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Simplest microscopic models

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• Revision of classical mechanics (vibrations and waves). Revision of fundamentals of the interaction of electromagnetic waves with matter in quantum mechanics, esp. that with isolated atoms.

• Classical models (Lorentzian oscillator and Drude response of free carriers) are very helpful and instructive. They also allow a specification of the link of microscopic and averaged quantities.

• The simples quantum models are based on perturbation theory. They form a convenient framework for understanding response functions related to one-electron picture of (direct and indirect) transitions of valence electrons in crystals.

Lorentzian oscillator

Charges bound elastically to their equilibrium positions are dislocated by the electrical force of the electromagnetic wave (the magnetic component is negligible). In a harmonic wave travelling along *z*, the wavelength is supposed to be large compared to the spatial structure of the investigated charges; the relevant quantity is then the displacement ***r*** of the charge *e* in the plane perpendicular to *z*. The force is proportional to the intensity of the electric field of the wave,

$$\vec{E}\left(z,t\right)=\vec{E}_o e^{i\left(k_z z-\omega t\right)} \quad .$$

Newtonian equation of motion for the displacement of damped harmonic oscillator of the mass *m* at an arbitrary position *z*:

$$m\frac{\mathrm{d}^2\vec{r}}{\mathrm{d}t^2}=-m\omega_o^2\vec{r}-\frac{m}{\tau}\frac{\mathrm{d}\vec{r}}{\mathrm{d}t}-e\vec{E}_o e^{-i\omega t} \quad .$$

Neglecting the contribution of possible vibrations at the eigenfrequency ω_o, which is small at times long compared to τ , the solution is a harmonic movement with the frequency ω ,

$$\vec{r}=-\frac{e}{m}\frac{1}{\omega_o^2-\omega^2-i\dfrac{\omega}{\tau}}\vec{E}_o e^{-i\omega t} \quad .$$

The complex values of intensity lead to complex values of the displacement (they have magnitude and *phase*).

The displacement of the charge produces the dipole moment

$$\vec{p} = -e\vec{r} = \alpha\vec{E} \ , \quad \alpha = \frac{e^2}{m}\frac{1}{\omega_o^2 - \omega^2 - i\dfrac{\omega}{\tau}} \ ,$$

proportional to the electric field; α is called electrical polarizability. It disappears for zero charge (no dipole moment) and infinite mass (no displacement). The frequency dependence exhibits a resonance close to the eigenfrequency of the oscillator.
With N oscillators in a unit volume, the volume density of the dipole moment (polarization) is

$$\vec{P} = N\vec{p} = N\alpha\vec{E} \equiv \chi\varepsilon_o\vec{E} \ ;$$

it is proportional to the intensity of the wave; the dimensionless coefficient (note the presence of the vacuum permittivity, SI units) χ is called susceptibility (“vaspriimčivost’” in Russian – the ability to accept the influence of the external field). The ensemble of oscillators is characterized by

$$\chi = \frac{Ne^2}{\varepsilon_o m}\frac{1}{\omega_o^2 - \omega^2 - i\dfrac{\omega}{\tau}} \ .$$

The SI unit of polarization is C/m^2, the same as that of area density of charge, or of the electric displacement D.

Dielectric function is dimensionless proportionality factor between the electric displacement and field intensity:

$$\vec{D} = \varepsilon\varepsilon_o\vec{E} = \varepsilon_o\vec{E} + \vec{P} = \varepsilon_o(1+\chi)\vec{E} \quad \rightarrow \quad \varepsilon = 1 + \chi \quad .$$

It represents the susceptibility added to to unity (the vacuum contribution to the electric displacement). The ensemble of charged oscillators with the same eigenfrequency and volume density *N* leads to

$$\varepsilon = 1 + \frac{Ne^2}{\varepsilon_o m}\frac{1}{\omega_o^2 - \omega^2 - i\dfrac{\omega}{\tau}} = 1 + \frac{S\omega_o^2}{\omega_o^2 - \omega^2 - i\dfrac{\omega}{\tau}} \quad \text{, where } S = \frac{Ne^2}{\omega_o^2\varepsilon_o m} \quad .$$

Here, S is dimensionless “oscillator strength”, determining the “magnitude of the spectral structure”; it has a further simple meaning, as it is equal to the contribution of the oscillators to static permittivity (dielectric function at zero frequency). The eigenfrequency of oscillators determines the “spectral position” and the damping time τ determines the “spectral width”.

The usual notation for the real and imaginary part of the dielectric function uses subscripts 1 and 2:

$$\varepsilon = \varepsilon_1 + i\varepsilon_2 \quad .$$

In the complex plane of frequencies, the dielectric function of Lorentzian oscillators has two poles (the roots of the denominator):

$$\varepsilon = 1 - \frac{S\omega_o^2}{(\omega-\omega_1)(\omega-\omega_2)} \quad ,$$

$$\omega_1 = -\frac{i}{2\tau} + \sqrt{\omega_o^2 - \frac{1}{4\tau^2}} \quad , \quad \omega_2 = -\frac{i}{2\tau} - \sqrt{\omega_o^2 - \frac{1}{4\tau^2}} \quad .$$

This form leads to a common approximate result fro the Lorentzian spectral profile in case of the weak damping. Namely, for

$\frac{1}{\tau} << \omega_o$, the approximation can be expressed as

$$\varepsilon \approx 1 - \frac{S\omega_o^2}{2\omega_o\left(\omega - \omega_o + \frac{i}{2\tau}\right)} = 1 + \frac{S\omega_o}{2}\frac{\omega_o - \omega}{(\omega_o-\omega)^2 + \frac{1}{4\tau^2}} + i\frac{S\omega_o}{2}\frac{\frac{1}{2\tau}}{(\omega_o-\omega)^2 + \frac{1}{4\tau^2}} \quad .$$

This approximation can be used only for the frequencies close to the eigenfrequency, due to the following approximation of the poles in the complex plane,

$$\omega_{1,2} \approx -\frac{i}{2\tau} \pm \omega_o \quad \text{and} \quad \omega - \omega_2 \approx 2\omega_o \quad ,$$

usable for small damping. Within this approximation, the imaginary part of ε is bell-shaped, symmetric lineshape about the eigenfrequency, with the maximum of

$$\varepsilon_{2,\max} = S\omega_o\tau \quad .$$

Full width at half-maximum (FWHM) is

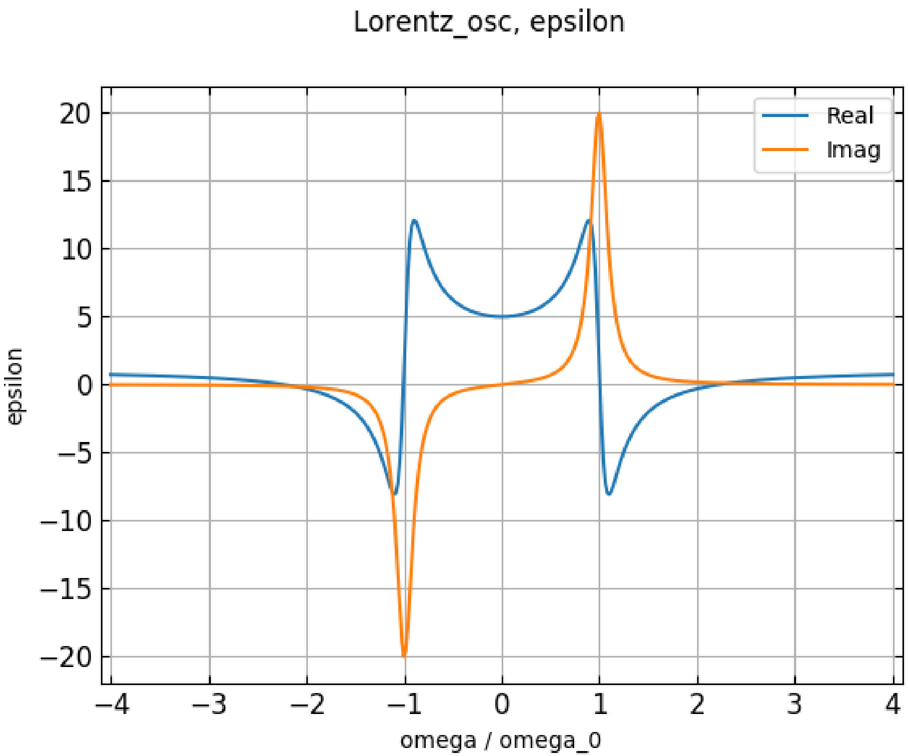
$$\Delta\omega = 1/\tau \quad .$$

Real part is antisymmetric about the eigenfrequency.

Spectral lineshapes on the real axis of frequencies complies with the general requirement

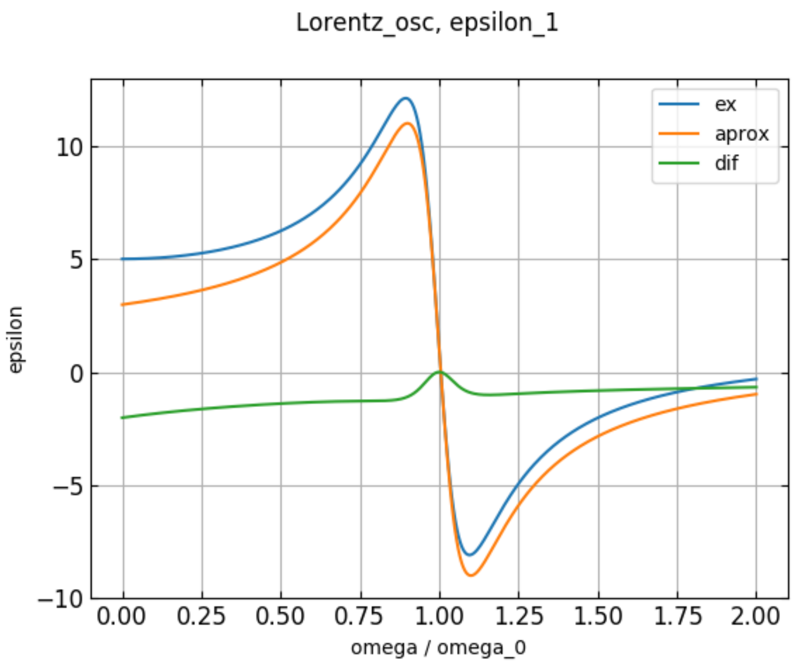
$$\varepsilon(-\omega) = \varepsilon^*(\omega) \quad ,$$

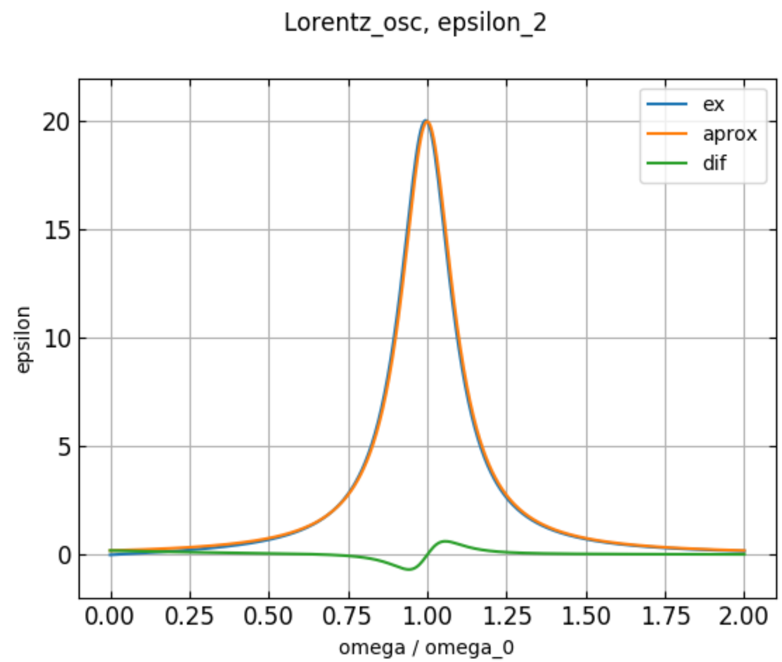
where the asterix denotes complex conjugation.



Dielectric function of Lorentz oscillators (S=4, tau*omega_0=5).

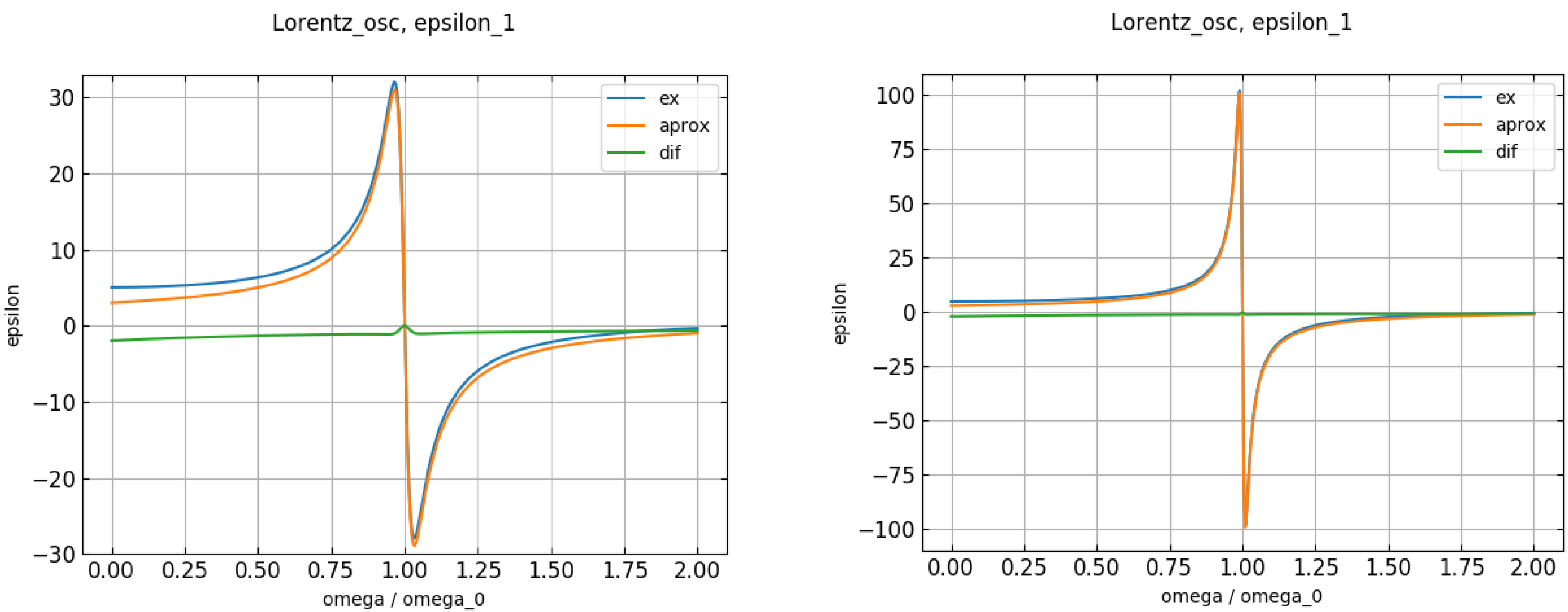
An example of the difference between the exact and approximate form of the Lorentzian lineshapes for the real (“dispersive”) and imaginary (“absorptive”) parts of the dielectric function:





Real (left) and imaginary (right) part of the dielectric function
(S=4, tau*omega_0=5),
exact (ex), approximate (aprox) forms and their difference (dif).

Relative agreement of the exact and approximate form improves for narrower Lorentzian profiles (longer times τ) :

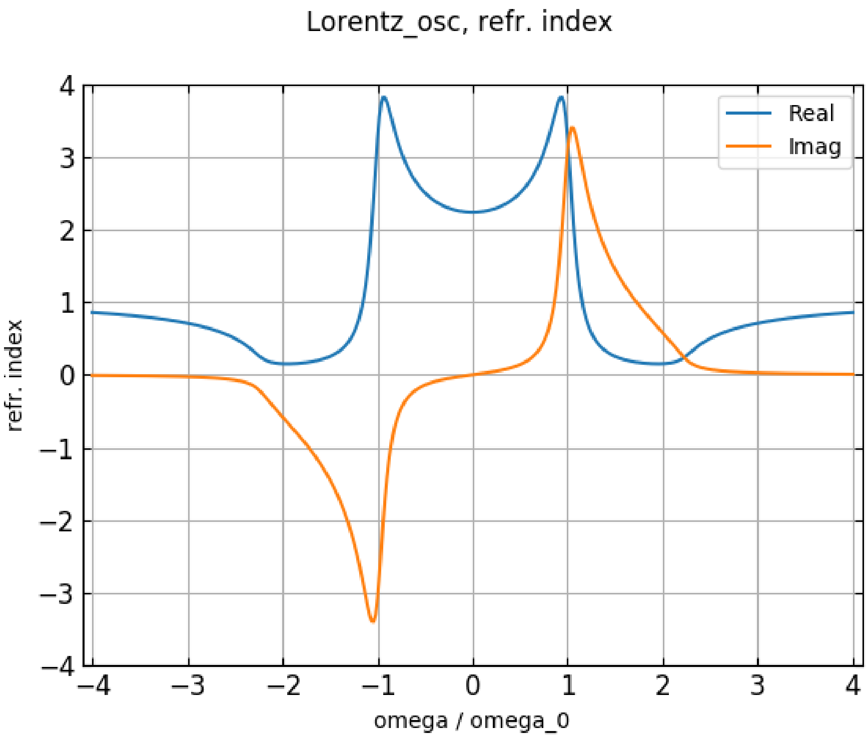


Real part of the Lorentzian dielectric function
(left: S=4, tau*omega_0=15, right: tau*omega_0=50),
exact (ex), approximate (aprox), difference (dif).

Refractive index is the square root of the dielectric function. Using the common conventions:

$$N = n + ik \;,\quad n = \sqrt{(\varepsilon_1 + \sqrt{\varepsilon_1^2 + \varepsilon_2^2})/2} \;,\quad k = \sqrt{(-\varepsilon_1 + \sqrt{\varepsilon_1^2 + \varepsilon_2^2})/2} = \frac{\varepsilon_2}{2n} \;,$$

where n and k are real. The real part (n) is always positive, the positive square root is assumed; the sign of k is the same as that of the imaginary part of the dielectric function – it describes the damping of the wave, travelling in the opposite direction for negative frequencies.

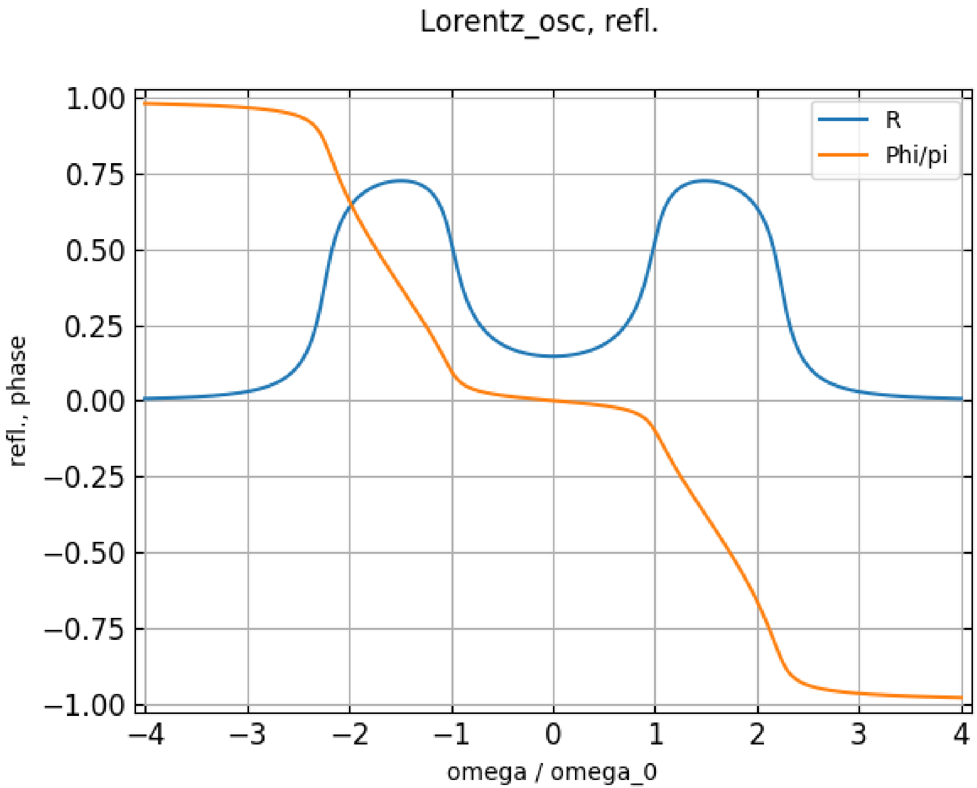


Complex refractive index of Lorentzian oscillators (S=4, tau*omega_0=5).

Complex refractive index determines the reflectivity at planar interfaces. Fresnel amplitude reflectance r for the normal incidence at the interface with vacuum (the unit refractive index) is

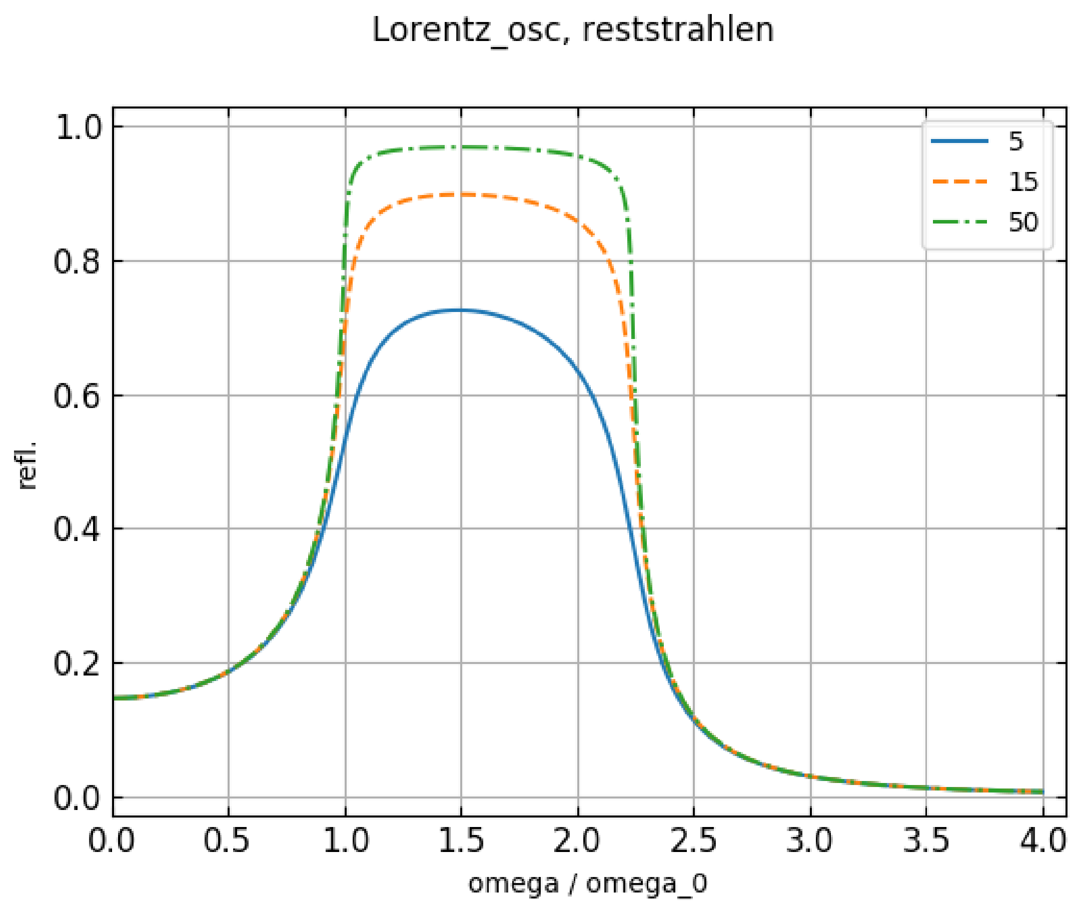
$$r = \sqrt{R} e^{i\Phi} = (n - 1 + ik)/(n + 1 + ik) \ ,$$

where R is the squared modulus of r, i.e., the power reflectivity.



Normal-incidence reflectivity and the phase angle of r (S=4, tau*omega_0=5).

The bands of large reflectivity above the eigenfrequency are called “reststrahlen”. They become more pronounced esp. for small damping of the oscillators.



Normal-incidence reflectvance (S=4, tau*omega_0=5, 15 a 50).

Complex conductivity

The velocity of the charge displacement in the Lorentz model is

$$\frac{\mathrm{d}\vec{r}}{\mathrm{d}t} = i\omega \frac{e}{m} \frac{1}{\omega_o^2 - \omega^2 - i\dfrac{\omega}{\tau}} \vec{E}_o e^{-i\omega t} \quad .$$

The current density produced by this movement equals to the charge transferred through unit area per unit time in the direction of the velocity. Assuming the concentration N of the oscillators, the current density is proportional to the field intensity, where the proportionality factor σ is called conductivity:

$$\vec{j} = Ne\frac{\mathrm{d}\vec{r}}{\mathrm{d}t} = i\omega \frac{Ne^2}{m} \frac{1}{\omega_o^2 - \omega^2 - i\dfrac{\omega}{\tau}} \vec{E}_o e^{-i\omega t} \equiv \sigma \vec{E}_o e^{-i\omega t} \quad .$$

The current density is usually not in phase with the driving force, which results in the complex-valued conductivity. Its SI unit is

$$\frac{\mathrm{A/m^2}}{\mathrm{V/m}} = \frac{1}{\Omega\mathrm{m}} \quad .$$

A convenient expression for the conductivity is

$$\sigma \equiv \sigma_1 + i\sigma_2 = -i\omega\varepsilon_o(\varepsilon - 1) = -i\omega \frac{Ne^2}{m} \frac{1}{\omega_o^2 - \omega^2 - i\dfrac{\omega}{\tau}}$$

$$= -i\omega \frac{S\varepsilon_o\omega_o^2}{\omega_o^2 - \omega^2 - i\dfrac{\omega}{\tau}} \quad \text{, where } \; S = \frac{Ne^2}{\omega_o^2\varepsilon_o m} \quad .$$

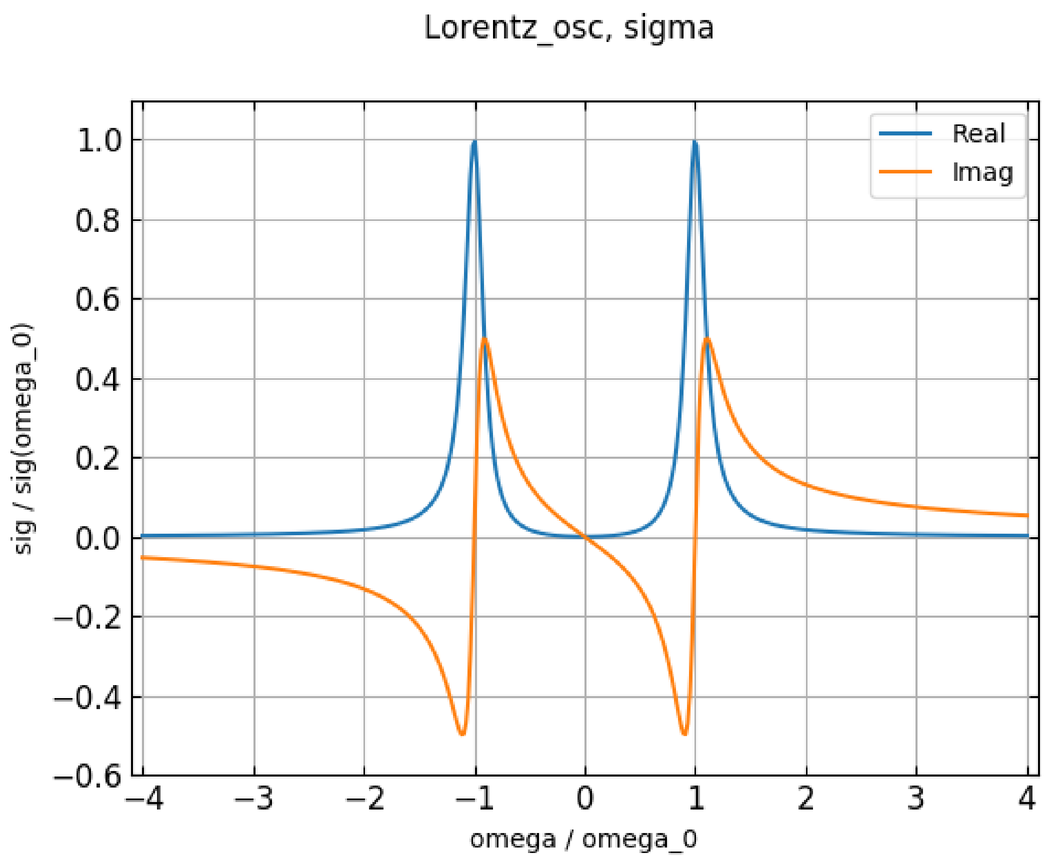
It uses the dimensionless oscillator strength sílu S. At the eigenfrequency, the conductivity is real,

$$\sigma(\omega_o) = S\varepsilon_o\omega_o^2\tau \; .$$

This value is convenient in expressing the dimensionless quantity

$$\frac{\sigma}{\sigma(\omega_o)} = -i\frac{\dfrac{\omega}{\tau}}{\omega_o^2 - \omega^2 - i\dfrac{\omega}{\tau}} = \frac{1}{1 + i\omega_o\tau(\omega_o/\omega - \omega/\omega_o)} \quad .$$

The spectral dependence of complex conductivity on real axis is even and odd in its real and imaginary parts, respectively. The real part decays for large frequencies as $1/\omega^2$, the imaginary part as $1/\omega$.



Conductivity of Lorentz oscillators (S=4, tau*omega_0=5).

Drude model for free charge carriers

The elastic bonding of charges to their equilibrium positions might disappear (e.g., for electrons in metals, or electrons and holes in semiconductors). This corresponds to the vanishing eigenfrequency of the Lorentzian oscillator. The displacement and velocity of the free charge carriers are

$$\vec{r} = \frac{e}{m}\frac{1}{\omega(\omega + i/\tau)}\vec{E}_o e^{-i\omega t} \quad , \quad \frac{\mathrm{d}}{\mathrm{d}t}\vec{r} = -i\frac{e}{m}\frac{1}{(\omega + i/\tau)}\vec{E}_o e^{-i\omega t} \quad .$$

Using the carrier density N and their mass m, we arrive at the dielectric function

$$\varepsilon = 1 - \frac{Ne^2}{\varepsilon_o m}\frac{1}{\omega\left(\omega + i\frac{1}{\tau}\right)} = 1 - \frac{\omega_p^2}{\omega^2 + \frac{1}{\tau^2}} + i\frac{\frac{\omega_p^2}{\tau}}{\omega\left(\omega^2 + \frac{1}{\tau^2}\right)} \quad \text{, where} \quad \omega_p = \sqrt{\frac{Ne^2}{\varepsilon_o m}} \quad .$$

The oscillator strength of the Lorentz formula is replaced by the square of *plasma frequency*; the name invokes the possibility of collective vibrations in the plasma of free carriers at this frequency.

NB: setting the eigenfrequency of the Lorentzian oscillator to zero provides an approximation of its behavior for large frequencies, with the motion independent of the elastic bonds.

The two poles of the Drude dielectric function are:

$$\omega_1 = 0 \quad \text{a} \quad \omega_2 = -\frac{i}{\tau} \quad .$$

As the modulus of complex frequency increases, the dielectric function approaches unity fast enough to warrant the unimportance of the pole at the origin in deriving the Kramers-Kronig relation

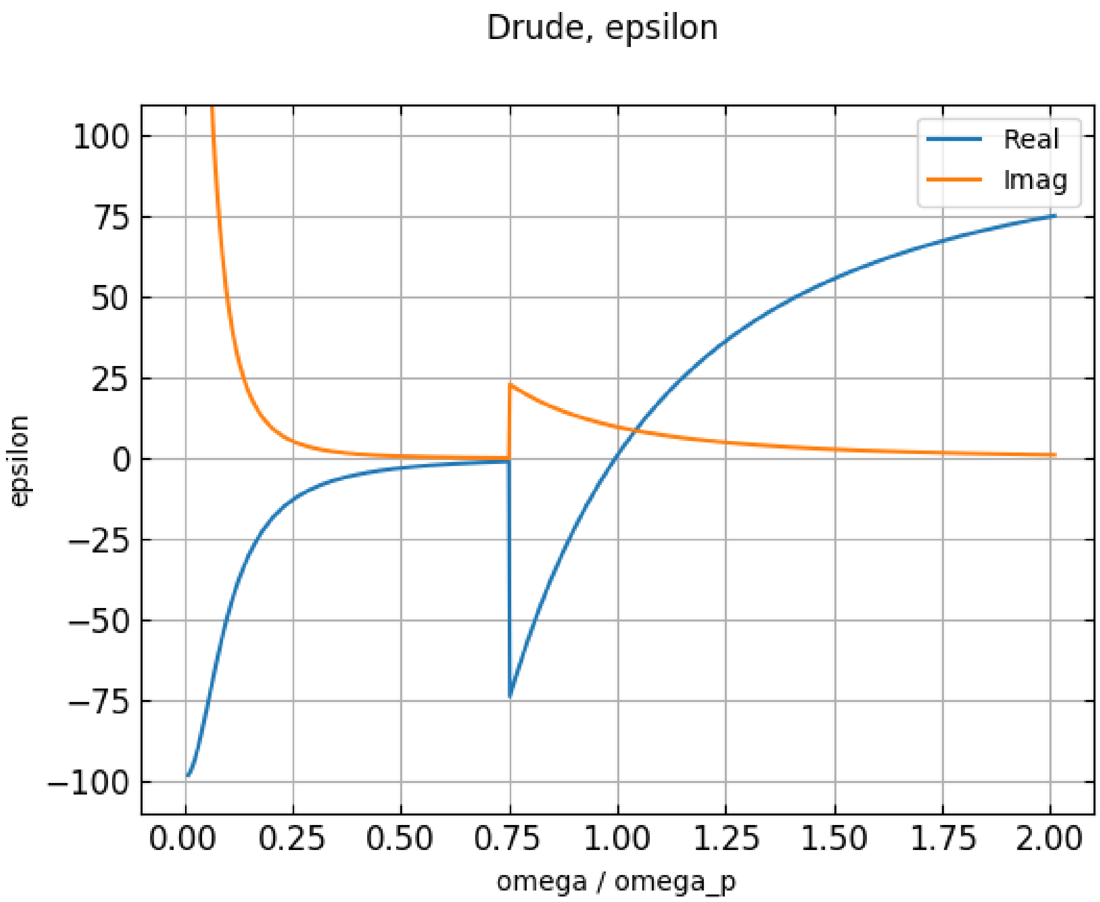
$$\varepsilon_2(\omega) = -\frac{2\omega}{\pi}\int_0^\infty \frac{\varepsilon_1(\Omega)-1}{\Omega^2-\omega^2}\mathrm{d}\Omega \quad .$$

The real part is on real axis is even, the imaginary part odd.
With increasing frequency, the real part is growing monotonically from

$$\varepsilon_1(0) = 1-(\omega_p\tau)^2$$

towards unity (the response of vacuum, as the charges are not able to follow the fast changes of the electromagnetic field); the imaginary part is singular at zero, and approaches zero as the inverse third power of frequency.

Note, in particular, the behavior of the real part (esp. the zero crossing close to the plasma frequency):



Dielectric function of the Drude model (omega_p=1, tau=10). Above 0.75, both parts are multiplied by 100.

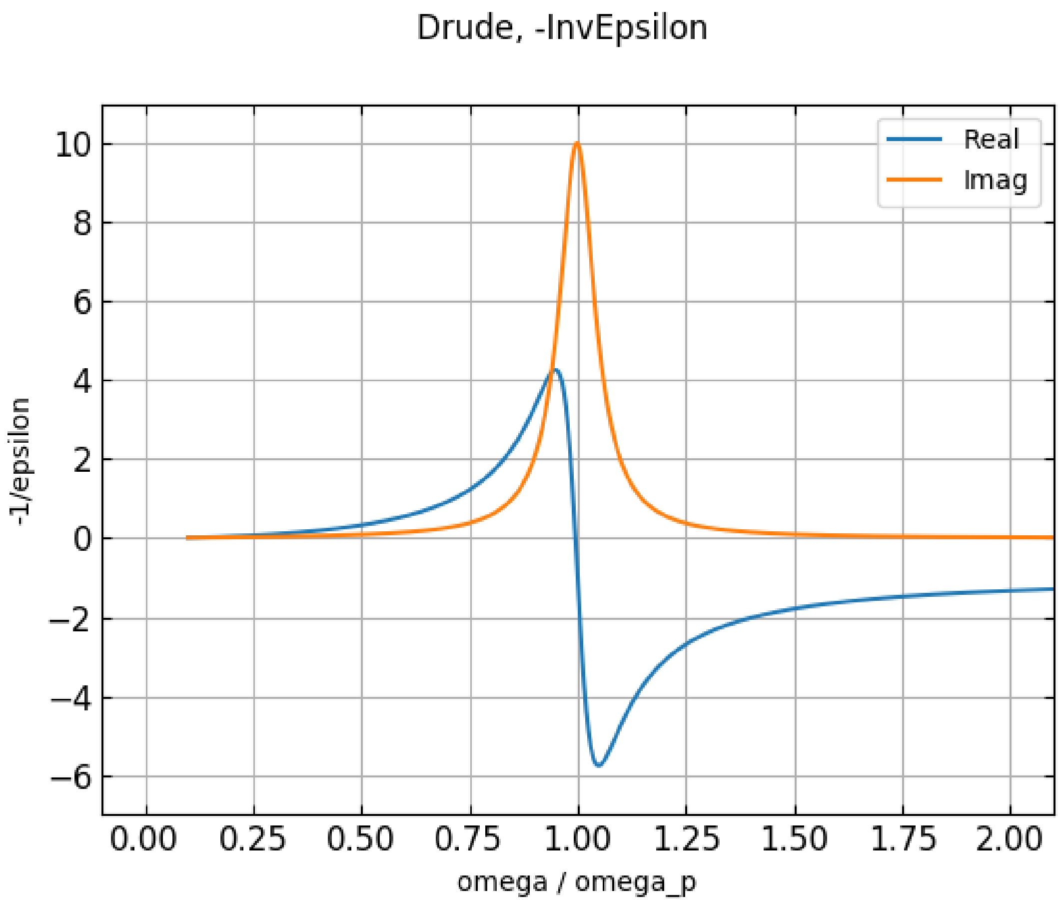
Negative inverse of the dielectric function,

$$-\frac{1}{\varepsilon} = \frac{\omega^2 + i\,\dfrac{\omega}{\tau}}{\omega_p^2 - \omega^2 - i\,\dfrac{\omega}{\tau}} \quad ,$$

ressembles (in a narrow neighborhood of the plasma frequency) the resonance of the Lorentz model. Its imaginary part is proportional to the absorbed energy of longitudinal waves, observable by the EELS technique (Electron Energy Loss Spectroscopy). Note the simple relation:

$$-\frac{1}{\varepsilon}(\omega_p) = -1 + i\omega_p\tau \quad .$$

The resonance at the plasma frequency has a nearly Lorentzian profile:



Negative inverse of the Drude dielectric function (tau*omega_p=10).

Conductivity is the convenient response function of free carriers; in the Drude model,

$$\sigma \equiv \sigma_1 + i\sigma_2 = -i\omega\varepsilon_o(\varepsilon - 1) = -i\varepsilon_o \frac{\omega_p^2\tau}{\omega\tau + i}$$

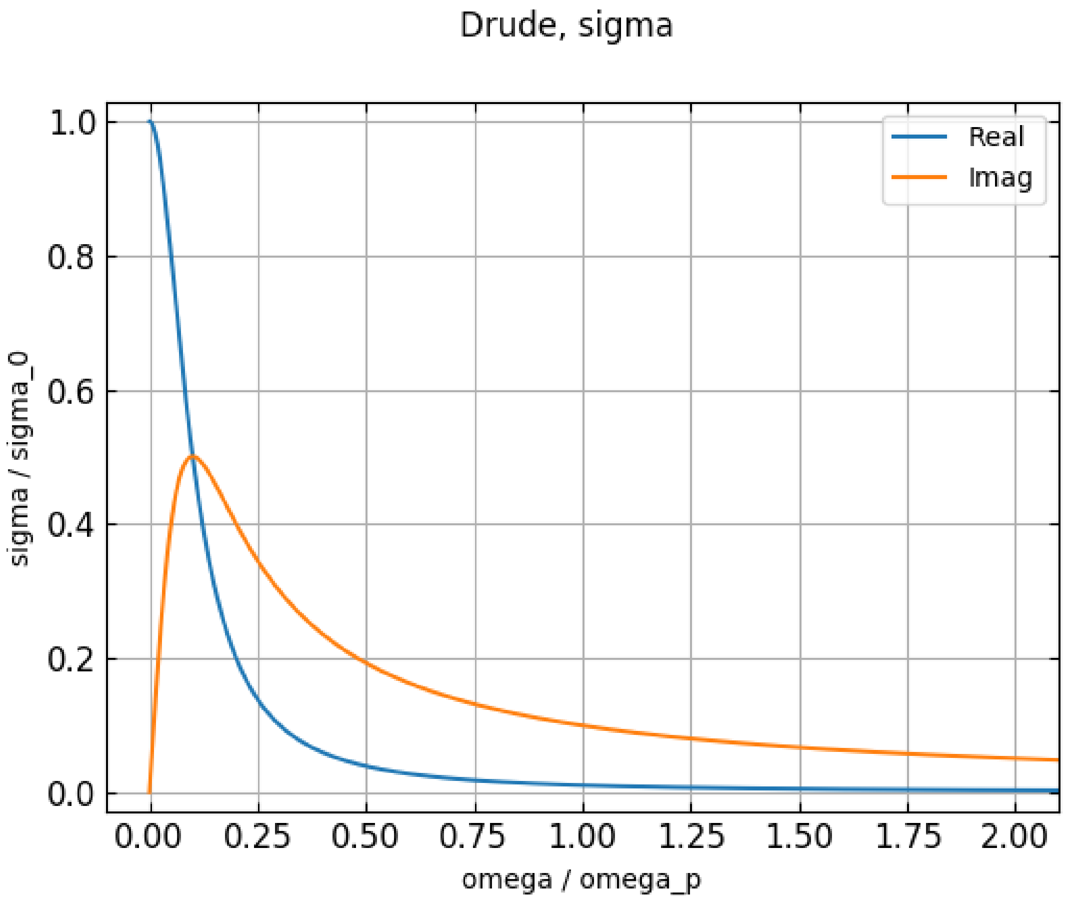
$$= \sigma_o\left(\frac{1}{(\omega\tau)^2+1} + i\frac{\omega\tau}{(\omega\tau)^2+1}\right) \text{ , where } \sigma_o = \varepsilon_o\omega_p^2\tau = \frac{Ne^2\tau}{m} \quad .$$

As expected, the dc conductivity is proportional to the damping time constant, and inversely proportional to the mass. The frequency dependence depends solely on the damping time.
Absorbed energy is proportional to the real part (cf. with the Joule heat U^2/R developed with the dc voltage U on the resistance R).
The simple frequency dependence of the absorptive (real) part allows for a direct check of the (general) sum rule

$$\frac{2}{\pi\varepsilon_o}\int_0^\infty \sigma_1(\Omega)\mathrm{d}\Omega = \omega_p^2 \ .$$

When the carrier concentration stays constant, possible changes in the frequency dependence of the absorption processes are limited by the constant area below the real part of conductivity.

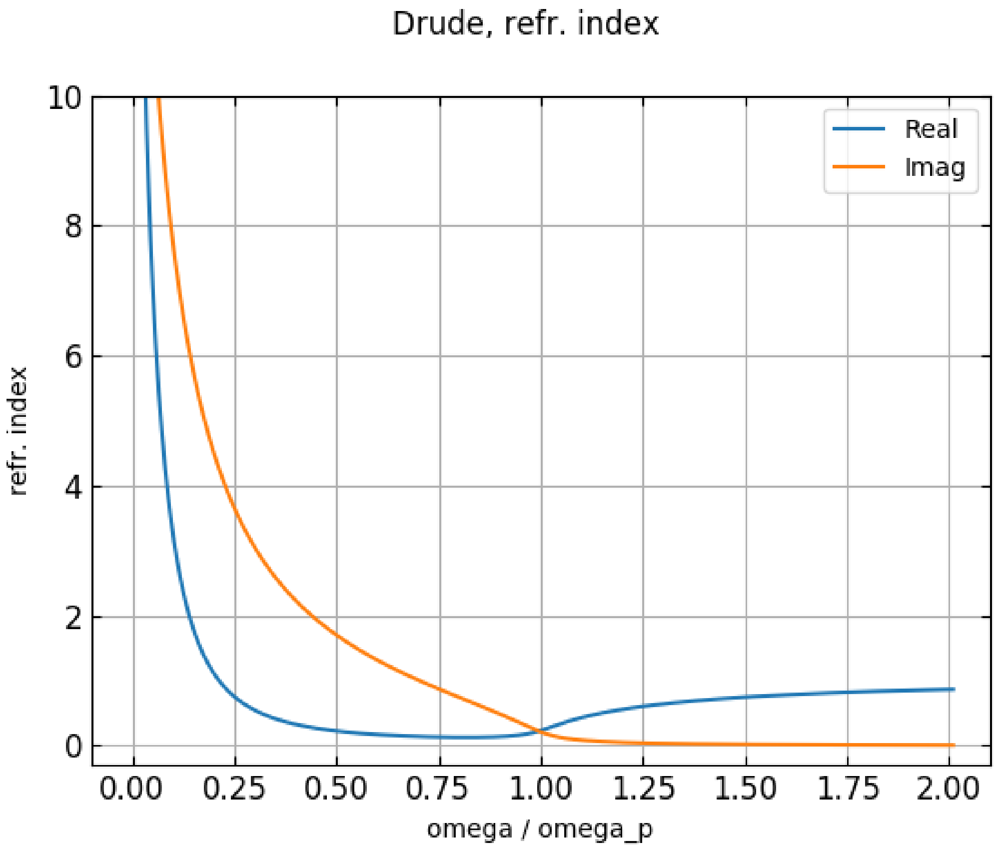
Spectral dependence of the complex conductivity has an even real, and odd imaginary part. The real part decays as $1/\omega^2$, the imaginary part as $1/\omega$, for high frequencies.



Complex conductivity of the Drude model (tau*omega_p=10).

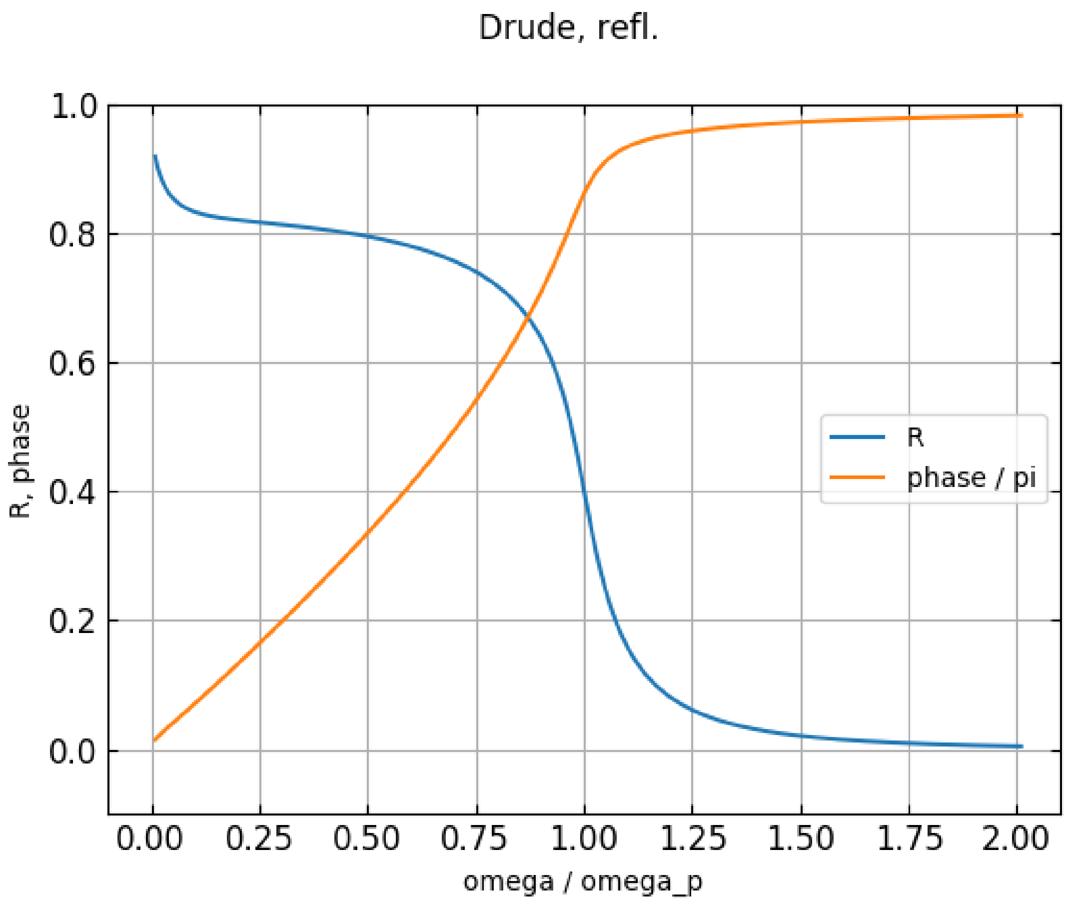
Both parts of the refractive index diverge with the frequency approaching zero, due to the divergence of the imaginary part of the dielectric function:

$$N = n + ik \ , \quad n = \sqrt{(\varepsilon_1 + \sqrt{\varepsilon_1^2 + \varepsilon_2^2})/2} \ , \quad k = \sqrt{(-\varepsilon_1 + \sqrt{\varepsilon_1^2 + \varepsilon_2^2})/2} = \frac{\varepsilon_2}{2n} \ ,$$



Complex refractive index of the Drude model (tau*omega_p=10).

Similar to the Lorentz model is the band of high reflectivity at the normal incidence; here it starts at the zero frequency:

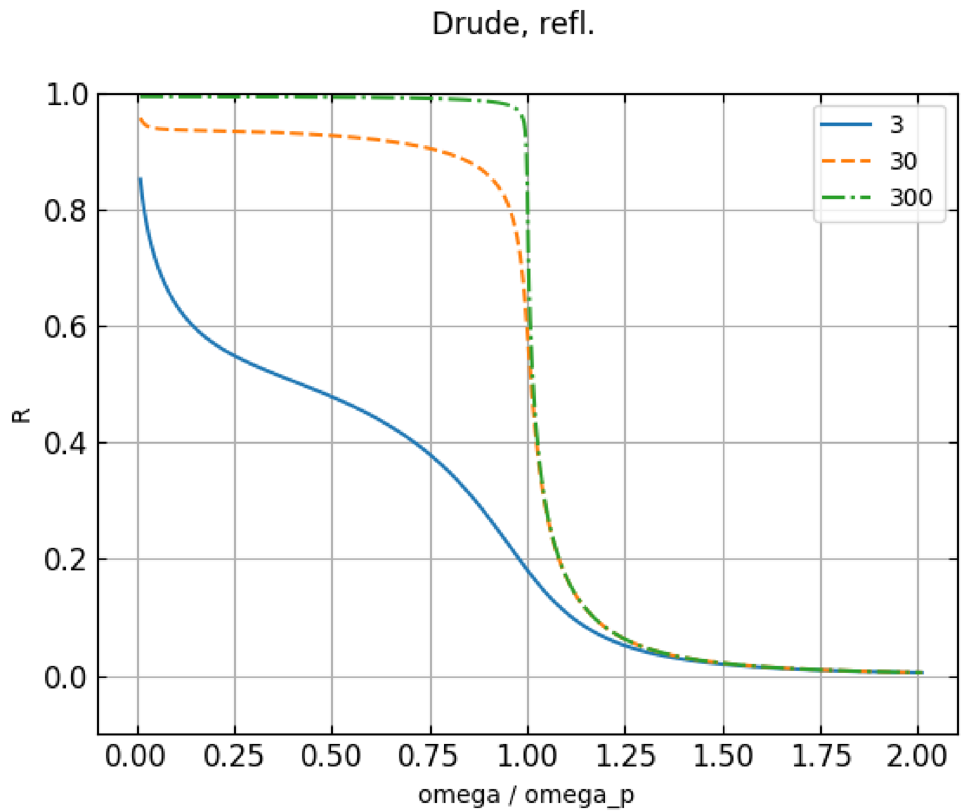


Normal-incidence reflectance and the phase of amplitude reflectance of the Drude model (tau*omega_p=10).

The large values of the reflectivity below the plasma frequency are the consequence of different importance of the closeness of the numerator and denominator in

$$R = \frac{(n-1)^2 + k^2}{(n+1)^2 + k^2} \;, \quad \text{namely } n << 1, \;\; \text{or } k >> n, \;\; \text{or } \; n >> 1 \;\; .$$

For weak damping, the normal-incidence reflectance is only weakly dependent on τ.



Normal-incidence reflectance of the Drude model (tau*omega_p=3, 30, and 300).

Travelling plane wave looses its amplitude in the direction of propagation (z), whenever the imaginary part of the refractive index is nonzero. The decrease of the amplitude is exponential, characterized by the "penetration depth of light". It results from the square of wavenumber,

$$k_z^2 = \varepsilon(\omega)\frac{\omega^2}{c^2} \ ,$$

where c is the light velocity in vacuum. The amplitude is diminished by $1/e$ of the initial value (about 37%) on the distance

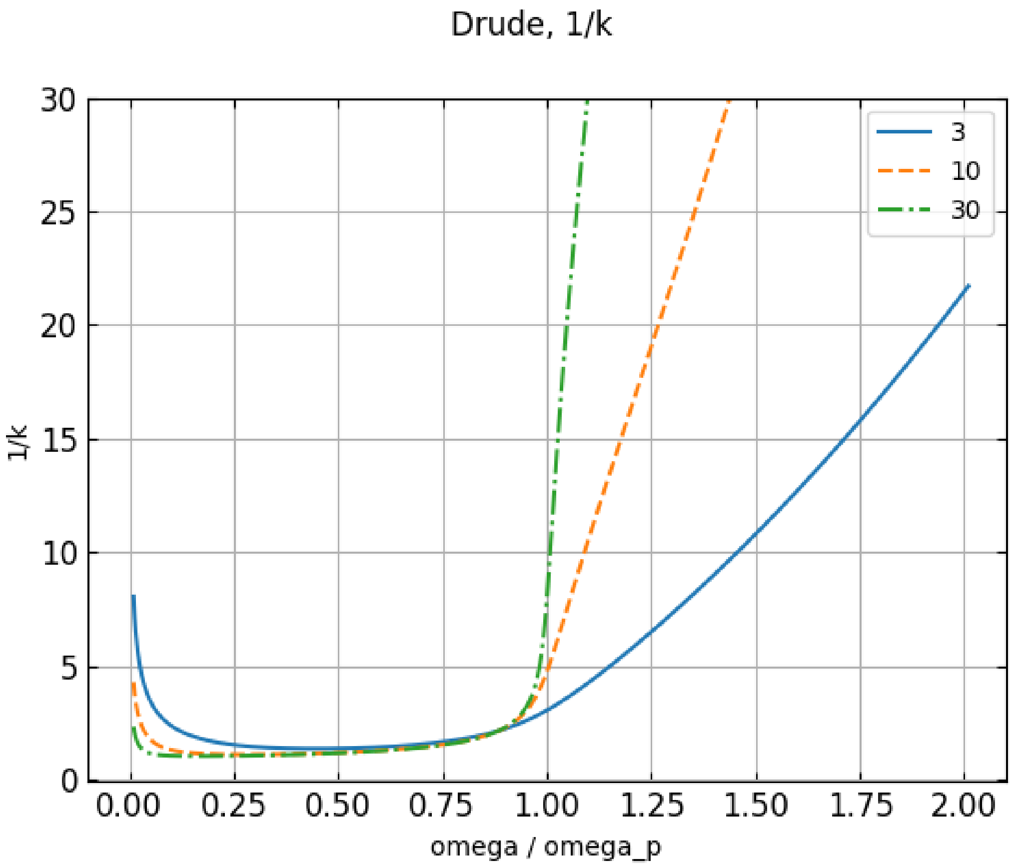
$$\delta_z = \frac{1}{\mathrm{Im}\{k_z\}} = \frac{c}{k\omega} \ ,$$

where k is the imaginary part of the refractive index. Spectral dependence of the penetration depth results from the multiplication of $1/k$ by the vacuum wavelength reduced by the factor of 2π .
When travelling this distance, the intensity is reduced by the factor $1/e^2$ (about 14%) of its initial value.

In the range of large reflectivity, the penetration dept is small. With the plasma frequency in the mid-infrared range, e.g.,

$$\lambda_{vac} = 10\ \mu\text{m}\ ,\ \ \nu_{vac} = 1000\ \text{cm}^{-1}\ ,\ \ \hbar\omega = 124\ \text{meV}\ ,$$

the penetration depth at the half of the plasma frequency is about 3 microns.



Inverse of the imaginary part of refractive index in the Drude model (tau*omega_p=3, 10, 30).

The usual term for the penetration length al low frequencies is "skin depth", as the field penetrates into small depths below the surface of conductors. In our model, the relevant quantity is

$$k_z \approx \frac{1+i}{\sqrt{2}} \frac{\omega_p}{\sqrt{\omega / \tau}} \frac{\omega}{c} \quad \text{for} \quad \omega << 1/\tau \quad .$$

The imaginary part of the refractive index increases towards zero as the square root of frequency; consequently, the penetration depth increases as its inverse. In the limit of small frequencies, the penetration depth can be expressed in terms of the dc conductivity as

$$\delta_z = \frac{1}{\operatorname{Im}\{k_z\}} \approx \sqrt{\frac{2}{\sigma_o \mu_o \omega}} \ ,$$

comprising the vacuum permeability.
For the dc conductivity of 10^5 1/Ohm.cm and the "optical" frequency of 1 THz, the penetration depth is about 160 nm, for the "radio" frequency of 100 MHz roughly 16 microns. The common form of the skin depth,

$$\delta_z = \sqrt{\frac{2\rho}{\mu\omega}} \ ,$$

contains the resistivity (the inverse of conductivity) and the permeability of the conductor; the latter might differ from the vacuum value at low frequencies.

Quantum transitions in perturbation theory

The light wave is composed by a train of photons, carrying quantized energy. They can be absorbed during the interaction with matter.

In the manybody system of condensed matter, elementary excitations in the form of quasiparticles can be identified (electrons, holes, excitons, phonons etc.).

The photon and quasiparticle fields influence each other via their interactions (“scattering”, “collisions”). One of the basic processes is the absorption of a photon, with the transfer of its energy to the quasiparticle system.

Other processes are possible, such as elastic or inelastic scattering of photons, when a photon survives the collision in a modified form (direction of propagation and/or energy). Important processes involve spontaneous or stimulated emission of photons, carrying energy taken from quasiparticles.

In the case of small changes of the studied system, caused by a weak optical field, the prediction of response functions can be based on the standard perturbation theory of quantum mechanics.

A convenient quantity to be calculated is the energy taken from a harmonic electromagnetic wave in a unit volume per unit of time, linked to the imaginary part of the dielectric function,

$$Q = \frac{1}{2}\omega\varepsilon_2\varepsilon_o \left\langle E^2 \right\rangle \ ,$$

which is proportional to the time average of the power of the wave. Its macroscopic form is usually the (Joule) heat.

The procedure involves a calculation of the increase of the mean energy of the condensed system, and use the above equation for the evaluation of the absorptive part of the dielectric function. The real part can be obtained via Kramers-Kronig transform of the imaginary part calculated for all frequencies.

Matter will be divided into small areas (of the volume *V*, with their dimensions much smaller than the wavelength of the optical field). In these areas, the electric field intensity of the wave is independent of the position; we retain solely the harmonic time dependence

$$\vec{E}\left(t\right) = \vec{E}_o e^{-i\omega t}$$

from the time t_o=0 of switching the perturbation on. Magnetic component will be neglected.

The perturbative part of hamiltonian can be expressed via the operator of dipole moment (charge times its displacement) as

$$H'(t) = \vec{d}\cdot\mathrm{Re}\left\{\vec{E}_o e^{-i\omega t}\right\} = \frac{\left(\vec{d}\cdot\vec{n}\right)E_o}{2}\left(e^{-i\omega t} + e^{i\omega t}\right) \ , \ \text{where} \ \ \vec{n} = \vec{E}_o / E_o$$

is a unit vector in the direction of force. The force performs work due to the displacement of the charge, equal to the scalar product of the vectors of force and displacement.

Assume the system in a stationary state i (with the energy E_i) at the initial time t_o. The probability of a transition to a stationary final state f (with the energy E_f) at the time T (which is the squared modolus of the probability amplitude) is

$$p_{if}(T,\omega) = \frac{1}{\hbar^2}\left|\left\langle f \left| \int_0^T H'(t) e^{i\frac{E_f - E_i}{\hbar}t} \mathrm{d}t \right| i \right\rangle\right|^2$$

$$= T\,\frac{\left|\left\langle f \left| \vec{d}\cdot\vec{n} \right| i \right\rangle\right|^2}{\hbar^2}\left[F(T,\omega_{if}-\omega)+F(T,\omega_{if}+\omega)\right]E_o^2 \;\;,\;\; \text{where}$$

$$\omega_{if} = \frac{E_f - E_i}{\hbar} \;\;,\;\; F(T,x) = \frac{\sin^2\left(\frac{T}{2}x\right)}{\frac{T}{2}x^2} \;\;.$$

For large T, the probability is negligible except for the fulfillment of the “resonance condition”

$$\omega = \pm\omega_{if} \;\;.$$

For $T \to \infty$ the function F can be replaced by the Dirac δ:

$$\int_{-\infty}^{\infty} F(T,x)\mathrm{d}x = \pi \quad \text{for any } T > 0 \; ; \qquad \lim_{T\to\infty} F(T,x) = \pi\delta(x) \; .$$

Owing to the transition $i \to f$, the light field performs work, which (per unit volume and time) reads

$$Q_{if}(\omega) = \frac{\hbar\omega p_{if}(T,\omega)}{TV} \to \frac{\pi\omega}{\hbar V}\left|\left\langle f\left|\vec{d}\cdot\vec{n}\right|i\right\rangle\right|^2 E_o^2\left[\delta(\omega_{if}-\omega)+\delta(\omega_{if}+\omega)\right] \; .$$

The work vanishes whenever the resonance condition is not fulfilled, and diverges otherwise. This is a consequence of the stationary initial and final states. Quasistationary states have finite lifetimes; for the exponential temporal dependence of the probability P_s of the decay of the state of mean energy E_o during the time t (P_n means the probability preserving the state during the time t),

$$P_n(t) = e^{-\frac{2\Gamma}{\hbar}t} \; , \quad P_s(t) = 1 - e^{-\frac{2\Gamma}{\hbar}t} \quad ,$$

the probability density of finding energy E is

$$\rho(E-E_o) = \frac{\Gamma}{\pi}\frac{1}{(E-E_o)^2+\Gamma^2} \; .$$

This is so called Breit-Wigner, or Lorentz, or Cauchy distribution.

The positive parameter Γ has the dimension of energy; it is inversely proportional to the lifetime of quasistationary ($\Gamma << E_o$) state,

$$\tau = \frac{\hbar}{2\Gamma} \quad .$$

For $\Gamma \to 0 \quad (\tau \to \infty) \ , \quad \rho(E - E_o) \to \delta(E - E_o) \ .$

Thus, the Fermi golden rule of the perturbation theory can be complemented by the assumption concerning the random values of the energy

$$E_{if} = E_f - E_i = \hbar\omega_{if}$$

taken from the wave via the $i \to f$ transition. The width parameters of the Breit-Wigner distribution of the initial and final energies can differ; assuming independent occurrence of both energies, the probability density of the energy difference is the convolution (Faltung, svjortka)

$$\rho(E_{if}) = \int_{-\infty}^{\infty} \frac{\Gamma_f / \pi}{(E - E_f^o)^2 + \Gamma_f{}^2} \frac{\Gamma_i / \pi}{(E_f - E_i - E_i^o - E)^2 + \Gamma_i{}^2} \mathrm{d}E$$

$$= \frac{(\Gamma_i + \Gamma_f)/\pi}{(E_{if} - E_{if}^o)^2 + (\Gamma_i + \Gamma_f)^2} \quad .$$

This is again the Breit-Wigner distribution; it is centered about the difference of the individual centers.

The width parameters and the corresponding relaxation times are

$$\Gamma_{if} = \Gamma_i + \Gamma_f \ , \quad \frac{1}{\tau_{if}} = \frac{\hbar}{2\Gamma_{if}} = \frac{1}{\tau_i} + \frac{1}{\tau_f} \ .$$

With the interpretation of inverse relaxation time as the frequency of collisions, the result for independent events concerning the initial and final states is the sum of frequencies.

The spectral dependence of the energy absorbed via transitions $i \to f$ between quasistationary states is broadened version of the delta-function singularity for stationary states. Multiplication by the probability density and summation over all possibilities leads to

$$\begin{aligned}
&\int_{-\infty}^{\infty} \left[\delta(\omega_{if} - \omega) + \delta(\omega_{if} + \omega) \right] \rho(\hbar\omega_{if}) \mathrm{d}(\hbar\omega_{if}) \\
&= \int_{-\infty}^{\infty} \left[\delta(x/\hbar - \omega) + \delta(x/\hbar + \omega) \right] \rho(x) \mathrm{d}(x) \\
&= \hbar\rho(\hbar\omega) + \hbar\rho(-\hbar\omega) \\
&= \hbar \frac{\Gamma_{if}}{\pi} \left[\frac{1}{(\hbar\omega - \hbar\omega_{if}^{o})^2 + \Gamma_{if}^2} + \frac{1}{(\hbar\omega + \hbar\omega_{if}^{o})^2 + \Gamma_{if}^2} \right] .
\end{aligned}$$

The resonances are of finite magnitude and width, they are centered close to $\omega = \pm\omega_{if}$.

The former result leads to the following approximate expression for the contribution of the $i \to f$ transitions to the imaginary part of the dielectric function,

$$(\Delta\varepsilon_2)_{if} = \frac{2Q_{i\,f}}{\omega\varepsilon_o \left\langle E^2 \right\rangle} = \frac{4Q_{i\,f}}{\omega\varepsilon_o E_o^2}$$

$$\approx \frac{4}{\varepsilon_o} \frac{\left| \left\langle f \left| \vec{d} \cdot \vec{n} \right| i \right\rangle \right|^2}{V} \left[\frac{\Gamma_{i\,f}}{(\hbar\omega - \hbar\omega_{if}^{\mathrm{o}})^2 + \Gamma_{if}^2} - \frac{\Gamma_{i\,f}}{(\hbar\omega + \hbar\omega_{if}^{\mathrm{o}})^2 + \Gamma_{if}^2} \right].$$

This formula can be further simplified, and, the need for the Kramers-Kronig transform (to obtain the real part) avoided.

Since

$$\frac{\gamma}{(\omega-\omega_o)^2+\gamma^2}-\frac{\gamma}{(\omega+\omega_o)^2+\gamma^2}$$

$$=\mathrm{Im}\left\{\frac{1}{\omega_o-\omega-i\gamma}+\frac{1}{\omega_o+\omega+i\gamma}\right\}=\mathrm{Im}\left\{\frac{2\omega_o}{\omega_o^2+\gamma^2-\omega^2-i2\omega\gamma}\right\}\ ,$$

the contribution to the absorptive part of the dielectric function can be expressed in the form

$$(\Delta\varepsilon_2)_{if}=\frac{4}{\varepsilon_o}\frac{\left|\left\langle f\left|\vec{d}\cdot\vec{n}\right|i\right\rangle\right|^2}{V}\frac{2\omega_{if}^{\mathrm{o}}}{\hbar}\mathrm{Im}\left\{\frac{1}{(\omega_{if}^{\mathrm{o}})^2+\frac{\Gamma_{if}^2}{\hbar^2}-\omega^2-i\omega\frac{2\Gamma_{if}}{\hbar}}\right\}\ .$$

This is to be compared with the result of classical Lorentz model for the complex dielectric function,

$$\varepsilon=1+\frac{S\omega_o^2}{\omega_o^2-\omega^2-i\,\frac{\omega}{\tau}}\quad .$$

The dimensionless "strength" of the $i \rightarrow f$ transitions is

$$S_{if} = \frac{8}{\varepsilon_o \hbar \omega_{if}^{o}} \frac{\left| \left\langle f \left| \vec{d} \cdot \vec{n} \right| i \right\rangle \right|^2}{V} \ ,$$

the eigenfrequency and damping time are

$$\omega_{o,if} = \sqrt{(\omega_{if}^{o})^2 + \frac{\Gamma_{if}^2}{\hbar^2}} \ , \ \ \tau_{if} = \frac{\hbar}{2\Gamma_{if}} \ .$$

The identical spectral dependencies of the imaginary parts imply identical spectra of the real parts, since they are related by Kramers-Kronig integral transform. Thus, in summing the contributions of (possibly many) independent contributions of transitions from different initial states to different final states, we may include the dispersive (real) part of the dielectric function in the sum:

$$\varepsilon(\omega) = 1 + \sum_{i,f} \frac{S_{if}\, \omega_{o,if}^2}{\omega_{o,if}^2 - \omega^2 - i\,\dfrac{\omega}{\tau_{if}}} \ .$$

Each of the terms has poles in the lower plane of complex frequencies.

The matrix element involving the charge and position,

$$D_{if} = \left\langle f \left| \vec{d} \cdot \vec{n} \right| i \right\rangle = e \left\langle f \left| \vec{r} \cdot \vec{n} \right| i \right\rangle \ ,$$

can be expressed in terms of the momentum operator, using the commutator of the unperturbed hamiltonian H_o with the position:

$$\left\langle f \left| H_o \vec{r} \right| i \right\rangle = E_f \left\langle f \left| \vec{r} \right| i \right\rangle \ , \ \left\langle f \left| \vec{r} H_o \right| i \right\rangle = E_i \left\langle f \left| \vec{r} \right| i \right\rangle \ ,$$

$$\left\langle f \left| \left[H_o , \vec{r} \right] \right| i \right\rangle = (E_f - E_i) \left\langle f \left| \vec{r} \right| i \right\rangle \ ,$$

$$\left\langle f \left| \vec{r} \right| i \right\rangle = \frac{\left\langle f \left| \left[H_o , \vec{r} \right] \right| i \right\rangle}{E_f - E_i} \ .$$

Since

$$\left[H_o , \vec{r} \right] = -i\hbar \frac{d\vec{r}}{dt} = -i\hbar \frac{\vec{p}}{m} \ ,$$

we arrive at

$$D_{if} = -i \frac{e\hbar}{m(E_f - E_i)} \left\langle f \left| \vec{p} \cdot \vec{n} \right| i \right\rangle \ .$$

The transition probability is proportional to

$$\left|D_{if}\right|^2 = \left|\frac{e\hbar}{m(E_f - E_i)}\right|^2 \left|\left\langle f \left| \vec{p} \cdot \vec{n} \right| i \right\rangle\right|^2 \quad .$$

This form is usually used for the one-electron transitions in crystals, which do not involve other excitations (such as phonons). As the momentum is proportional to the *k*–vector of the Bloch states, the matrix element is zero for states of different *k* (the state vectors are orthogonal). The allowed transitions are called “direct” (in *k*-space). This selection rule can also be interpreted as the requirement of momentum conservation, since the momentum of the involved photon is negligible.