscillator, and c is the oscillator width. In Eq. (3), the oscillator strength has been set to unity. If E_0 is selected in a central position of the desired range and c is adapted to better fit that range, the function in Eq. (3) provides a sort of window function. The main drawback of the oscillator is that it does not provide a relatively constant value in the desired spectral range. Furthermore, its real part does not decay towards small energies.

An analytical function $H_1(E)$ with the desired filtering profile in the imaginary part over the target spectrum $[E_1, E_2]$ can be generated through integration of the Lorentz oscillator for its central energy over that spectrum:

$$H_1(E) = \frac{2}{\pi} \int_{E_1}^{E_2} O(E; E_0, c) dE_0 = \frac{1}{\pi} [L(E; E_2, c) - L(E; E_1, c)] \quad (4)$$

with

$$L(E; E_i, c) \equiv \ln(E_i^2 - E^2 - icE) \quad (5)$$

In Eq. (5) \ln stands for the natural logarithm; the latter must be understood as the logarithm principal value, i.e., its imaginary part lies in the interval $(-\pi, \pi]$; the principal value is often represented as Log .

Fig. 1 plots the real and imaginary parts of $H_1(E)$ for the particular choice of $E_1=25$ eV, $E_2=780$ eV and $c=1$ eV, which will match a spectral range of available optical-constant data of SrF_2 thin film in an example in the next section. Per construction, the imaginary part of H_1 reproduces the desired window behaviour, particularly for small values of c , so that it is valued close to 1 in most of the (E_1, E_2) range. On the other hand, the real part of H_1 decays at large energies but it does not at small energies, reproducing the Lorentz oscillator asymptotic behaviour. However, for some of the new sum rules that are derived below, the presence of powers of energy will compensate for this lack of decay of the real part at small energies. The real part of H_1 is far from constant and it seems that the two parts of the window function cannot be made simultaneously constant in the desired spectral range.

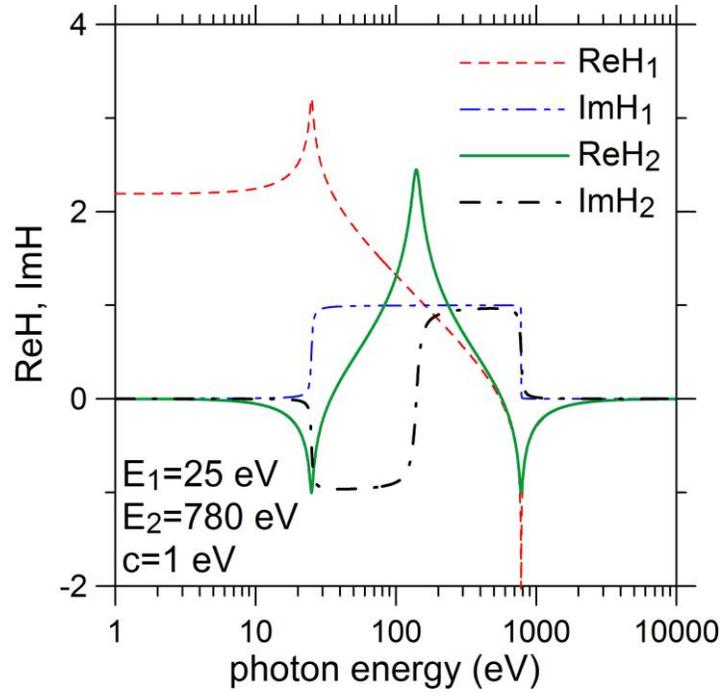


Fig. 1. Window functions H_1 and H_2 for the particular choice of $E_1=25$ eV, $E_2=780$ eV, and $c=1$ eV

The limitation to have a single c parameter to define the function variation width, which turns H_1 relatively more abrupt at E_2 compared with E_1 , can be overcome by defining separated parameters c_1 and c_2 at E_1 and E_2 , respectively, in Eq. (4). However, by doing this the asymptotic decay at large energies is reduced. A new function can be defined to recover the decay:

$$H_2(E) = \frac{1}{\pi} \left[L(E; E_2, c_2) + L(E; E_1, c_1) - 2L\left(E; \sqrt{E_1 E_2}, \frac{c_1 + c_2}{2}\right) \right] \quad (6)$$

with $c_2=c_1 E_2/E_1$. Fig. 1 also displays H_2 . H_2 succeeds in decaying to zero on both limits. Table 1 summarizes the asymptotic decay of the two functions.

Table 1. Asymptotic decay of the real and imaginary part of H_1 and H_2

Window function	Asymptotic decay			
	$E \rightarrow 0$		$E \rightarrow \infty$	
	Re	Im	Re	Im
H_1	E^0	E^1	$(E_1^2 - E_2^2)/\pi E^2$	E^{-3}
H_2	E^2	E^3	$[-(E_2 - E_1)^2 + (c_2 - c_1)^2]/4\pi E^2$	E^{-3}

Other useful window functions can be defined by multiplying the integrand in Eq. (4) with positive or negative powers of E_0 ; these powers will replace the flat imaginary part plotted in Fig. 1 with the corresponding positive or negative power functionality of the added term. This gives a further degree of freedom that enables biasing the specific spectral range to one of its energy edges.

2.2 New sum rules involving window functions

Sum rules were said above to be useful tests to evaluate the accuracy of a set of optical constants. By virtue of the superconvergence theorem¹, the asymptotic decay of the optical constants at high energies enables us obtaining the well-known sum rules:

$$\int_0^{\infty} E' k(E') dE' = \frac{\pi \hbar^2 \omega_p^2}{4} \quad (7)$$

$$\int_0^{\infty} [n(E') - 1] dE' = 0 \quad (8)$$

The first sum rule is one of various possible expressions of the so called f -sum rule, which relates the number density of electrons to k (or to other functions like ϵ , $1/\epsilon$, or the oscillator strength) through plasma frequency $\omega_p^2 = N_e e^2 / m \epsilon_0$, which depends on electron density N_e , electron mass and charge and vacuum permittivity. The second expression is called the inertial sum rule, which expresses that the average value of the refractive index throughout the spectrum is unity.

Window functions will be used here for the generation of new sum rules that give more weight to data in the desired spectral range. To derive the new sum rules we will use a procedure similar to the one used by Altarelli *et al.*¹ to derive the nowadays standard sum rules, which is based on the superconvergence theorem. This job is possible because the above window functions are analytic in the upper complex plane, have the correct parity, and the window function times the refractive index decays fast enough at large energies. In the sum-rule development we will use the large-energy asymptotic behavior of the optical constants¹:

$$n(E) - 1 \rightarrow -\frac{\omega_p^2}{2E^2} + O(E^{-\alpha}) \quad (9)$$

and

$$k(E) \rightarrow O(E^{-2} \log^{-\beta} E) \quad (10a)$$

or

$$k(E) \rightarrow O(E^{-\gamma}) \quad (10b)$$

with $\alpha > 2$ and either $\beta > 1$ or $\gamma > 2$, depending on which of the two usual asymptotic decays is assumed for k .

By replacing the usual expression of KK analysis for n and k with the modified expressions of Eqs. (2a) and (2b) that involve a window function, by using the asymptotic behaviour of the optical constants and of the window functions, which is summarized in table 1, and by using the superconvergence theorem, we obtain the following new sum rules:

$$\int_0^{\infty} E^i \text{Im}\{H_i(E') [N(E') - 1]\} dE' = 0, \quad i = 1, 2 \quad (11)$$

$$\int_0^{\infty} \text{Re}\{H_i(E') [N(E') - 1]\} dE' = 0, \quad i = 1, 2 \quad (12)$$

$$\int_0^{\infty} E^3 \text{Im}\{H_i(E') [N(E') - 1]\} dE' = \frac{\pi \hbar^2 \omega_p^2}{4} [E^2 \text{Re} H_i(E)]_{\infty}, \quad i = 1, 2 \quad (13)$$

$$\int_0^{\infty} E^3 \text{Im}\{H_1(E') [N(E') - 1]\} dE' = \frac{\hbar^2 \omega_p^2}{4} (E_1^2 - E_2^2) \quad (13a)$$

$$\int_0^{\infty} E^3 \text{Im}\{H_2(E') [N(E') - 1]\} dE' = \frac{\hbar^2 \omega_p^2}{4} \left[-(E_2 - E_1)^2 + \frac{1}{4} (c_2 - c_1)^2 \right] \quad (13b)$$

$$\int_0^{\infty} E^i \text{Re}\{H_i(E') [N(E') - 1]\} dE' = 0, \quad i = 1, 2 \quad (14)$$

where the term $E^2 \text{Re} H_i(E)_{\infty}$ represents the limit at infinite energy of function $E^2 \text{Re} H_i$, which is given in table 1. Differently to Eq. (7), Eq. (11) is equalled to zero due to the increased large-energy decay given by H_i . On the other hand, new sum rule (13) replaces (7) in involving the plasma frequency, and hence the number of electrons. Eqs. (13a) and (13b) particularize Eq. (13) for H_1 and H_2 , respectively.

Due to the decay of H_2 at small energies for both real and imaginary parts, we obtain two new sum rules only valid for H_2 :

$$\int_0^{\infty} E'^{-1} \text{Im}\{H_2(E')[N(E')-1]\}dE' = 0 \quad (15)$$

$$\int_0^{\infty} E'^{-2} \text{Re}\{H_2(E')[N(E')-1]\}dE' = 0 \quad (16)$$

New sum rules (13) and (14) involve an extra E^2 term over the standard ones given by (7) and (8), which turns irrelevant the lack of decay of the real part of H_1 at small energies, at the cost of losing the increased decay given by the window functions at large energies. On the other hand, E term in sum rule (11) provides the decay at short energies that was not present in $\text{Re}H_1$; therefore, for this sum rule we have a decreased contribution to the sum rule at both energy limits and for both real and imaginary parts. Regarding H_2 , it provides decreased contributions at both energy limits in new sum rules (11), (12), and (15), whereas sum rules (13), (14), and (16) lack some enhanced decay on one limit, which combines with an accelerated asymptotic decay on the other limit.

We have then six new sum rules, each of which is tunable in the desired energy range $[E_1-E_2]$ through either H_1 or H_2 . Sum rules resulting in a null integral need some criterion to evaluate how close to zero is the integral when using discrete data that involve experimental errors. We will define a verification parameter in analogy to the one used by Altarelli et al.³

$$\zeta = \frac{\int_0^{\infty} E^m \text{Re}\{H(E)[N(E)-1]\}dE}{\int_0^{\infty} |E^m \text{Re}\{H(E)[N(E)-1]\}|dE} \quad (17)$$

for sum rules involving a real part (12, 14, and 16). For sum rules involving an imaginary part [(11) and (15)] we just replace the real with the imaginary part in Eq. (17). Shiles et al¹¹ considered that ζ be considered acceptable if it stands within ± 0.005 . In a straightforward generalization of Shiles criterion, we propose the same top value for ζ in the new sum rules.

The new sum rules involve data both of n and k , whereas standard sum rules (7) and (8) involve data of only one of them. This is not a complication since the purpose of the new sum rules is to apply them after KK analysis, which results in the determination of one optical constant out of the other.

The new sum rules will be compared with the standard ones in the next section.

3 Application of the new sum rules to evaluate experimental data and discussion

3.1 SrF_2

The new sum rules will be applied on available experimental data in order to display their capacity to enhance the weight of the desired spectral range. This feature will be used to give more weight both to a measured range over extrapolations and also to a range that was covered with an extrapolation. Finally we will let the window function scan over a wide photon energy range.

We start applying the new sum rules to a self-consistent set of data reported for thin films of SrF_2 ¹². Data sources for the characterization of SrF_2 included experimental data in the ranges of 0.01-0.1 eV^{13,14}, 9.8-35 eV¹⁵, 25-780 eV¹². At photon energies up to 3×10^4 eV, where no experimental data were available, an independent-atom approximation was used in Ref. 12 that combined the optical constants of Sr ¹⁶ with the semi-empirical data of Henke et al.¹⁷ for F; the latter was downloaded from the web of the Center for X-Ray Optics (CXRO)¹⁸. For energies in the 3×10^4 to 4×10^5 eV range, the calculations of Chantler et al.¹⁹ were used. One difficulty to make a self-consistent characterization was the lack of data in the 0.1-9.8 eV range, which was covered with an interpolation by fitting the surrounding ranges with a set of eight Lorentz oscillators. We apply below the new sum rules to the range of 25-780 eV, which involves experimental measurements, and to the extrapolation range of 0.1 to 9.8 eV.

We start applying the inertial sum rule, both in its original expression [Eq. (8)] and in the new sum rules [Eqs. (11), (12), and (14) to (16)]. To display the contribution of each energy range to the sum rules, we

plot the integral through function $I(E)$, which for the sum rules involving a real part (12, 14, and 16) it is defined as:

$$I(E) \equiv \int_0^E E'^m \operatorname{Re}\{H_i(E')[N(E')-1]\}dE', \quad m = -2,0,2 \quad (18)$$

with $m=0,2,-2$, respectively. For sum rules involving an imaginary part, we just replace the real for the imaginary part in Eq. (18), with $m=1$ (Eq. 11) or -1 (Eq. 15). In order to display the contribution of the different spectral ranges to the sum rule, the upper limit of the integral is left as the function variable. For accurate optical constants, the integral must tend to zero in the infinity limit. Figs. 2-left and 2-right plot all sum rules with H_1 and H_2 , respectively, with parameters $E_1=25$ eV, $E_2=780$ eV, and $c=c_1=1$ eV. The new sum rules are also applied in the range of extrapolation: Figs. 3-left and 3-right plot sum rules with H_1 and H_2 , respectively, with parameters $E_1=0.1$ eV, $E_2=9.8$ eV, $c=c_1=0.01$ eV. The integral of the standard sum rule, i.e., with no window function, is also plotted. All curves were normalized to the largest value over the spectrum to simplify the comparison. The small-energy range data taken from Rodríguez-de Marcos¹², which come from Bosomworth¹⁴, did not reach a small enough energy as to calculate the sum rules with more weight on the small-energy range. To solve this, we extrapolated Bosomworth data down to 10^{-5} eV with a power function.

The series of sum rules is seen to shift the spectral range that most contributes to the integral. There is a correlation between the energy range $[E_1-E_2]$ selected in the window function and the range of largest contribution to the sum rule, but the specific range mostly contributing to the sum rule also depends on the variation of the optical constants over the spectrum. It also depends on the E^m term of the specific sum rule: the range mostly contributing to the sum rule shifts to larger or smaller energies with more or less positive energy powers, respectively. Among the derived sum rules, the one that a priori better matches the window range is expected to be the one with no energy term, i.e., Eq. (12), although the effective range obviously depends on the specific optical constants. In the examples of Figs. 2 and 3, the sum rules with E powers of 0 and ± 1 are the ones that better adapt to the window range. In most cases, the energy range contributing to the integral is considerably narrower for the sum rules with window functions compared to the standard sum rule. There are some exceptions, like sum rules given by Eq. (11) (Fig. 2-left) and Eqs. (15) and (16) (Fig. 3-right), which are attributed to the specific distribution of n and k over the spectrum; narrower distributions in the latter three cases can be obtained by just using narrower window functions.

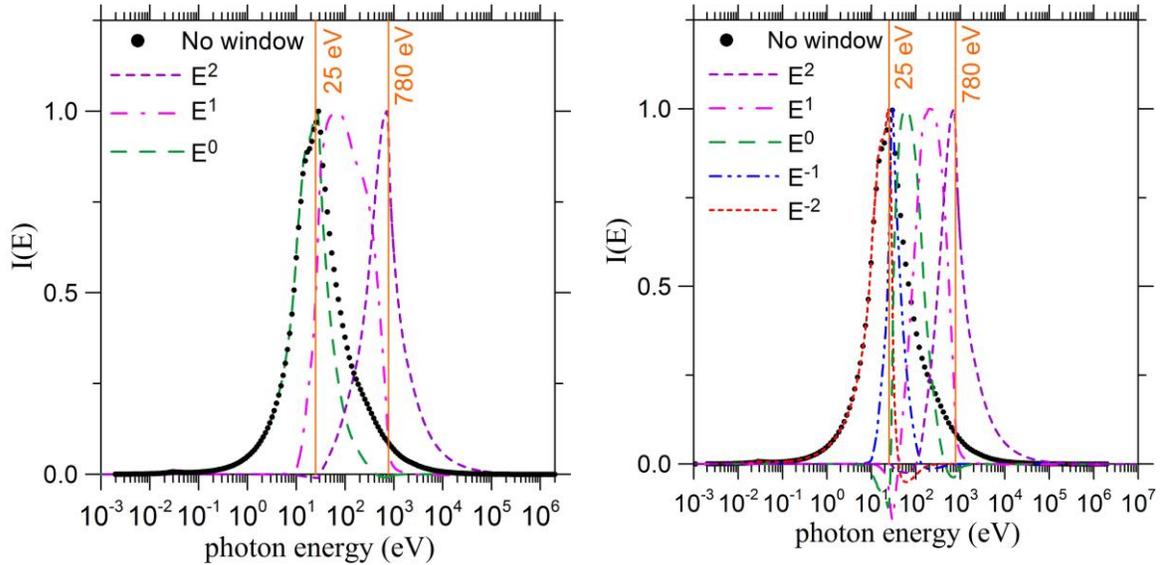


Fig. 2. $I(E)$ for H_1 (left) and H_2 (right) for sum rules (11), (12) and (14)-(16), compared to the standard rule (8) (no window). Data used are the optical constants of SrF_2 ¹². The window is defined by $E_1=25$ eV, $E_2=780$ eV, and $c=1$ eV. For H_2 , c corresponds to c_1 in Eq. (6) and $c_2=c_1E_2/E_1$. The sum rules are identified in the legend by the power of photon energy in the integral.

The present procedure enables the selection of the energy range in a direct way. This contrasts with a procedure used in the literature³ consisting in the use of sum rules that involve powers of the refractive index (in fact of $N-1$) along with powers of photon energy; the application of the latter sum rules does not enable properly selecting the spectral range, since the resulting weight over the spectrum exclusively depends on the spectral profile of the optical constants of the material, whilst the energy power merely introduces a bias to larger or smaller energies.

Table 2 displays Shiles's parameter ζ for the optical constant data of SrF_2 with the two window functions and all sum rules, compared to the case of no window. For the present data, ζ takes very low values, well below the aforementioned limit of ± 0.005 . Hence in this case, not only the global accuracy of the full set of data is good (presented as "no window"), but it is also good for all the specific ranges defined by the window functions and the different sum rules. For other particular data sets, the above sum-rule calculation might have resulted in that a specific range involves a lower accuracy (through a higher Shiles's parameter) than with the ordinary sum rule; that result would suggest that a more accurate set of data would be needed at that range. When ζ is as small as for many of the numbers in table 2, that number may be affected by the limited data accuracy, so that the differences over small numbers in table 2 might not be significant.

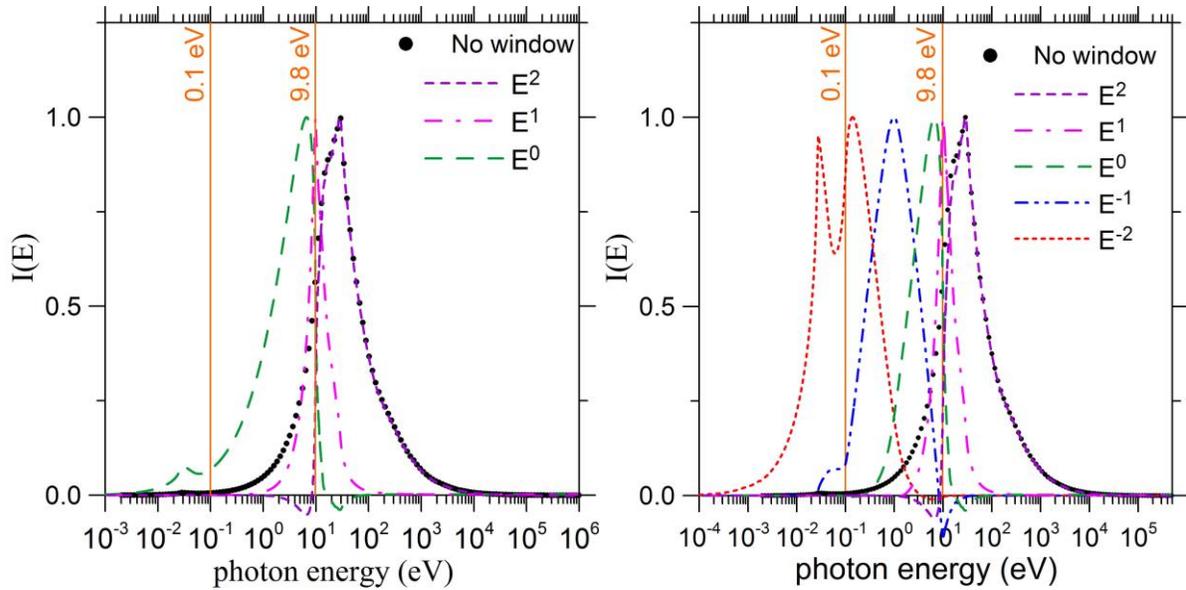


Fig. 3. $I(E)$ for H_1 (left) and H_2 (right) for sum rules (11), (12) and (14)-(16), compared to the standard rule (8) (no window). Data used are the optical constants of SrF_2 ¹². The window is defined by $E_1=0.1$ eV, $E_2=9.8$ eV, and $c=0.01$ eV. For H_2 , c corresponds to c_1 in Eq. (6) and $c_2=c_1E_2/E_1$. The sum rules are identified in the legend by the power of photon energy in the integral.

Table 2. Shiles's parameter calculated with SrF_2 data using both the standard sum rule and new sum rules with window functions H_1 and H_2 with the indicated energy ranges^a

Window function	Sum rule	ζ	
		$E_1=25$ eV, $E_2=780$ eV, $c=1$ eV	$E_1=0.1$ eV, $E_2=9.8$ eV, $c=0.01$ eV
H_1	$E^0\text{Re}[H(N-1)]$	0.0002	0.0002
	$E^1\text{Im}[H(N-1)]$	-0.0009	-0.0009
	$E^2\text{Re}[H(N-1)]$	0.0002	0.0002
H_2	$E^{-2}\text{Re}[H(N-1)]$	0.00007	0.00003
	$E^{-1}\text{Im}[H(N-1)]$	0.00006	-0.00005
	$E^0\text{Re}[H(N-1)]$	-0.0003	0.001
	$E^1\text{Im}[H(N-1)]$	-0.0006	0.0004
	$E^2\text{Re}[H(N-1)]$	0.0003	0.0006
no window	$\text{Re}(N-1)$	-0.000001	

^aFor H_2 , c corresponds to c_1 in Eq. (6) and $c_2=c_1E_2/E_1$

The past examples illustrate the case of window functions tuned at two specific energy ranges. More general information can be obtained by making a certain window function to vary continuously. Hence we have defined window functions centered at a variable energy E_w with the window parameters satisfying $E_w=(E_1E_2)^{0.5}$, $E_2/E_1=3$, and $c_{1(2)}=E_{1(2)}/10$. The window central energy E_w has been set to span a wide spectral range. Fig. 4 plots ζ vs E_w for the above set of optical constants of SrF_2 and for the five sorts of inertial-like sum-rules developed for function H_2 . The figure highlights the limits suggested by Shiles et al.¹¹. Parameter ζ comfortably stands well away from these limits for all five sum rules, which strengthens the conclusion of good consistency of the data set all over the spectrum. ζ is very smooth in the 0.1-9.8-eV range of the interpolation with eight Lorentz oscillators, it slightly oscillates at energies larger than 9.8 eV, corresponding to experimental data, and the largest oscillations are below 0.1 eV, where data of crystalline (instead of thin film) SrF_2 had to be used.

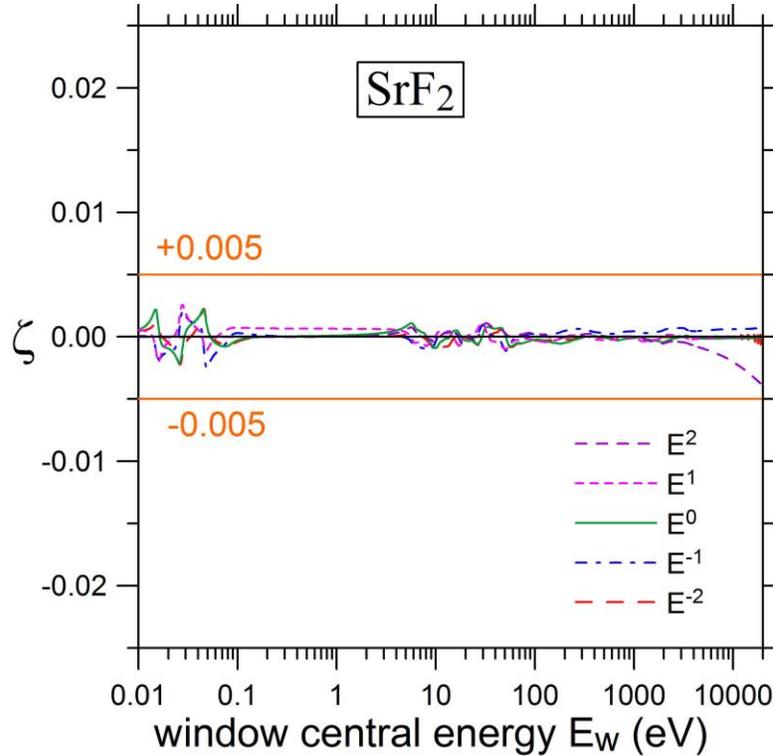


Fig. 4. Shiles's parameter ζ versus the central energy E_w of window functions for all five inertial-like sum rules calculated with the optical constants of SrF_2 . The sum rules are identified in the legend by the power of photon energy in the integral. Window function is H_2 and its parameters are: $E_w=(E_1E_2)^{0.5}$, $E_2/E_1=3$, $c_{1(2)}=E_{1(2)}/10$

Summarizing the results with sum rules akin to inertial sum rule:

- There is a correlation between the energy range of the window function and the range of largest contribution to the sum rule.
- For a given set of window parameters, a positive (negative) energy power in the sum rule can be selected to shift the contributing range to larger (smaller) energies.
- The energy range mostly contributing to the sum rule can be considerably narrowed with the use of window functions.
- The application of inertial-like sum rules spanning a wide range of photon energies can display the local sources of inaccuracies of the set of optical constants.

Let us now focus on f -sum rule. In Fig. 5, the new f -sum rule of Eq. (13) is applied with H_1 window function and it is compared with the usual sum rule of Eq. (7); data are again for SrF_2 and come from the same source. The figure plots the following function, obtained out of Eq. (13a):

$$n_{\text{eff}}(E) = \frac{4m\epsilon_0}{\hbar^2 N_a e^2 (E_1^2 - E_2^2)} \int_0^E E'^3 \text{Im}\{H_1(E') [N(E') - 1]\} dE' \quad (19)$$

where N_a stands for atom density. In the large-energy limit, $n_{\text{eff}}(\infty) = \sum_i Z_i$, i.e., the summation over all atomic numbers Z_i of atoms in the molecule; this number is 56 for SrF_2 . After correcting for relativistic effects, the number decreases to 55.71²⁰. $n_{\text{eff}}(\infty)$ obtained for the plotted data are 55.72 (no window) and 55.74 both for the use of H_1 with $E_1=9.8$ eV, $E_2=100$ eV, $c=0.5$ eV, and with $E_1=25$ eV, $E_2=780$ eV, $c=1$ eV. According to Rodríguez de Marcos et al.¹², SrF_2 density was set at 3.98 g/cm³. The agreement between integrated data and the theoretical prediction is excellent for all cases and in fact this coincidence must be partly fortuitous due to uncertainty in optical constant data and in the film density.

The new sum rule with a window function succeeds in narrowing the spectral range of largest contribution to the integral. This narrowing is obtained by pushing the small-energy limit to larger energies, whereas the other limit is not affected. This asymmetrical behavior is attributed to the E^3 term in the integral, which tends to shift the contributing range to larger energies, enhancing the contribution of the large-energy end of the selected range compared to the small-energy end.

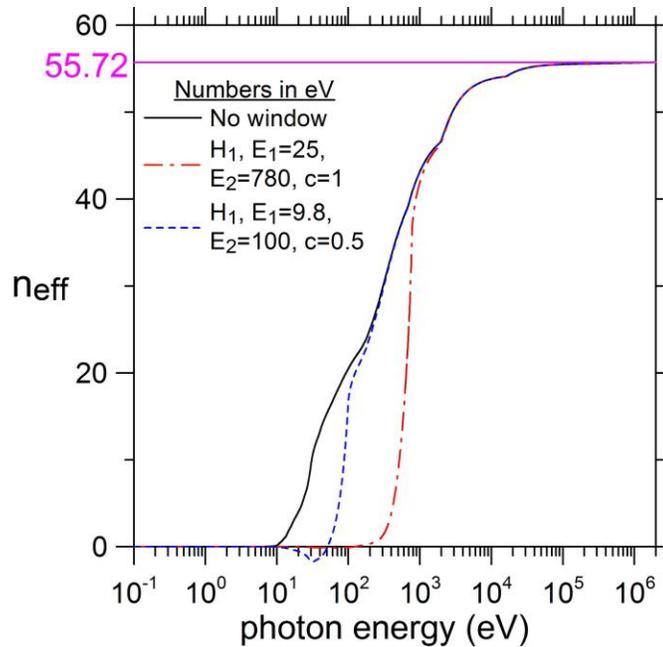


Fig. 5. $n_{\text{eff}}(E)$ for sum rule (13a) with H_1 , compared to the standard rule 7 (no window). The optical constants of SrF_2 are used in the calculations¹⁶. Window parameters are displayed

3.2 Al

Window functions were also applied to evaluate the consistency of the optical constants of a metal. Al was selected for being a common metal that is used in optical coatings from the near-infrared to the extreme ultraviolet and Al optical constants are well known in most of the spectrum. An excellent paper by Shiles et al.¹¹ obtained self-consistent optical constants of Al in a broad spectral range. It was obtained from a large collection of optical constant data in the literature. Here we will address the application of the inertial-like sum rules to Al data both with and without window functions. It is significant for the discussion below that Al optical constants at photon energies smaller than 0.04 eV were obtained in Ref. 11 by extrapolation with a Drude model. The inertial sum rule with no window function applied to Al has been found to be strongly dependent on the specific Drude model extrapolation used in this low-energy range. In fact, half of the spectrum contributing with a refractive index satisfying $n > 1$ comes from energies below 0.04 eV, i.e., the range of application of the Drude model. Therefore, various extrapolations using slightly different Drude parameters, which produced similarly smooth connections of the optical constants, resulted in largely different Shiles's evaluation parameters ζ ranging from more negative than -0.015 to more positive than +0.015. Additionally, a good simultaneous fit of

both n and k could not be obtained with any pair of Drude parameters. The reason for this may be that Drude model can only fit the free-electron (i.e., intraband) part of the optical constants, but often interband contributions are not negligible. With the Drude model applied in Ref. 11, a value of $\zeta=-0.002$ was obtained. Therefore, here we selected Drude parameters to match the value of -0.002 , as calculated with no window function. These parameters were $\omega_p=1.75\times 10^{16} \text{ s}^{-1}$ and $\tau=1.32\times 10^{-14} \text{ s}$, which result in a conductivity of $\sigma=3.23\times 10^{17} \text{ s}^{-1}$, in good agreement with the value of $3.21\times 10^{17} \text{ s}^{-1}$ obtained in Ref. 11.

The strong dependence of the inertial sum rule on the specific extrapolation of Al optical constants at small energies tends to invalidate the application of this rule when no window function is used. In general, the divergence of the optical constants of metals at small energies complicates the accurate calculation of the inertial sum rule. Hence the use of window functions, particularly H_2 for its strong decay at small energies, is expected to effectively overcome this problem.

As with SrF_2 , H_2 window function was made to cross the spectrum of Al data and ζ was calculated as a function of the central energy of the window function E_w , with the edges satisfying $E_w=(E_1E_2)^{0.5}$, $E_2/E_1=3$, and $c_{1(2)}=E_{1(2)}/10$. In the calculation of the inertial-like sum rules, optical constants of Al in Ref. 11 and the aforementioned Drude model were used. The results are plotted in Fig. 6. Now ζ considerably grows compared with the example of SrF_2 . Some energies are highlighted in the picture: the energy under which the Drude model is applied (0.04 eV), and Al $L_{2,3}$ (72.95, 72.55 eV), and K (1559.6 eV) edges. The transition to the Drude model is noticeable in Fig. 6 with an oscillation of ζ , but still within the limits of Shiles's acceptable values. But larger oscillations, well beyond Shiles's limits, are seen close to $L_{2,3}$ edge, where Al optical constants have a strong feature; one has to keep in mind that the present windows are centered at E_w but they extend from $E_1=E_w/(3)^{1/2}$ to $E_2=E_w\times(3)^{1/2}$, which broadens the range at which this edge contributes to sum rules. The energy power of the specific sum rule also plays a role in this. In fact, Ref. 12 encounters that their data on k are too high between $L_{2,3}$ edge and 500 eV and the authors decreased these data guided with the application of f -sum rule. Hence the oscillation found here close to $L_{2,3}$ edge may be highlighting the uncertainty involved in the optical constant determination in this range. Above $L_{2,3}$ edge, ζ keeps high and it features high peaks at energies above roughly 3,000 eV. This behavior might be influenced by Al K edge, by the connection at 4,000 eV of two different sources of optical constants, and/or by the extrapolation at 10,000 eV with a power function. Therefore, Fig. 6 illustrates a case that, even though the evaluation parameter calculated with no window function ($\zeta=-0.002$) is well within the suggested limits of Shiles et al.¹², the application of window functions reveal weaknesses of the optical constants at specific spectral ranges, which can include uncertainty in optical constant calculation, rough connections of optical constants from various sources, or inaccurate extrapolations. Unlike the standard inertial sum rule without window functions, the use of window functions gives us information not only on the global accuracy of the optical constants, but on the specific spectral range where the inaccuracy is present.

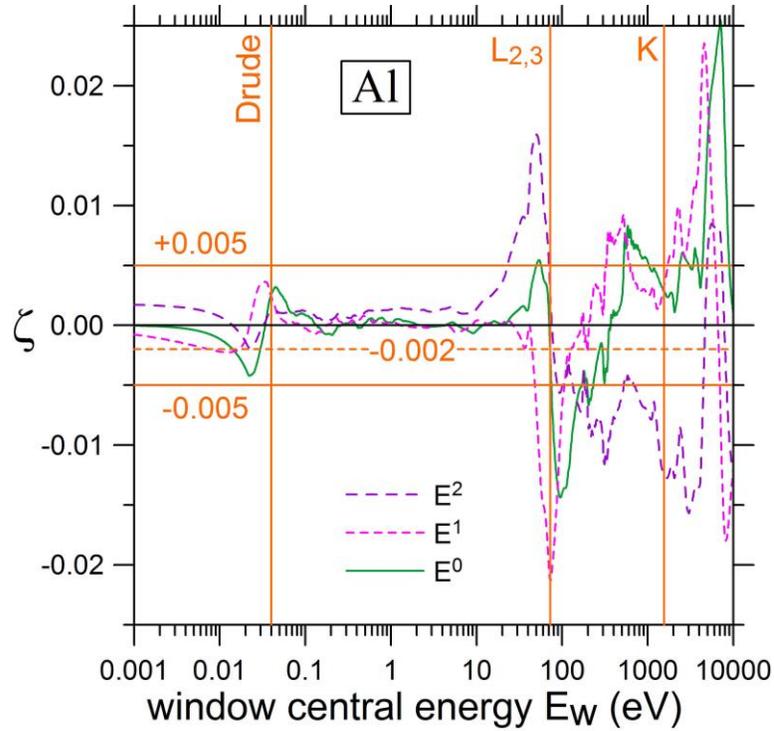


Fig. 6. Shiles's parameter ζ versus the central energy E_w of window functions for three inertial-like sum rules calculated with the optical constants of Al. The sum rules are identified in the legend by the power of photon energy in the integral. Window function is H_2 and its parameters are: $E_w=(E_1E_2)^{0.5}$, $E_2/E_1=3$, $c_{1(2)}=E_{1(2)}/10$. Shiles's suggested limits for ζ (± 0.005) and ζ value obtained in Ref. 11 for Al optical constants (-0.002) are displayed.

4. Conclusions

Window functions have been constructed to enhance the contribution of the spectral range of interest to sum rules for the evaluation of optical constant accuracy. In the desired spectral range, the imaginary part of the window functions could be made relatively constant. Outside that range, the two parts of one generated window function strongly decrease towards larger energies and the imaginary part also towards small energies. A second window function with its real part also decaying at small energies was also generated. The asymptotic decay of window functions was used to obtain a multiplicity of sum rules akin to the inertial sum rule. This multiplicity of sum rules combined with the selection of a photon energy range provides a double way to tune the spectral contribution within the sum rule. A tuneable version of f -sum rule in the small-energy range was also obtained.

Window functions were applied to real optical constant data of SrF_2 and Al thin films; in both cases, standard inertial sum rule with no window functions result in good values of the evaluation parameter. For SrF_2 , window functions tuned either at a certain experimental set of optical constants or at a range covered with an interpolation resulted in good values of the evaluation parameter, suggesting optical constant accuracy particularly at these specific ranges. A window function whose central energy continuously crossed the spectrum was applied to inertial-like sum rules of both SrF_2 and Al optical constants. For SrF_2 , good data accuracy determined through an evaluation parameter was found all over the spectrum, suggesting good consistency at every spectral range. However, for Al optical constants inaccuracies were observed at specific ranges. Hence the new sum rules with window functions are useful to discover a specific data range that is not accurate enough even though the standard inertial sum rule with no window function may not display this due to the compensation of inaccuracies in one spectral range with those in another one.

These new tools for sum-rule generation are called to improve the analysis of optical constant sets.

Acknowledgments

We acknowledge support by Spanish Programa Estatal de Investigación Científica y Técnica de Excelencia, Secretaría de Estado de Investigación, Desarrollo e Innovación, project number AYA2013-42590-P.

- ¹ M. Altarelli, D. L. Dexter, H. M. Nussenzveig, and D. Y. Smith, “Superconvergence and Sum Rules for the Optical Constants”, *Phys. Rev. B* **6**, 4502-4509 (1972).
- ² A. Villani and A. H. Zimerman, “Generalized f-sum rules for the optical constants”, *Phys. Lett.* **44A**, 295-297 (1973).
- ³ M. Altarelli, D. Y. Smith, “Superconvergence and sum rules for the optical constants: Physical meaning, comparison with experiment, and generalization”, *Phys. Rev. B* **9**, 1290-1298 (1974).
- ⁴ F. W. King, “Sum rules for the optical constants”, *J. Math. Phys.* **17**, 1509-1514 (1976).
- ⁵ D. Y. Smith, “Dispersion theory, sum rules, and their application to the analysis of optical data”, in *Handbook of optical constants of solids*, ed. E. D. Palik (Academic Press, San Diego, 1985, 1998), Chap. 3.
- ⁶ Y.-C. Liu, S. Okubo, “Tests of new π -N superconvergent dispersion relations”, *Phys. Rev. Lett.* **19**, 190-192 (1967).
- ⁷ A. Villani and A. H. Zimerman, “Superconvergent sum rules for the optical constants”, *Phys. Rev. B* **8**, 3914-3916 (1973).
- ⁸ G. Bimonte, “Generalized Kramers-Kronig transform for Casimir effect computations”, *Phys. Rev. A* **81**, 062501 (2010).
- ⁹ G. Bimonte, “Making precise predictions of the Casimir force between metallic plates via a weighted Kramers-Kronig transform”, *Phys. Rev. A* **83**, 042109 (2011).
- ¹⁰ V. Lucarini, J. J. Saarinen, K. -E. Peiponen, E. M. Vartiainen, *Kramers-Kronig relations in optical materials research* (Springer Series in optical sciences, Springer, 2005).
- ¹¹ E. Shiles, T. Sasaki, M. Inokuti, and D. Y. Smith, “Self-consistency and sum-rule tests in the Kramers-Kronig analysis of optical data: applications to aluminium,” *Phys. Rev. B* **22**, 1612–1628 (1980).
- ¹² L. Rodríguez-de Marcos, J. I. Larruquert, J. A. Aznárez, M. Fernandez-Perea, R. Soufli, J. A. Méndez, S. L. Baker, E. M. Gullikson, “Optical constants of SrF₂ thin films in the 25–780-eV spectral range”, *J. Appl. Phys.* **113**, 143501 (2013).
- ¹³ W. Kaiser, W. G. Spitzer, R. H. Kaiser, and L. E. Howarth, “Infrared Properties of CaF₂, SrF₂, and BaF₂,” *Phys. Rev.* **127**, 1950-1954 (1962).
- ¹⁴ D. R. Bosomworth, “Far-Infrared Optical Properties of CaF₂, SrF₂, BaF₂, and CdF₂”, *Phys. Rev.* **157**, 709-715 (1967).
- ¹⁵ J. Frandon, B. Lahaye, and F. Pradal, “Spectra of Electronic Excitations in CaF₂, SrF₂, and BaF₂ in the 8 to 150 eV Range”, *Phys. Status Solidi B* **53**, 565-575 (1972).
- ¹⁶ L. Rodríguez-de Marcos, J. I. Larruquert, J. A. Aznárez, M. Vidal-Dasilva, S. García-Cortés, J. A. Méndez, L. Poletto, F. Frassetto, A. M. Malvezzi, D. Bajoni, A. Giglia, N. Mahne, S. Nannarone, “Transmittance and optical constants of Sr films in the 6-1,220 eV spectral range”, *J. Appl. Phys.* **111**, 113533 (2012).
- ¹⁷ B. L. Henke, E. M. Gullikson, and J. C. Davis, *At. Data Nucl. Data Tables* **54**, 181 (1993).
- ¹⁸ http://henke.lbl.gov/optical_constants/
- ¹⁹ C. T. Chantler, K. Olsen, R. A. Dragoset, J. Chang, A. R. Kishore, S. A. Kotochigova, and D. S. Zucker, “X-ray form factor, attenuation and scattering tables,” *J. Phys. Chem. Ref. Data* **29**, 597–1048 (2000); C. T. Chantler, “Theoretical Form Factor, Attenuation and Scattering Tabulation for Z=1-92 from E=1-10 eV to E=0.4-1.0 MeV”, *J. Phys. Chem. Ref. Data* **24**, 71–643 (1995); available online: <http://physics.nist.gov/PhysRefData/FFast/html/form.html>
- ²⁰ Downloaded from Physical Reference Data, Physics Laboratory at NIST: <http://physics.nist.gov/PhysRefData/FFast/Text/cover.html>.