development of micro-instrumentation, by combining scanning near-field microscopy with SERS.

See also: Nanostructures, Optical Properties of; Plasmons; Polaritons; Scattering, Inelastic: Raman; Semiconductors, Optical and Infrared Properties of; Time-Resolved Optical Spectroscopies; Treated Surfaces, Optical Properties of.

PACS: 78.; 78.20. − e; 78.20.Ci; 78.30. − j; 33.20.Fb; 68.43.Pq; 78.67.Bf; 78.68. + m; 78.40.Kc; 71.36. + c; 71.45.Gm

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Optical Sum Rules and Kramers–Kronig Relations

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Introduction

The optical properties of atoms, molecules, and solid materials have been an active field of research for the past two centuries and have given the most precise information on the microscopic structure of matter. Since the early nineteenth century, it was known that absorption peaks in the light intensity occur at specific frequencies and that a corresponding dispersion occurs in the frequency dependence of the dielectric function $\varepsilon(\omega)$ (or in the refractive index $n(\omega)$).

It may be recalled that in any medium all the optical functions (dispersion, absorption, reflection, etc.) depend on the frequency ω and on the momentum of the photon $\hbar k = \hbar(2\pi/\lambda)$, $\hbar$ being the reduced Planck constant. They can all be expressed in terms of the dielectric functions $\tilde{\varepsilon}(k, \omega)$ extended to the complex plane. From Maxwell equations, it can be seen that its imaginary part can be expressed in terms

of the conductivity σ, so that

$$\tilde{\varepsilon}(k, \omega) = \varepsilon_1(k, \omega) + i\varepsilon_2(k, \omega)$$
$$= 1 + 4\pi\chi(k, \omega) + \frac{4\pi\sigma(k, \omega)}{\omega}i \qquad [1]$$

where the real susceptibility χ is defined in terms of the polarization P (dipole moment per unit volume) and of the electric field E by

$$\chi(k, \omega) = \frac{P(k, \omega)}{E} \qquad [2]$$

If the susceptibility is also extended to the complex plane to include the conductivity, so that

$$\tilde{\chi}(k, \omega) = \chi(k, \omega) + \frac{i\sigma(k, \omega)}{\omega} = \chi_1 + i\chi_2 \qquad [3]$$

where the subscripts 1 and 2 denote the real and imaginary parts, respectively, the usual expression for the complex dielectric function obtains $\tilde{\varepsilon}(k, \omega) = 1 + 4\pi\tilde{\chi}(k, \omega)$. This also defines a complex

refractive index

$$\tilde{n}(\boldsymbol{k}, \omega) = \sqrt{\tilde{\varepsilon}}(\boldsymbol{k}, \omega) = n(\boldsymbol{k}, \omega) + \mathrm{i}\kappa(\boldsymbol{k}, \omega) \quad [4]$$

The absorption of radiation can be related to the conductivity induced by the electric field by considering the energy lost per unit time per unit volume

$$\frac{\mathrm{d}W}{\mathrm{d}t} = \boldsymbol{J} \cdot \boldsymbol{E} = \frac{\mathrm{d}\boldsymbol{P}}{\mathrm{d}t} \cdot \boldsymbol{E} = \sigma E^2 \quad [5]$$

so that the absorption coefficient $\eta(\omega)$, defined as $\mathrm{d}W/\mathrm{d}x = -\eta W = (\mathrm{d}W/\mathrm{d}t)\,(n/c)$, is given by

$$\eta = \left| \frac{\mathrm{d}W}{\mathrm{d}t} \right| \frac{n}{Wc} = \frac{4\pi\sigma}{nc} = \frac{\omega\varepsilon_2}{nc} = \frac{2\omega\kappa}{c} \quad [6]$$

Also the reflection and transmission amplitudes can be obtained from the dielectric function through Fresnel relations, which in the case of normal incidence from vacuum to a medium are

$$\frac{E_r}{E_0} = r = \frac{\tilde{n} - 1}{\tilde{n} + 1}, \qquad \frac{E_t}{E_0} = t = \frac{2}{\tilde{n} + 1} \quad [7]$$

$R = |r|^2$ and $T = n|t|^2$ being the reflectivity and the transmittance, respectively.

In crystalline materials, the optical constants are tensors (second-rank tensors in the linear approximation), but this aspect may be neglected and isotropic media may be considered for the purpose. The results obtained will apply to all tensorial components.

For electromagnetic waves, the magnetic susceptibility is considered unitary and one can also use the dipolar approximation ($\hbar k \simeq 0$) because of the very small light momentum (neglect of spatial dependence).

The above-described optical functions give the electromagnetic properties of matter. Their detailed dependence on frequency is related to the microscopic structure of the material considered and to its interaction with the radiation field. Here, the general properties of the optical functions that depend only on time causality are considered.

Elementary Description of Sum Rules

The traditional phenomenological model for the optical constants is the Lorentz oscillator model, where the equation of motion from the equilibrium position of any specific electron in terms of any oscillator frequencies ω_j and of damping γ_j, is given by

$$\frac{\mathrm{d}^2 x}{\mathrm{d}t^2} + \omega_j^2 x + \frac{\gamma_j\,\mathrm{d}x}{\mathrm{d}t} = \frac{eE}{m} \quad [8]$$

From this, for the complex dielectric function in a volume V for a number of resonance frequencies ω_j, one obtains

$$\tilde{\varepsilon}(\omega) = 1 + \frac{4\pi e^2}{mV} \left(\sum_j \frac{f_j}{(\omega_j^2 - \omega^2) - \mathrm{i}\gamma_j\omega} \right) \quad [9]$$

where the oscillator strength f_j gives the intensity of the resonance frequency ω_j with damping constant γ_j. The conservation of the electron number and the asymptotic behavior ($\omega \to \infty$) of [9], made to coincide with that of any free electrons ($f_i = 1$, $\omega_j = 0$, $\gamma_j = 0$), immediately gives the f-sum rule, first demonstrated in 1925 by W Thomas, F Reiche, and W Kuhn, and called the TRK sum rule:

$$\sum_j f_j = n \quad [10]$$

This states that the sum of the oscillator strengths of all optical transitions is equal to the total number of electrons n.

Although the TRK sum rule was derived with classical mechanics, it is worth mentioning that the quantum description of the oscillator strength implies that, for the sum rule to hold, the commutation relations between momentum and position operator must also hold, as pointed out by Heisenberg. In fact one can see, by expressing the optical functions in terms of the transition probability rates, observing that electrons are excited from state i to state f, with a probability rate given by the Fermi golden rule

$$P_{if} = \frac{2\pi}{\hbar} |\langle f|eEx|i \rangle|^2 \delta(E_f - E_i - \hbar\omega) \quad [11]$$

that the quantum mechanical expression for the imaginary part of the dielectric function is

$$\varepsilon_2(\omega) = 4\pi^2 \sum_{ij} |\langle f|ex|i \rangle|^2 \delta(E_f - E_i - \hbar\omega) \quad [12]$$

Considering in expression [9] that

$$\lim_{\gamma \to 0} \frac{\gamma}{(\omega_j - \omega)^2 + (\gamma/2)^2} = 2\pi\delta(\omega_j - \omega) \quad [13]$$

and comparing with [12] it is obtained that the quantum mechanical expression for the oscillator strength is

$$f_{fi} = \frac{2m}{\hbar^2} |\langle f|x|i \rangle|^2 (E_f - E_i) \quad [14]$$

Taking into account the general Heisenberg expression for the time dependence of the displacement x,

$$m\dot{x} = \frac{m}{i\hbar}[x, H] \qquad [15]$$

where the square brackets denote commutators, and considering the expression for eigenstates,

$$H|j\rangle = E_j|j\rangle \qquad [16]$$

one obtains for the oscillator strength

$$
\begin{aligned}
f_{fi} &= \frac{2m}{\hbar^2}\langle i|x|f\rangle\langle f|x|i\rangle(E_f - E_i) \\
&= \frac{1}{i\hbar}(\langle i|x|f\rangle\langle f|p_x|i\rangle \\
&\quad - \langle i|p_x|f\rangle\langle f|x|i\rangle)
\end{aligned} \qquad [17]
$$

which, summing over the final states, gives

$$\sum_f f_{fi} = \frac{1}{i\hbar}\langle i|[x, p_x]|i\rangle = 1 \qquad [18]$$

because of Heisenberg commutation rules $[x, p_x] = i\hbar$. Summing over all occupied initial states, one obtains immediately the TRK sum rule [10].

In general, the oscillator strength depends continuously on the frequency, so that the TRK sum rule can be expressed in terms of the imaginary part of the dielectric function as

$$\int_0^\infty \omega\varepsilon_2(\omega)\,d\omega = \frac{2\pi^2 e^2}{m}\varrho \qquad [19]$$

which relates the total radiation absorbed to the total electron density $\varrho = n/V$.

This is a very important property, because it gives a general constraint which the absorption of the medium must obey. When the sum rule [19] is saturated at a given frequency, no further absorption can occur at higher frequencies. This explains why in light elements (low electron density) hard X-rays are not absorbed and hard γ-rays pass through all materials. The sum rule [19] is also useful to check the results of approximate calculations or experiments. It must always be obeyed by the exact optical functions.

Kramers–Kronig Dispersion Relations

A connection between sum rules and the causality principle was established on the basis of the relation between the real and the imaginary parts of the susceptibility $\tilde{\chi}(\omega)$. This can be obtained by considering the complex ω plane and observing that the susceptibility does not have poles on the upper plane because the polarization can be expressed from the time-dependent response operator $G(\tau)$ as

$$P(t) = \int_{-\infty}^{+\infty} G(\tau)E(t - \tau)\,d\tau \qquad [20]$$

with the condition $G(\tau) = 0$ for $\tau < 0$ due to time causality. Then, taking the Fourier transform, one obtains

$$\tilde{P}(\omega) = \tilde{\chi}(\omega)E(\omega) \qquad [21]$$

with

$$\tilde{\chi}(\omega) = \int_0^\infty G(\tau)\exp(i\omega\tau)\,d\tau \qquad [22]$$

The fact that $\tilde{\chi}(\omega)$ is analytic in the upper complex plane gives, using the Cauchy theorem on a contour closed to infinity where $\tilde{\chi}(\omega)$ goes to zero (see **Figure 1**)

$$\tilde{\chi}(\omega) = \frac{1}{\pi i}\fint_{-\infty}^{+\infty} \frac{\tilde{\chi}(\omega')}{\omega' - \omega}\,d\omega' \qquad [23]$$

where the line on the integral denotes that the principal part must be considered. Since $\chi(-\omega) = \chi^*(\omega)$, the standard form of Kramers–Kronig (KK) relations is obtained:

$$\chi_1(\omega) = \frac{2}{\pi}\fint_0^\infty \frac{\omega'\chi_2(\omega')}{\omega'^2 - \omega^2}\,d\omega' \qquad [24a]$$

$$\chi_2(\omega) = \frac{-2\omega}{\pi}\fint_0^\infty \frac{\chi_1(\omega')}{\omega'^2 - \omega^2}\,d\omega' \qquad [24b]$$

In the case of metals, besides the pole at ω, the function $\tilde{\chi}(\omega')/(\omega' - \omega)$ has an additional pole at $\omega' = 0$ because $\sigma(0) \neq 0$. This can be taken into account by considering the function $\tilde{\chi} - (\sigma(0)/\omega)i$, which does not have such a pole and is analytic
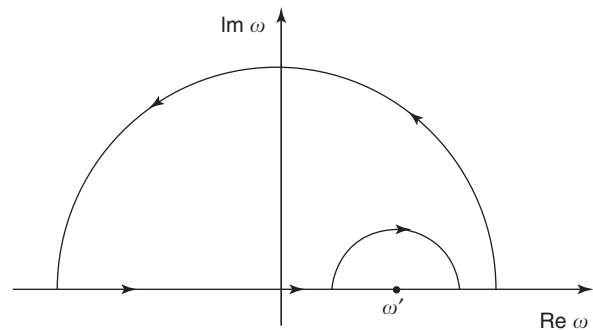

Figure 1 Indication of the contour on the complex plane where the integral of the function $\chi(\omega')/(\omega' - \omega)$ by Cauchy theorem is equal to $i\pi\chi(\omega)$.

on the upper plane. Then dispersion relations [23] and [24] apply, provided the term $-\sigma(0)/\omega$ is added to the imaginary part of $\tilde{\chi}(\omega)$ and the principal part of the integrals is considered along the entire real axis, including the point at $\omega = 0$, where $\tilde{\chi}_2(\omega')$ has a pole.

The above KK relations are very useful because they relate the dispersion to the absorption. Similar relations can be obtained for the other optical constants $\tilde{\sigma}$, $\tilde{n}(\omega)$, r, and $\text{Im}(1/\varepsilon)$.

They can all be connected to specific sum rules by considering the asymptotic behavior which can be obtained from the KK relations, and comparing it to that which is obtained from a specific model of the material system. Since the asymptotic behaviors must coincide, sum rules are obtained. It can be seen immediately that the TRK sum rule [10] or [19] can be obtained when one considers the asymptotic behavior from [24a] by using the so-called super-convergence theorem, which amounts to letting $\omega' \to 0$ in the denominator, and comparing it with the asymptotic behavior from expression [9] ($\omega_j \to 0$ in the denominator).

As a consequence of the above discussion, one can conclude that sum rules and KK dispersion relations derive from the causality principle only, and from a knowledge of the short-time (or high-frequency) behavior of the system. Complicated properties due to electron–electron interaction or external potentials are not relevant for sum rules and Kramers–Kronig relations. Also the quantum mechanical approach is not essential.

A revival of the field of sum rules started in the early 1970s after the discovery of the refractive index sum rule by Altarelli, Dexter, Nussezveig, and Smith (ADNS), which states for the real part of the refractive index

$$\fint_0^\infty (n(\omega) - 1)\, d\omega = 0 \qquad [25]$$

After that new sum rules and more KK-type relations were derived for all optical functions and are now being used to interpret a variety of effects. New KK relations and sum rules have also been found in nonlinear optics. Sum rules can now be explored in the entire frequency range using the properties of synchrotron radiation. They are also being used as stringent tests for approximate theories.

KK Relations and Linear Sum Rules

The KK relations [24] for the complex susceptibility function have been derived by direct integration, but causality and KK relations have more direct implications; they can be summarized in what is known as a Titchmarsh theorem, which states the following: any square integrable function $f(\omega)$ which fulfills one of the three conditions below fulfills all three of them:

1. the inverse Fourier transform $F(t)$ of $f(\omega)$ vanishes for $t < 0$,
2. $f(\omega)$ is the limit for $\varepsilon \to 0^+$ of a function $\tilde{f}(\omega + i\varepsilon)$ that is analytic in the upper half plane and square integrable on the real axis and on any line parallel to it, and
3. $\tilde{f}(\omega)$ verifies the KK identity

$$\tilde{f}(\omega) = \frac{1}{\pi i} \fint_{-\infty}^{\infty} \frac{\tilde{f}(\omega')}{\omega' - \omega}\, d\omega' \qquad [26a]$$

or equivalently for $F(t)$ real,

$$f_1(\omega) = \frac{2}{\pi} \fint_0^\infty \frac{\omega' f_2(\omega')}{\omega'^2 - \omega^2}\, d\omega'$$
$$f_2(\omega) = -\frac{2\omega}{\pi} \fint_0^\infty \frac{f_1(\omega')}{\omega'^2 - \omega^2}\, d\omega' \qquad [26b]$$

The above theorem proves that KK relations are a direct consequence of time causality, but it also implies that any combinations of analytic functions satisfy KK relations if they are square integrable. For establishing KK relations, it is not necessary to know the explicit form of the causal response function, which is determined by the specific operator being considered, by the Hamiltonian, and by the time-dependent perturbing potential. One only needs to know its asymptotic behavior which can be obtained in the classical approximation from the Lorentz oscillator model, or in the quantum theory from the quantum expression of the response function at time zero. The same holds for the sum rules, which are obtained by comparing the above described asymptotic behavior with that obtained from KK relations.

Consider the optical case in the dipole approximation. The interaction Hamiltonian can then be written as

$$H' = -\mathbf{P} \cdot \mathbf{E}(t) \qquad [27]$$

where $\mathbf{P} = \sum_i e\mathbf{r}_i$ is the polarization (it can be used as an operator in quantum mechanics) and $\mathbf{E}(t)$ is the electric field, which is taken as a sinusoidal function. While in the classical approximation one considers directly the time dependence of the $\mathbf{P}_+$ (Lorentz oscillator model), in the quantum mechanical approach the response function can be obtained from the trace of the density matrix operator ϱ_0 on the ground state

of the system, and to the first order is given by

$$G_p(\tau) = \mathrm{Tr}\left\{\frac{1}{-i\hbar}\,[P(-\tau),\,\varrho_0]P\right\} \qquad [28]$$

where $P(\tau)$ is defined in the interaction representation. This gives, for the susceptibility, the expression

$$\chi(\omega) = \frac{1}{\hbar}\sum_n |\langle 0|P|n\rangle|^2$$
$$\times\left\{\frac{1}{\omega - \omega_{n0} + i\varepsilon} - \frac{1}{\omega + \omega_{n0} + i\varepsilon}\right\} \qquad [29]$$

where ε is an arbitrarily small frequency which accounts for the adiabatic switching of the perturbation.

The sum rules can now be obtained from the two expressions of the asymptotic behavior, which must coincide. The first is given by the zero-time response function and its derivatives, and can be obtained integrating by part the Fourier transform of $G(\tau)$, with $G(\infty) = 0$:

$$\chi_{\omega\to\infty}(\omega) = \int_0^\infty G(\tau)\,\exp(-i\omega\tau)\,\mathrm{d}\tau$$
$$= \frac{G(0^+)}{-i\omega} + \frac{G'(0^+)}{-\omega^2} + \frac{G''(0^+)}{-i\omega^3}$$
$$+ \frac{G'''(0^+)}{\omega^4} + \cdots \qquad [30]$$

where the time derivatives are denoted with the apex. The second is obtained from the KK relations [24] with the superconvergence theorem,

$$\chi_1 \underset{\omega\to\infty}{=} -\frac{2}{\pi\omega^2}\int \omega'\chi_2(\omega')\,\mathrm{d}\omega' + O(\omega^{-2}) \qquad [31a]$$

$$\chi_2 \underset{\omega\to\infty}{=} -\frac{2}{\pi\omega}\int \chi_1(\omega')\,\mathrm{d}\omega' + O(\omega^{-1}) \qquad [31b]$$

By computing the limits of expression [30], it can be seen that $G(0^+) = 0$, $G'(0^+) = \omega_p^2/4\pi$, etc. One can see immediately that two sum rules are obtained: The first from the asymptotic behavior of the real part is the TRK sum rule

$$\int_0^\infty \omega'\chi_2(\omega')\,\mathrm{d}\omega' = \frac{\pi}{2}\frac{\mathrm{d}}{\mathrm{d}t}G(t)\big|_{t=0^+} = \frac{1}{8}\omega_p^2 \qquad [32]$$

where $\omega_p^2 = 4\pi e^2\varrho/m$. The second refers to the asymptotic behavior [31b] of the imaginary part of the susceptibility which, by comparing with [30] is

$$\int_0^\infty \chi_1(\omega')\,\mathrm{d}\omega' = \frac{\pi}{2}G(t)\big|_{t=0^+} = 0 \qquad [33]$$

where the second equality can be obtained from the quantum mechanical expression [28] of $G(t)$ or from the Lorentz oscillator model.

In the case of metals, the imaginary part of $\chi(\omega)$ has a pole $\omega = 0$ due to the fact that the conductivity $\sigma(\omega)$ is different from zero at zero frequency. As shown for the KK relations, this can be handled by adding to $\tilde{\chi}(\omega)$ the term $(-(\sigma(0)/\omega)i)$ which cancels the pole, preserving the properties of the function. This is the dominant term in the asymptotic behavior for $\omega\to\infty$, so that, by comparing with [31b] the sum rule for metals is obtained:

$$\int_0^\infty \chi_1(\omega')\,\mathrm{d}\omega' = \frac{\pi}{2}\sigma(0) \qquad [34]$$

Other similar sum rules can be obtained for all optical constants (conductivity σ, refractive index $\tilde{n}$, $\varepsilon^{-1}(\omega)$) in the same way as described above, because they are all related to the real and imaginary parts of the susceptibility. Since conductivity is related to the susceptibility by $\sigma(k,\omega) = -i\omega\chi$, the sum rule [32] gives directly

$$\int_0^\infty \mathrm{Re}\,\sigma(k,\,\omega)\,\mathrm{d}\omega' = \frac{\omega_p^2}{8} \qquad [35]$$

which has been used in superconductors. Analogous to eqn [33] is the ADNS sum rule [25] for the real part of the index of refraction, which can be obtained immediately from the observation that the dispersion relations [26b] apply to $\tilde{n}(\omega) - 1$ for both the metallic and nonmetallic media, and that the asymptotic behavior of the complex refractive index is

$$\tilde{n}_{\omega\to\infty}(\omega) \simeq 1 - \frac{\omega_p^2}{2\omega^2} + O(\omega^{-2}) \qquad [36]$$

As a consequence, the ADNS sum rule [25] is obtained for both metallic and nonmetallic media.

Longitudinal Sum Rules

Sum rules can also be obtained for the longitudinal dielectric function $\varepsilon_l(\boldsymbol{k},\omega)$. This is given by the response of the electron density to an external scalar perturbation, which in $\boldsymbol{k}$ space takes the form

$$\Delta\varrho(\boldsymbol{k},\omega) = \chi_l(\boldsymbol{k},\omega)\phi(\boldsymbol{k},\omega) \qquad [37]$$

The relation between $\chi_l(\boldsymbol{k},\omega)$ and $\varepsilon_l(\boldsymbol{k},\omega)$ is obtained from the Maxwell equations

$$\varepsilon_l^{-1}(\boldsymbol{k},\,\omega) = 1 + \frac{4\pi e}{k^2}\chi_l(\boldsymbol{k},\omega) \qquad [38]$$

A number of phenomena are related to the longitudinal dielectric function, such as the screening of charges, the scattering of electrons, with the expression for the probability for unit time and unit volume that an electron transfers momentum k, and energy $\hbar\omega$ to the medium:

$$P(\boldsymbol{k}, \omega) = -\frac{8\pi e^2}{k^2 \hbar V} \, \text{Im} \, \varepsilon_l^{-1}(\boldsymbol{k}, \omega) \qquad [39]$$

The sum rules for $\varepsilon_l^{-1}(\boldsymbol{k}, \omega)$ can be obtained with the same procedure used for the optical susceptibility and are

$$\int_0^\infty [\text{Re} \, \varepsilon_l^{-1}(k, \omega) - 1] \, \text{d}\omega = 0 \qquad [40]$$

and

$$\int_0^\infty \omega \, \text{Im} \, \varepsilon_l^{-1}(k, \, \omega) \, \text{d}\omega = \frac{\pi}{2} \, \omega_p^2 \qquad [41]$$

where $\omega_p^2 = (4\pi e^2/m)\varrho$ is the plasma frequency. This can be referred to the density of the valence electrons to give the contribution of plasma resonances in metals, but when ϱ includes all the electrons of the medium the sum rule is saturated for $k \to 0$ so that no other longitudinal excitations are present.

Relativistic and Spatial-Dependent Corrections

One can extend the sum rules beyond the dipole approximation, by considering spatial dispersion and the relativistic definition of the current from the Dirac equation. One must consider the fact that k is related to ω by the expression $\varepsilon(k,\omega)\omega^2 = k^2(\omega)c^2$ so that one must take this into account when performing the integration over frequency.

One can be limited to first-order contributions because of the small value of $|k|$ in optics. The lowest-order contribution is of order k^2 because the linear term vanishes due to time reversal. Following Ginzburg and Meiman, a Taylor expansion about $k = 0$ can be obtained as

$$\varepsilon\left(\frac{\partial^2 \varepsilon}{\partial k^2} \frac{\omega\sqrt{\varepsilon}}{c}, \, \omega\right)$$
$$\simeq \varepsilon(0, \omega) + \frac{\omega^2}{2c^2} \, \varepsilon\left(\frac{\omega\sqrt{\varepsilon}}{c}, \, \omega\right) \frac{\partial^2 \varepsilon}{\partial k^2}\bigg|_{t=0} \qquad [42]$$

which gives

$$\varepsilon\left(\frac{\omega\sqrt{\varepsilon}}{c}, \, \omega\right) \simeq \frac{\varepsilon(0, \omega)}{1 - (\omega^2/2c^2) \, (\partial^2\varepsilon/\partial k^2)|_{k=0}} \qquad [43]$$

The calculation of the second derivative of the dielectric function with an inclusion of relativistic corrections has been carried out by Scandolo, Bassani, and Lucarini; it is rather complex and is not to be reported here. When the result is substituted in the frequency dependence [43], its asymptotic behavior is obtained, and the sum rules can be derived in the usual way with spatial dispersion and relativistic corrections. The sum rule on the real part of the susceptibility is unchanged and gives zero, and that on the imaginary part is modified by a contribution which depends on the expectation value of the kinetic energy of the electrons on the total ground state of the system $T_0 = \langle 0|\frac{1}{2}mv^2|0\rangle$. The result is

$$\int_0^\infty \omega' \varepsilon_2(\omega') \, \text{d}\omega' = \frac{\pi}{2} \, \omega_p^2 \left(1 - \frac{2}{3} \frac{T_0}{mc^2}\right) \qquad [44]$$

This correction is very small, of the order of $\approx 10^{-3}$ in Al, where tests of the sum rule have been made, but it may be easily detected in heavy materials using synchrotron radiation up to very high frequencies.

Applications

Applications of the above described sum rules and KK relations are innumerable and have been of great help in understanding the basic properties of optics in condensed matter. They explain immediately why above a given frequency, all materials are transparent to the electromagnetic radiation.

They show immediately the strict connection between the absorption edge in solids and the value of the static dielectric constant.

The KK dispersion relations have allowed the determination of the optical constants from the measurements of only one of them on the entire optical spectrum (for instance, the reflectivity in semiconductors, where the transmittance cannot be measured because it is too small). In that case, KK dispersion relations can be derived for the reflectivity amplitude. They connect the measured reflectivity R to the phase θ through the function

$$\ln r = \ln |r| + i\theta = \tfrac{1}{2} \ln R(\omega) + i\theta(\omega) \qquad [45]$$

which has been proven to have the required analytic behavior in the upper half of the complex ω plane. One can then obtain the phase, and from eqn [7] the complex refractive index and all optical constants. This has allowed the knowledge of the optical transitions in solids, and consequently of the electronic band structure over an extended energy range.

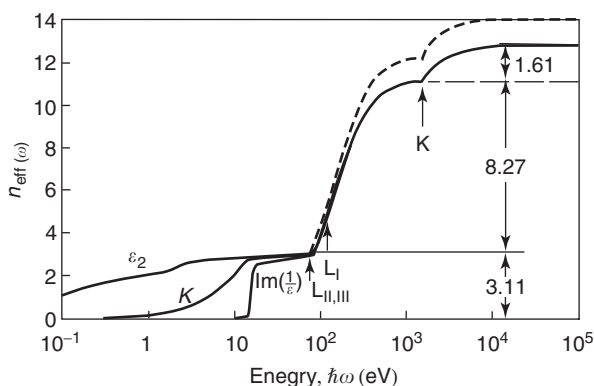The availability of synchrotron radiation of frequency over a very extended range has furthermore

Figure 2 Sum rule for ε_2, κ, and $-\text{Im}(\varepsilon_l^{-1})$: in Al, the solid line shows the saturation at $n = 13$. (E Shiles, T Sasaki, M Inokuti, and DY Smith (1980) *Physical Review B* 22: 1612.)

allowed the direct verification of the sum rules. **Figure 2** reports the results obtained on the metal Al. Further, more detailed analysis on heavy materials would allow the verification of the relativistic and spatial dispersive correction given by expression [44].

See also: Elemental Semiconductors, Electronic States of; Interaction of Light and Matter; Optical Absorption and Reflectance; Optical Properties of Materials; Semiconductor Compounds and Alloys, Electronic States of; Semiconductor Optics.

PACS: 78.20. – e; 78.40. – q; 11.55.Hx

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Organic Semiconductors

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Introduction: Materials

Organic semiconductors are molecular materials with vanishing density of states around the Fermi energy and an energetic gap of ~ 1–5 eV between the highest occupied and the lowest unoccupied states. Contrary to inorganic semiconductors, the optical and transport gaps may differ by more than 1 eV because they are related to different kinds of crystal excitations: the optical response is dominated by Frenkel excitons arising from neutral molecular excitations, and the transport gaps refer to charge transfer (CT) between different molecular sites in the limit of infinite intermolecular distance.

The highest valence band results from the highest occupied molecular orbital (HOMO), and the lowest conduction band from the lowest unoccupied molecular orbital (LUMO). Two contributions to the band dispersion have to be distinguished: strong interactions between adjacent covalently bound building blocks in long oligomers or polymers, and weak intermolecular interactions. The latter give rather small transfer matrix elements between adjacent molecules, restricting the bandwidths of the charge carriers to typically less than 0.5 eV.

Three material classes can be distinguished: polymers, crystalline or amorphous solids composed of identical polycyclic molecules, and organic salts composed of two different kinds of molecules. In the last case, the condensed phase favors electron transfer from the sites with the smaller ionization potential toward the molecules with the stronger electron affinity. The electronic states of polymers and oligomers with a large number of repeating units are covered elsewhere in the encyclopedia (refer "See also" section), and the present article concentrates on the properties of solids composed of identical molecules. Some prototypic planar molecules forming one or several semiconducting crystal phases are discussed, compare **Figure 1**. The optical properties of the monomers are related to the electronic orbitals involved in the dipole-allowed transitions, highlighting the importance of the deformation in the relaxed excited state of the molecule both for the optical response and for resonant Raman spectra.