New dispersion equations for insulators and semiconductors valid throughout radio-waves to extreme ultraviolet spectral range

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Abstract
A new formulation of optical dispersion in terms of complex index of refraction, \( N(E) \) as a function of photon energy, \( E \), applicable to insulators and semiconductors, is introduced. Previous formulations, developed over the past 200 years, are either valid only over a limited spectral range, or do not accurately fit experimental data, or do not conform to the Principle of Causality. The new formulation overcomes these shortcomings. Its validity is established based on theoretical and experimental considerations. The theoretical basis stems from consistency with Titchmarsh’s Theorem, a comprehensive mathematical expression of the Principle of Causality. In accordance with Titchmarsh’s Theorem, the expressions for the real and imaginary parts of \( N(E) \), the refractive index, \( n(E) \), and extinction coefficient, \( k(E) \), are shown to be skew reciprocal Hilbert Transforms. Also, the expression for the inverse Fourier Transform of \( N(E) \) is shown to be a complex-valued causal function of time. The causal function is identified as the polarization of the medium, \( P(t) \), if photons reach the medium at an initial time equal to zero. \( P(t) \) is associated with photon excitations of electrons and other quantum constituents of the media. The experimental basis of the formulation stems from demonstrating exceptionally close agreement with published experimental \( n(E) \) and \( k(E) \) data of different forms of insulators and semiconductors. Specifically, the formulation is applied to data of Water, Ice, SiO\(_2\)-Glass, LiF, Polyethylene, a-Si, InSb, GaP, and As\(_2\)Se\(_3\). Data for Water span thirteen orders of magnitude, and fourteen for Ice, over the spectral range of Radio-Waves to EUV. Data of the other materials involved smaller spectral ranges. Results indicate that fewer fitting parameters are needed over any segment of the electromagnetic spectrum, compared to other formulations. These theoretical and experimental findings suggest the formulation represents a universal description of optical dispersion of insulators and semiconductors.

1. Introduction
Optical dispersion, i.e., the dispersion of light by materials, has been the subject of many investigations over several hundred years and is the focus of numerous formulations that describe this phenomenon. Optical dispersion of any material, and hence such formulations, depend on photon energy, \( E \), or the wavelength of light, \( \lambda \), and also on the nature of the material and its fabrication conditions as well. The quantities \( E \) and \( \lambda \) are related through \( \lambda = \frac{hc}{E} \), where \( h \) is Planck’s constant and \( c \) the speed of light in vacuum. Numerically, \( \lambda(\text{nm}) = \frac{1239.8}{E(\text{eV})} \). Dispersion formulations are expressed in terms of optical functions such as the real and imaginary parts of the complex index of refraction \( N(E) = n(E) - ik(E) \), i.e., the refractive index, \( n(E) \), and extinction coefficient, \( k(E) \), or the real and imaginary parts of the complex dielectric function \( \varepsilon(\omega) = \varepsilon_1(\omega) - i\varepsilon_2(\omega) \), where \( \omega \) represents angular frequency and is related to photon energy by \( E = \frac{h\omega}{2\pi} \equiv h\omega \).

Optical functions, \( n(E) \) and \( k(E) \), are intrinsic material properties and may be thought of as the fingerprint of a material, but they cannot be measured directly. They are determined from extrinsic measurements that depend on them, for example, reflectance and transmittance, or ellipsometric parameters. Therefore, there is a
need to establish a relation between these measurements and optical functions. This involves formulating models of \( n(E) \) and \( k(E) \) which can be used to analyze the extrinsic measurement data.

By inspecting the \( n(E) \) and \( k(E) \) spectra of an 'ideal' insulator or semiconductor, over a very wide range, the following picture emerges:

The energy band gap, \( E_g \), can be identified, indicating the onset of electron absorption of photons for energies above \( E_g \). The value of \( E_g \) depends on the particular material, and can occur anywhere from Infrared (IR) to Vacuum-Ultraviolet (VUV) energies.

In the region around \( E_g \) there is typically an exponential-type rise in \( k(E) \), Urbach’s edge formula [1] is usually used to describe \( k(E) \) when \( E \approx E_g \). See [2] for examples of applications of Urbach’s edge formula.

Above \( E_g \), up to the Extreme-Ultraviolet (EUV) region, peaks in the spectra of \( n(E) \) and \( k(E) \) are attributed to inter-band electron transitions caused by photon absorption. The original Forouhi-Bloomer [3, 4] and Tauc-Lorentz [5] models are widely used to describe the spectra in this region. For comparative studies of these two models, see Easwarakhanthan et al [6], Laidani et al [7] and Gao et al [8].

Below \( E_g \), there is a spectral regime where all insulators and semiconductors are practically transparent. In this regime, the value of \( k(E) \) is close to zero, less than \( 10^{-5} \), typically. This is a region indicative of negligible 'optical activity’. Depending on the value of the band gap, this transparent region can fall anywhere between deep UV down to the IR range. The Cauchy and Sellmeier models, which were developed in the nineteenth century, are usually used to describe \( n(E) \) in the transparent regime [9, 10], where the minute values of \( k(E) \) are taken as equal to zero. Historically, and traditionally, the Cauchy and Sellmeier models are expressed in terms of \( n \) versus \( \lambda \). There are innumerable examples of the utilization of Cauchy and Sellmeier models in the literature. See, for instance Kedenburg et al [11] and Daimon and Masumura, [12]. Interestingly, Poelman and Smet [13] indicate that the original Forouhi-Bloomer equations can yield very good results in this regime as well.

Below the transparent regime, down to the Far-Infrared (Far-IR), a good measure of ‘optical activity’ occurs. Photon excitations of phonons and molecular-spinors are attributed to the activity, which results in spectral peaks in \( n(E) \) and \( k(E) \). We have taken the liberty of borrowing the term ‘spinor’ from quantum dynamics to represent quantized molecular rotational modes [14]. The Lorentz Oscillator [15, 16] is the most-widely quoted and generally-accepted model describing \( n(E) \) and \( k(E) \) in this regime. Other approaches describing \( n(E) \) and \( k(E) \) have been developed by Meneses et al [17, 18] and Carati et al [19].

Below the Far-IR, somewhere in the Microwaves down to Radio-Waves, a strong peak is observed in the spectrum of \( k(E) \). Complementing the \( k(E) \) spectrum, \( n(E) \) appears as a reverse ‘rounded step function’, approaching the square root of the static dielectric constant, as \( E \rightarrow 0 \). The spectra of \( n(E) \) and \( k(E) \) in this region, referred to as the relaxation spectra, are attributed to proton mobility, and are described by the Debye relaxation equation. See, for example, Artemov and Volkov [20].

Regardless of the particular model, there is no single formulation able to adequately describe experimental data for \( n(E) \) and \( k(E) \), over especially wide ranges of the electromagnetic spectrum, spanning Radio-Waves EUV energies.

In this paper, a new formulation for \( n(E) \) and \( k(E) \) that addresses this insufficiency is presented. We maintain that the new formulation can be used to replace all previous formulations describing the \( n \) and \( k \) spectra of insulator and semiconductor materials.

The new equations are an outcome of modifying the original Forouhi-Bloomer (F-B) Equations [3, 4]. The modification results in a new formulation for \( n(E) \) and \( k(E) \) that is completely consistent with the mathematical expression of Causality stipulated by Titchmarsh’s Theorem [21].

To support the validity of the new formulation, we apply it to experimental \( n(E) \) and \( k(E) \) data of a selected set of materials, all with interesting properties and practical applications. The materials in this selected set are Water, Ice, SiO2-Glass, LiF, Polyethylene, a-Si, InSb, GaP, and As2Se3.

The paper is organized as follows. In section 2, the original F-B equations are presented and used as a starting point in section 3 to derive the new equations for \( n(E) \) and \( k(E) \). In section 4, the K-K requirements for physical validity of dispersion formulations are reviewed. In section 5, we explore the physical validity of the new formulation and show its connection to the Principle of Causality via Titchmarsh’s Theorem. In section 6, the new F-B equations for \( n(E) \) and \( k(E) \) are applied to published experimental \( n(E) \) and \( k(E) \) data of the above mentioned materials. Conclusions follow in section 7. Appendices A1–A3 provide proofs of the new formulation’s agreement with elements of Titchmarsh’s Theorem.

2. Background

2.1. The original Forouhi-Bloomer (F-B) formulation for \( n(E) \) and \( k(E) \)
The original F-B equations were published in 1986 and involved \( n(E) \) and \( k(E) \) of amorphous insulators and semiconductors [3]. The work was extended to crystalline materials in 1988 [4].
The term ‘amorphous’ was used for those materials dominated by short range order that exhibit one peak in their \( n(E) \) and \( k(E) \) spectra in the Near Infrared-Visible-Ultraviolet (NIR-Vis-UV) spectral range. Materials that exhibit more than one peak in this range, where long range order dominates, were termed ‘crystalline’. However, when viewed over a wider range of photon energies, from Radio-Waves to EUV energies and beyond, all materials, including ‘amorphous’ materials, exhibit more than one peak in their \( n(E) \) and \( k(E) \) spectra.

The original formulation dealt with inter-band electron transitions which occur at photon energies above the energy band gap, \( E_g \). Inter-band transitions typically appear somewhere in the NIR to EUV range, anywhere from approximately 0.5 eV to 25 eV or higher.

The formulation was based on time-dependent perturbation theory applied to a continuous medium, perturbed by a flow of photons. The perturbation induces electron transitions with a finite lifetime, from lower occupied electron energy states in the valence band to higher unoccupied states in the conduction band. This led to the following expression for \( k(E) \) [3, 4]:

\[
k(E) = \sum_{j=1}^{q} \frac{A_j (E - E_g)^2}{E^2 - B_j E + C_j}, \quad E > E_g
\]

(1)

The expression for \( n(E) \) was derived from the Hilbert Transform of \( k(E) \):

\[
n(E) = n(\infty) + \sum_{j=1}^{q} \frac{B_{0j} E + C_{0j}}{E^2 - B_j E + C_j}, \quad E > E_g
\]

(2)

where the sum is over the number of peaks, \( 'q' \) in the \( n(E) \) and \( k(E) \) spectra [3, 4].

The parameter \( A_j \) in equation (1) is a dimensionless constant, and is proportional to inter-band electron transition probabilities.

The factor \( (E^2 - B_j E + C_j) \) in the denominator originates from the recognition that the lifetime of the excited state is not infinite. The quantity \( B_j = 2(E_{j-1} - E_0) \), the energy difference between initial and final states involved in the electron transition. The quantity \( C_j = [(B_j^2/4) + (\hbar^2/2\tau_j)] \) where \( \tau_j \) represents the lifetime of the \( j \)th excited electron state.

The quantity \( (E - E_g)^2 \) in the numerator of equation (1) represents the joint density of states, where \( E_g \) is the optical energy band gap. It is based on the assumption that electron states are distributed parabolically in the valence and conduction bands of the medium.

The parameters \( B_{0j}, C_{0j} \) in equation (2), are not independent, but depend on \( A_j, B_j, C_j, \) and \( E_g \):

\[
B_{0j} = \frac{A_j}{Q_j} \left[ -\frac{B_j^2}{2} + E_g B_j + E_g^2 + C_j \right]
\]

(3)

\[
C_{0j} = \frac{A_j}{Q_j} \left[ (E_g^2 + C_j) \frac{B_j}{2} - 2E_g C_j \right]
\]

(4)

where:

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

(5)

2.2. Concerns with original F-B equations

A number of years after their 1986 and 1988 publications, it was argued by Jellison and Modine [5] that the original F-B equations were not physically valid for two main reasons:

1. \( \lim_{E \to \infty} k(E) \equiv k(\infty) \neq 0 \).

2. The expressions for \( n(E) \) and \( k(E) \) are asymmetric functions of \( E \).

Regarding the first concern, experimental evidence indicates that \( k(\infty) = 0 \). Also, from a theoretical point of view, at extremely high energies, the perturbation of a medium caused by photon-electron interactions, breaks down, and the photons behave as if in a vacuum, in which case, \( k(\infty) \) should be equal to zero.

Furthermore, \( n(E) \) and \( k(E) \) cannot be related as Hilbert Transforms of each other, as stipulated by the Principle of Causality (See section 4.3), if \( k(\infty) \neq 0 \).

The second concern represents a breach of the symmetry requirements of the Kramers-Kronig (K-K) Dispersion Relations. The K-K relations constrain \( n(E) \) and \( k(E) \) to be symmetric and anti-symmetric functions of \( E \), respectively.
3. Deriving new dispersion equations for \( n(E) \) and \( k(E) \)

3.1. Deriving a new expression for \( k(E) \) for \( E > E_g \)

In the original equation for \( k(E) \), \( \lim_{k \to \infty} k(E) = 0 \). A simple remedy to this issue would be to subtract the contribution of \( k(\infty) \) from \( k(E) \) and re-formulate optical dispersion in terms of

\[
[N(E) - N(\infty)] = [n(E) - n(\infty)] - i[k(E) - k(\infty)]
\]

(6)

Obviously, \([N(E) - N(\infty)] \to 0\) as \( |E| \to \infty\), so that \([n(E) - n(\infty)]\) and \([k(E) - k(\infty)]\) can be derived as Hilbert Transforms of each other. We remark that the subtraction of \( n(\infty) \) from \( n(E) \) has always been factored into formulations of optical dispersion [15].

In the original formulation, the density of states in the numerator of \( k(E) \) has a quadratic dependence on \( E \). If \( k(\infty) \) is subtracted from \( k(E) \), then the numerator of \( k(E) \) will depend linearly on \( E \). For example, consider the case with \( q = 1 \), i.e., when there is one peak in \( k(E) \), then \( k(\infty) = A \). Letting \( k'(E) \equiv [k(E) - k(\infty)]\):

\[
k'(E) \equiv [k(E) - k(\infty)] = \frac{A(E - E_g)^2}{E^2 - BE + C} - A
\]

(7)

equation (7) shows that the subtraction of \( k(\infty) \) from \( k(E) \) produces a linear dependence on \( E \) in the numerator of \( k'(E) \). However, in order to achieve the correct behavior of \( k'(E) \) at the energy band gap, we find that we must go beyond just subtracting \( k(\infty) \) from \( k(E) \).

Originally, the quantity \( E_g \) was understood as representing the optical energy bandgap, such that \( k(E) \) equals zero when \( E \) equals \( E_g \). According to equation (7), \( k'(E_g) = -A \neq 0 \) and therefore, the quantity \( E_g \) loses its meaning. In order to overcome this dilemma, we rewrite equation (7) in the following way:

\[
k'(E) = \frac{A'(E - E'_g)}{E^2 - BE + C}
\]

(8)

where

\[
A' = A(B - 2E_g)
\]

(9)

\[
E'_g = \frac{C - E_g^2}{B - 2E_g}
\]

(10)

Examining equation (8), it is seen that \( E'_g \) has the correct attributes of energy band gap: it has the dimensions of energy and also \( k'(E) = 0 \) if \( E = E'_g \), as required, i.e., \( k'(E'_g) = 0 \).

Dropping the ‘primes’ in \( k'(E) \), \( A' \), and \( E'_g \) in equation (8), the extinction coefficient can be expressed as:

\[
k(E) = \frac{A(E - E_g)}{E^2 - BE + C}
\]

(11)

We now make the assumption that the general expression for the extinction coefficient can be represented by a sum of terms, with each term having the same form as \( k(E) \) in equation (11):

\[
k(E) = \sum_{j=1}^{q} \frac{A_j(E - E_g)}{E^2 - B_jE + C_j}, \quad E > E_g
\]

(12)

The total number of terms, \( q \), in equation (12) is taken as equal to the number of peaks in \( k(E) \).

Based on the result for a single peak, we assume that \( A_j \) is proportional to the probability for electron transitions. This point is emphasized because we expect, in general, \( A'_j \) is also proportional to the probability of other types of transitions caused by photon interactions with phonons, molecular-spinors (quantized molecular rotational modes) and mobile-protons.

We continue to assume that the numerator, \( (E - E_g) \), represents the joint density of states, albeit a linear function of \( E \), as opposed to the quadratic function for \( k(E) \) in original F-B equation.

Furthermore the factor \( (E^2 - B_jE + C_j) \) in the denominator is still associated with the energy difference between initial and final electron states, as well as the finite lifetime of excited states.

3.2. Deriving a new expression for \( n(E) \) for \( E > E_g \)

The next step is to obtain an expression for the counterpart of \( k(E) \), namely, \( n(E) \). As discussed in 4.3, the Principle of Causality, via Titchmarsh’s Theorem [21], specifies \([n(E) - n(\infty)]\) as the Hilbert Transform of \([k(E) - k(\infty)]\), analogous to the K-K Dispersion Relations:
\[ n(E) - n(\infty) = H \left( [k(E) - k(\infty)] \right) = \frac{1}{\pi} \oint \frac{\delta \Phi}{E - E'} dE' \]  \hspace{1cm} (13)

The symbol \( \Phi \) in front of the integral of equation (13) stands for the Cauchy Principle Value of the integral over a closed loop in the complex \( E \) plane and is equal to the sum of the residues within the loop and on the boundary of the loop.

Appendix A.3 shows the steps involved in evaluating the principle value integral in equation (13) to obtain:

\[ n(E) - n(\infty) = \sum_{j=1}^{q} \frac{D_j E + F_j}{E^2 - B_j E + C_j}, \quad E > E_g \]  \hspace{1cm} (14)

where:

\[ D_j = \frac{A_j}{Q_j} \left( E_g - \frac{B_j}{2} \right) \]  \hspace{1cm} (15)

\[ F_j = \frac{A_j}{Q_j} \left( C_j - \frac{E_g B_j}{2} \right) \]  \hspace{1cm} (16)

The quantity \( Q_j \) is given, as before, by equation (5).

### 3.3. New equations for \( n(E) \) and \( k(E) \) for \( E < E_g \)

The formulation in section 3.1 was designed to represent \( n(E) \) and \( k(E) \) above the band gap. Below the band gap, there is not enough photon energy to induce electron inter-band transitions. Existing models, such as those mentioned in the Introduction, do not provide a complete description of \( n(E) \) and \( k(E) \), starting from \( E = E_g \) down to Radio-Waves energies. Taking a phenomenological approach, we will assume that \( n(E) \) and \( k(E) \) spectra below the band gap can be represented by setting \( E_g = 0 \) in equations (12) and (14).

With \( E_g = 0 \), equations (12) and (14) reduce to:

\[ k(E) = \sum_{j=1}^{p} \frac{A_j E}{E^2 - B_j E + C_j}, \quad E < E_g \]  \hspace{1cm} (17)

\[ n(E) = n(\infty) + \sum_{j=1}^{p} \frac{D_j E + F_j}{E^2 - B_j E + C_j}, \quad E < E_g \]  \hspace{1cm} (18)

\[ D'_j = - \frac{A_j B_j}{2 Q_j}, \]  \hspace{1cm} (19)

\[ F'_j = \frac{A_j C_j}{Q_j} \]  \hspace{1cm} (20)

In equations (17) and (18), we assume that below the gap, the parameter \( A_j \) is related to the probability for phonon, molecular-spinor (quantized molecular rotational modes), or mobile-proton transitions. Furthermore, we continue to assume that the denominator is a manifestation of finite lifetimes of the excited quantized states involved in the transitions of these quantum constituents. The parameter \( Q_j \) in equations (14)–(16) and (18)–(20) will still equal \( h/2 \tau_p \), where \( \tau_p \) is now construed as the lifetime of the \( j \)th excited state to which these quantized constituents transfer. This is analogous to the definition of \( Q_j \) in equation (5).

As in the case for \( n(E) \) and \( k(E) \) above the band gap, the density of states below the gap follows a linear dependence on \( E \).

The linear dependence on \( E \) of the density of states, for quantum states both above and below the band gap, is a consequence of fulfilling the requirement that \( k(\infty) = 0 \).

### 3.4. Expressions for \( n(E) \) and \( k(E) \) applicable to entire radio-wave to EUV spectral range

We will now assume that the equations for \( n(E) \) and \( k(E) \) consist of two parts, one part for the region below the energy band gap given by equations (17) and (18); and the other for the region above the energy band gap given by equations (12) and (14).

Therefore, we will assume that the complete equations for \( n(E) \) and \( k(E) \) can be given as:

\[ k(E) = \sum_{j=1}^{p} \frac{A_j E}{E^2 - B_j E + C_j} + \sum_{i=1}^{q} \frac{A_i (E - E_g)}{E^2 - B_i E + C_i} \]  \hspace{1cm} (21)  

\[ n(E) = n(\infty) + \sum_{j=1}^{p} \frac{D_j E + F_j}{E^2 - B_j E + C_j} + \sum_{i=1}^{q} \frac{D_i E + F_i}{E^2 - B_i E + C_i} \]  \hspace{1cm} (22)

Equations (21) and (22) are the new F-B dispersion equations with \( D_j, F_j, D'_j \) and \( F'_j \) given by equations (15), (16), (19) and (20), respectively.
In the above formulation, \( \lim_{E \to \infty} n(E) \equiv n(\infty) \). When fitting the new F-B dispersion equations, equations (21) and (22), to experimental data, the value of \( n(\infty) \) is not assumed equal to one, the classical value. The quantity \( n(\infty) \) is taken as \( 1 + a' \), where \( a' \) is a constant that compensates for any neglected dispersion terms [3, 4]. When all terms, including the terms at the upper end of the spectral range, are considered in the sum, then \( a \to 0 \), as \( E \to \infty \), and the classical result is obtained, i.e., \( n(\infty) \to 1 \).

Note that when applying equation (21) to experimental data, \( k(E) \) may fall below zero at certain values of \( E \) for certain combinations of the parameters \( A_j, B_j, \) and \( C_j \) in both sums of equation (21). In which case, the value of \( k(E) \) should be set to zero.

4. Traditional requirements for physical validity of expressions for \( n(E) \) and \( k(E) \)

4.1. The Kramers-Kronig (K-K) relations

Traditionally, formulations of optical dispersion are considered physically valid if they are consistent with the Kramers-Kronig (K-K) relations. The K-K relations are a set of conditions, derivable from the Principle of Causality [22, 23]. In particular, all physically valid formulations for the complex index of refraction \( N(E) \equiv n(E) - ik(E) \) are expected to comply with the following three K-K conditions:

1. Restriction on the limits of \( n(E) \) and \( k(E) \) as \( E \) tends to infinity:
   \[
   \lim_{E \to \infty} n(E) \equiv n(\infty) = 1, \quad \lim_{E \to \infty} k(E) \equiv k(\infty) = 0
   \]

2. Compliance with K-K dispersion relations that connect \( n(E) \) and \( k(E) \) as skew reciprocal Hilbert Transforms:
   \[
   n(E) = 1 + P \int_{-\infty}^{\infty} \frac{k(E')}{E - E'} dE' \tag{23}
   \]
   \[
   k(E) = -P \int_{-\infty}^{\infty} \frac{[n(E') - 1]}{E - E'} dE' \tag{24}
   \]

3. Adherence to the Kramers-Kronig (K-K) symmetric and anti-symmetric constraints for \( n(E) \) and \( k(E) \):
   \[
   n(E) = n(-E) \tag{25}
   \]
   \[
   k(E) = -k(-E) \tag{26}
   \]

The new F-B dispersion equations, equations (21) and (22), are consistent with the first two requirements, but not the third, but not the symmetry constraints stated in the third requirement.

4.2. Arguments supporting the K-K symmetry requirements

Since the K-K symmetry constraints are considered to be a criterion for physical validity of dispersion formulations, it is important to understand how they arise. The necessity for the K-K symmetry constraints encompasses several loosely connected arguments [5, 15, 23].

1. One argument states that without the K-K symmetry constraints, the integrals of the Hilbert Transforms for \( n(E) \) and \( k(E) \), equations (23) and (24), will cover both negative and positive energies. It is purported to be preferable for the Hilbert Transform integrals to cover only positive energies. Thus, if \( n(E) = n(-E) \) and \( k(E) = -k(-E) \), then the Hilbert Transforms in the K-K Dispersion Relations can be expressed in terms of integrals that do not cover negative energies, i.e.:
   \[
   [n(E) - 1] = \mathcal{H}\{k(E)\} \equiv \frac{1}{\pi} \int_{-\infty}^{\infty} \frac{k(E')}{E - E'} dE' = \frac{2}{\pi} \int_{0}^{\infty} \frac{E'k(E')}{E^2 - E'^2} dE' \tag{27}
   \]
   \[
   k(E) = -\mathcal{H}\{[n(E) - 1]\} \equiv -\frac{1}{\pi} \int_{-\infty}^{\infty} \frac{[n(E') - 1]}{E - E'} dE' = \frac{2E}{\pi} \int_{0}^{\infty} \frac{[n(E) - 1]}{E^2 - E'^2} dE' \tag{28}
   \]

However, this is a circular argument, since the right hand sides of equations (27) and (28) do not actually eliminate negative energies. Rather, the right hand sides of these equations are essentially statements that \( n(E) = n(-E) \) and \( k(E) = -k(E) \).
2. A second argument states that the Lorenz Oscillator model $\varepsilon(\omega)$ can be used as an archetype to represent optical dispersion. Since $\varepsilon_1(\omega) = \varepsilon_1(-\omega)$ and $\varepsilon_2(\omega) = -\varepsilon_2(-\omega)$, it is argued that it should represent dispersion properties in general. Although this notion is very elegant, the Lorenz Oscillator model does not adequately describe experimental data for $n(E)$ and $k(E)$ over any reasonably-extended energy range.

3. Another argument arises from the desire to impart physical meaning to $\mathcal{F}^{-1}[N(E)]$, the inverse Fourier Transform of $N(E)$ by constraining it to be a real-valued function of time. This will be the case if the K-K symmetry constraints, equations (25) and (26), hold. Thus with the new formulation, since $n(E)$ and $n(E)$ are asymmetric, $\mathcal{F}^{-1}[N(E)]$ is complex-valued. Nevertheless, we are able to impart physical meaning to $\mathcal{F}^{-1}[N(E)]$, as discussed in section 5.4.

4. Lastly, Jellison and Modine [5] argue that $k(E)$ must necessarily be anti-symmetric in order for ‘time-reversal symmetry’ to hold. However, ‘time reversal symmetry’ states that if $P(t)$ and $N(E)$ are Fourier Transform pairs, then and $P(-t)$ and $N(-E)$ are also Fourier Transform pairs. ‘Time reversal symmetry’ holds regardless of any symmetry characteristics of $n(E)$ and $k(E)$ [24].

Therefore, it seems that the arguments mentioned above do not satisfactorily support the K-K symmetry constraints as a necessary condition for the validity of dispersion equations. In the next section we demonstrate, by invoking Titchmarsh’s Theorem, that the K-K constraints are not a necessary condition of Causality, and consequently, should not be the arbiter of physical validity of dispersion formulations.

5. The principle of causality and new F-B dispersion equations

5.1. Titchmarsh’s theorem

The three requirements of the K-K Dispersion Relations presented in section 4.1, are a restricted version of Titchmarsh’s Theorem. Like the K-K Relations, Titchmarsh’s Theorem is a mathematical representation of the Principle of Causality [21]. However, it is more general. The theorem does not place any restriction on the symmetry characteristics of $n(E)$ and $k(E)$. In this section we show that the new F-B formulation satisfies Titchmarsh’s Theorem and consequently is consistent with Causality.

Titchmarsh’s Theorem consists of three elements related to formulations of dispersion, including optical dispersion [21]. In the specific case of optical dispersion involving the complex index of refraction, it must be stated in terms of $[N(E) - N(\infty)]$, rather than $N(E)$ alone since $N(\infty) = 0$, rather $N(\infty) = 1$.

The theorem states that if $[N(E) - N(\infty)]$ is square integrable along the real $E$ axis, and satisfies one of the three conditions below, $[N(E) - N(\infty)]$ automatically satisfies the other two.

(i) The inverse Fourier Transform of $[N(E) - N(\infty)]$ vanishes for $t < 0$.

(ii) $[N(E) - N(\infty)]$ is holomorphic (complex analytic) in the lower half complex $E$ plane, and is square integrable along any line parallel to the real $E$ axis in the lower half complex $E$ plane.

(iii) $\text{Re}[N(E) - N(\infty)]$ and $\text{Im}[N(E) - N(\infty)]$ are skew reciprocal Hilbert Transforms.

In appendix A.1, we show that $[N(E) - N(\infty)]$ is square integrable. In section 6.2 we give the details of proving the new formulation for $[N(E) - N(\infty)]$ satisfies the first element of Titchmarsh’s Theorem; in which case $[N(E) - N(\infty)]$ will necessarily satisfy the other two elements. We show this is the case in Appendices A2 and A3.

5.2. Inverse Fourier Transform of $[N(E) - N(\infty)]$: first element of Titchmarsh’s Theorem

Titchmarsh’s Theorem states:

$$\mathcal{F}^{-1}[[N(E) - N(\infty)]] \equiv P(t) = \frac{1}{\pi} \int_{-\infty}^{\infty} ([N(E) - N(\infty)]e^{iEt})dE$$

(29)

It can be shown from equations (21) and (22) if $E > E_k^*$:

$$[N(E) - N(\infty)] = \sum_j \left[ \frac{D_j E + F_j}{E^2 - B_j E + C_j} - i \frac{A_j (E - E_k^*)}{E^2 - B_j E + C_j} \right]$$

$$= \sum_j \frac{A_j}{Q_j} \left( Q_j + i\alpha_j \right) \left[ \frac{1}{\gamma_j + iE} \right]$$

(30)
where
\[ \alpha_j = \frac{B_j}{2}, \quad E > E_g \]  

(31)

If \( E < E_g \), \([N(E) - N(\infty)]\) still has the same form as equation (30) but with \( \alpha_j \) given as:
\[ \alpha_j = \frac{B_j}{2}, \quad E < E_g \]  

(32)

\[ \gamma_j = Q_j - \frac{iB_j}{2} \]  

(33)

Since \( \text{Re}(\gamma_j) = Q_j \equiv \hbar / 2\tau_j > 0 \), incorporating equation (30) into equation (29) yields:
\[ P(t) \equiv \sum_j P_j(t) = \sum_j Q_j e^{i\tau_j} e^{-\frac{\tau_j}{2\tau_j} t} u(t) \]  

(34)

where
\[ Q_j = \frac{A_j}{Q_j}(Q_j + i\alpha_j) \]  

(35)

The quantity \( u(t) \) in equation (34) is the unit step function:
\[ u(t) = \begin{cases} 1, & t > 0 \\ 0, & t < 0 \end{cases} \]  

(36)

Therefore, \( P(t) \equiv \mathcal{F}^{-1}[[N(E) - N(\infty)]] \) vanishes for \( t < 0 \), and \( P(t) \) behaves as a Causal Function.

5.2.1. Consistency check
As a consistency check, it is found that by working backwards and taking the Fourier Transform of \( P(t) \) in equation (34), the new F-B expression for \([N(E) - N(\infty)]\) is recovered, i.e., \([N(E) - N(\infty)] = \mathcal{F}(P(t)) \).

As a further consistency check, note that the formulation for each term in \([N(E) - N(\infty)]\) is consistent with Parseval’s Theorem [21]. Letting \([N(E) - N(\infty)] \equiv \frac{\Delta(E - E_g)}{E - \hbar / 2\tau_j + C_j} - i\frac{\Delta(E - E_g)}{E - \hbar / 2\tau_j + C_j} \), Parseval’s Theorem states:
\[ \int_{-\infty}^{\infty} |P_j(t)|^2 dt = \int_{-\infty}^{\infty} |[N(E) - N(\infty)]|^2 dE \]  

(37)

From equations (34) and (36),
\[ \int_{-\infty}^{\infty} |P_j(t)|^2 dt = \int_{-\infty}^{\infty} |Q_j e^{i\tau_j} e^{-\frac{\tau_j}{2\tau_j} t} u(t)|^2 dt = \int_{0}^{\infty} |Q_j e^{-\frac{\tau_j}{2\tau_j} t}|^2 dt \]

Noting that \( \tau_j \equiv \hbar / 2Q_j \):
\[ \int_{-\infty}^{\infty} |P_j(t)|^2 dt = \frac{1}{2 Q_j} \left( E_g^2 - B_j E_g + C_j \right) \quad E > E_g \]  

(38)

or
\[ \int_{-\infty}^{\infty} |P_j(t)|^2 dt = \frac{1}{2 Q_j} C_j \quad E < E_g \]  

(39)

From appendix A1, \int_{-\infty}^{\infty} |[N(E) - N(\infty)]|^2 dE = \frac{\pi A^2_j}{Q_j} (E_g^2 - B_j E_g + C_j), \quad E > E_g \), and \int_{-\infty}^{\infty} |[N(E) - N(\infty)]|^2 dE = \frac{\pi A^2_j}{Q_j} C_j, \quad E < E_g \).

Thus, the results for \( \mathcal{F}^{-1}[[N(E) - N(\infty)]] \equiv P(t) \) are consistent with Parseval’s Theorem, up to a factor of \((\hbar / 2\pi)\).

5.2.2. Discussion: insights regarding \( \mathcal{F}^{-1}[[N(E) - N(\infty)]] \equiv P(t) \)
The first element of Titchmarsh’s Theorem whereby \( \mathcal{F}^{-1}[[N(E) - N(\infty)]] = 0 \) for \( t < 0 \), mathematically expresses the concept that no effect can precede its cause; in which case \( \mathcal{F}^{-1}[[N(E) - N(\infty)]] \) is referred to as a causal function of time. Since polarization behaves in a causal manner, we will assume that the causal function \( P(t) \) represents polarization of the medium at time \( t \), if photons reach the medium at time \( t = 0 \), as implied by Roman [25].

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5.2.2.1. Complex nature of polarization function, \( P(t) \)

The polarization causal function, \( P(t) \), given by equation (34), is a complex function of time. The complex nature of \( P(t) \) is due to an inherent property of Fourier Transform pairs [24]. If \( n(E) \) and \( k(E) \) are asymmetric functions of \( E \), then \( \mathcal{F}^{-1}\{[N(E) - N(\infty)]\} \equiv P(t) \) is necessarily complex-valued, as in the present case.

On the other hand, if \( n(E) \) and \( k(E) \) satisfy the K-K symmetry constraints, and if \( k(\infty) = 0 \), then \( \mathcal{F}^{-1}\{N(E) - N(\infty)\} \) will be a real-valued function of time. As a case in point, consider the expression for the complex dielectric function of the Lorentz Oscillator, \( \varepsilon(\omega) = \varepsilon_1(\omega) - i\varepsilon_2(\omega) = 1 + \omega_p^2 / (\omega_0^2 - \omega^2 + i\Gamma\omega) \), where \( \omega_p \) is the plasma frequency, \( \omega_0 \) is the resonance frequency, and \( \Gamma \) is a damping factor. The inverse Fourier Transform of \( [\varepsilon(\omega) - \varepsilon(\infty)] \) can be shown to be a real-valued Causal Function since \( \varepsilon_1(\omega) = \varepsilon_1(-\omega) \) and \( \varepsilon_2(\omega) = -\varepsilon_2(-\omega) \), and \( \varepsilon(\infty) = 0 \). Specifically:

\[
\mathcal{F}^{-1}\{[\varepsilon(\omega) - \varepsilon(\infty)]\} = \mathcal{F}^{-1}\{[\varepsilon(\omega) - 1]\} = \frac{\omega_p^2}{\Omega} e^{-\Gamma t/2} \sin(\Omega t) u(t) \tag{40}
\]

where

\[
\Omega^2 = \omega_0^2 - \frac{\Gamma^2}{4} \tag{41}
\]

5.2.2.2. Connection between polarization function and peaks in \( k(E) \)

We now demonstrate that \( |P_j(t)| \), the magnitude of each term in the sum for \( P(t) \), is proportional to the position of a corresponding peak in \( k(E) \), which we denote as \( |E_{\text{max}}| \). By differentiating \( k(E) \) with respect to \( E \) and setting the result equal to zero, \( |E_{\text{max}}| \) is found to be:

\[
|E_{\text{max}}| = E_g + \sqrt{E_g^2 - B_j E_g + C_j} \text{ for } E > E_g \tag{42}
\]

or

\[
|E_{\text{max}}| = \sqrt{C_j} \text{ for } E < E_g \tag{43}
\]

Inserting expressions for \( Q_j \) and \( \alpha_j \), equations (5) and (31) or (32), into equation (35) gives:

\[
|\mathcal{R}_j| = \frac{A_j}{Q_j} \sqrt{E_g^2 - B_j E_g + C_j} \text{ for } E > E_g \tag{44}
\]

or

\[
|\mathcal{R}_j| = \frac{A_j}{Q_j} \sqrt{C_j} \text{ for } E < E_g \tag{45}
\]

At any time \( t > 0 \):

\[
|P_j(t)| = |\mathcal{R}_j| e^{-\frac{\omega_p^2}{\Omega}} = \frac{A_j}{Q_j} (|E_{\text{max}}| - E_g) e^{-\frac{\omega_p^2}{\Omega}} \text{ for } E > E_g \tag{46}
\]

or

\[
|P_j(t)| = |\mathcal{R}_j| e^{-\frac{\omega_p^2}{\Omega}} = \frac{A_j}{Q_j} (|E_{\text{max}}|) e^{-\frac{\omega_p^2}{\Omega}} \text{ for } E < E_g \tag{47}
\]

According to equation (46), if \( E > E_g \), the magnitude of each term in \( P(t) \), \( |P_j(t)| \), is proportional to \( |E_{\text{max}}| \), the energy at which the \( j \)th peak in \( k(E) \) occurs. Such peaks are attributed to inter-band electron transitions.

Likewise, from equation (47), if \( E < E_g \), \( |P_j(t)| \propto |E_{\text{max}}| \). These peaks are attributed to phonon, molecular-spinor or mobile-proton transitions.

Furthermore, \( P_j(t) \) decays exponentially according to \( e^{-\frac{\omega_p^2}{\Omega}} \), so that as \( t \to \infty \), equilibrium is eventually restored in the medium as polarization dies out.

6. Experimental verification

In this section we apply the new formulation to available published \( n(E) \) and \( k(E) \) data of nine different insulators and semiconductors. Section 6.1 is devoted to two of the nine materials, namely Water and Ice. An in-depth examination of their optical properties is given. In section 6.2, we apply the formulation to the other seven materials: SiO\(_2\)-Glass, LiF, Polyethylene, a-Si, InSb, GaP, and As\(_2\)Se\(_3\). However, we do not provide the same detailed considerations to these other materials, in order to avoid repetitious discussions.
6.1. Water and Ice

Water and Ice were chosen as examples of a liquid and crystalline insulator, respectively. As the most common substances on Earth’s surface, reliable and consistent experimental data is available in tabular form for these materials. The data are published for extremely wide energy ranges: thirteen orders of magnitude for Water and fourteen for Ice, spanning the Radio-Waves to EUV range. Furthermore, as pointed out by Khorram [26], physically valid equations for \( n(E) \) and \( k(E) \) are important for studies of atmospheric and oceanic events, as well as for improving models of global warming and climate change, which rely on the optical properties Water and Ice.

For Water, the available experimental data for \( n(E) \) and \( k(E) \) span thirteen orders of magnitude, from \( 1.24 \times 10^{-11} \) to 124 eV \( \cong 100 \) km to 10 nm. Part of the experimental data was published by Querry et al. [27]. Two sets of data were compiled. The first set spanned the range from \( 1.24 \times 10^{-7} \) to 124 eV (Radio-Waves to EUV energies). In terms of the wavelength of light, this range corresponds to 10.0 meters to 10.0 nm. The second set spanned the range from \( 6.309 \times 10^{-2} \) eV to 1.0064 eV (IR to NIR energies). The second set included a denser collection of data points than the first set in this shorter energy range.

A third set of data for Water, spanning the range from \( 1.24 \times 10^{-11} \) to \( 10^{-6} \) eV was obtained by digitizing the plots presented by Mesenbrink [28].

For Ice, the available experimental data span fourteen orders of magnitude, from \( 1.24 \times 10^{-13} \) to 28 eV \( \cong 10,000 \) km to 43 nm. Part of the experimental data was compiled by Warren and Brandt [29], spanning the range from 2.0 meters to 44.3 nm (6.2 \( \times 10^{-7} \) to 28 eV). The data from \( 1.24 \times 10^{-13} \) to \( 10^{-6} \) eV are obtained by digitizing the plots given by Mesenbrink [28], which are primarily based on the experimental and theoretical spectra of Ice by Johari [30].

The \( n(E) \) and \( k(E) \) spectra of Water and Ice are sensitive to temperature [31]. The data for Water presented by Querry et al [27] are compiled from work by several investigators, and are believed to have been taken at a temperature anywhere from 25 °C to 35 °C. The data for Ice, compiled by Warren and Brandt [29] were taken at \(-7 \) °C; whereas the data by Mesenbrink [28] are ‘valid for a temperature of \(-20 \) °C’. Therefore, occasional spread in the data and a mismatch between the data and the calculated plots presented in this paper should be expected.

Section 6.1 begins by describing the trends of experimental \( k(E) \) data of Water and Ice, followed by a discussion of the energy band gap, \( E_g \). Next, the method of analysis is discussed, and after that, the fitted results are presented. Table I provides a summary of the results obtained in the analysis, including all the parameters involved for plotting the spectra of \( n(E) \) and \( k(E) \).

6.1.1. Trend in the experimental data of \( k(E) \) for Water and Ice

The experimental \( k(E) \) data of Water and Ice are plotted in figures 1 and 2, respectively. Local maxima in the data are referred to as ‘peaks’ and are represented by a solid black arrow. These peaks are readily identifiable as local maxima in the tabulated data of \( k(E) \), and have a precise corresponding position, \( E_{\text{max}} \). ‘Shoulders’ are represented by dashed arrows. The description of ‘shoulders’ are less precise. They are not exactly local maxima, but a bump in the data. Each ‘shoulder’ means an additional term in the equations, which will result in improving the fit between the experimental data and the theoretical calculations. The double dashed arrow on the log-log plot is there to indicate that the fine structural features in the NIR to UV region, appearing below the horizontal dashed line marking \( k(E) \) values below \( 10^{-5} \), were lumped together as one term in the calculation of \( n(E) \) and \( k(E) \).

By inspecting the experimental \( k(E) \) spectra of Water and Ice in figures 1 and 2, there appear to be four distinct regions with various ‘peaks’ and ‘shoulders’. These four regions are:

(i) Relaxation Spectra, Radio-Waves through Microwaves energies, from approximately \( 10^{-11} \) to \( 10^{-3} \) eV for Water, and \( 10^{-13} \) to \( 10^{-3} \) eV for Ice: a prominent peak in the \( k(E) \) spectrum appears in this region which is attributed to mobile-proton transitions.

(ii) Microwaves to NIR energies, from approximately \( 10^{-3} \) to 1.0 eV for Water and Ice: this is a region of high ‘optical activity’, signified by noticeable values of \( k(E) \). Eight peaks and one shoulder for Water, and nine peaks plus one shoulder for Ice, can be observed, due to photon excitations of phonons and molecular-spinors. As previously mentioned, we borrowed the term ‘spinor’ from quantum dynamics to represent quantized rotational objects.

(iii) NIR to UV energies, from approximately 1.0 eV to 7 eV: this is a region where both Water and Ice are practically transparent. In this region, the \( k(E) \) spectrum appears to be flat and equal to zero when viewed on the linear-log scale. However, there are very fine variations in the \( k(E) \) spectrum that are only discernable on the log-log scale. The values for \( k(E) \) in this region range from \( 10^{-5} \) and smaller, and signify very minor
Table 1. Parameters for Water and Ice Related to figures 4 and 5.

\[ k(E) = \frac{A_E}{\Sigma_{j=1}^{2} E^2 - B_j E + C_j} + \sum_{j=1}^{2} A_j (E - E_j) + \sum_{j=1}^{2} \frac{D_j E + F_j}{E^2 - B_j E + C_j}, \quad n(E) = n(\infty) + \sum_{j=1}^{2} \frac{D_j E + F_j}{E^2 - B_j E + C_j} \]

| Experimental data | Peak/Shoulder as Labeled in figures 1 and 2 | Position of Peak/Shoulder, \( E_{\text{max}} \) (eV) | Number of Terms in the Sum for Calculation | Calculated Position of Peak/Shoulder |
|------------------|--------------------------------------------|---------------------------------|-----------------------------------------------|----------------------------------|
| Region           | Watera                                   | From Experimental Data         | \( E_j \) (eV) | \( A_j \) (eV) | \( B_j \) (eV) | \( C_j \) (eV) |
| Radio-Waves to EUV | 1.24 x 10^{-11} to 1.24 x 10^2 eV [27, 28] (100 km to 10 nm) | (i) 1 | 1.3056E-04 | 5.5779E-04 | 0.0000E + 00 | 1.1788E-08 | 1.0857E-04 |
|                  |                                           | (ii) 2 | \( \sim 1.0E-03 \) | 9.7149E-04 | 0.0000E + 00 | 3.1340E-07 | 5.5982E-04 |
|                  |                                           | 3 3.1877E-02 | 7.2728E-03 | 1.9347E-02 | 2.9009E-04 | 1.7032E-02 |
|                  |                                           | 4 7.2333E-02 | 1.7027E-03 | 1.4427E-01 | 5.5522E-03 | 7.4513E-02 |
|                  |                                           | 5 2.0334E-01 | 8.0428E-06 | 4.0765E-01 | 2.0386E-01 |
|                  |                                           | 6 2.6384E-01 | 4.7317E-04 | 8.3639E-01 | 2.6655E-01 |
|                  |                                           | 7 4.2204E-01 | 6.3592E-01 | 4.1865E-01 |
|                  |                                           | 8 6.3592E-01 | 6.3592E-01 | 4.1865E-01 |
|                  |                                           | 9 8.5574E-01 | 8.5574E-01 | 8.7658E-01 |
|                  |                                           | (iii) No Number (Dashed Double-Arrow) | 4.5000E-01 | 0.0000E + 00 | 6.7082E-00 |
| Radio-Waves to EUV | 1.24 x 10^{-13} to 2.8 x 10^1 eV [28, 29] (10,000 km to 44.3 nm) | (i) 1 | 8.2673 | 5.5157E-02 | 1.5848E-20 | 9.9987E-23 | 9.9993E-12 |
|                  |                                           | 2 ~10.0 | 4.3608E-02 | 2.0569E-01 | 1.0657E+02 | 10.4155 |
|                  |                                           | 3 14.452 | 5.8741E-02 | 2.5925E+01 | 1.7504E+02 | 13.5512 |
|                  |                                           | 4 ~18.0 | 5.4217E-02 | 3.4916E+01 | 3.1899E+02 | 18.1348 |
|                  |                                           | 5 ~25.0 | 8.0616E-02 | 5.0399E+01 | 6.4933E+02 | 25.5950 |
|                  |                                           | (ii) 2 | 1.8154E-02 | 3.0444E-02 | 1.6089E-02 | 2.8039E-04 | 1.6745E-02 |
|                  |                                           | 3 ~2.0E-02 | 5.6092E-05 | 3.0877E-02 | 3.1204E-04 | 1.7664E-02 |
|                  |                                           | 4 2.6178E-02 | 1.4952E-04 | 5.2024E-02 |

\( E_j = \sqrt{E_j^2 + E_j B_j + C_j} \)
Table 1. (Continued.)

| Experimental data | Region | Peak/Shoulder as Labeled in figures 1 and 2 | Position of Peak/Shoulder, $E_{\text{max}}$ (eV), From Experimental Data | Number of Terms in the Sum for Calculation | $E_i$ (eV) | $A_j$ (eV) | $B_j$ (eV) | $C_j$ (eV$^2$) | Calculated Position of Peak/Shoulder

Water$^a$

| 5 | 1.0076E-01 | $p = 11$ | 8.2799E-04 | 1.9573E-01 | 9.7566E-03 | 9.8776E-02 |
| 6 | 2.0209E-01 | — | 2.1959E-04 | 3.8872E-01 | 2.9835E-02 | 1.9579E-01 |
| 7 | 2.7320E-01 | | 1.8424E-05 | 5.5173E-01 | 7.3527E-02 | 2.7808E-01 |
| 8 | 4.0292E-01 | | 3.5438E-04 | 8.0621E-01 | 1.6271E-01 | 4.0337E-01 |
| 9 | 6.1990E-01 | | 6.7154E-04 | 1.2200E+00 | 3.8626E-01 | 6.2150E-01 |
| 10 | 8.3041E-01 | b | 4.0853E-04 | 1.7200E+00 | 7.692E-01 | 8.7231E-01 |
| (iii) No Number (Dashed Double-Arrow) | | | 2.3326E-01 | 2.0328E-09 | 5.4408E+00 | 2.3326E+00 |
| (iv) | | | 8.6397 | 7.5 | 6.9804E-02 | 1.6957E+01 | 7.2997E+01 | 8.5814 |
| | | | 10.2462 | | 3.4898E-03 | 2.0758E+01 | 1.0815E+02 | 10.4176 |
| | | | 16.7994 | | 1.7829E+00 | 2.9284E+01 | 2.4126E+02 | 16.3250 |

$^a$ $n(\infty) = 1 + a > 1$. The parameter 'a' compensates for the limited range of experimental data. As the range increases, $a \to 0$ and $n(\infty) \to 1$.

$^b$ Fine structural variations in $k(E)$ are treated as a single peak, i.e., a single term, in Region (iii).
optical activity. The peaks in Region (iii) are lumped together as a single term in the fitting calculation, indicated by a double-dashed arrow in figures 1 and 2.

(iv) UV to EUV energies, from approximately 7 eV and up: after the transparent region, the next region starts with a sharp rise in $k(E)$ at around 7 eV, and manifests two peaks and three shoulders for Water, and three peaks for Ice. These structures are attributed to electron-photon interactions. Also, there appears to be two shoulders associated with the $k(E)$ spectrum of Ice in this region. They were not considered, since their inclusion did not improve the fit between the data and the calculated spectra.
6.1.2. Energy band gap, $E_g$

The determination of $E_g$, the energy band gap, and the mechanism for the onset of photon absorption by electrons, has been the subject of many experimental and theoretical investigations. Here the key points related to $E_g$ of Water and Ice are presented. These points are also pertinent to the other insulators and semiconductors described in section 6.2.

The sharp rise in $k(E)$ at the beginning of Region (iv) is indicative of the onset of inter-band photon absorption by electrons. In our formulation, the energy at which this commences represents the optical energy band gap, $E_g$. This is shown in figure 3 for (a) Water and (b) Ice. The data for these materials are represented by solid green triangles connected by a solid green line to better visualize the absorption edges.

It is seen that the band gap occurs at $E_g = 7.3$ eV for Water and 7.5 eV for Ice. These are consistent with the values cited in the literature. For further discussions, refer to articles by Fang et al [32] for Water, and by Parravicini and Resca [33] for Ice.

6.1.3. Method of analysis and the results

The Levenberg-Marquardt method of regression analysis was used to fit the data to equations (21) and (22). This method involves an iterative improvement to values of the parameters in the equations for $n(E)$ and $k(E)$, in order to minimize the sum of the squares of the differences between the calculated plots and experimental data.

We would first like to mention that each term in the new F-B equations for $n(E)$ and $k(E)$ involves three unknown parameters, $A_j$, $B_j$, and $C_j$. The total number of unknowns to be determined in the fitting calculation for $n(E)$ and $k(E)$ is then equal to the number of terms multiplied by three.

In order to determine the number of terms, the number of peaks in the $k(E)$ data need to be counted. Figures 1 and 2 show that Region (i) is dominated by one spectral peak in $k(E)$. Therefore, one term is sufficient to account for the relaxation spectrum of $k(E)$, and necessarily, one term for $n(E)$. In Region (ii) there are eight peaks in $k(E)$ for Water, and nine peaks for Ice in $k(E)$. However, in order to improve the fits, we added one extra term in Region (ii) for Water and Ice.

In Region (iii), it would seem that no term is needed in the calculation since $k(E)$ appears to be flat on the linear-log scale of figures 1 and 2. However, because of the very small scale variations of $k(E)$ observed on the log-log scale of these figures, one extra term was incorporated in the analysis, indicated by a double-dashed arrow in figures 1(b) and 2(b). This extra term was necessary to improve the fit to the data.

In Region (iv), there are two peaks for Water and three peaks for Ice. The peaks are indicated as solid arrows in figures 1 and 2. The number of peaks are taken as the initial number of terms used to fit the data in the calculation. In addition, three extra terms in Region (iv) for Water were included. These extra terms appear as ‘shoulders’ in the $n$ and $k$ spectra. As mentioned before, the ‘shoulders’ are indicated as dashed arrows in figures 1 and 2.

For Water, a total of 15 terms were used in the calculation of $n(E)$ and $k(E)$ to cover the range from $\sim 10^{-11}$ to 124 eV. Therefore, the total number of parameters, $A_j$, $B_j$, $C_j$, that needed to be determined were equal to $3 \times 15 = 45$, plus one for $n(\infty)$. For Ice, a total of 14 terms were used in the calculation to cover the range from 0 to 124 eV.
\[ 10^{-13} \text{ to } 28 \text{ eV}. \] In this case, the total number of parameters, \(A_j, B_g, C_j\), were equal to \(3 \times 14 = 42\), plus one for \(n(\infty)\). All parameters for Water were determined simultaneously. Similarly, for Ice.

The value of the position of the \(j\text{th}\) peak in \(k(E), [E_{\text{max}}]\), can be used as a starting point in the regression analysis to determine \(C_j\).

For \(E < E_g\), according to equation (43), \([E_{\text{max}}] = \sqrt{C_j}\), which can be used to obtain initial values for \(C_j\) as \([E_{\text{max}}]\) below the band gap.

According to equation (42) for \(E > E_g\), \([E_{\text{max}}] = E_g + \sqrt{E_g^2 - B_gE_g + C_j}\). An initial value for \(C_j\) can also be obtained by setting the value of \([E_{\text{max}}]\) equal to \(\sqrt{C_j}\) (which amounts to ignoring \(E_g\) and the other terms in the radical).

As an example, in table 1 for Water, the value of \([E_{\text{max}}]\) for the third peak above the gap, obtained from the experimental data, is 14.432 eV and the value obtained from the regression analysis for \(\sqrt{C_j} = 17.7504\) is 13.23 eV.

Taking the value of the position of the peaks as a starting point for obtaining an initial value for \(C_j\) in the regression analysis is an important first step in obtaining convergence to the best values of \(A_j, B_g, \) and \(C_j\). This scheme applies in general, including to the other seven materials under consideration section 6.2.

The results of our analysis are presented in figures 4 and 5, depicting the calculated and experimental \(n(E)\) and \(k(E)\) spectra for Water and Ice, respectively.

### 6.2 SiO\(_2\)-Glass, LiF, Polyethylene, a-Si, InSb, GaP and As\(_2\)Se\(_3\)

The purpose of section 6.2 is to demonstrate the scope of the applicability of the new F-B equations for \(n(E)\) and \(k(E)\) by applying them to the experimental data of different types of materials besides Water and Ice. These materials include amorphous, crystalline, and polymer-like insulators, as well as amorphous, isotropic and anisotropic crystalline semiconductors. Specifically the equations are applied to the \(n(E)\) and \(k(E)\) data for SiO\(_2\)-Glass [34], LiF [35], Polyethylene [36], a-Si [37], InSb [38], GaP [38], and As\(_2\)Se\(_3\) [39].

As with the analysis of the data of Water and ice, the Levenberg-Marquardt method of regression was used to fit the data to equations (21) and (22) for these seven materials, in the same way as was used to fit the data to Water and Ice in Section 5.2.3. The results are presented in figures 6–12. However, the energy ranges presented are smaller than those of Water and Ice in Section 5.2.3. The results are presented in figures 4 and 5, depicting the calculated and experimental \(n(E)\) and \(k(E)\) spectra for Water and Ice, respectively.

Excellent fits based on the new F-B equations are achieved, even for a limited range of data, regardless of whether the range is above or below \(E_g\). The results of our analysis are summarized in table 2.

**6.2.1 Silicon Dioxide (SiO\(_2\)-Glass)**

SiO\(_2\)-Glass is an amorphous insulator with energy band gap equal to 9.0 eV [41]. Figures 6(a) and (b) shows the fits of equations (21) and (22) for \(n(E)\) and \(k(E)\) to the experimental data of SiO\(_2\)-Glass published by Philipp [34]. The data spanned the range from 0.031 to 25 eV, well below and well above the band gap. Therefore both sums in each of these equations were needed to obtain the fits. Five terms were used below the gap, and four above, in the calculation to achieve the fits in this range. The number of parameters totaled 28, including one for \(n(\infty)\).

**6.2.2 Lithium Fluoride (LiF)**

The crystalline form of LiF is an insulator with the highest UV transmission and largest band gap \(E_g\) for of any material. However, different values for its band gap, determined experimentally and theoretically, have been reported in the literature, ranging from \(-8\) to \(16\) eV [42, 43]. Figures 7(a) and (b) shows the fits of equations (21) and (22) for \(n(E)\) and \(k(E)\) to the experimental data of LiF published by Palik and Hunter [35]. Consistent with the experimental data, we have taken \(E_g = 12\) eV for calculations. The data spanned the range from 0.025 to 25 eV, well below and well above the band gap. Therefore both sums in each of these equations were needed to obtain the fits. Five terms were used below the gap, and four above, in the calculation to achieve the fits in this range. The number of parameters totaled 28, including one for \(n(\infty)\).

**6.2.3 Polyethylene—(\(C_2H_4\)\)_n**

Polyethylene is polymer-like insulator with an energy band gap equal to 6.9 eV [44]. Figure 8 shows the fits of equations (21) and (22) for \(n(E)\) and \(k(E)\) to the experimental data of Polyethylene compiled by Ashok et al [36]. We selected data that span the range from 5.0 to 60 eV, just below and well above the band gap. Only the sums on the right hand sides of these equations were used to obtain the fits. Four terms were used above the gap in the calculation to achieve the fits in this range. The number of parameters totaled 13, including one for \(n(\infty)\).
6.2.4. Amorphous Silicon (a-Si)
Amorphous Silicon (a-Si) is the non-crystalline form of Silicon, and as such can represent a number of materials, each with a slightly different disordered microstructures, depending on the processing conditions that produced the material. Thus, a unique set of $n(E)$ and $k(E)$ spectra, and by extension, a unique energy band gap, cannot be assigned to a-Si. It is reported to be anywhere between 1.5 to 1.6 eV \([45]\), and 1.5 to 2.0 eV \([46]\).

Figure 9 shows the fits of equations (21) and (22) for $n(E)$ and $k(E)$ to the experimental data of a-Si published by \([37]\). We chose to limit the range of data from 1.5 eV to 6.0 eV to demonstrate that one term would be sufficient to fit the data in this range. The bang gap was taken to be 1.5 eV. The total number parameters to achieve the fit is therefore equal to four, including one for $n(\infty)$.

6.2.5. Indium Antimonide (InSb)
The crystalline form of InSb is a semiconductor with the smallest value of the energy band gap of any crystalline semiconductor, equal to 0.17 eV \([47]\). Figure 10 shows the fits of equations (21) and (22) for $n(E)$ and $k(E)$ to the experimental data of crystalline InSb published by Aspnes and Studna \([38]\). The data range was limited to 1.5 to 6.0 eV, well above the band gap. Only the sums on the right hand sides of these equations were used to obtain the
fits. Six terms were used in the calculation to achieve the fits shown in figure 10. The number of parameters totaled 19, including one for \( n(\infty) \).

6.2.6. Gallium Phosphide (GaP)

The crystalline form of GaP is a semiconductor with energy band gap equal to 2.25 eV [48]. Figure 11 shows the fits of equations (21) and (22) for \( n(E) \) and \( k(E) \) to the experimental data of GaP published by Aspens and Studna [38]. The data range was limited to 1.5 to 6.0 eV, which starts at an energy slightly below \( E_g \). Only the sums on the right hand sides of these equations were used to obtain the fits. The sums on the left hand side of these equations were not apparently needed. Five terms were used in the calculation to achieve the fits shown in figure 11. The number of parameters totaled 16, including one for \( n(\infty) \).

6.2.7. Arsenic Selenide (As₂Se₃)

The anisotropic crystalline form of As₂Se₃ is a semiconductor with an energy band gap equal to 1.77 eV [48]. The published experimental data by Treacy [39] for \( n(E) \) and \( k(E) \) of this material along the so-called a-axis, was used to fit equations (21) and (22), the new equations for \( n(E) \) and \( k(E) \). In order to demonstrate that equations (21) and (22) can be applied to limited spectral ranges where \( E \ll E_g \), we selected data that only
spanned the range from 0.0062 to 0.062 eV, well below $E_g$. Therefore, just the sums in the left hand sides these equations were used to obtain the fits, and thus $E_g$ was not part of the equations. Five terms were used in the calculation to achieve the fits in this range. The number of parameters totaled 16, including one for $n(\infty)$. 

6.3. Discussion: number of parameters involved in the fits

One of the appeals of the new formulation is that it requires fewer fitting parameters than other formulations to describe $n(E)$ and $k(E)$ spectra for any material over any given spectral range. As a case in point, we would like to call attention to the results of the following two analysis.

(1) Daimon and Masumura [12] measured the refractive index $n$ of distilled water at various wavelengths, from 182 nm to 1129 nm (6.812 to 1.098 eV), at temperatures of 19 °C, 21.5 °C, and 24 °C. They assumed that
$k(\lambda) = 0$ in this spectral range and were able to fit their $n(\lambda)$ data to a four-term Sellmeier dispersion formula, which required eight fitting parameters for just $n(\lambda)$.

For example, with the present formulation, the data for the 21.5 °C temperature can be fitted with only one term, using four parameters, specified in table 2, with $E_g$ taken as 7.3 eV. See figure 13.

(1) Kitamura et al [49] were able to fit the experimental $n$ and $k$ data of Amorphous Quartz (which is essentially SiO$_2$-Glass) in the 7 m to 50 m wavelength range (0.0248 to 0.177 eV) that were measured and tabulated by Popova et al [40], to the dispersion formula proposed by Meneses et al [17, 18], using 25 fitting parameters.

With the present formulation, it can be shown that only five terms, with a total of 16 parameters specified in table 2, including one for $n(\infty)$, would be sufficient to fit the data. See figure 14.
7. Conclusion

7.1. Key theoretical and experimental findings

A new formulation of optical dispersion in terms of the complex index of refraction, \( N(E) = n_E - ik_E \), applicable to insulators and semiconductors, was introduced. The quantities \( n_E \) and \( k_E \) represent the refractive index and extinction coefficient as functions of photon energy, \( E \).

The motivation for developing the formulation was the desire to derive a universal set of equations that can replace the variety of different equations that are usually used to describe \( n_E \) and \( k_E \) over limited regions of the Radio-Waves to EUV spectral range.

This was accomplished by modifying the original F-B dispersion equations for \( n_E \) and \( k_E \), resulting in new set of equations consistent with the Principe of Causality via Titchmarsh’s Theorem.

These new equations for \( n_E \) and \( k_E \) were shown to be skew reciprocal Hilbert Transforms, in accordance with Titchmarsh’s Theorem, a result analogous to the K-K Dispersion Relations.

In addition, the inverse Fourier Transform of \( [N(E) - N(\infty)] \), denoted as \( P(t) \), was determined to be a complex-valued causal function of time. We identified the causal function, \( P(t) \), as the complex polarization of the medium at time \( t \), if photons reached the medium at time \( t = 0 \). This is consistent with the fact that
polarization behaves in a causal manner. The expression for polarization, \( P(t) \), decays exponentially, so that as \( t \to \infty \), equilibrium is eventually restored in the medium.

The polarization, \( P(t) \), was associated with positions of the peaks in \( k(E) \), which are generated by photon excitations of quantum constituents of the medium, such as electrons, phonons, molecular-spinors (quantized molecular rotational modes), or mobile-protons.

Traditionally, formulations of dispersion are required to be consistent with the Kramers-Kronig (K-K) Dispersion Relations which are a mathematical expression of Causality. However, the new formulation does not satisfy the symmetry conditions of the K-K Relations. By noting that Titchmarsh’s Theorem is a more general representation of Causality and that the K-K Relations are a restricted version of the theorem, we are able to assert that the new formulation is theoretically valid.

In order to obtain experimental verification, the new formulation was applied to published experimental \( n(E) \) and \( k(E) \) data of nine insulator and semiconductor materials with different molecular bonding arrangements: liquid and solid, amorphous, isotropic and anisotropic crystalline, and polymer. These materials were Water, Ice, SiO\(_2\)-Glass, LiF, Polyethylene, a-Si, InSb, GaP, and As\(_2\)Se\(_3\). Excellent fits were achieved in all cases, regardless of any particular spectral range of available experimental data, whether above or below \( E_g \). For Water and Ice, the spectral range spanned the entire Radio-Waves to EUV. For the other materials, the ranges of the data were not as extensive. For SiO\(_2\)-Glass and LiF, the range spanned IR to EUV, and for Polyethylene, UV to EUV. For a-Si, InSb, and GaP, the range covered NIR-Visible-UV. For As\(_2\)Se\(_3\), the range was well below \( E_g \), in the IR only.

In addition, it appeared that fewer parameters were needed to achieve the fits, compared to other formulations.

We believe that, based on the results presented in this paper, we achieved our goal to derive a universal formulation for \( n(E) \) and \( k(E) \) of insulators and semiconductors that can replace other formulations used to describe optical dispersion.

### 7.2. Future relevant work

In reviewing the published \( n \) and \( k \) spectra of various insulator and semiconductor materials, authored by different investigators, it becomes apparent that there is a large scatter in the data for practically the same material, especially at overlapping spectral ranges. Utilizing the new universal formulation, one can revisit the determination of the optical constants of insulators and semiconductors from the analysis of measured reflectance and transmittance spectra, or other spectral measurements, to create a comprehensive library of accurate \( n(E) \) and \( k(E) \) data, covering Radio-Waves to EUV, and perhaps up to x-ray region.

Additionally, we have preliminary results that show the new formulation can also describe \( n(E) \) and \( k(E) \) spectra of metals. However, this is a work in progress, since for the case of metals, we are not yet able to confidently give physical meaning to the parameters in the new equations we derived for \( n(E) \) and \( k(E) \).
Table 2. Parameters for SiO₂-Glass, LiF, Polyethylene, a-Si, InSb, GaP, As₅Se₃, Distilled Water 21.5 °C, and Amorphous Quartz, Related to figures 6–14.

\[
k(E) = \sum_{j=1}^{A_1} \frac{A_j E}{E^2 - B_j E + C_j} + \sum_{j=1}^{A_2} \frac{A_j(E - E_j)}{E^2 - B_j E + C_j} + \frac{\sum_{j=1}^{A_3} D_j' E + F_j'}{2Q_j}, \quad D_j' = \frac{A_j C_j}{Q_j}, \quad F_j' = \frac{A_j C_j}{Q_j}
\]

| Experimental Data          | Number of Terms in the Sum for the Calculation | \( A_1 \) (eV) | \( B_1 \) (eV) | \( C_1 \) (eV²) | \( n(\infty) \)² |
|-----------------------------|------------------------------------------------|----------------|----------------|----------------|-----------------|
| SiO₂-Glass 0.031–25 eV [34] | \( \rho = 5 \)                                   | —              | 5.1915E-04     | 1.1489E-01     | 3.3119E-03      | 1.05            |
|                             |                                                | 1.5900E-04     | 1.9475E-01     | 9.3303E-03     |                 |                 |
|                             |                                                | 6.4532E-04     | 2.6990E-01     | 1.8245E-02     |                 |                 |
|                             |                                                | 7.5949E-05     | 2.9619E-01     | 2.1951E-02     |                 |                 |
| LiF 0.0248–25 eV [35]       | \( \rho = 5 \)                                   | —              | 2.1074E-04     | 7.7218E-02     | 1.4920E-03      | 1.00            |
|                             |                                                | 4.5244E-04     | 8.1546E-02     | 1.6675E-03     |                 |                 |
|                             |                                                | 1.8785E-03     | 9.1390E-02     | 2.1209E-03     |                 |                 |
|                             |                                                | 3.8073E-03     | 1.1976E-01     | 3.7512E-03     |                 |                 |
| Polyethylene 7.2–60 eV [36] | \( \rho = 4 \)                                   | 6.9            | 8.1711E-02     | 1.7334E-01     | 7.5451E+01      | 1.03            |
|                             |                                                | 7.4984E-02     | 1.9372E-01     | 9.4705E+01     |                 |                 |
|                             |                                                | 1.5274E+00     | 2.5497E-01     | 1.7493E+02     |                 |                 |
| a-Si 1.5–6.0 eV [37]        | \( \rho = 1 \)                                   | 1.5            | 5.1807E+00     | 6.6882E+00     | 1.4989E+01      | 1.30            |
| InSb 1.5–6.0 eV [38]        | \( \rho = 6 \)                                   | 0.17           | 1.2046E-02     | 3.7667E+00     | 3.5693E+00      | 1.90            |
| GaP 1.5–6.0 eV [38]         | \( \rho = 5 \)                                   | 2.25           | 9.6758E-04     | 5.9343E+00     | 8.8155E+00      | 1.94            |
| As₅Se₃ – anisotropic crystalline along a-axis 0.0062–0.0562 eV [39] | \( \rho = 5 \)                                   | 1.1389E-05     | 2.6397E-02     | 1.7428E-04     | 3.36            |
| Distilled Water, 25 °C 182–1129 nm [12] 6.812–1.098 eV | \( \rho = 1 \)                                   | 7.3            | 1.7000E-02     | 1.8037E+01     | 8.1337E+01      | 1.27            |
| Amorphous Quartz (SiO₂-Glass) 7–50 μm [40] (0.177–0.0248 eV) | \( \rho = 5 \)                                   | —              | 4.1148E-04     | 1.1161E-01     | 3.1370E-03      | 1.56            |

\* \( n(\infty) = 1 + a > 1 \). The parameter "a" compensates for the limited range of experimental data. As the range increases, \( a \to 0 \) and \( n(\infty) \to 1 \).

\( b \) Values of \( E_q \) for As₅Se₃ and Amorphous Quartz are, respectively, 1.77 eV and 9.0 eV. However \( E_q \) as not part of the equations for \( n(\infty) \) and \( k(E) \) since the experimental data were in a range well below the bandgap.
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Figure 13. Solid lines are calculated plots of $n(E)$ and $k(E)$ spectra of Water at 21.5 °C, with $E_g = 7.3$ eV and parameters specified in Table 2. $n$: experimental data \([12]\) are in the range from 182 to 1129 nm (6.812 to 1.098 eV), starting just below $E_g$. In this range, $k$: was assumed to be equal to zero \([12]\). Calculated $n$ and $k$ spectra are plotted from 150 to 1200 nm.

Figure 14. Solid lines are calculated plots of $n(E)$ and $k(E)$ spectra of Amorphous Quartz (SiO$_2$-Glass), with $E_g = 9.0$ eV and parameters specified in Table 2. $n$: and $k$: experimental data \([40]\) are in the range from 7 to 50 μm (0.177 to 0.0248 eV), well below $E_g$. Calculated spectra are extended down to 4 μm. In (a) and (b), spectra of $n$ and $k$ are plotted separately for clarity.
Appendix

A.1. Square integrability of \([N(E) - N(\infty)]\)

From equations (12) and (14) if \(E > E_g\),

\[
[N(E) - N(\infty)] = \sum_{j=1}^{d} \frac{D_j E + F_j}{E^2 - B_j E + C_j} - i \frac{A_j(E - E_g)}{E^2 - B_j E + C_j} \tag{A1.1}
\]

To show that \([N(E) - N(\infty)]\) is square integrable, it is sufficient to show that each term in the sum of equation (A1.1) is square integrable. Taking the square of the absolute value of the \(j\)th term yields:

\[
\left| \frac{D_j E + F_j}{E^2 - B_j E + C_j} - i \frac{A_j(E - E_g)}{E^2 - B_j E + C_j} \right|^2 = \frac{A_j}{Q_j} \left( \frac{E_g^2 - B_j E_g + C_j}{E^2 - B_j E + C_j} \right)
\]

where

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

Integrating equation (A1.2) over the real \(E\) axis gives:

\[
\int_{-\infty}^{\infty} \frac{A_j}{Q_j} \left( \frac{E_g^2 - B_j E_g + C_j}{E^2 - B_j E + C_j} \right) dE = \frac{A_j}{Q_j} \int_{-\infty}^{\infty} \frac{1}{(E^2 - B_j E + C_j)} dE = \frac{\pi A_j^2 C_j}{Q_j^2}
\]

(A1.3)

And if \(E < E_g\) set \(E_g = 0\) in the result of equation (A1.3):

\[
\left( \frac{A_j}{Q_j} \right)^2 \int_{-\infty}^{\infty} \frac{C_j}{(E^2 - B_j E + C_j)} dE = \frac{\pi A_j^2 C_j}{Q_j^2}
\]

(A1.4)

From equations (A1.3) and (A1.4), it is seen that the \(j\)th term in the sum for \([|N(E) - N(\infty)|]^2\) is finite. Consequently, each term in the sum for \([N(E) - N(\infty)]\) is square integrable, and therefore, \([N(E) - N(\infty)]\) itself is square integrable.

A.2. Proof that \([N(E) - N(\infty)]\) is (a) holomorphic (complex analytic) in the lower half complex \(E\) plane, and (b), square integrable over any line in the lower half plane parallel to the real \(E\) axis.

(a) Inserting equation (33) into equation (30), it is found that \([N(E) - N(\infty)]\) only has singularities in the upper half of the complex plane at \(E_j = \frac{b_j}{2} + iQ_j\), and none in the lower half plane. Furthermore, \([N(E) - N(\infty)]\) has no terms involving branch points or branch cuts.

Therefore, the new expression for \([N(E) - N(\infty)]\) is holomorphic (complex analytic) in the lower half complex \(E\) plane.

(b) This part of the proof follows Titchmarsh’s proof [21] which was derived for a case when \(N(E)\) is defined with a plus sign in front of \(\text{Im}[N(E)]\), i.e., \(N(E) \equiv \text{Re}[N(E)] + \text{Im}[N(E)]\). Consequently the condition in section A2 would apply to any line in the upper half plane parallel to the real axis, rather than the lower half. Also, Titchmarsh’s proof did not involve a sum of terms for \(\text{Re}[N(E)]\) and \(\text{Im}[N(E)]\).

It is sufficient to prove that each term in the new F-B expression for \([N(E) - N(\infty)]\) is square integrable in the lower half complex plane, along any line parallel to the real \(E\) axis. Let

\[
[N(E) - N(\infty)]_j \equiv \frac{D_j E + F_j}{E^2 - B_j E + C_j} - i \frac{A_j(E - E_g)}{E^2 - B_j E + C_j} \tag{A2.1}
\]

represent the \(j\)th term in the sum involving \([N(E) - N(\infty)]\), and let \(P(t)\), represent the \(j\)th term in the sum for \(P(t)\).

Consider Parseval’s Theorem for Fourier Transforms [21]. Parseval’s Theorem states:

\[
\int_{-\infty}^{\infty} |[N(E) - N(\infty)]_j|^2 \, dE = \int_{-\infty}^{\infty} |P(t)|^2 \, dt
\]

(A2.2)

if \([N(E) - N(\infty)]_j\) is the Fourier Transform of \(P(t)\).
Let $E \to u + iv$ such that $v$ is constant in the lower half complex $E$ plane (i.e., $v < 0$), so that when $v \to 0$, $E \to u$, defines the real axis. Then, $\int [N(u + iv) - N(\infty)]$ is the Fourier Transform of $e^{-|v|^2}P(t)$, since $v$ is negative. From equation (A.2.2):

$$
\int_{-\infty}^{\infty} \left| \left[ N(u + iv) - N(\infty) \right] \right|^2 \, dE = \int_{-\infty}^{\infty} \left| P(t) \right|^2 \, e^{-|v|^2} \, dt < \int_{-\infty}^{\infty} \left| P(t) \right|^2 \, dE \quad (A2.3)
$$

Therefore, since each term in $\int [N(E) - N(\infty)]$ is square integrable along the real $E$ axis as shown in section A1:

$$
\int_{-\infty}^{\infty} \left| \left[ N(u + iv) - N(\infty) \right] \right|^2 \, dE < \int_{-\infty}^{\infty} \left| \left[ N(E) - N(\infty) \right] \right|^2 \, dE \quad (A2.4)
$$

and $\int [N(E) - N(\infty)]$ is square integrable along any line parallel to the real $E$ axis in the lower half complex plane parallel to the real axis.

**A.3. Proof that $[n(E) - n(\infty)]$ and $[k(E) - k(\infty)]$ are skew reciprocal Hilbert Transforms**

This proof involves showing that:

$$
[n(E) - n(\infty)] = \mathcal{H} \left[ \left[ k(E) - k(\infty) \right] \right] \equiv \frac{1}{\pi} \int_{|E| = \infty} \frac{k(E') - k(\infty)}{E - E'} \, dE' \quad (A3.1)
$$

and

$$
k(E) - k(\infty) = -\mathcal{H} \left[ \left[ n(E) - n(\infty) \right] \right] \equiv -\frac{1}{\pi} \int_{|E| = \infty} \frac{n(E') - n(\infty)}{E - E'} \, dE' \quad (A3.2)
$$

In equations (A3.1) and (A3.2), $k(\infty) = 0$. The symbol $\mathcal{H}$, in front of the integrals of equations (A3.1) and (A3.2), stands for the Cauchy Principle Value of the integral over a closed loop in the complex $E$ plane, and is equal to the sum of the residues within the loop and on the boundary of the loop.

The loop is defined to be a closed semicircle with radius, $r = |E'|$, residing in the lower half complex $E$ plane, and diameter along the real $E'$ axis, and center at the origin.

The reason we evaluate the integral in the lower half complex $E$ plane, is because we chose to define $N(E)$ with a minus sign in front of its imaginary part, $k(E)$. If we had used the convention of a plus sign, then the integration would occur in the upper half complex $E$ plane.

On the semicircle, $|E'|$ is equal to a constant and can be expressed as $E' = |E'| \, e^{i\theta}$. Therefore, on the semicircle $dE' = i|E'| \, e^{i\theta} \, d\theta$. Taking the limit as $|E'| \to \infty$, the integrals in equations (A3.1) and (A3.2) can be expressed as two integrals, one over the semicircle from $0$ to $-\pi$ and one over the real axis from $-\infty$ to $\infty$.

$$
[n(E) - n(\infty)] = \frac{1}{\pi} \int_{|E'| = \infty} \left[ \lim_{|E'| \to \infty} \int_{-\pi}^{\pi} \frac{k(E')}{E - E'} \, e^{i\theta} \, d\theta \right] + \int_{-\infty}^{\infty} \frac{k(E')}{E - E'} \, dE' \quad (A3.3)
$$

$$
k(E) = \frac{1}{\pi} \int_{|E'| = \infty} \left[ \lim_{|E'| \to \infty} \int_{-\pi}^{\pi} \frac{n(E') - n(\infty)}{E - E'} \, e^{i\theta} \, d\theta \right] + \int_{-\infty}^{\infty} \frac{n(E') - n(\infty)}{E - E'} \, dE' \quad (A3.4)
$$

Since $k(E') = \sum \frac{A_j(E' - E_g)}{E'^2 - B_jE' + C_j}$ and $[n(E') - n(\infty)] = \sum \frac{D_jE' + F_j}{E'^2 - B_jE' + C_j}$, if $E > E_g$, the integral over the semicircle vanishes as $|E'| \to \infty$, because in each case, the numerator goes as $|E'|^2$ and the denominator, as $|E'|^3$ as $|E'| \to \infty$. Likewise for $E < E_g$.

We will evaluate equations (A3.1) and (A3.2) for the case where $E > E_g$. If $E < E_g$, simply take the result for $E > E_g$ and set $E_g = 0$.

Based on equations (12) and (14), if $E > E_g$ equations (A3.3) and (A3.4) reduce to:

$$
[n(E) - n(\infty)] = \frac{1}{\pi} \sum_{j=1}^{q} \int_{-\infty}^{\infty} \frac{A_j(E' - E_g)}{(E'^2 - B_jE' + C_j)(E - E')} \, dE' \quad (A3.5)
$$

$$
k(E) = -\frac{1}{\pi} \sum_{j=1}^{q} \int_{-\infty}^{\infty} \frac{D_jE' + F_j}{(E'^2 - B_jE' + C_j)(E - E')} \, dE' \quad (A3.6)
$$

In equations (A3.5) and (A3.6) the integral and the sum were interchanged.

The principle value of the integrals in equations (A3.5) and (A3.6) is equal to the sum of the residues within the semicircle and residues on the real $E$ axis, which we denote as $r_j$ and $s_j$, respectively.

To obtain the residues, note that the denominators in equations (A3.5) and (A3.6) can be written as:

$$(E'^2 - B_jE' + C_j)(E - E') = \left( E' - \frac{B_j}{2} - iQ \right) \left( E' - \frac{B_j}{2} + iQ \right)(E - E') \quad (A3.7)$$
where $Q_{i}^{2} = C_{j} - \frac{B_{j}^{2}}{4}$. From equation (A3.7), it is seen that there are poles in the lower half plane at $E' = \left(\frac{B_{j}}{2} - iQ_{j}\right)$, and one pole on the real axis resides at $E' = E$.

First consider the residues associated with $[n(E) - n(\infty)]$ in equation (A3.5). The contribution to the integral from the residues at the poles $E' = \left(\frac{B_{j}}{2} - iQ_{j}\right)$ is:

$$2\pi \tau = \sum_{j=1}^{q} 2\pi \eta_{j} \equiv \sum_{j=1}^{q} \frac{A_{j}}{Q_{j}} (E_{g} - E_{g}) + \left(\frac{E_{g} - B_{j}}{2}\right)E + \left(\frac{C_{j} - B_{j}E_{g}}{2}\right)\left(E^{2} - B_{j}E + C_{j}\right)$$  \hspace{1cm} (A3.8)

The contribution to the residue from the pole on the real $E$ axis is:

$$\pi \tau = \sum_{j=1}^{q} \tau_{j} \equiv \sum_{j=1}^{q} \left[A_{j} \frac{iQ_{j}(E_{g} - E_{g})}{(E^{2} - B_{j}E + C_{j})}\right]$$  \hspace{1cm} (A3.9)

Combining equations (A3.8) and (A3.9), it is seen that the imaginary terms cancel, yielding:

$$2\pi \tau + \pi \tau = \sum_{j=1}^{q} \frac{A_{j}}{Q_{j}} \left(E_{g} - \frac{B_{j}}{2}\right)E + \left(\frac{C_{j} - B_{j}E_{g}}{2}\right)\left(E^{2} - B_{j}E + C_{j}\right) = \sum_{j=1}^{q} \left[\frac{D_{j}E + F_{j}}{E^{2} - B_{j}E + C_{j}}\right]$$  \hspace{1cm} (A3.10)

where:

$$D_{j} = \frac{A_{j}}{Q_{j}} \left(E_{g} - \frac{B_{j}}{2}\right)$$  \hspace{1cm} (A3.11)

$$F_{j} = \frac{A_{j}}{Q_{j}} \left(C_{j} - \frac{E_{g}B_{j}}{2}\right)$$  \hspace{1cm} (A3.12)

Therefore:

$$[n(E) - n(\infty)] = \sum_{j=1}^{q} \frac{D_{j}E + F_{j}}{E^{2} - B_{j}E + C_{j}}, \hspace{0.5cm} E > E_{g}$$  \hspace{1cm} (A3.13)

in agreement with equations (14)–(16). If $E < E_{g}$, take $E_{g} = 0$ in equations (A3.11)–(A3.13) and obtain:

$$[n(E) - n(\infty)] = \sum_{j=1}^{p} \frac{D'_{j}E + F'_{j}}{E^{2} - B_{j}E + C_{j}}, \hspace{0.5cm} E < E_{g}$$  \hspace{1cm} (A3.14)

in agreement with equation (18), where $D'_{j}$ and $F'_{j}$ are given by equations (19) and (20). Combing equations (A3.13) and (A3.14) yields the complete new expression for $[n(E) - n(\infty)]$, given by equation (22). Thus, in general, $[n(E) - n(\infty)]$ is the Hilbert Transform of $k(E)$.

To see if $k(E)$ is minus the reciprocal Hilbert Transform of $[n(E) - n(\infty)]$, i.e., if

$$\sum_{j=1}^{q} \frac{A_{j}(E - E_{g})}{E^{2} - B_{j}E + C_{j}} = -\frac{1}{\pi} \sum_{j=1}^{q} \int_{-\infty}^{\infty} \frac{D_{j}E' + F_{j}}{E^{2} - B_{j}E' + C_{j}}(E - E')dE',$$

apply the same procedure that was used to obtain $[n(E) - n(\infty)]$ as the Hilbert Transform of $k(E)$. It is important to remember to take into account the minus sign in front of the Hilbert Transform of $[n(E) - n(\infty)]$. Doing so yields the expected result, namely:

$$k(E) = \sum_{j=1}^{q} \frac{A_{j}(E - E_{g})}{E^{2} - B_{j}E + C_{j}}, \hspace{0.5cm} E > E_{g}$$  \hspace{1cm} (A3.15)

in agreement with equation (12). Taking $E_{g} = 0$ in equation (A3.15) yields:

$$k(E) = \sum_{j=1}^{q} \frac{A_{j}(E)}{E^{2} - B_{j}E + C_{j}}, \hspace{0.5cm} E < E_{g}$$  \hspace{1cm} (A3.16)

Combing equations (A3.15) and (A3.16), the complete new F-B equation for $k(E)$ is identical to equation (21). Thus, in general, $k(E)$ is minus the reciprocal Hilbert Transform of $[n(E) - n(\infty)]$.

Therefore, we have proved that in the new F-B formulation, $[n(E) - n(\infty)]$ and $k(E)$ are skew reciprocal Hilbert Transforms, in agreement with Titchmarsh’s Theorem.
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