Optical dispersion equations for metals applicable to the Far-IR through EUV spectral range

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Abstract
The long-standing problem of finding a general formulation of optical dispersion for metals, valid over a wide spectral range of photon energy $E$ is tackled. To this end, equations for refractive index $n$ and extinction coefficient $k$ as functions of $E$ are developed. Functions $n(E)$ and $k(E)$ respectively represent real and imaginary parts of complex index of refraction $N(E)$. Previous formulations, most of which are based on various combinations of Drude and Lorentz models, are either useable only over a limited spectral range or do not accurately fit experimental data. The formulation overcomes these shortcomings by exploiting concepts set forth by Forouhi and Bloomer in 1986, 1988 and 2019 publications pertaining to optical dispersion of semiconductors and insulators. These concepts are centered on time-dependent perturbation theory and consistency with principle of causality. The new expression for $k(E)$ is based on three types of events initiated by photon-electron interactions in metals: intraband electron dipole transitions; interband electron dipole transitions; inelastic collisions of electrons. Expression for $n(E)$ is obtained as Hilbert transform of $k(E)$. It is demonstrated that the new dispersion equations satisfy Titchmarsh’s Theorem, a mathematical theorem that conveys the principle of causality, which in turn establishes the theoretical validity of the formulation. Equations for $n(E)$ and $k(E)$ are fitted to published experimental data of metals encompassing all metal groups of the periodic table. Reported data span various ranges of energy, from far-infrared to extreme-ultraviolet. Excellent fits between calculated and experimental spectra are achieved. Having established consistency with Titchmarsh’s Theorem and by extension, causality, plus agreement with experimental findings suggests this formulation represents a valid description of optical dispersion of metals.

1. Introduction
Valid dispersion equations for metals can provide a deeper understanding of the interaction between photons and electrons in metals, and also may be linked to their chemical and physical properties. In addition, such equations may serve to characterize and model the thin film metallic constituents of integrated circuits and optoelectronic devices.

In this paper a new formulation for optical dispersion of metals is presented in terms of refractive index $n$ and extinction coefficient $k$ as functions of photon energy $E$. The quantities $n(E)$ and $k(E)$ correspond to the real and imaginary parts of the complex index of refraction $N(E) = n(E) - ik(E)$.

The function $k(E)$ provides a measure of energy transfer by photons to the medium, while $n(E)$ represents elastic scattering of photons by the medium, i.e., the quantum equivalent of refraction of electromagnetic waves after they pass through an interface from one medium to another.

Thus, $k(E)$ is related to an action by photons upon the medium, while $n(E)$ is related to an action by the medium upon photons. This reciprocal action process can be traced to the principle of causality which states that no effect can precede its cause, and links $n(E)$ and $k(E)$ as skew reciprocal Hilbert Transforms.

As an alternative to $N(E)$, the complex dielectric function $\varepsilon(\omega) = \varepsilon_1(\omega) - i\varepsilon_2(\omega)$ is also used to describe the interaction between photons and a medium. The quantity $\omega$ which represents photon angular frequency is
proportional to $E$ whereby $\omega = E/\hbar$. The dielectric function is related to $N(E)$ by $\varepsilon = N^2$, so that $\varepsilon_1 = n^2 - k^2$ and $\varepsilon_2 = 2nk$.

For metals, accurate determination of $n(E)$ and $k(E)$ can be challenging. In many instances, after years of investigations, there are still differences in the data reported for the same metal by different researchers. For example, Olmon et al [1] reviewed the values of $\varepsilon(\omega)$ the dielectric function of Au, published over the past six decades, and found large variations between the data. Also, Yang et al [2] reviewed the published optical data of Ag over almost the same time period and found large inconsistencies.

The root of the problem is that $n(E)$ and $k(E)$ are not determined by direct measurements. They are determined by analysis of measurable quantities that depend on them, such as experimental spectra of reflectance $R(E)$, transmittance $T(E)$, or of ellipsometric functions $\psi(E)$ and $\Delta(E)$. Accuracy of the resulting spectra will depend on (1) the accuracy of the measurements and (2) the physical validity of the model used to analyze the measured data.

Measurements are affected by preparation of suitable metal samples, in bulk form or as a thin film. For bulk samples, it is difficult to prepare flat optical-quality mirror-polished surfaces. A rough surface, albeit small, causes scattering of light, specifically in the visible-ultraviolet (Vis-UV) range, which will hinder accurate measurement of spectra of specular reflectance or ellipsometric parameters. As for thin film samples, surface roughness and oxidation, grain size variations and anisotropy, as well as poor adhesion to the substrate, can adversely affect the accuracy of measured spectra. Furthermore, structural morphology and film thickness may affect the determination of the dielectric function. See for example Yakubovsky et al [3].

The other part of the problem is with analysis of experimental data, requiring a dispersion model to determine the optical functions $n(E)$ and $k(E)$ or $\varepsilon_1(\omega)$ and $\varepsilon_2(\omega)$. Traditionally, the Lorentz oscillator model, developed at the end of the 19th century, and the free-electron Drude model, proposed at the turn of the 20th century, are still used to describe optical functions of metals. Offspring involving various combinations, and at times ‘improvements’, of the Drude and Lorentz models are also utilized.

For instance, the critical point model was introduced in 1998 by Leng et al [4] to describe the optical properties of silicon by generalizing the Lorentz model. In 1992, Brendel and Borrmann [5] proposed a model of solids constructed as a convolution of a Gaussian function with a Lorentz oscillator function. A similar model was proposed earlier in 1985 by Efimov and Makarova [6]. Further combinations of the Drude, Lorentz, critical point, and Efimov-Makarova models have also been used for analysis of experimental results [7–20].

There are several concerns with these models. Some of them involve many fitting parameters, some are only valid for limited spectral ranges, while some are expressed by a complicated form (involving complicated integration, for example). Also, some are not consistent with the principle of causality.

The aim of this paper is to start fresh and develop valid expressions for optical dispersion relations for metals from a starting point not centered on the Drude or Lorentz models. To this end, insights gained from previous Forouhi-Bloomer (F-B) dispersion equations for insulators and semiconductors [21–23] provide our course of action. Thus, the preceding methodology is applied to metals. The ensuing material presented in this paper is the result of doing so.

Consequently, equations for $n(E)$ and $k(E)$ are deduced and successfully applied to published experimental data of metal elements covering all the metal groups in the periodic table, from group 1 to group 15. The experimental data span spectral ranges from far-infrared (Far-IR) through extreme-ultraviolet (EUV) energies, and anywhere in between. These elements include alkali, alkaline-earth, rare-earth/lanthanide, transition, noble transition, and poor metals.

The connection of the formulation to various concepts in physics is discussed including complex polarization, Drude model for complex conduction, and low energy limit of $n(E)$ and $k(E)$.

2. Background

The new formulation of optical dispersion for metals presented in this paper is a sequel to the formulation for insulators and semiconductors developed by F-B [21–23]. The common thread between the two formulations is the application of the principle of causality to first order quantum mechanical interactions between photons and a medium. The foundation for applying the principle of causality is furnished by Titchmarsh’s Theorem [24], a theorem relating causality to the physics of dispersion. The connection to quantum mechanics relies on time dependent perturbation theory applied to a continuous medium, perturbed by a flow of photons.

2.1. F-B 1986 and 1988 expressions for $n(E)$ and $k(E)$

In 1986 and 1988, expressions for $n(E)$ and $k(E)$ of amorphous and crystalline insulators and semiconductors were deduced, applicable to the near-infrared to ultraviolet (NIR–UV) spectral range [21, 22]. The formulation dealt with interband electron dipole transitions which occur at photon energies above the energy bandgap $E_g$. First, the expression for $k(E)$ was deduced from first order time-dependent perturbation theory. The origin of the term ‘electron dipole transitions’ stems from first order time dependent perturbation theory which leads to transition probabilities proportional to electron dipole moments. In order to satisfy the principle of causality, it was necessary to
we look to our previous work, there may be more than one threshold energy, \( k(\infty) \), of the order of 10 k\( E\), \( E\), \( E\) is practically zero, of the order of 10 k\( E\), \( n(\infty) \) as the Hilbert Transform of \( k(E) \). The first sum in equations (3) and (4) represents photon interactions that occur when \( E < E_g \). The second sum represents interactions that occur when \( E > E_g \). The parameters \( D_j^j \) and \( F_j^j \) are not independent, but depend on \( A_j^j, B_j, C_j \), \( A_j^j, B_j, C_j \) all have physical meaning. See section 3.3.1 for details.

2.2. F-B 2019 expression for \( n(E) \) and \( k(E) \)

The original formulation for insulators and semiconductors was improved upon in 2019 in order achieve the expected behavior for \( k(E) \) in the limit \( E \to \infty \), which expresses that \( k(\infty) = 0 \). Also, the condition that \( k(E) = 0 \) when \( E = E_g \) was incorporated. Furthermore, the equations covered the spectral energy range not only for \( E > E_g \), but also for \( E < E_g \) [23]:

\[
k(E) = \sum_{j=1}^k \frac{A_j^j E}{E^2 - B_j E + C_j^j} + \sum_{j=1}^g \frac{B_j E + C_0}{E^2 - B_j E + C_j}
\]

(1)

\[
n(E) = n(\infty) + \sum_{j=1}^k \frac{A_j^j (E - E_g)}{E^2 - B_j E + C_j} + \sum_{j=1}^g \frac{B_j E + C_0}{E^2 - B_j E + C_j}
\]

(2)

where the sums are over the number of peaks in \( k(E) \) generated by interband dipole transitions.

The parameters \( B_0 \) and \( C_0 \) are not independent, but rather depend on \( A_j, B_j, C_j, \) and \( E_g \) [21, 22].

Besides \( E_0 \) and \( n(\infty) \), the independent parameters \( A_j, B_j, \) and \( C_j \) all have physical meaning. See section 3.3.1 for details.

3. New dispersion equations for \( n(E) \) and \( k(E) \) of metals

The new dispersion equations for \( n(E) \) and \( k(E) \) of metals are deduced based on a simplistic view of their electronic structure. We adopt the view that the electronic structure consists of an arrangement of core electrons filling all available states in inner energy bands plus conduction electrons that partially fill available states of the outermost energy bands. The equations are the result of assuming that photon interactions induce three types of events that affect \( k(E) \) of metals: (1) intraband electron transitions; (2) interband electron transitions; (3) inelastic collisions of electrons. Furthermore, we assume that first order time dependent perturbation theory can be used to describe these events. To implement this assumption for \( k(E) \), we look to our previous work [21–23] for guidance. Once \( k(E) \) is determined, \( n(E) \) is derived as the Hilbert Transform of \( k(E) \) (see section 4.2.1.3.).

3.1. Intraband and interband electron dipole transitions

To first order, intraband and interband electron dipole transitions may occur, stimulated by photon interactions. In this case, electrons transfer from occupied states to either unoccupied states in the same energy band (undergoing intraband transitions) or to unoccupied states in a higher energy band (undergoing interband transitions).

For the case of intraband transitions, there is no threshold energy to overcome associated with this event. For the case of interband transitions, there is a minimum photon energy, or threshold energy, necessary to induce the transfer of electrons.

The interband threshold energy in metals is analogous to the energy bandgap \( E_g \) in insulators and semiconductors with a distinct difference. All insulators and semiconductors have a transparent region for a range of energies where \( k(E) \) is practically zero, of the order of 10^{-5} \text{ eV} \, or less. \( E_g \) is the energy at the edge of this transparent range (the absorption edge) where the beginning of a sharp rise in the spectrum of \( k(E) \) occurs, indicative of the onset of photon absorption. On the other hand, in metals, there is no sharp rise in \( k(E) \) at the edge of a transparent regime that delineates the inception of photon absorption. To visualize these statements, the absorption edge in the experimental \( k(E) \) spectrum of a typical insulator, crystalline \( \text{SiO}_2 \), is shown in figure 1(a), The data is by Philipp [25]. The energy at which the edge occurs is around 9 eV, which represents the value of \( E_g \) for this insulator. In figure 1(b) the lack of an absorption edge in the spectrum of \( k(E) \) is portrayed for a typical metal, Cr, based on data by Lynch and Hunter [26].

We assume that the threshold energy of an interband transition in metals is manifested as a local minimum in \( k(E) \). As there may be more than one local minimum in \( k(E) \), there may be more than one threshold energy,
which we denote by \(X_j\). The factor \(X_j\) plays a role in metals somewhat similar to \(E\). Therefore, we assume (5) for intraband and interband electron transitions can be represented as a sum of electron transitions as described by equation (1), but with \(\Delta = k_A j \Delta q j 1\) specifically subtracted from \(k_E\) and where \(X_j\) takes the place of the lone parameter \(E\). Therefore, for intraband and interband transitions we assume:

\[
k(E) = \sum_{j=1}^{q} \left[ \frac{A_j (E - X_j)^2}{E^2 - B_j E + C_j} - A_j \right]
\]

Intraband Transitions: \(X_j = 0\)
Interband Transitions: \(X_j > 0\)

3.2. Inelastic collisions of electrons

Photon energy can be transferred to the lattice prompting phonon creation, which in turn can stimulate inelastic collisions of the loosely bound or ‘free’ conduction electrons in a metal. The effect of these inelastic collisions on \(k(E)\) is manifested mostly in the IR range and below. This is because if \(E > E_{IR}\), the effect of photon interactions leading to intraband and interband transitions on \(k(E)\) is more assertive. On the other hand, if \(E < E_{IR}\) photon energy may not be enough to excite electron transitions to unoccupied states in the metal, and therefore, only the effect of inelastic free electron collisions is manifested.

We assume that the influence on \(k(E)\) due to inelastic electron collisions can be constructed from the 2019 expression for the component of \(k(E)\) that deals with \(E < E_g\). This component is given by the first sum in equation (3):

\[
\sum_{j=1}^{q} \frac{A_j^* E}{E^2 - B_j E + C_j}
\]

Based on physical considerations, which are discussed in the next section, section 3.3.1, we eliminate the parameter \(B_j^*\). Accordingly, we assume that \(k(E)\) due to inelastic electron collisions is given by:

\[
k(E) = \sum_{j=1}^{p} \frac{A_j^* E}{E^2 + C_j}
\]

3.3. Complete equations for \(n(E)\) and \(k(E)\) of metals

Piecing together the three effects that contribute to \(k(E)\) of metals from equations (5) and (6) yields:

\[
k(E) = \sum_{j=1}^{q} \left[ \frac{A_j (E - X_j)^2}{E^2 - B_j E + C_j} - A_j \right] + \sum_{j=1}^{p} \left[ \frac{A_j^* E}{E^2 + C_j} \right]
\]

Taking the Hilbert Transform of equation (7) to obtain \(n(E)\) yields (See section 4.2.1.3.):

\[
n(E) = n(\infty) + \sum_{j=1}^{q} \left[ \frac{D_j E + F_j}{E^2 - B_j E + C_j} \right] + \sum_{j=1}^{p} \left[ \frac{A_j^* (C_j)^{\frac{1}{2}}}{E^2 + C_j} \right]
\]

where,

\[n(\infty) = 1\]
In equation (8), \( n(\infty) \) is taken as equal to one in the analysis of the experimental data for the metals considered in this paper. This is in accordance with the classical theory of electromagnetism and experimental results. Occasionally, if the spectral range of the measurement is limited, \( n(\infty) \) may be treated as floating parameter in the analysis and may converge to a value that is different than one.

The parameters \( D_j \) and \( F_j \) in equation (8) are not independent, but depend on \( A_j, \ B_j, \ C_j, \) and \( X_j \):

\[
D_j = \frac{A_j}{Q_j} \left( -\frac{B_j^2}{2} + B_j X_j - X_j^2 + C_j \right)
\]

\[
F_j = \frac{A_j}{Q_j} \left( (X_j^2 + C_j) \frac{B_j}{2} - 2X_j C_j \right)
\]

where,

\[
Q_j = \left( C_j - \frac{B_j^2}{4} \right)^{1/2}
\]

Equations (7)–(11) represent the complete new formulation for \( n(E) \) and \( k(E) \) of metals.

3.3.1. Physical significance of parameters

The physical significance of parameters in the 1986, 1988, and 2019 equations for \( n(E) \) and \( k(E) \) of insulators and semiconductors play a considerable role in comprehending the physical significance of the parameters \( X_j, \ A_j, \ B_j, \ C_j, \ A'_j \) and \( C'_j \), in equations (7) and (8).

As previously discussed, \( X_j \) is the threshold energy for interband transitions, analogous to \( E_g \). The meanings of \( A_j, B_j, C_j \) relate to intraband and interband electron dipole transitions and are similar to the original meanings of \( \lambda_i, B_i, C_i \) in equations (1)–(4) for \( n(E) \) and \( k(E) \) insulators and semiconductors [21–23]. However, the meanings for the parameters \( A'_j \) and \( C'_j \) are somewhat different since they are associated with inelastic collisions of ‘free’ electrons.

According to the 1986 and 1988 publications, \( A_j \) is unitless and proportional to the probability for \( j \)th electron dipole electron transition between initial and excited states \([a]|j|b\rangle \). The parameter \( B_j \) has energy units and is related to the \( j \)th energy difference between \([a]|j|b\rangle \), i.e., \( B_j/2 = (E_b - E_a) \approx \Delta E_j \). The parameter \( C_j \) is given as \( C_j = [(B_j^2/4) + Q_j^2] \equiv [(B_j^2/4) + (\hbar^2/4\tau_j)] \) and has energy units squared. The parameter \( \tau_j \) represents the lifetime of the \( j \)th excited electron state, and is related inversely to \( Q_j \), whereby \( \tau_j = \hbar/2Q_j \).

Similarly to \( A_j, A'_j \) is a probability factor. It is related to the probability that the \( j \)th conduction electron contributes to inelastic collisions, and unlike \( A_j, A'_j \) is not unitless, but has units of energy. As previously mentioned in section 3.2, the parameter \( B'_j \) does not enter into the expressions for \( n(E) \) and \( k(E) \) associated with inelastic collisions. This is because, according to the 2019 F-B publication [23], \( B'_j \) is proportional to the \( j \)th energy difference between states involving various quantum entities (e.g., phonons, etc.), whereas the collision process is not associated with transitions between energy states in the metal. However, similar to \( C_j, \ C'_j \) is related to a time parameter by:

\[
C'_j = \frac{\hbar^2}{4\tau'_j}
\]

whereby the parameter \( \tau'_j \) now represents the mean time between collisions, \( C'_j \) has energy units squared.

The new formulation for \( [N(E) - N(\infty)] \) involves two components, \( N_1(E) \) and \( N_2(E) \) such that \( [N(E) - N(\infty)] = \{N_1(E) + N_2(E)\} - N(\infty) \), where:

\[
N_1(E) = \sum_{j=1}^{d} [N_1(E)]_j = \sum_{j=1}^{d} \left[ \frac{D_j E + F_j}{E^2 - B_j E + C_j} \right] - \left[ \frac{A_j (E - X_j)^2}{E^2 - B_j E + C_j} - A_j \right]
\]

\[
N_2(E) = \sum_{j=1}^{p} [N_2(E)]_j = \sum_{j=1}^{p} \left[ \frac{A'_j (C'_j)^{1/2}}{E^2 + C'_j} \right] - \left[ \frac{A'_j E}{E^2 + C'_j} \right]
\]

The first component, \( N_1(E) \), is due to intraband \((X_j = 0)\) and interband \((X_j \neq 0)\) electron dipole transitions; the second, \( N_2(E) \), to inelastic electron collisions.

4. Theoretical validity

We submit that consistency with the principle of causality is one of two criteria that determines the validity of equations related to the process of dispersion. The other criterion is agreement with experimental data. In this section, we establish that the new formulation is consistent with the principle of causality and therefore satisfies the first criterion for validity of the new dispersion equations for metals.
4.1. The link between causality and dispersion equations
In 1956 Toll proved the logical equivalence between causality and the validity of dispersion equations [27]. Causality is expressed by the notion that no effect can precede its cause, a notion conveyed in a theorem by Titchmarsh [24], which is the basis of Toll’s proof.

4.2. Titchmarsh’s theorem
In order to determine if the new formulation is consistent with causality, we utilize Titchmarsh’s Theorem which consists of three equivalent conditions. A prerequisite to applying the theorem to optical dispersion is that the complex index of refraction should be analytically extendable in the lower half complex plane, with no poles or essential singularities as \( |E| \to \infty \). This prerequisite can be met if \( N(E) \) is confined to be square integrable along the real \( E \) axis. However, \( N(E) \) on its own will not satisfy this prerequisite, since \( n(\infty) \) is not equal to zero. Furthermore, depending on the formulation, \( k(E) \) may tend to be a constant as \( E \to \infty \). Consequently, in general, in order to ensure square integrability, Titchmarsh’s three conditions should be applied to \( [N(E) - N(\infty)] \) rather than to just \( N(E) \).

4.2.1. The three conditions of Titchmarsh’s Theorem
According to the theorem, if \( [N(E) - N(\infty)] \) satisfies any one of the following three conditions, it will automatically satisfy the other two. We demonstrate, however, that it satisfies all three conditions in order to erase any doubt regarding the formulation’s consistency with causality and its validity.

4.2.1.1. Condition (i)
Condition (i) stipulates that the function \( \mathcal{F}^{-1}[N(E) - N(\infty)] \) is a causal function, where the operator \( \mathcal{F}^{-1} \) denotes the inverse Fourier Transform. Explicitly:

\[
\mathcal{F}^{-1}[N(E) - N(\infty)] = \frac{1}{h} \int_{-\infty}^{\infty} [N(E) - N(\infty)] e^{i(E/h)t} dE = 0 \quad \text{for} \quad t < 0 \tag{15}
\]

Condition (i), stated by equation (15), suggests the notion of cause and effect of optical dispersion; namely if photons reach the medium at \( t = 0 \), their effect on the medium cannot occur at times corresponding to \( t < 0 \). \( \mathcal{F}^{-1}[N(E) - N(\infty)] \) has two components, \( \mathcal{F}^{-1}[N_1(E)] \) and \( \mathcal{F}^{-1}[N_2(E)] \). Taking the inverse Fourier Transforms of \( N_1(E) \) and \( N_2(E) \) in equations (13) and (14) yields:

\[
\mathcal{F}^{-1}[N_1(E)] = \sum_{j=1}^{q} \mathcal{F}^{-1}[[N_1(E)]_j] = \sum_{j=1}^{q} \frac{1}{h} A_j \left\{ 2Q \left( \frac{B_j}{2} - X_j \right) + i \left[ Q_j^2 - \left( \frac{B_j}{2} - X_j \right)^2 \right] \right\} \\
\times (e^{-t/2}) (e^{(iB_j/2h)t}) u(t) \tag{16}
\]

and

\[
\mathcal{F}^{-1}[N_2(E)] = \sum_{j=1}^{p} \mathcal{F}^{-1}[[N_2(E)]_j] = \sum_{j=1}^{p} \frac{1}{h} A_j' (e^{-t/2'}) u(t) \tag{17}
\]

The quantity \( u(t) \) is the unit step function such that:

\[
u(t) = \begin{cases} 
1, & t > 0 \\
0, & t < 0
\end{cases} \tag{18}
\]

Therefore, \( \mathcal{F}^{-1}[N(E) - N(\infty)] \) is a causal function since the summands of its two components vanish for \( t < 0 \).

4.2.1.2. Condition (ii)
Condition (ii) stipulates that the function \( [N(E) - N(\infty)] \) is holomorphic (complex analytic) in the lower half complex \( E \) plane, and square integrable along any line parallel to the real \( E \) axis in the lower half complex \( E \) plane. Based on equations (13) and (14), it can be shown that the summands \([N_1(E)]_j\) and \([N_2(E)]_j\) of the

\[\text{The reason we deal with the lower half complex } E \text{ plane is because we adopt the convention of defining the complex index of refraction } N(E) \text{ with a minus sign in front of its imaginary part } k(E), \text{ i.e., we express } N(E) = n(E) - ik(E). \text{ This is the convention generally used when applying the Fresnel coefficients to formulate reflectance and transmittance for the analysis of experimental data from a stack of thin films [28]. If we had adopted the convention of a plus sign in front of the imaginary part of } N(E), \text{ then this statement would apply to the upper half complex } E \text{ plane.}\]
components of $[N(E) - N(\infty)]$ have singularities only in the upper half of the complex plane at $E_j = \frac{B_j}{Z} + iQ_j$ and $E_j = i(C_j)^{1/2}$ and none in the lower half plane. Furthermore, it can be shown that $[N_1(E_j)]$ and $[N_2(E_j)]$ are square integrable along any line parallel to the real $E$ axis in the lower half complex $E$ plane. The particulars of this proof involve square integrability of $[N_1(E)]$ and $[N_2(E)]$, along with Parseval’s Theorem, as demonstrated by Titchmarsh.

### 4.2.1.3. Condition (iii)
Condition (iii) stipulates that the real and imaginary parts of $[N(E) - N(\infty)]$ are skew reciprocal Hilbert Transforms, i.e.,

$$
[n(E) - n(\infty)] = \mathcal{H} \left\{ [k(E) - k(\infty)] \right\}
= \frac{1}{\pi} \int \frac{[k(E')] - k(\infty)}{E - E'} dE' 
$$

(19)

$$
[k(E) - k(\infty)] = -\mathcal{H} \left\{ [n(E) - n(\infty)] \right\}
= -\frac{1}{\pi} \int \frac{[n(E')] - n(\infty)}{E - E'} dE' 
$$

(20)

where $\mathcal{H}$ denotes the Hilbert Transform. The symbol ‘$P$’ in front of the closed integrals of equations (19) and (20) stands for the Cauchy Principle Value of the integral, evaluated over a closed loop in the complex $E$ plane. Equation (19) was used to obtain the expressions for $[n(E) - n(\infty)]$ given by equations (2), (4) and (8).

Condition (iii) expressed by equations (19) and (20) seems to be the same as the well-known Kramers-Kronig (K-K) relations. However, equations (19) and (20) are not quite the same. The K-K relations constrain $n(E)$ and $k(E)$ to be symmetric and anti-symmetric functions of $E$, and no such restriction applies to these equations.

In particular, the sums of the components of $[n(E) - n(\infty)]$ and $k(E)$ related to intraband and interband electron dipole transitions, given by the real and imaginary parts of $[N_1(E)]$, in equation (13), are asymmetric functions of $E$. Nevertheless, they satisfy dispersion relations given by equations (19) and (20). Thus, the symmetry/anti-symmetry constraints of the K-K relations are not a necessary condition of Titchmarsh’s Theorem, and by extension, not a necessary condition of causality.

The expressions for $[n(E) - n(\infty)]$ and $k(E)$ related to inelastic electron collisions, given by the real and imaginary parts of $[N_2(E)]$, in equation (14), are also skew reciprocal Hilbert Transforms. In this case $n(E)$ and $k(E)$ are symmetric and anti-symmetric functions of $E$ and are therefore consistent with the K-K relations.

Since the summation of each term in the expression for $[N(E) - N(\infty)]$ satisfies the three conditions of Titchmarsh’s Theorem, $[N(E) - N(\infty)]$ is consistent with causality, and consequently, may be regarded as a valid theoretical description of optical dispersion of metals.

### 5. Experimental validity

#### 5.1. Overview
In this section, equations (7) and (8) are applied to the published $n(E)$ and $k(E)$ data of selected elements, representing all metal groups from 1 to 15 of the Periodic Table shown in figure 2, in the next section. The criterion for selecting these elements is based on the availability of reliable $n(E)$ and $k(E)$ data reported in a tabular form in the literature that span relatively wide spectral ranges. Any data for which $E > 150$ eV were excluded in this work. In some cases, all available data were used, while in other cases, due to inconsistencies of the reported data, a limited range was used.

In figures 3–25, calculated and experimental plots of $n(E)$ and $k(E)$ spectra of the selected metals are presented. In all plots, red solid circles (●) and green open diamonds (○) represent experimental data points, while solid blue —— and orange ——— lines represent the calculated spectra. Depending on the spectral range, the spectra are plotted either on log-log scales, linear-log scales, or linear-linear scales. In general, small mismatches between calculated and experimental spectra when plotted on log-log scales seem to be amplified. If the same data are plotted on linear-log scales, the mismatches are hardly noticeable.

All fitting parameters were simultaneously obtained from the analysis, and are listed in table 1 for Al, and in table 2 for the other materials presented in this work. Most of the experimental data of metals discussed in this paper can be found in tabular form at [https://refractiveindex.info/](https://refractiveindex.info/).

#### 5.2. Periodic table
The Periodic Table in figure 2, with its fifteen groups and six periods for non-radioactive metals, serves as a reference for each of the metal elements considered in this paper. These selected metals are outlined in bold.
metal groups are labeled as: alkali, alkaline-earth, rare-earth/lanthanide, transition, noble transition, and poor metals.

5.3. Analysis method

The Levenberg-Marquardt non-linear least square curve fitting regression algorithm is used to analyze published experimental data of $n(E)$ and $k(E)$ for the materials included in this paper. This method involves an iterative improvement to values of the $A_j$, $B_j$, $C_j$, $X_j$ ($j = 0$ to $q$), and $A'_j$, $C'_j$, ($j = 0$ to $p$), in order to minimize the sum of the squares of the differences between the calculated plots and experimental data. The value of $n(\infty)$ was fixed at one for all examples considered here.

In principle, each observed peak and shoulder in the experimental spectra contributes a term to the sums of equations (7) and (8). In some cases, extra terms may be needed in order to improve the correspondence between calculated and experimental data.

5.4. Methodology of applying formulation to experimental data

The methodology of utilizing equations (7) and (8) to analyze various energy ranges of experimental data is provided below in section 5.3.1–5.3.4 for the case of aluminum (Al). Out of all the metals we considered, Al was chosen as an archetype, because the data, which was published by Hagemann et al. [47], had the widest spectral range, spanning eight orders of magnitude, from $0.001 \times 10^5$ eV. However, we only considered data from $0.001$–$150$ eV. Most importantly, the data for this very wide spectral range were obtained by the same team of researchers, from one type of Al sample. No apparent inconsistencies in the data were noticed.

5.4.1. Far-IR to EUV energies: $0.001$–$150$ eV

For this range, both sums in equations (7) and (8) were involved. A total of nine terms were used in the calculation for Al to cover five orders of magnitude of experimental data, from $0.001$–$150$ eV; two terms were related to intraband ($X_j = 0$), and four to interband ($X_j \neq 0$) electron dipole transitions ($q = 6$), while three terms represented inelastic collisions of electrons ($p = 3$). Experimental data and calculated plots are depicted in figure 3. The mismatches between experimental and calculated plots of $n(E)$ seen at around 1 eV and 10 eV are actually minute. These mismatches are magnified since spectra are plotted on a log-log scale.
5.4.2. Far-IR to NIR energies: 0.001–0.5 eV
For this range, only the second sum, representing inelastic collisions of electrons, is needed. Photon energy is not large enough in this range to induce intraband or interband electron transitions. A total of three terms ($p = 3$) were used in the calculation for $n(E)$ and $k(E)$ of Al. Experimental data and calculated plots are depicted in figure 4. As expected, the parameters in table 1, related to inelastic collisions of electrons, are almost the same but not identical, since the range of data selected for the analysis were different.

5.4.3. NIR to EUV energies: 0.5–30 eV
For this range, only the first sum is needed, representing intraband and interband electron transitions. Any contribution to $n(E)$ and $k(E)$ of Al due to inelastic electron collisions is over-shadowed by that of intraband and interband transitions. A total of three terms ($q = 3$), were used in the calculation; one term was related to intraband ($X_i = 0$), and two to interband ($X_j = 0$) electron dipole transitions. Experimental data and calculated plots are depicted in figure 5.
5.4.4. EUV energies: 30–150 eV
For this range, only the first sum is needed. As in the previous case with photon energies between 0.5–30 eV, any contribution to $n(E)$ and $k(E)$ due to inelastic collisions is overshadowed by that of intraband and interband transitions. A total of four terms ($q = 4$), were used in the calculation for $n(E)$ and $k(E)$; three terms were related to intraband ($X_j = 0$), and one to interband ($X_j \neq 0$) electron dipole transitions. Experimental data and calculated plots are depicted in figure 6.

5.5. Results of analysis of experimental $n(E)$ and $k(E)$ data of assorted metal elements
5.5.1. Alkali metals
Alkali metals occupy periods 2–7 in group 1 of the periodic table. Lithium (Li), sodium (Na), potassium (K), rubidium (Rb), cesium (Cs), and francium (Fr) belong to this group. These metals are monovalent and highly reactive due to their tightly bound core electrons and weakly held single conduction band electron [49] which may be treated as unbound or ‘free’ in various interactions. Details of analysis results for Li are first presented. This is followed by comparison of results for Li and its congeners (elements in the same group) Na, K, Rb, and Cs to show an example of a pattern in optical properties of metals in the same group. Francium, a radioactive metal that occurs only in very minute quantities, was excluded.
Table 1. Fitting parameters $A_j$, $B_j$, $C_j$, $X_j$, $A'_j$, and $C'_j$ for Al associated with calculated spectra of figures 3–6. Data by Hagemann et al [47].

\[
k(E) = \sum_{j=1}^{q} \left[ \frac{A_j(E - X_j)^2}{E^2 - B_jE + C_j} \right] + \sum_{j=1}^{q} \left[ \frac{A'_jE}{E^2 + C'_j} \right] n(E) = 1 + \sum_{j=1}^{p} \left[ \frac{D_jE + E_j}{E^2 - B_jE + C_j} \right] + \sum_{j=1}^{p} \left[ \frac{A'_j(C'_j)^2}{E^2 + C'_j} \right]
\]

| Energy Range (eV) | Number of Terms 1st Sum | $A_j$ (eV) | $B_j$ (eV) | $C_j$ (eV)$^2$ | $X_j$ (eV) | Number of Terms 2nd Sum | $A'_j$ (eV) | $C'_j$ (eV)$^2$ |
|-------------------|-------------------------|-----------|-----------|---------------|-----------|-------------------------|-----------|---------------|
| 0.001–150         | $q = 6$                 | 4.5025E-04| 1.8418E+02| 8.6055E+03    | 0.0000E+00| $p = 3$                | 1.1796E+00| 1.3167E-07    |
| Figure 3          |                         | 1.1761E-04| 2.3834E+02| 1.4328E+04    | 0.0000E+00|                        | 2.3902E+00| 2.0565E-05    |
|                   |                         | 1.5820E+00| 2.9810E+00| 2.2458E+00    | 1.3989E+00|                        | 9.1226E+00| 1.4591E-03    |
|                   |                         | 3.0561E-01| 3.0202E+01| 2.3386E+02    | 1.6059E+01|                        |           |               |
|                   |                         | 4.6742E-01| 1.4018E+01| 1.8572E+02    | 1.8508E+01|                        |           |               |
|                   |                         | 1.0319E-02| 1.4597E+02| 5.3283E+03    | 7.1811E+01|                        |           |               |
| 0.001–0.5         | $q = 0$                 | —         | —         | —              | —         | $p = 3$                | 1.1733E+00| 1.2744E-07    |
| Figure 4          |                         |           |           |               |           |                        | 2.3814E+00| 1.9981E-05    |
|                   |                         |           |           |               |           |                        | 9.1650E+00| 1.4538E-03    |
| 0.5–30            | $q = 3$                 | 2.0848E+04| 5.9790E-04| 1.9118E-07    | 0.0000E+00| $p = 0$                | —         |               |
| Figure 5          |                         | 1.6860E+00| 2.9822E+00| 2.2548E+00    | 1.3874E+00|                        |           |               |
|                   |                         | 6.5061E-01| 1.9089E+01| 1.8075E+02    | 1.8115E+01|                        |           |               |
| 30–150            | $q = 4$                 | 8.8421E-03| 1.6338E+02| 8.9982E+03    | 0.0000E+00| $p = 0$                | —         |               |
| Figure 6          |                         | 7.1924E-05| 1.8705E+02| 8.7820E+03    | 0.0000E+00|                        |           |               |
|                   |                         | 3.4354E+03| 3.8651E+01| 3.7401E+02    | 0.0000E+00|                        |           |               |
|                   |                         | 1.2760E-02| 1.4556E+02| 5.2990E+03    | 7.1605E+01|                        |           |               |
Table 2. Fitting parameters $A_j$, $B_j$, $C_j$, $X_j$, $A_j'$, and $C_j'$ for assorted metal elements, associated with calculated spectra of figures 7–25.

$$k(E) = \sum_{j=1}^{q} \left( \frac{A_j (X_j)^2}{E^2 + B_j E + C_j} - A_j \right) + \sum_{j=1}^{p} \left( \frac{A_j' E}{E^2 + C_j'} \right)$$

$$n(E) = 1 + \sum_{j=1}^{q} \left( \frac{D_j E + F_j}{E^2 + F_j} \right) + \sum_{j=1}^{p} \left( \frac{A_j' (C_j')^2}{E^2 + C_j'} \right)$$

| Metal   | Energy Range (eV) | Number of Terms | 1st Sum | 2nd Sum | Number of Terms | 2nd Sum | 2nd Sum |
|---------|-------------------|-----------------|---------|---------|-----------------|---------|
|         |                   |                 | $A_j$   | $B_j$   | $C_j$           | $X_j$   | $A'_j$  | $C'_j$ |
| Li      | 0.45–100          | $q = 6$         | 1.2879E+00 | 2.000E+20 | 3.775E-01 | 0.000E+00 | 5.804E+00 | 1.342E-06 |
| Figure 7(a) | 0.45–10.65 [29]   |                 | 1.5019E-04 | 1.255E+02 | 3.967E+03 | 0.000E+00 | 1.255E+00 | 1.395E+00 |
| 7(b)    | 51.57–100 [30]    |                 | 1.3399E+00 | 6.596E+00 | 1.766E+01 | 0.000E+00 | 1.255E+00 | 5.726E+00 |
| 8(a)    |                   |                 | 3.1698E-05 | 1.608E+02 | 6.506E+03 | 0.000E+00 | 1.349E+00 | 5.726E+00 |
| Na      | 0.5–4.9           | $q = 1$         | 7.8426E-01 | 1.139E+01 | 1.129E+02 | 1.078E+01 | 5.498E+00 | 5.126E+05 |
| Figure 8(b) | 0.5–4.0 [31]     |                 | 1.4483E-02 | 1.088E+02 | 2.962E+03 | 5.353E+01 | 1.255E+00 | 1.255E+00 |
| K       | 0.5–10.7          | $q = 1$         | 7.4593E-01 | 5.257E+00 | 1.352E+01 | 4.349E+00 | 3.760E+00 | 1.029E-08 |
| Figure 8(c) | 0.5–4.0 [31]     |                 | 1.4483E-02 | 1.088E+02 | 2.962E+03 | 5.353E+01 | 1.255E+00 | 1.255E+00 |
| Rb      | 0.5–10.5          | $q = 2$         | 1.787E+00 | 4.209E+00 | 5.828E+00 | 0.000E+00 | 3.636E+00 | 5.622E-09 |
| Figure 8(d) | 0.5–4.0 [34]     |                 | 6.138E+00 | 4.193E+00 | 6.139E+00 | 2.870E+00 | 3.636E+00 | 5.622E-09 |
| Cs      | 0.5–9.6           | $q = 2$         | 1.534E+00 | 3.117E+00 | 4.129E+00 | 0.000E+00 | 2.990E+00 | 1.988E-09 |
| Figure 8(e) | 0.5–4.0 [34]     |                 | 2.734E+00 | 3.259E+00 | 4.948E+00 | 2.822E+00 | 2.990E+00 | 1.988E-09 |
| Be      | 1–100 [37]        | $q = 4$         | 1.196E+00 | 3.207E+00 | 5.739E+00 | 0.000E+00 | 5.310E+00 | 1.868E-10 |
| Figure 9 |                   |                 | 2.069E-01 | 1.063E+01 | 3.390E+01 | 0.000E+00 | 5.310E+00 | 1.868E-10 |

Alkali-Earth Metals: Group 2

|         |                   |                 | $A'_j$  | $C'_j$ |
|---------|-------------------|-----------------|---------|---------|
|         |                   |                 | 5.908E+00 | 1.342E-06 |

Alkali Metals: Group 1

|         |                   |                 | 5.908E+00 | 1.342E-06 |

Alkali-Earth Metals: Group 2

|         |                   |                 | 5.908E+00 | 1.342E-06 |

Alkali Metals: Group 1

|         |                   |                 | 5.908E+00 | 1.342E-06 |

Alkali-Earth Metals: Group 2

|         |                   |                 | 5.908E+00 | 1.342E-06 |

Alkali Metals: Group 1

|         |                   |                 | 5.908E+00 | 1.342E-06 |

Alkali-Earth Metals: Group 2

|         |                   |                 | 5.908E+00 | 1.342E-06 |

Alkali Metals: Group 1

|         |                   |                 | 5.908E+00 | 1.342E-06 |

Alkali-Earth Metals: Group 2

|         |                   |                 | 5.908E+00 | 1.342E-06 |

Alkali Metals: Group 1

|         |                   |                 | 5.908E+00 | 1.342E-06 |

Alkali-Earth Metals: Group 2

|         |                   |                 | 5.908E+00 | 1.342E-06 |
Table 2. (Continued.)

\[
k(E) = \sum_{j=1}^{a} \left[ A_j (E - X_j)^2 - A_i \right] + \sum_{j=1}^{c} A_j^2 E^2 + C_j \]
\[n(E) = 1 + \sum_{j=1}^{c} D_j E + F_j \]
\[+ \sum_{j=1}^{c} A_j^2 E^2 + C_j \]

| Metal       | Energy Range (eV) | Number of Terms | Number of Terms 1st Sum | Number of Terms 2nd Sum | \(A_j\) (eV) | \(B_j\) (eV) | \(C_j\) (eV)² | \(X_j\) (eV) | \(A^\prime_j\) (eV) | \(C^\prime_j\) (eV)² |
|-------------|-------------------|-----------------|-------------------------|-------------------------|-------------|-------------|--------------|-------------|----------------|----------------------|
| Sc          | 6.5–100           | 8               |                         |                         | 9.6763E+00 | 5.2587E-01 | 1.1709E+00  | 0.0000E+00  | 6.5               | 0.0000E+00  |
| Figure 10   | 6.5–100 [38]      |                 | 6.4552E-02              | 2.7655E+00              | 1.9124E+00 | 0.0000E+00  |
|             | 20–100 [40]       |                 | 1.1477E-01              | 1.7757E+01              | 7.8991E+00 | 8.7494E+00  |
|             |                   |                 | 2.1235E-01              | 2.0574E+01              | 1.3463E+02 | 1.9290E+01  |
|             |                   |                 | 1.2665E-02              | 2.9103E+01              | 2.1234E+02 | 1.2449E+01  |
|             |                   |                 | 2.4231E-02              | 5.7880E+01              | 8.3526E+02 | 2.6862E+01  |
|             |                   |                 | 7.0794E-02              | 6.8870E+01              | 1.2052E+03 | 2.9744E+01  |
|             |                   |                 | 2.9141E-02              | 8.4740E+01              | 1.8402E+03 | 6.1482E+01  |
| Lu          | 3–100 [39]        | 6               |                         |                         | 7.3398E+02 | 8.4654E-03 | 5.2433E-05  | 0.0000E+00  | 3.1350E-02       | 7.8744E+02  |
| Figure 11   |                   |                 | 7.2086E-04              | 7.0816E+01              | 1.2602E+03 | 0.0000E+00  |
|             |                   |                 | 1.4335E-03              | 8.1129E+01              | 1.6587E+03 | 0.0000E+00  |
|             |                   |                 | 2.8258E-01              | 7.2020E+00              | 1.4682E+01 | 4.8393E+00  |
|             |                   |                 | 1.5723E-01              | 2.1774E+01              | 1.4103E+02 | 2.0190E+01  |
|             |                   |                 | 3.1350E-02              | 5.5891E+01              | 7.8744E+02 | 2.2689E+01  |

Rare-Earth/Lanthanide Metals: Group 3

Forouhi and Bloomer
\[ k(E) = \frac{1}{2} \sum_{j=1}^{q} \left( A_j (E - X_j)^2 - A_j \right) + \sum_{j=1}^{p} \frac{A_j' E}{E^2 + C_j' (E^2 + C_j' \cos \theta)} n(E) = 1 + \sum_{j=1}^{q} \frac{D_j E + F_j}{E^2 + B_j E + C_j} + \sum_{j=1}^{p} \frac{A_j (C_j')^3}{E^2 + C_j' \cos \theta} \]

| Metal  | Energy Range (eV) | Number of Terms 1st Sum | Number of Terms 2nd Sum | Transition Metals: Groups 4–10 |
|--------|-------------------|--------------------------|--------------------------|-------------------------------|
| Ti     | 0.15–6.46         | \( q = 8 \)              | \( A_j, B_j, C_j, X_j \) | \( A_j', C_j' \)              |
|        | [40, 41]          |                          |                          |                               |
|        | 4.9603E+01        | 3.1809E-02               | 3.7123E-04               | 0.0000E+00 \( p = 1 \)       |
|        | 1.5889E-02        | 5.5996E-01               | 7.9198E-02               | 2.1485E+00, 2.5814E-02        |
|        | 3.0202E-01        | 2.8777E+00               | 2.6433E+00               | 0.0000E+00                    |
|        | 1.7213E+00        | 7.3664E-01               | 1.4730E-01               | 0.0000E+00                    |
|        | 2.9135E-02        | 1.2722E+01               | 4.3300E+01               | 0.0000E+00                    |
|        | 1.1915E-02        | 6.6058E-01               | 1.1163E+01               | 0.0000E+00                    |
|        | 3.5089E+00        | 5.8424E-01               | 8.5431E-02               | 2.8689E-01                    |
|        | 2.4351E+01        | 7.5882E-01               | 1.5991E-01               | 4.0443E-01                    |
| V      | 0.5–6.0 [42]      | \( q = 4 \)              |                          |                               |
|        | [40, 41]          |                          |                          |                               |
|        | 3.0755E-03        | 1.7394E-03               | 1.6098E-06               | 0.0000E+00 \( p = 0 \)       |
|        | 5.3377E-03        | 1.1766E+01               | 3.5072E+01               | 0.0000E+00                    |
|        | 6.4371E-01        | 5.0408E+00               | 7.8323E+00               | 5.4068E-01                    |
|        | 4.6032E-01        | 2.5250E+00               | 1.6560E+00               | 1.1454E+00                    |
| Cr     | 0.7–29.5 [26]     | \( q = 8 \)              |                          |                               |
|        | [40, 41]          |                          |                          |                               |
|        | 4.2498E+01        | 1.0026E-01               | 4.2147E-03               | 0.0000E+00 \( p = 0 \)       |
|        | 1.5034E+00        | 1.9736E+00               | 1.9484E+00               | 0.0000E+00                    |
|        | 2.4932E-02        | 6.5225E+00               | 1.2117E+01               | 0.0000E+00                    |
|        | 2.6502E-02        | 1.2735E+01               | 4.2466E+01               | 0.0000E+00                    |
|        | 5.5203E-02        | 2.6988E+01               | 1.9989E+02               | 0.0000E+00                    |
|        | 1.4913E-02        | 3.9145E+01               | 4.0378E+02               | 0.0000E+00                    |
|        | 3.9563E-01        | 5.5633E+00               | 8.1749E+00               | 4.0099E+00                    |
| Mn     | 0.64–6.6 [43]     | \( q = 5 \)              |                          |                               |
|        | [40, 41]          |                          |                          |                               |
|        | 1.0686E+01        | 7.3671E-03               | 1.3569E-05               | 0.0000E+00 \( p = 0 \)       |
|        | 9.6718E-01        | 8.9674E-01               | 2.1973E-01               | 0.0000E+00                    |
|        | 7.9615E-00        | 7.9291E-01               | 4.1115E-01               | 0.0000E+00                    |
|        | 2.3461E-00        | 8.3145E-00               | 3.1452E-00               | 0.0000E+00                    |
|        | 8.5160E-01        | 5.5348E-00               | 5.1323E-01               | 0.0000E+00                    |
| Fe     | 0.0062–6.6        | \( q = 2 \)              |                          |                               |
|        | [40, 41]          |                          |                          |                               |
|        | 1.7134E-01        | 5.3716E+00               | 8.6637E+00               | 0.0000E+00 \( p = 4 \)       |
|        | 1.0621E-04        | 5.5570E+01               | 7.7201E-02               | 0.0000E+00                    |
|        | 2.0–6.6 [43]      |                          |                          |                               |
Table 2. (Continued.)

\[
k(E) = \sum_{j=1}^{\infty} \frac{A_j(E - X_j)^2 - A_j}{E^2 - B_jE + C_j} + \sum_{j=1}^{\infty} \frac{A_jE}{E^2 + C_j} + \sum_{j=1}^{\infty} \frac{D_jE + F_j}{E^2 + C_j}
\]
\[
n(E) = 1 + \sum_{j=1}^{\infty} \frac{D_jE + F_j}{E^2 + C_j} + \sum_{j=1}^{\infty} \frac{A_j(C_j)^{1/2}}{E^2 + C_j}
\]

| Metal | Energy Range (eV) | Number of Terms 1st Sum | \(A_j\) | \(B_j\) (eV) | \(C_j\) (eV) \(^2\) | \(X_j\) (eV) | Number of Terms 2nd Sum | \(A'_j\) (eV) | \(C'_j\) (eV) \(^2\) |
|-------|------------------|-------------------------|--------|-------------|-----------------|-------------|-------------------------|-------------|-----------------|
| Co    | 0.64–6.6 \(^{[43]}\) | \(q = 5\) | 9.3563E+01 | 2.6622E-03 | 1.7719E-06 | 0.0000E+00 | \(p = 0\) | — | — |
|       |                  |                         | 9.0381E+01 | 6.7054E-02 | 5.0440E-02 | 0.0000E+00 |                       |             |                 |
| Ni    | 0.64–6.6 \(^{[43]}\) | \(q = 4\) | 3.5768E+01 | 2.3844E-02 | 1.4236E-04 | 0.0000E+00 | \(p = 0\) | — | — |
|       |                  |                         | 1.1097E-02 | 1.2170E+01 | 3.8607E+01 | 0.0000E+00 |                       |             |                 |
| Zn    | 0.022–3.44 \(^{[45]}\) | \(q = 2\) | 7.5849E+01 | 3.0269E+01 | 7.0369E+00 | 0.0000E+00 | \(p = 2\) | 5.7277E+00 | 1.7901E-08 |
|       |                  |                         | 3.0994E+01 | 2.4825E+00 | 6.7293E+00 | 4.7334E+00 |                       |             |                 |
| Cu    | 0.005–100 \(^{[47]}\) | \(q = 6\) | 8.5227E+00 | 5.7907E-01 | 1.9976E+00 | 3.5295E+00 |                       |             |                 |
|       |                  |                         | 8.1001E-01 | 3.0451E+00 | 2.7832E+00 | 7.0796E+00 |                       |             |                 |

Transition Metals: Group 12

| Metal | Energy Range (eV) | Number of Terms 1st Sum | \(A_j\) | \(B_j\) (eV) | \(C_j\) (eV) \(^2\) | \(X_j\) (eV) | Number of Terms 2nd Sum | \(A'_j\) (eV) | \(C'_j\) (eV) \(^2\) |
|-------|------------------|-------------------------|--------|-------------|-----------------|-------------|-------------------------|-------------|-----------------|
| Hg    | 0.2–19.5 \(^{[46]}\) | \(q = 6\) | 9.1717E+00 | 1.6277E+01 | 2.9318E-02 | 0.0000E+00 | \(p = 1\) | 9.7739E+00 | 1.2432E+00 |
|       |                  |                         | 2.6592E+00 | 2.3844E+00 | 1.4236E-04 | 0.0000E+00 |                       |             |                 |
| Cu    | 0.005–100 \(^{[47]}\) | \(q = 6\) | 8.5227E+00 | 5.7907E-01 | 1.9976E+00 | 3.5295E+00 |                       |             |                 |
|       |                  |                         | 8.1001E-01 | 3.0451E+00 | 2.7832E+00 | 7.0796E+00 |                       |             |                 |

Noble Transition Metals: Group 11

| Metal | Energy Range (eV) | Number of Terms 1st Sum | \(A_j\) | \(B_j\) (eV) | \(C_j\) (eV) \(^2\) | \(X_j\) (eV) | Number of Terms 2nd Sum | \(A'_j\) (eV) | \(C'_j\) (eV) \(^2\) |
|-------|------------------|-------------------------|--------|-------------|-----------------|-------------|-------------------------|-------------|-----------------|
| Cu    | 0.005–100 \(^{[47]}\) | \(q = 6\) | 2.3230E-01 | 5.1758E+00 | 7.4078E+00 | 0.0000E+00 | \(p = 3\) | 1.2828E+00 | 2.0586E-06 |
|       |                  |                         | 2.7286E-02 | 1.0414E+01 | 2.8334E+01 | 0.0000E+00 |                       |             |                 |
| Cu    | 0.005–100 \(^{[47]}\) | \(q = 6\) | 5.9774E-03 | 2.8905E+01 | 2.1450E+02 | 0.0000E+00 |                       |             |                 |
|       |                  |                         | 1.9468E-04 | 5.2178E+01 | 6.8185E+02 | 0.0000E+00 |                       |             |                 |
| Cu    | 0.005–100 \(^{[47]}\) | \(q = 6\) | 9.9160E-05 | 1.7600E+02 | 7.2610E+03 | 0.0000E+00 |                       |             |                 |
| Cu    | 0.005–100 \(^{[47]}\) | \(q = 6\) | 2.8591E+00 | 4.5451E+00 | 6.4141E+00 | 2.7111E+00 |                       |             |                 |
Table 2. (Continued.)

\[
k(E) = \sum_{j=1}^{q} \left( \frac{A_j (E - X_j)^2}{E^2 - B_j E + C_j} - A_j \right) + \sum_{j=1}^{q} \frac{A'_j E}{E^2 + C'_j} \quad n(E) = 1 + \sum_{j=1}^{q} \frac{B_j E + C_j}{E^2 - B_j E + C_j} + \sum_{j=1}^{q} \frac{A'_j (C'_j)^2}{E^2 + C'_j}
\]

| Metal | Energy Range (eV) | Number of Terms 1st Sum | \(A_j\) (eV) | \(B_j\) (eV) | \(C_j\) (eV)^2 | \(X_j\) (eV) | Number of Terms 2nd Sum | \(A'_j\) (eV) | \(C'_j\) (eV)^2 |
|-------|-------------------|--------------------------|-------|-------|----------------|-------|--------------------------|-------|-------|
| Ag    | 0.005–100 [47]    | \(q = 6\)                | 1.1506E-01 | 7.9557E+00 | 1.5901E+01 | 0.0000E+00 | \(p = 2\)                | 3.2217E+00 | 3.057E+06 |
|       |                   |                          | 4.0112E-03 | 1.2214E+01 | 3.7960E+01 | 0.0000E+00 |                          | 5.5014E+00 | 2.0519E-04 |
|       |                   |                          | 2.1548E-04 | 1.5200E+02 | 5.8010E+03 | 0.0000E+00 |                          |                          |         |
|       |                   |                          | 2.4853E+01 | 7.9473E+00 | 1.5871E+01 | 3.9908E+01 |                          |                          |         |
|       |                   |                          | 2.0719E-01 | 2.8170E+01 | 8.3333E+00 | 0.0000E+00 |                          |                          |         |
|       |                   |                          | 1.1424E-01 | 4.4090E+01 | 1.8001E+00 | 0.0000E+00 |                          |                          |         |
| Au    | 0.005–100 [47]    | \(q = 8\)                | 5.2726E+00 | 1.4552E-01 | 8.9896E-03 | 0.0000E+00 | \(p = 3\)                | 5.0645E-01 | 3.3662E-07 |
|       |                   |                          | 2.4217E-02 | 6.0394E+00 | 9.3383E+00 | 0.0000E+00 |                          | 1.7049E+00 | 8.3606E-06 |
|       |                   |                          | 6.1301E-01 | 6.9045E+00 | 1.4213E+01 | 0.0000E+00 |                          | 5.6827E+00 | 9.6685E-04 |
|       |                   |                          | 1.2395E-02 | 1.6605E+01 | 7.1422E+01 | 0.0000E+00 |                          |                          |         |
|       |                   |                          | 9.2252E+02 | 2.4360E+01 | 8.3333E+00 | 0.0000E+00 |                          |                          |         |
|       |                   |                          | 1.2977E-02 | 4.3735E+01 | 1.8001E+00 | 0.0000E+00 |                          |                          |         |
|       |                   |                          | 1.3276E-02 | 5.9693E+01 | 8.3333E+00 | 0.0000E+00 |                          |                          |         |
|       |                   |                          | 3.8406E+00 | 5.4503E+00 | 1.8001E+00 | 0.0000E+00 |                          |                          |         |
| Pb    | 0.7–3.6 [48]      | \(q = 2\)                | 4.0149E+01 | 1.8769E+00 | 1.5839E+02 | 0.0000E+00 | \(p = 0\)                | —     | —     |
|       |                   |                          | 5.1442E-01 | 4.9064E+00 | 7.0092E+00 | 7.6924E-01 |                          |                          |         |
| Bi    | 0.6–100 [47]      | \(q = 6\)                | 8.9918E+00 | 3.7941E+00 | 3.7941E+00 | 0.0000E+00 | \(p = 1\)                | 1.5500E+01 | 1.3912E+00 |
|       |                   |                          | 3.1502E-04 | 5.9579E+00 | 7.8567E+02 | 0.0000E+00 |                          |                          |         |
|       |                   |                          | 2.9282E-01 | 5.7047E+01 | 1.6566E+03 | 0.0000E+00 |                          |                          |         |
|       |                   |                          | 2.0824E-01 | 2.0860E+04 | 2.7284E+12 | 0.0000E+00 |                          |                          |         |
|       |                   |                          | 1.6759E+00 | 2.0000E+02 | 3.4580E+01 | 1.4656E+01 |                          |                          |         |
|       |                   |                          | 2.5163E-02 | 4.8849E+01 | 5.9688E+02 | 2.3224E+01 |                          |                          |         |

* Values of the calculated parameters for Al, which is a Poor Metal, can be found in Table 1.
5.5.1. Lithium (Li)

Lithium occupies period 2, group 1 of the periodic table. It is the lightest of the metals and the lightest solid element.

Figures 7(a) and (b) depict calculated fits of equations (7) and (8) to experimental data. In figure 7(a) the spectra are plotted on a log-log scale, and in figure 7(b), partial spectral data are plotted on a linear-log scale in order to better see spectral details. The data were combined from two separate studies: from 0.45–10.65 eV by Rasigni and Rasigni [29]; from 51.57–100 eV by Henke et al [30]. The reported data point at 0.15 eV by Rasigni and Rasigni [29] was not included in the analysis, since it was obviously wrong: the $n$ and $k$ data at 0.15 eV did not correspond to values for $\varepsilon_1$ and $\varepsilon_2$.

A total of seven terms were used in the calculation, four terms representing intraband transitions, two interband transitions and one inelastic collision. The large gap in data, from 10.6 to 51.57 eV, is filled in by the calculated spectra which precisely fit the very fine structural details of the experimental data.

![Figure 7. Calculated and experimental $n(E)$ and $k(E)$ spectra of Li plotted on (a) log-log scale and (b) partially linear-log scale. Data by Rasigni and Rasigni [29] from 0.45–10.6 eV, combined with data by Henke et al [30] from 51.57–100 eV. The calculated spectra continue through the gap in the data, from 10.6 to 51.57 eV. Corresponding fitting parameters are given in table 2.](image)

5.5.1.1. Comparison of $n(E)$ and $k(E)$ spectra of alkali metals

Typically, congeners have closely related physical and chemical properties [49]. Therefore, we expect that congeners will also have similar optical properties. In figures 8(a)–(e) the calculated and experimental $n(E)$ and $k(E)$ spectra for Li, Na, K, Rb, and Cs are displayed on a linear-log scale.

By extending the calculated spectra, based on equations (7) and (8), beyond the experimental data points into lower energies, the similarity of the optical spectra of alkali metals is more apparent.

5.5.2. Alkali-earth metals

Alkali-earth metals occupy group 2 of the periodic table. Beryllium (Be), magnesium (Mg), calcium (Ca), strontium (Sr), barium (Ba), and radium (Ra) belong to this group. They have somewhat similar chemical and electrical properties as alkali metals, but are not as soft and are less reactive. Out of the six alkali-earth metals, the experimental $n(E)$ and $k(E)$ data of beryllium was selected for analysis.

5.5.2.1. Beryllium (Be)

Beryllium occupies period 2, group 2 of the periodic table. Its calculated and experimental spectra are depicted in figure 9. The experimental data were compiled by Arakawa et al [37] spanning 1.0 to 100 eV. A total of five terms were used in the calculation. Out of the five terms, two represented intraband, two interband transitions, and one inelastic collisions.

5.5.3. Rare-earth/lanthanide metals

Rare-earth/lanthanide metals occupy group 3 of the periodic table. This group consists of seventeen metals, comprising fifteen lanthanides in period 6, plus scandium (Sc) and yttrium (Y) in periods 4 and 5, respectively. Sc and Y are considered rare earth elements since they tend to occur in the same ore deposits as the lanthanides.

\footnote{Also, Lynch and Hunter [50] reported values for $n(E)$ and $k(E)$ below 0.75 eV which did not correspond to those reported by Rasigni and Rasigni [29], while referencing these authors.}
and exhibit similar chemical properties. Out of the seventeen rare-earth/lanthanide metals, the experimental $n(E)$ and $k(E)$ data of Sc and Lu were selected for analysis.

5.5.3.1. Scandium (Sc)

Scandium has similar electronic properties as the transition metals and is sometimes classified as such. Its calculated and experimental spectra is depicted in figure 10. The experimental data for Sc span 6.5–100 eV and were a combination of two studies: Larruquert et al [38] from 6.5–100 eV, supplemented with data by Fernández-Perea et al [51] from 20–100 eV. A total of eight terms were used in the calculation to cover the range of data, from 6.5–100 eV. Out of the eight terms, two represented intraband electron transitions and six interband transitions. The effect of inelastic collisions is not manifested in this energy range for Sc.
5.5.3.2. Lutetium (Lu)

Lutetium is the heaviest of the lanthanides. Its calculated and experimental spectra are depicted in figure 11. The experimental data for Lu were taken from García-Cortés et al.\textsuperscript{[39]} spanning 3.0–100 eV. A total of six fitting parameters are given in table 2.
terms were used in the calculation. Out of the six terms, three represented intraband transitions and three interband transitions. The effect of inelastic collisions is not manifested in this energy range for Lu.

5.5.4. Transition metals

Transition metals are defined in two different ways, leading to two different series of classifications. The first way defines transition metals as those metals acting as a bridge between two sides of the periodic table; in particular, as a bridge between the first three groups on the left side of the periodic table, and the last six groups on the right side. By this definition, metals in periods 4, 5, 6 that span groups 4–12 are classified as transition metals. In this case, group 12 metals, zinc, cadmium and mercury are included.

The other definition involves the stability of ions which the metal forms based on its electronic structure. Specifically, the second way defines transition metals as those that form one or more stable ions in which the ‘d’ orbitals are not completely filled [49]. Zinc, cadmium and mercury do not satisfy this definition since the ions formed by these metals have ‘d’ orbitals that are completely filled.

The chemical properties of transition metals do not change very much with atomic number unlike those of other elements [49] and therefore, it might be expected that the same holds true for their optical properties. However, based on our results, it is difficult to state with any certainty that the $n(E)$ and $k(E)$ spectra of transition metals are similar.

This section presents analysis of eight of the transition metals in the fourth period, namely titanium (Ti), vanadium (V), chromium (Cr), manganese (Mn), iron (Fe), cobalt (Co), nickel (Ni), and zinc (Zn), plus mercury, a congenor of zinc, which occupies the sixth period. Note that Zn’s other congenor was not considered due to lack of available reported experimental data. Noble metals, copper, silver and gold, which are also classified as transition metals, are dealt with separately in section 5.5.6.

5.5.4.1. Titanium (Ti)

Titanium occupies group 4 of the periodic table. It is the lightest of the transition metals. The experimental data for titanium were reported by Lynch et al [40] combined with data by Lynch and Hunter [41], spanning 0.15–6.46 eV. A total of nine terms were used in the calculation to cover this range of data. Out of the nine terms, six represented intraband transitions, two interband transitions, and one inelastic collision. Figure 12(a) shows the calculated and experimental spectra based on the entire measured energy range and figure 12(b) shows a magnified portion of the
spectra spanning 0.2–0.4 eV in order to highlight the details. The calculated spectra of $n(E)$ and $k(E)$ of Ti fill in the gap between data points at ~0.28 and 0.31 eV, indicating the presence of spectral peaks and valleys within the gaps, rather than a simple structure less line between the two endpoints of the gaps. In particular, the calculated spectra indicate a local minimum in $k(E)$ at ~0.285 eV and local maxima in $n(E)$ and $k(E)$ at ~0.295 eV and 0.305 eV, respectively.

5.5.4.2. Vanadium (V)
Vanadium occupies group 5 of the periodic table. Its calculated and experimental spectra are depicted in figure 13. The experimental data were taken from Nestell and Christy [42] spanning 0.5–6.0 eV. A total of four terms were used in the calculation. Out of the four terms, two represent intraband electron transitions, and two interband transitions. The effect of inelastic collisions is not manifested in this energy range for V.

![Figure 13](image)

5.5.4.3. Chromium (Cr)
Chromium occupies group 6 of the periodic table. Its calculated and experimental spectra are depicted in figure 14. The experimental data were reported by Lynch and Hunter [26], covering the NIR–EUV range from 0.7–29.5 eV. A total of eight terms from the first sum in equations (7) and (8) were used in the calculation; six terms were related to intraband electron transitions, and two terms to interband electron dipole transitions. Since $E > 0.5$ eV, the effect of inelastic collisions is not manifested in this energy range for Cr.

![Figure 14](image)
5.5.4.4. Manganese (Mn)
Manganese occupies group 7 of the periodic table. Its calculated and experimental spectra are depicted in figure 15. The experimental data were taken from Johnson and Christy [43] spanning 0.64–6.6 eV. A total of five terms were used in the calculation, all of which represented intraband transitions. The effect of interband transitions and inelastic collisions is not manifested in this energy range.

![Figure 15](image)

**Figure 15.** Plot of calculated and experimental $n(E)$ and $k(E)$ spectra of Mn. Data by Johnson and Christy [43] from 0.64–6.6 eV. Corresponding fitting parameters are given in table 2.

5.5.4.5. Iron (Fe)
Iron occupies group 8 of the periodic table. It is the most abundant of all metals. Its calculated and experimental spectra are depicted in figure 16. The experimental data from Ordal et al. [44] spanning 0.0062–1.86 eV was combined with the experimental data of Johnson and Christy [43] spanning 2.0–6.6 eV. A total of six terms were used in the calculation to cover the total range from 0.0062–6.6 eV. Two terms represented intraband transitions, and four inelastic collisions. In this range photon energy was not high enough to induce interband transitions.

![Figure 16](image)

**Figure 16.** Calculated and experimental $n(E)$ and $k(E)$ spectra of Fe. Data from 0.0062–1.86 eV is by Ordal et al [44], and from 2.0–6.6 eV by Johnson and Christy [43]. Corresponding fitting parameters are given in table 2.

5.5.4.6. Cobalt (Co)
Cobalt occupies group 9 of the periodic table. The bright blue color, ‘cobalt-blue’, is one of Co’s oxides, cobalt-aluminate (CoAl$_2$O$_4$). Its calculated and experimental spectra are depicted in figure 17. The experimental data were taken from Johnson and Christy [43] spanning 0.64–6.6 eV. A total of five terms were used in the calculation to cover this range. All five terms represent intraband transitions. No interband transitions were present. The effect of inelastic collisions is not manifested in this energy range for Co.
5.5.4.7. Nickel (Ni)
Nickel occupies group 10 of the periodic table. Its calculated and experimental spectra are depicted in figure 18. The experimental data were taken from Johnson and Christy [43] spanning 0.64–6.6 eV. A total of four terms were used in the calculation to cover this range. Out of the four terms, three terms represent intraband transitions, and one interband transitions. The effect of inelastic collisions is not manifested in this energy range for Ni.

5.5.4.8. Zinc (Zn)
Zinc occupies group 12 of the periodic table. Although the stable ions formed by Zn and its congeners, Cd and Hg, have ten electrons that completely fill their ‘d’ orbitals [49], they are often classified as transition metals since they bridge the first three groups of the periodic table with the last six groups. Its calculated and experimental spectra are depicted in figure 19. The experimental data were taken from Querry [45] spanning 0.022–3.44 eV. A total of four terms were used in the calculation to cover this range. Out of the four terms, one term was related to intraband transitions, one to interband transitions, and two to inelastic collisions.
5.5.4.9. Mercury (Hg)
Mercury, a congener of Zn and Cd, occupies the sixth period of group 12 in the periodic table. It is the only metal element that is a liquid at room temperature. Compared to other metals, Hg is a poor conductor of heat, but a fair conductor of electricity.

Its calculated and experimental spectra are depicted in figure 20. It is seen that the calculated spectra match the fine structural details in the data occurring at ∼8–10 eV. The experimental data of Hg were taken from Inagaki et al. [46] spanning 0.2–19.5 eV. A total of seven terms were used in the calculation to cover this range. Out of the seven terms, three terms were related to intraband transitions, three to interband transitions, and one to inelastic collisions.

5.5.5. Noble transition metals
The noble metals, copper, silver, and gold are congeners of group 11 and occupy periods 4, 5, and 6 of the periodic table. They are classified as transition metals because they form stable ions in which the ‘d’ orbitals are not completely filled [49]. As might be expected, their calculated $n(E)$ and $k(E)$ are very similar since they are in the same group. Sometimes noble metals are defined as those which are basically inert and resistant to corrosion and oxidation in humid air. In this case, copper is excluded as a noble metal. Nevertheless, we show that the calculated and experimental $n(E)$ and $k(E)$ spectra of copper follow the same pattern of behavior as that of gold and silver. Six other inert metals besides silver and gold are sometimes included under this classification: ruthenium, rhodium, palladium, osmium, iridium, platinum.
5.5.5.1. Copper (Cu)
Copper is the lightest of the noble metals. It is soft, malleable, and ductile, with very high electrical and thermal conductivity. Its calculated and experimental spectra are depicted in figure 21. The experimental data were taken from Hagemann et al [47] spanning 0.005–100 eV. A total of nine terms were used in the calculation to cover this range of experimental data. Out of the nine terms, five terms represented intraband transitions, one interband transitions, and three inelastic collisions.

![Figure 21. Calculated and experimental n(E) and k(E) spectra of Cu. Data by Hagemann et al [47] from 0.005–100 eV. Corresponding fitting parameters are given in table 2.](image)

5.5.5.2. Silver (Ag)
Silver is a 'precious' metal occupying the fifth period of group 11 of the periodic table. It is soft, and exhibits the highest electrical and thermal conductivity and highest reflectivity of any metal. The experimental data were taken from Hagemann et al [47] spanning 0.005–100 eV. The calculated fits for Ag are shown in figure 22. The figure shows a mismatch between calculated and experimental spectrum of n(E) in the ~1–4 eV range. However, as in the case of Al, the mismatch is actually small, but is magnified since the data were plotted on a log-log scale. A total of eight terms were used in the calculation for n(E) and k(E) to cover the range of experimental data. Out of the eight terms, three represented intraband transitions, three interband transitions, and two inelastic collisions.

![Figure 22. Calculated and experimental n(E) and k(E) spectra of Ag. Data by Hagemann et al [47] from 0.005–100 eV. Corresponding fitting parameters are given in table 2.](image)

5.5.5.3. Gold (Au)
Like silver, gold is a 'precious' metal occupying the sixth period, group 11 of the periodic table. It has a bright yellowish gold color, and is dense, soft, malleable, and ductile. It can be drawn into a very thin wire and then stretched considerably before it breaks. Also, it is one of the least reactive chemical elements.
The experimental data were taken from Hagemann et al [47] spanning 0.005–100 eV. The calculated fits are shown in figure 23. The figure shows a slight mismatch between calculated and experimental spectrum of $n(E)$ from $\sim 1\sim 3$ eV. However, as in the case of Al and Ag, the mismatch is actually magnified since the data were plotted on a log-log scale. A total of eleven terms were used in the calculation to cover the range of experimental data. Out of the eleven terms in the calculation, seven represented intraband transitions, one interband transitions, and three inelastic collisions.

5.5.6. Poor metals or post transition metals
Poor metals are elements on the right-hand side of the periodic table whose conduction electrons occupy the p-orbitals. Poor metals is not a rigorous term, but the grouping is generally taken to include aluminum (Al), gallium (Ga), Indium (In), thallium (Tl), tin (Sn), lead (Pb), and bismuth (Bi). Poor metals generally have lower melting and boiling points, and greater softness than transition metals.

The $n(E)$ and $k(E)$ results of two poor metals, Pb and Bi, are presented in next two sections. Al which is also classified as a poor metal is discussed in detail in section 5.4.

5.5.6.1. Lead (Pb)
Lead occupies the sixth period of group 14 of the periodic table. Pb is a heavy metal that is denser than most common materials. It is soft and malleable, and also has a relatively low melting point. Lead has the highest atomic number of any stable element. Up until 2003 it was believed that Bismuth held that position.
The experimental data are by Mathewson and Myers [48] spanning 0.7–3.6 eV. The calculated and experimental spectra are depicted in figure 24. A total of two terms were used in the calculation. Out of the two terms, one represented intraband transitions and one interband transitions. The effect of inelastic collisions is not manifested in this energy range for Pb.

5.5.6.2. Bismuth (Bi)

Bismuth occupies the sixth period of group 15 of the periodic table. Bi has one of the lowest values of thermal conductivity. It was long considered the element with the highest atomic mass that is stable, but in 2003 it was discovered to be extremely weakly radioactive with a half-life of more than a billion times the estimated age of the universe. Because of its tremendously long half-life, bismuth may still be considered stable for all intents and purposes. The calculated and experimental spectra are depicted in figure 25. The experimental data were by Hagemann et al [47] spanning 0.6–100 eV. A total of seven terms were used in the calculation to cover this range of data. Out of the seven terms, four represented intraband transitions, two interband transitions and one inelastic collisions.

![Figure 25. Calculated and experimental n(E) and k(E) spectra of Bi. Data by Hagemann et al [47] from 0.6–100 eV. Corresponding fitting parameters are given in table 2.](image)

6. Discussion: relation to other physical concepts

6.1. Polarization

As previously discussed, Condition (i) of Titchmarsh’s Theorem embodies the principle of causality [24] by stipulating that the inverse Fourier Transform of the complex index of refraction, \( \mathcal{F}^{-1}[N(E) - N(\infty)] \), is a causal function. However, the theorem does not attribute any physical meaning to \( \mathcal{F}^{-1}[N(E) - N(\infty)] \). Nevertheless, as implied by Roman [52], we propose that it corresponds to polarization, which is consistent with the fact that polarization behaves in a causal manner. Thus, polarization does not occur at times corresponding to \( t < 0 \), if photons reach the metal at \( t = 0 \).

Let \( P(t) \) represent polarization, such that \( \mathcal{F}^{-1}[N(E) - N(\infty)] \equiv P(t) \). Then according to equations (16) and (17), \( P(t) \) consists of two components, \( \mathcal{F}^{-1}[N_i(E)] \equiv P_1(t) = \sum_{j=1}^{q} A_j \left( e^{-j/2\tau_j} \right) u(t) \) and \( \mathcal{F}^{-1}[N_2(E)] \equiv P_2(t) = \sum_{j=1}^{q} B_j \left( e^{-j/2\tau_j} \right) u(t) \).

Explicitly, \( [P_1(t)]_j = \frac{1}{n} \sum_{j=1}^{q} \left[ 2Q_j \left( \frac{k}{\tau_j} - X_j \right) + i \left( Q_j^2 - \left( \frac{k}{\tau_j} - X_j \right)^2 \right) \right] \left( e^{-j/2\tau_j} \right) u(t) \) and \( [P_2(t)]_j = \frac{1}{n} \sum_{j=1}^{q} \left[ \frac{1}{\tau_j} \left( e^{-j/2\tau_j} \right) u(t) \right] \). We assume that \( P_1(t) \) represents polarization prompted by electron dipole transitions (intraband or interband), and \( P_2(t) \), polarization prompted by inelastic collisions of conduction electrons.

As indicated by equations (16) and (17), \( [P_1(t)]_j \) and \( [P_2(t)]_j \), decay exponentially as \( \exp[-t/2\tau_j] \) or \( \exp[-t/2\tau_j^\prime] \). The parameter \( \tau_j \) represents the lifetime of the \( j \)th excited electron state and the parameter \( \tau_j^\prime \) represents the mean time between collisions. In the limit as \( t \rightarrow \infty \), polarization dies out and equilibrium is restored.

Furthermore, the complex-valued and real-valued nature of \( P_1(t) \) and \( P_2(t) \) is due to the behavior of Fourier Transform pairs [53]. Accordingly, since \( n(E) \) and \( k(E) \) for intraband and interband transitions are asymmetric functions of \( E \), \( [P_1(t)]_j \) is complex-valued. By contrast, since \( n(E) \) and \( k(E) \) for inelastic electron collisions are symmetric and anti-symmetric functions of \( E \), \( [P_2(t)]_j \) is real-valued.
In addition, since $[P(t)]_k$ contains the factor $\exp[i(Bt/2\hbar)t]$, the real and imaginary parts of polarization associated with intraband and interband transitions oscillate with a frequency $\omega = \frac{\hbar}{2\hbar} \equiv \frac{(\Delta E_k)}{\hbar}$, where $\Delta E_k = (E_n - E_p)$ is proportional to the $j$th energy difference between initial and excited electron states, $|a_j\rangle$ and $|b_j\rangle$.

6.2. Connection to complex conductivity

In general, the complex index of refraction $N(E) = n(E) - ik(E)$ is related to the complex dielectric function $\varepsilon(\omega) = \varepsilon_1(\omega) - i\varepsilon_2(\omega)$, which in turn is related to the complex optical conductivity $\sigma(\omega) = \sigma_1(\omega) - i\sigma_2(\omega)$ by

$$\varepsilon(\omega) = 1 - \frac{4\pi\sigma(\omega)}{\varepsilon_0\omega}$$

where $\varepsilon_0$ represents the vacuum permittivity. Consider the free electron Drude model for $\varepsilon(\omega)$, valid in the low energy spectral range, given by:

$$\varepsilon(\omega) = \frac{\omega_p^2}{\omega^2 - i\omega\tau}$$

(22)

where $\omega_p$ represents plasma frequency and $\tau$ the average mean time between collisions of electrons. Incorporating equation (22) into equation (21) yields the Drude model for $\sigma(\omega)$:

$$\sigma_1(\omega) = \frac{\sigma_0}{1 + \omega^2\tau^2}$$

(23)

$$\sigma_2(\omega) = \frac{\sigma_0}\omega\tau}{1 + \omega^2\tau^2}$$

(24)

where $\omega^2\tau/4\pi$ is replaced by $\sigma_0$, the DC-conductivity.

Substituting $\omega = E/\hbar$ in equations (23) and (24), and letting $\sigma_0 = A_0\tau/\hbar$ and $\tau = \hbar^2/C_0$ yields:

$$\sigma_1(\omega) = \frac{A_0(C_0)^{\omega_5}}{E^2 + C_0}$$

(25)

$$\sigma_2(\omega) = \frac{A_0E}{E^2 + C_0}$$

(26)

Now, consider the present model for $n(E)$ and $k(E)$ corresponding to inelastic collisions of conduction or ‘free’ electrons, given by the real and imaginary parts of equation (14) for $N(E)$. Assuming one term in the sum is sufficient to describe $n(E)$ and $k(E)$ in the low IR energy range, then:

$$n(E) = \frac{A'(C')^{\omega_6}}{E^2 + C'}$$

(27)

$$k(E) = \frac{A'E}{E^2 + C'}$$

(28)

Equations (25) and (26) show that the functional forms of the Drude model for $\sigma_1(\omega)$ and $\sigma_2(\omega)$ match the functional forms of $n(E)$ and $k(E)$ in the low energy range given by equations (27) and (28).

As a specific example, consider figure 26 which shows a side by side comparison of $n(E)$ and $k(E)$ and $\sigma_1(\omega)$ and $\sigma_2(\omega)$ of Ag, and provides a visual correspondence between these functions.

In figure 26(a) the calculated fits of equations (27) and (28) for $[n(E) - 1]$ and $k(E)$ of Ag are based on partial experimental data by Yang *et al.* [2], covering the range from 0.05–1.0 eV. (The entire range of data spans 0.05–4.14 eV.) The values of $A'$ and $C'$ in equations (27) and (28) were determined to be $A' = 8.5714$ and $C' = 2.7323 \times 10^{-4}$, in accordance with the methodology described in sections 5.3 and 5.4.

In figure 26(b) the calculated and experimental spectra of equations (25) and (26) for $\sigma_1(\omega)$ and $\sigma_2(\omega)$ of Ag is a direct reprint from Yang *et al.* [2].

As these figures demonstrate, the shapes of the spectra of $n(E)$ and $k(E)$ representing inelastic ‘free’ electron collisions of Ag, match the shapes of spectra for the real and imaginary parts of complex conductivity $\sigma_1(\omega)$ and $\sigma_2(\omega)$. 

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6.3. Behavior of \( n(E) \) and \( k(E) \) at very low energies

When extended down to very low energies to the Far-IR and THz regimes, at around \( 10^{-3} \) eV–\( 10^{-4} \) eV, the calculated spectrum of \( k(E) \) predicts the existence of peak, for a number of metal elements, including Li, Al, Fe, Cu, Ag and Au. In addition, the calculated spectrum of \( n(E) \) in the low energy regime predicts that \( n(E) \) flattens out at a very high value, sometime between \( 10^3 \) and \( 10^5 \). Such behavior in \( n(E) \) and \( k(E) \) is analogous to the behavior of \( n(E) \) and \( k(E) \) for water and ice in the relaxation regime at \( \sim 10^{-4} \) eV and \( \sim 10^{-11} \) eV, respectively. However, the value for \( n(E) \) of water and ice in the relaxation regime is significantly lower, around 9. The extremely high value of \( n(E) \) in the low energy regime is somewhat justifiable. This is because, in principle, for a perfect conductor, \( \lim_{E \to 0} n(E) \to \varepsilon_0 \to \infty \), where \( \varepsilon_0 \) represents the static dielectric constant. Experimental measurements are needed to verify the results in the very low energy spectral range.

7. Conclusion

7.1. The takeaway

A new formulation is introduced for the complex index of refraction of metals, \( N(E) = n(E) - ik(E) \). The formulation is the result of assuming the interaction between photons and metals induces three types of events that affect \( k(E) \): intraband electron dipole transitions; interband electron dipole transitions; inelastic collisions of conduction electrons. Based on these events an expression for \( k(E) \) is obtained, followed by an expression for its counterpart, \( n(E) \), determined from the Hilbert Transform of \( k(E) \). The question of theoretical validity of these expressions is tackled first, after which consistency with experimental data is examined.

At the heart of theoretical validity is an esoteric mathematical theorem by Titchmarsh. Although esoteric, the theorem has a real-world side to it; in particular, it conveys the principle of causality and its connection to the physics of dispersion. Meanwhile, Toll proved the logical equivalence between causality and the validity of dispersion equations [27]. The basis of the proof is Titchmarsh’s Theorem. Thus, the theoretical validity of the formulation is centered on consistency with causality laid out by Titchmarsh’s Theorem.

Causality is a statement that effect cannot precede its cause and, according to Titchmarsh’s Theorem, is expressed by stipulating \( \mathcal{F}^{-1} \{ [N(E) - N(\infty)] \} \) behaves as a causal function; namely, it vanishes for \( t < 0 \). The operator \( \mathcal{F}^{-1} \) denotes inverse Fourier Transform. As a result of the causal condition, two more equivalent conditions follow. One is related to analyticity of \( [N(E) - N(\infty)] \), which specifies it as holomorphic in the lower half complex \( E \) plane and allows it to be analytically extended into that plane. The other deals with the real and imaginary parts of \( [N(E) - N(\infty)] \), specifying them to be skew reciprocal Hilbert Transforms, analogous to the well-known Kramers-Kronig (K-K) relations. The K-K relations are usually considered to be the standard for expressing the concept of optical dispersion and its connection to causality. However, they are a limited version of the more general relations by Titchmarsh. Specifically, the K-K relations constrain \( n(E) \) and \( k(E) \) to be symmetric and anti-symmetric functions of \( E \), whereas Titchmarsh’s Theorem does not. Thus, although the new expressions for \( n(E) \) and \( k(E) \) are asymmetric functions of \( E \), it is demonstrated that they are skew.
reciprocal Hilbert Transforms. Furthermore, it is established that the new formulation satisfies all three conditions of Titchmarsh’s Theorem, and therefore, theoretically, is a valid representation of optical dispersion.

Several aspects of relating the formulation to other physical concepts are discussed. These aspects include polarization, the Drude model for complex conductivity, and the behavior of \( n(E) \) and \( k(E) \) in the limit \( E \to 0 \).

Having dealt with theoretical aspects of the formulation, attention is then turned to experimental considerations. To this end, the published experimental data of \( n(E) \) and \( k(E) \) were examined for 23 metal elements belonging to Groups 1 through 15 of the periodic table. Calculated spectra determined from the new equations for \( n(E) \) and \( k(E) \) of all these metals were obtained. Excellent agreement is obtained for the fits between calculated and corresponding experimental data. The calculated spectra even fit very fine features of the \( n(E) \) and \( k(E) \) data. Also, our results indicate that calculated \( n(E) \) and \( k(E) \) spectra of metals in the same group, for example Alkaline metals, are very similar. This result is not unexpected since metals in the same group also exhibit similar physical and chemical behavior.

Based on the formulation’s theoretical validity plus its agreement with experimental data spanning the Far-IR through EUV energies, our takeaway is that the new formulation is a wide-ranging representation of optical dispersion for metals.

7.2. Future relevant work
7.2.1. \( n(E) \) and \( k(E) \) measurements in the low energy regime
Our results predict a peak in \( k(E) \) along with an extremely high constant value in \( n(E) \) in the very low energy regime, anywhere from Far-IR through terahertz (THz) energies. However, finding data in this low energy spectral range for metals is challenging. To obtain such data, we are in the process of setting up experiments to measure the transmittance of a thin layer of a metal (e.g., gold) deposited on a silicon substrate. We know that silicon is semi-transparent in the THz regime. Therefore, if a maximum in \( k(E) \) of gold is present in this regime, then the transmittance spectrum should show a minimum in the THz spectral range.

7.2.2. Non-metals, metalloids, metal alloys
We have preliminary results that show the present dispersion equations can be applied to materials not designated as metals in the periodic table. Such materials include silicon, germanium, and tellurium which are metalloids; cubic-carbon (diamond) and selenium which are non-metals; plus, permalloy and brass which are metal alloys. These results may be presented in a future publication.

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