

# Supplementary Materials: Determination of Optical Properties of Undoped Amorphous Selenium (*a*-Se) Films by Dielectric Modeling of Their Normal-Incidence Transmittance Spectra

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## Appendix A

### Formulations of specular transmittance and reflectance of multi-layered structures

Various methodologies (Tauc, 1972; Tauc, 1979; Heavens, 1991; Azzam & Bashara, 1987; Ward, 1994; Dragoman & Dragoman, 2002; Stenzel, 2005; Case, 1983; Peng & Desu, 1994; Birgin et al., 1999; Richards, 1998; Chambouleyron & Martínez, 2001; Truong & Tanemura, 2006; Kasap & Capper, 2006; Palik, 1998; Dressel & Grüner, 2002; Reitz et al., 1993; Jackson, 1998; Born & Wolf, 2002; Jafar, 2013; Nichelatti, 2002; Dresselhaus, 2001) were used to derive theoretical formulations of specular transmittance  $T(\lambda)$  and reflectance  $R(\lambda)$  of *multi-layered* structures at which monochromatic light waves are *obliquely incident*. The  $E^+ - E^-$  transfer matrix method (Born & Wolf, 2002; Jafar, 2013) is an elegant approach to accomplish this aim. The *normal-incidence*  $T(\lambda)$ - and  $R(\lambda)$ - formulas for *three-* and *four-* layered structures comprising of dissimilar thin and thick layers are less tangled and often written explicitly in terms of optical constants of these layers, which are handy in the analysis of their as-measured normal-incidence reflectances and transmittances.

#### A.1 $E^+ - E^-$ transfer matrix formulation for transmission and reflection of multi-layered stacks

The  $E^+ - E^-$  transfer matrix method, which holds for both *s-* and *p-* polarized light waves (Jafar, 2013), is used to derive specular  $T(\lambda)$ - and  $R(\lambda)$ - relations for the {layer 1/layer 2/layer 3/.../layer  $m$ }-stacking on which monochromatic light waves of wavelength  $\lambda$  and spectral bandwidth (SBW)  $\Delta\lambda$  are incident *obliquely*. The  $T(\lambda)$ - and  $R(\lambda)$ - relations are wieldy if *first* and *last* layers are *semi-infinite* air media ( $\hat{n}_1 = \hat{n}_m = n_{\text{air}} + j0 \cong 1$  and  $d_1 = d_m = \infty$ ) and for *normal incidence* as hitches from wave polarization and angle of incidence become irrelevant. If layer  $l$  has index of refraction  $n_l$  and is thin with thickness  $d_l$  such that  $\Delta\lambda \ll \lambda^2/2\pi n_l d_l$ , and with smooth, parallel-plane surfaces, the back and forth light wave reflections inside it and interference between them are both significant. So, the problem is treated by a *coherent approach* where the complex electric field vectors of individual reflected and transmitted light waves are added to give *net* field vectors to find the relevant light intensities (Jafar, 2013). For a thick layer with  $\Delta\lambda \gg \lambda^2/2\pi n_l d_l$ , multiple internal wave reflections is important with no interference effect, and *incoherent method* is used to sum up *algebraically light intensities* of all individual reflected/transmitted waves to get the  $T(\lambda)$ - and  $R(\lambda)$ - formulas (Jafar, 2013). For *monochromatic* light *obliquely* incident at a stack of  $i = 1, 2, 3, \dots, m$  successive layers with  $(i - 1)$ -interfaces, the matrix formula relating the amplitude of its complex electric field vector to the amplitudes of the complex electric field vectors of reflected and transmitted light plane waves has the form (Born & Wolf, 2002; Jafar, 2013)

$$\begin{pmatrix} \hat{E}_+^1 \\ \hat{E}_-^1 \end{pmatrix} = \mathbf{M} \begin{pmatrix} \hat{E}_+^f \\ \hat{E}_-^f \end{pmatrix} = \hat{\mathbf{I}}_1 \cdot \hat{\mathbf{T}}_2 \cdot \hat{\mathbf{I}}_2 \cdot \hat{\mathbf{T}}_3 \cdot \hat{\mathbf{I}}_3 \cdot \hat{\mathbf{T}}_4 \cdot \hat{\mathbf{I}}_4 \cdot \hat{\mathbf{T}}_5 \cdot \hat{\mathbf{I}}_5 \cdot \hat{\mathbf{T}}_{i-1} \cdot \hat{\mathbf{I}}_{i-1} \cdot \hat{\mathbf{T}}_i \begin{pmatrix} \hat{E}_+^f \\ \hat{E}_-^f \end{pmatrix} = (\hat{\mathbf{I}}_1 \cdot \prod_{m=2}^{m=i-1} \mathbf{C}_m) \begin{pmatrix} \hat{E}_+^f \\ \hat{E}_-^f \end{pmatrix} \quad (\text{A1})$$

The amplitudes  $\hat{E}_+^1$  and  $\hat{E}_-^1$  are, respectively, the components of electric fields of light plane waves moving to and reflected from the interface of the first layer of the  $i$ th-layered stack, while  $\hat{E}_+^f$  and  $\hat{E}_-^f$  correspond to the amplitudes of electric fields of light waves transmitted and reflected from the interface of its last layer.  $\mathbf{M}$ , a

characteristic matrix of the  $i$ th-layered structure, is the product of the  $m$ th-layer's coefficient matrix  $\hat{\mathbf{I}}_m$  and transmission matrix  $\hat{\mathbf{T}}_m$ - that is, the matrix  $\mathbf{C}_m \equiv \hat{\mathbf{T}}_m \hat{\mathbf{I}}_m$  ( $m \geq 2$ ), which are described by (Jafar, 2013)

$$\hat{\mathbf{I}}_m = \begin{pmatrix} \frac{1}{\hat{\epsilon}_m} & 0 \\ 0 & \hat{\epsilon}_m \end{pmatrix}; \hat{\mathbf{T}}_m = \begin{pmatrix} e^{-j\hat{\delta}_m} & 0 \\ 0 & e^{j\hat{\delta}_m} \end{pmatrix}; \hat{\mathbf{C}}_m = \begin{pmatrix} \frac{1}{\hat{\epsilon}_m} & \hat{\epsilon}_m e^{-j\hat{\delta}_m} \\ \hat{\epsilon}_m e^{j\hat{\delta}_m} & \hat{\epsilon}_m \end{pmatrix} \quad (\text{A2})$$

The matrix  $\hat{\mathbf{I}}_m$  relates to reflection and transmission coefficients  $\hat{r}_m$  and  $\hat{t}_m$  at the  $m$ -( $m+1$ ) interface, with  $\hat{r}_m \equiv \hat{r}_{m,m+1} = -\hat{r}_{m+1,m}$ ,  $\hat{t}_m \equiv \hat{t}_{m,m+1} \neq \hat{t}_{m+1,m}$ , and  $\hat{r}_{m,m+1}^2 + \hat{t}_{m,m+1}\hat{t}_{m+1,m} \equiv 1$ , hold for  $s$ - and  $p$ -polarized waves, while  $\hat{\mathbf{T}}_m$  contains a complex phase angle  $\hat{\delta}_m \equiv \delta'_m + j\delta''_m \equiv (2\pi d_m/\lambda) \hat{n}_m \cos \hat{\theta}_m = (2\pi d_m/\lambda) (u_m + j v_m)$  due to a single wave traversal in  $m$ th-layer of thickness  $d_m$  and refractive index  $\hat{n}_m$ , where  $u_m$  and  $v_m$  are real quantities equal to  $n_m$  and  $\kappa_m$  for normal incidence (Born & Wolf, 2002; Reitz et al., 1993). The geometric meaning of a complex angle of incidence  $\hat{\theta}_m$  cannot be realized in the usual way; yet, it equals to complex angle of reflection and is related to complex angle of refraction via a modified form of Snell's law (Born & Wolf, 2002; Jafar, 2013). Derivation of vector-/scalar-quantities related to light reflection and refraction at a two-media interface does not appeal to geometry and their obliquely-/normal- incidence formulas remain formally correct, with the net reflection and transmission coefficients  $\hat{r}_{\text{net}}$  and  $\hat{t}_{\text{net}}$  of a multi-layered stack being defined as

$$\hat{r}_{\text{net}} \equiv \frac{\hat{E}_-^1}{\hat{E}_+^1} \quad \text{and} \quad \hat{t}_{\text{net}} \equiv \frac{\hat{E}_+^f}{\hat{E}_+^1} \quad (\text{A3})$$

The obliquely-incidence intensity reflection and transmission coefficients  $R_{ll'}$  and  $T_{ll'}$  at interface of adjacent  $l$ - and  $l'$ - layers can be expressed in terms of  $\hat{n}_l$ ,  $\hat{n}_{l'}$  and their conjugates  $\hat{n}_l^*$  and  $\hat{n}_{l'}^*$  via Fresnel's reflection and transmission coefficients  $\hat{r}_{ll'}$ ,  $\hat{t}_{ll'}$ ,  $\hat{r}_{ll'}^*$  and  $\hat{t}_{ll'}^*$  (Born & Wolf, 2002; Jafar, 2013), with the normal-incidence  $R_{ll'}$ - and  $T_{ll'}$ - formulas are

$$R_{ll'} \equiv \hat{r}_{ll'} \hat{r}_{ll'}^* \quad \text{and} \quad T_{ll'} \equiv \text{Re} \left( \frac{\hat{n}_{l'}}{\hat{n}_l} \right) \hat{t}_{ll'} \hat{t}_{ll'}^* \quad (\text{A4})$$

For normal incidence, the coefficients  $\hat{r}_{ll'}$  and  $\hat{t}_{ll'}$ , and the net expressions for the specular reflectance  $R(\lambda)$  and transmittance  $T(\lambda)$  of the whole  $i$ th-layered structure can be found from the following formulations (Reitz et al., 1993; Jackson, 1998; Born & Wolf, 2002; Jafar, 2013; Nichelatti, 2002; Dresselhaus, 2001)

$$\hat{r}_{ll'} \equiv \frac{\hat{n}_l - \hat{n}_{l'}}{\hat{n}_l + \hat{n}_{l'}} = \frac{(n_l - n_{l'}) + j(\kappa_l - \kappa_{l'})}{(n_l + n_{l'}) + j(\kappa_l + \kappa_{l'})} \quad (\text{A5})$$

$$\hat{t}_{ll'} \equiv \frac{2\hat{n}_l}{\hat{n}_l + \hat{n}_{l'}} = \frac{2(n_l + j\kappa_l)}{(n_l + n_{l'}) + j(\kappa_l + \kappa_{l'})} \quad (\text{A6})$$

$$R(\lambda) \equiv \hat{r}_{\text{net}} \hat{r}_{\text{net}}^* \quad \text{and} \quad T(\lambda) \equiv \text{Re} \left( \frac{\hat{n}_m^*}{\hat{n}_1} \right) \hat{t}_{\text{net}} \hat{t}_{\text{net}}^* \quad (\text{A7})$$

Where the coefficients  $\hat{r}_{\text{net}}$  and  $\hat{t}_{\text{net}}$  are the conjugates of  $\hat{r}_{\text{net}}$  and  $\hat{t}_{\text{net}}$  of the structure, while  $\hat{n}_1^*$  and  $\hat{n}_m^*$  are the conjugates of the complex indices of refraction  $\hat{n}_1$  and  $\hat{n}_m$  of its first (incident) and last ( $m$ th-) layers.

#### A.2 Specular Transmittance and Reflectance of Three-Layered Structures

Let layer 2 in a {layer 1/layer 2/layer 3}-stack to be made from linear, isotropic, and non-magnetic material of complex index of refraction  $\hat{n}_2(\lambda) \equiv n_2(\lambda) + j\kappa_2(\lambda)$  and to have finite thickness  $d_2$  and smooth, parallel-plane surfaces. If the first and third layers are semi-infinite transparent air media ( $d_1 = d_3 = \infty$  and  $n_1 = n_3 \equiv 1$ ), we have a layer standing freely in air, while if layer 2 is laid on a thick and highly absorbing layer 3, so no light waves will be reflected back or come out from it, layer 3 is said to be infinite. Layer 2 may be a coherent thin film or an incoherent thick slab.

##### A.2.1 Coherent Thin Layer Bounded by two Different Semi-Infinite Media

For a coherent thin, absorbing layer 2, multiple internal reflections of light plane waves inside it and interference between them are both important. Use equations (A1), (A2), and (A3) for  $i = 3$  to get a couple of formulas for the reflection  $\hat{r}_{\text{net}} \equiv \hat{E}_-^1/\hat{E}_+^1 = \hat{r}_{123}$  and transmission  $\hat{t}_{\text{net}} \equiv \hat{E}_+^3/\hat{E}_+^1 = \hat{t}_{123}$  coefficients of a 123-structure for light plane waves obliquely incident on it from the side of layer 1 (along the 123-route) as

$$\hat{r}_{123} = \frac{\hat{r}_{12} + \hat{r}_{23} e^{j(2\delta_2)}}{1 + \hat{r}_{12} \hat{r}_{23} e^{j(2\delta_2)}} \quad \text{and} \quad \hat{t}_{123} = \frac{\hat{t}_{12} \hat{t}_{23} e^{j\delta_2}}{1 + \hat{r}_{12} \hat{r}_{23} e^{j(2\delta_2)}} \quad (\text{A8})$$

The  $\hat{r}_{\text{net}} \equiv \hat{E}_-^3 / \hat{E}_+^3 = \hat{r}_{321}$  and  $\hat{t}_{\text{net}} \equiv \hat{E}_+^1 / \hat{E}_+^3 = \hat{t}_{321}$  formulas for light waves *obliquely incident* from the side of layer 3 (321-route) can be found by *replacing number 1* in equation (A8) by *number 3* and *vice versa*, viz.

$$\hat{r}_{321} = \frac{\hat{r}_{32} + \hat{r}_{21} e^{j(2\delta_2)}}{1 + \hat{r}_{32} \hat{r}_{21} e^{j(2\delta_2)}} \quad \text{and} \quad \hat{t}_{321} = \frac{\hat{t}_{32} \hat{t}_{21} e^{j\delta_2}}{1 + \hat{r}_{32} \hat{r}_{21} e^{j(2\delta_2)}} \quad (\text{A9})$$

We can find the  $R_{123}(\lambda)$ -,  $R_{321}(\lambda)$ -,  $T_{123}(\lambda)$ -, and  $T_{321}(\lambda)$ - formulas in terms of  $\hat{r}_{ll'}$  and  $\hat{t}_{ll'}$  or *real scalar* reflection and transmission coefficients  $\rho_{ll'}$  and  $\tau_{ll'}$ , defined as  $\hat{r}_{ll'} \equiv \rho_{ll'} \exp(j\phi_{ll'})$  and  $\hat{t}_{ll'} \equiv \tau_{ll'} \exp(j\chi_{ll'})$ , where  $\phi_{ll'}$  and  $\chi_{ll'}$  are *real* phase-angle changes on wave reflection and transmission at interfaces of  $l$ - $l'$  layers (Born & Wolf, 2002; Jafar, 2013). At *normal incidence*,  $\rho_{ll'}$ ,  $\tau_{ll'}$ ,  $\phi_{ll'}$ , and  $\chi_{ll'}$  are given in terms of  $n_l$ ,  $n_{l'}$ ,  $\kappa_l$ , and  $\kappa_{l'}$  by (Born & Wolf, 2002; Jafar, 2013)

$$\rho_{ll'}^2 \equiv \frac{(n_l - n_{l'})^2 + (\kappa_l - \kappa_{l'})^2}{(n_l + n_{l'})^2 + (\kappa_l + \kappa_{l'})^2} \quad \text{and} \quad \tan \phi_{ll'} = -\frac{2(n_l \kappa_{l'} - n_{l'} \kappa_l)}{(n_l^2 + \kappa_l^2) - (n_{l'}^2 + \kappa_{l'}^2)} \quad (\text{A10})$$

$$\tau_{ll'}^2 \equiv \frac{4(n_l^2 + \kappa_l^2)}{(n_l + n_{l'})^2 + (\kappa_l + \kappa_{l'})^2} \quad \text{and} \quad \tan \chi_{ll'} = -\frac{(n_l \kappa_{l'} - n_{l'} \kappa_l)}{(n_l^2 + \kappa_l^2) + n_l n_{l'} + \kappa_l \kappa_{l'}} \quad (\text{A11})$$

For normal incidence,  $\delta_2 \equiv (2\pi n_2 d_2 / \lambda) + j(2\pi \kappa_2 d_2 / \lambda)$  and in terms of  $\rho_{ll'}$ ,  $\tau_{ll'}$ ,  $\phi_{ll'}$ ,  $d_2$ ,  $\alpha_2 \equiv 2\delta_2'' / d_2$ , and  $\delta_2'$ , the normal-incidence  $R_{123}(\lambda)$ -,  $T_{123}(\lambda)$ -,  $R_{321}(\lambda)$ -, and  $T_{321}(\lambda)$ - formulas of a four-layered structure having the {semi-infinite layer 1/thin layer 2/semi-infinite layer 3}-stacking become (Born & Wolf, 2002; Jafar, 2013)

$$R_{123}(\lambda) = \frac{\rho_{12}^2 + \rho_{23}^2 e^{-2\alpha_2 d_2} + 2\rho_{12}\rho_{23} e^{-\alpha_2 d_2} \cos(2\delta_2' - \phi_{12} + \phi_{23})}{1 + \rho_{12}^2 \rho_{23}^2 e^{-2\alpha_2 d_2} + 2\rho_{12}\rho_{23} e^{-\alpha_2 d_2} \cos(2\delta_2' + \phi_{12} + \phi_{23})} \quad (\text{A12})$$

$$T_{123}(\lambda) = \frac{\left(\frac{n_3}{n_1}\right) \tau_{12}^2 \tau_{23}^2 e^{-\alpha_2 d_2}}{1 + \rho_{12}^2 \rho_{23}^2 e^{-2\alpha_2 d_2} + 2\rho_{12}\rho_{23} e^{-\alpha_2 d_2} \cos(2\delta_2' + \phi_{12} + \phi_{23})} \quad (\text{A13})$$

$$R_{321}(\lambda) = \frac{\rho_{32}^2 + \rho_{21}^2 e^{-2\alpha_2 d_2} + 2\rho_{32}\rho_{21} e^{-\alpha_2 d_2} \cos(2\delta_2' - \phi_{32} + \phi_{21})}{1 + \rho_{32}^2 \rho_{21}^2 e^{-2\alpha_2 d_2} + 2\rho_{32}\rho_{21} e^{-\alpha_2 d_2} \cos(2\delta_2' + \phi_{32} + \phi_{21})} \quad (\text{A14})$$

$$T_{321}(\lambda) = \frac{\left(\frac{n_1}{n_3}\right) \tau_{32}^2 \tau_{21}^2 e^{-\alpha_2 d_2}}{1 + \rho_{32}^2 \rho_{21}^2 e^{-2\alpha_2 d_2} + 2\rho_{32}\rho_{21} e^{-\alpha_2 d_2} \cos(2\delta_2' + \phi_{32} + \phi_{21})} \quad (\text{A15})$$

Note that  $\rho_{ll'} = \rho_{l'l}$  and  $\phi_{12} = \phi_{21}$  and  $\phi_{23} = \phi_{32}$  and vanish if all layers are transparent ( $\kappa_1 = \kappa_2 = \kappa_3 = 0$ ), with  $R_{123}(\lambda) = R_{321}(\lambda)$ , but  $\tau_{ll'} \neq \tau_{l'l}$  and  $\chi_{ll'} \neq \chi_{l'l}$  except under constraints, so  $T_{123}(\lambda) = T_{321}(\lambda)$  if layers 1 and 3 are transparent ( $\kappa_1 = \kappa_3 = 0$ ), irrespective of whether layer 2 is transparent or absorbing ( $\kappa_2 \geq 0$ ).

#### A.2.2 Incoherent Thick Layer Surrounded by two Dissimilar Semi-Infinite Media

Formulas for *normal-incidence* specular reflectance and transmittance of an *incoherent thick* layer 2 bounded by two semi-infinite layers 1 and 3 can be found from the  $R_{123}(\lambda)$ -,  $T_{123}(\lambda)$ -,  $R_{321}(\lambda)$ -, and  $T_{321}(\lambda)$ - equations (A12) to (A15) by *eliminating effect of interference* between back and forth wave reflections at the layer 2-interfaces with its adjacent media. This may be attained by treating the phase-change angle  $\delta_2'$  as an arbitrary random angle and averaging transmittance and reflectance formulas via integrating them with respect to  $\delta_2'$  for all its values between  $-\infty$  and  $\infty$  (Richards, 1998), which is an awkward procedure. Instead, we can derive them using a much less tangled approach, based on algebraic summation of individual intensities of reflected and transmitted light waves at interfaces of the *incoherent layer* 2 with its semi-infinite adjoining layers 1 and 3 (Richards, 1998; Born & Wolf, 2002; Jafar, 2013; Nichelatti, 2002; Dresselhaus, 2001). The results are cited below for light waves travelling along 123- and 321-routes as

$$T_{123}(\lambda) = \frac{\left(\frac{n_3}{n_1}\right) |\hat{t}_{12}|^2 |\hat{t}_{23}|^2 e^{-\alpha_2 d_2}}{1 - |\hat{r}_{12}|^2 |\hat{r}_{23}|^2 e^{-2\alpha_2 d_2}} = \frac{T_{12} T_{23} e^{-\alpha_2 d_2}}{1 - R_{21} R_{23} e^{-2\alpha_2 d_2}} \quad (\text{A16})$$

$$R_{123}(\lambda) = |\hat{r}_{12}|^2 + \frac{|\hat{t}_{12}|^2 |\hat{r}_{23}|^2 |\hat{t}_{21}|^2 e^{-2\alpha_2 d_2}}{1 - |\hat{r}_{12}|^2 |\hat{r}_{23}|^2 e^{-2\alpha_2 d_2}} = R_{12} + \frac{T_{12} R_{23} T_{21} e^{-2\alpha_2 d_2}}{1 - R_{21} R_{23} e^{-2\alpha_2 d_2}} \quad (\text{A17})$$

$$T_{321}(\lambda) = \frac{\left(\frac{n_1}{n_3}\right) |\hat{t}_{32}|^2 |\hat{t}_{21}|^2 e^{-\alpha_2 d_2}}{1 - |\hat{r}_{32}|^2 |\hat{r}_{21}|^2 e^{-2\alpha_2 d_2}} = \frac{T_{32} T_{21} e^{-\alpha_2 d_2}}{1 - R_{32} R_{21} e^{-2\alpha_2 d_2}} \quad (\text{A18})$$

$$R_{321}(\lambda) = |\hat{r}_{32}|^2 + \frac{|\hat{t}_{32}|^2 |\hat{r}_{21}|^2 |\hat{t}_{23}|^2 e^{-2\alpha_2 d_2}}{1 - |\hat{r}_{32}|^2 |\hat{r}_{21}|^2 e^{-2\alpha_2 d_2}} = R_{32} + \frac{T_{32} R_{21} T_{23} e^{-2\alpha_2 d_2}}{1 - R_{32} R_{21} e^{-2\alpha_2 d_2}} \quad (\text{A19})$$

### A.3 Four-Layered Structures With two Stacked Layers Bounded by two Semi-Infinite Media

If part of light waves passing to layer 3 of a three-layered stack emerges into a *semi-infinite layer* 4 ( $d_4 = \infty$ ) to form a *four-layered* stack, two types of which worth debating. One in which layers 2 and 3 are *coherently thin* with dissimilar absorption coefficients  $\alpha_2$  and  $\alpha_3$ . The other consists of a *coherent thin* layer 2 of thickness  $d_2$  and an *incoherent thick* layer 3 of thickness  $d_3$  ( $\gg d_2$ ) as a dielectric or semiconducting thin film grown on a thicker transparent substrate, both of which bounded by air. This {*air/thin film/thick substrate/air*}-stack is common in most thin film optical studies.

#### A.3.1 Two Coherent Thin Stacked Layers Confined Between two Semi-Infinite Layers

When layers 2 and 3 are *coherently thin* and bounded by *semi-infinite first* and *fourth* layers, equations (A1), (A2), and (A3) can be applied to this 1234-structure ( $i = 4$ ) to get its *obliquely-incident* complex Fresnel reflection and transmission coefficients  $\hat{r}_{1234}$  and  $\hat{t}_{1234}$  in terms of  $\hat{r}_{ll'}$  and  $\hat{t}_{ll'}$ , at the *three* interfaces of its adjacent  $l$  and  $l'$  layers, and of  $\delta_2 \equiv \delta_2' + j\delta_2''$  and  $\delta_3 \equiv \delta_3' + j\delta_3''$  produced upon a *single traversal* of light waves inside the *coherent thin* layers 2 and 3, respectively, as given below

$$\hat{r}_{1234} = \frac{\left[ \hat{r}_{12} + \hat{r}_{23} e^{-2\delta_2''} e^{j(2\delta_2')} \right] + \hat{r}_{34} \hat{r}_{23} e^{-2\delta_3''} e^{j(2\delta_3')} \left[ \hat{r}_{12} \hat{r}_{23} + \hat{r}_{23} e^{-2\delta_2''} e^{j(2\delta_2')} \right]}{\left[ 1 + \hat{r}_{12} \hat{r}_{23} \hat{r}_{23} e^{-2\delta_2''} e^{j(2\delta_2')} \right] + \hat{r}_{34} e^{-2\delta_3''} e^{j(2\delta_3')} \left[ \hat{r}_{23} + \hat{r}_{12} \hat{r}_{23} e^{-2\delta_2''} e^{j(2\delta_2')} \right]} \quad (\text{A20})$$

$$\hat{t}_{1234} = \frac{\hat{t}_{12} \hat{t}_{23} e^{-\delta_2''} \hat{t}_{34} e^{-\delta_3''} e^{j(\delta_2' + \delta_3')}}{\left[ 1 + \hat{r}_{12} \hat{r}_{23} \hat{r}_{23} e^{-2\delta_2''} e^{j(2\delta_2')} \right] + \hat{r}_{34} e^{-2\delta_3''} e^{j(2\delta_3')} \left[ \hat{r}_{23} + \hat{r}_{12} \hat{r}_{23} e^{-2\delta_2''} e^{j(2\delta_2')} \right]} \quad (\text{A21})$$

$\delta_2' = 2\pi n_2 d_2 / \lambda$ ,  $\delta_3' = 2\pi n_3 d_3 / \lambda$ ,  $2\delta_2'' = 4\pi \kappa_2 d_2 / \lambda = \alpha_2 d_2$ , and  $2\delta_3'' = 4\pi \kappa_3 d_3 / \lambda = \alpha_3 d_3$  at normal incidence and the formulas of transmittance  $T_{1234} \equiv \text{Re}(\hat{n}_4^* / \hat{n}_1^*) \hat{t}_{1234} \hat{t}_{1234}^*$  and reflectance  $R_{1234} \equiv \hat{r}_{1234} \hat{r}_{1234}^*$  of this four-layered stack are much involved and cannot be applicable in algebraic methods if they are expressed explicitly in terms of complex indices of refraction of its layers. Yet, these theoretical  $R_{1234}$ - and  $T_{1234}$ -formulas can be used in analysis of measured reflectance and/or transmittance data using conventional numeric iterative curve-fitting techniques.

#### A.3.2 Air-Supported Stack of a Coherent Thin Film Placed on an Incoherent Thick Absorbing Slab

The normal-incidence  $T_{1234}$ -formula of an air-supported {thin film/thick substrate}-stack is not much intricate and can be used in both analytical and curve-fitting techniques. One might get this formula by substituting the  $\hat{t}_{1234}$ -equation (A21) and its complex conjugate  $\hat{t}_{1234}^*$  into  $T_{1234} \equiv \text{Re}(\hat{n}_4^* / \hat{n}_1^*) \hat{t}_{1234} \hat{t}_{1234}^*$ , with  $\hat{n}_1 = \hat{n}_4 = 1$ , and eliminate effects of interference between multiple reflections in the incoherent thick substrate via averaging the  $T_{1234}$ -integral over random phase angles  $\delta_3'$ . This job is arduous, but for such a {*semi-infinite layer 1/thin layer 2/thick layer 3/semi-infinite layer 4*}-stack, one can adopt more irresistibly methodological and analytical approaches (Jafar, 2013) to derive the general formulations for both of its specular  $R_{1234}(\lambda)$  and  $T_{1234}(\lambda)$  in terms of the intensity reflection and transmission coefficients at the respective interfaces of its adjacent neighboring layers. Alternatively, we can simply *re-number* the layers of a three-layered structure composing of an incoherent thick layer bounded by two semi-infinite layers to turn into a four-layered structure if we replace its layer 2 with a stack of a semi-infinite layer 1 and a coherent thin layer 2 to form a 1234-stacking. Replace  $R_{12}(\lambda)$ ,  $R_{21}(\lambda)$ ,  $T_{12}(\lambda)$ ,  $T_{21}(\lambda)$ ,  $R_{23}(\lambda)$ ,  $R_{32}(\lambda)$ ,  $T_{23}(\lambda)$ , and  $T_{32}(\lambda)$  appear in equations (A16) to (A19) by  $R_{123}(\lambda)$ ,  $R_{321}(\lambda)$ ,  $T_{123}(\lambda)$ , and  $T_{321}(\lambda)$  of equations (A12) to (A15) via altering their numeric permutations as: number 1 on the left is replaced by 12 and number 1 on the right by 21, while numbers 2 and 3 are re-named 3 and 4, respectively. Whatever the adopted derivation approach, the resulting  $R_{1234}(\lambda)$ - and  $T_{1234}(\lambda)$ -formulas are valid for *normal*- or *obliquely*-incidence light waves travelling from the side of layer 1 and can re-written in compacted forms in terms of the various intensity reflection and transmission at the interfaces of adjacent layers of this four-layered structure as (Jafar, 2013)

$$R_{1234}(\lambda) = R_{123}(\lambda) + \frac{T_{123}(\lambda) T_{321}(\lambda) R_{34}(\lambda) e^{-2\alpha_3(\lambda) d_3}}{1 - R_{321}(\lambda) R_{34}(\lambda) e^{-2\alpha_3(\lambda) d_3}} = R_{12}(\lambda) + \frac{T_{12}(\lambda) R_{23}(\lambda) T_{21}(\lambda) e^{-2\alpha_2(\lambda) d_2}}{1 - R_{21}(\lambda) R_{23}(\lambda) e^{-2\alpha_2(\lambda) d_2}}$$

$$+ \frac{\frac{T_{12}(\lambda)T_{23}(\lambda)e^{-\alpha_2(\lambda)d_2}}{1-R_{21}(\lambda)R_{23}(\lambda)e^{-2\alpha_2(\lambda)d_2}} \frac{T_{32}(\lambda)T_{21}(\lambda)e^{-\alpha_2(\lambda)d_2}}{1-R_{32}(\lambda)R_{21}(\lambda)e^{-2\alpha_2(\lambda)d_2}} R_{34}(\lambda)e^{-2\alpha_3(\lambda)d_3}}{1-R_{32}(\lambda) + \frac{T_{32}(\lambda)R_{21}(\lambda)T_{23}(\lambda)e^{-2\alpha_2(\lambda)d_2}}{1-R_{32}(\lambda)R_{21}(\lambda)e^{-2\alpha_2(\lambda)d_2}} R_{34}(\lambda)e^{-2\alpha_3(\lambda)d_3}} \quad (A22)$$

$$T_{1234}(\lambda) = \frac{T_{123}(\lambda) T_{34}(\lambda) e^{-\alpha_3 d_3}}{1-R_{321}(\lambda) R_{34}(\lambda) e^{-2\alpha_3 d_3}} = \frac{\frac{T_{12}(\lambda)T_{23}(\lambda)e^{-\alpha_2(\lambda)d_2}}{1-R_{21}(\lambda)R_{23}(\lambda)e^{-2\alpha_2(\lambda)d_2}} R_{34}(\lambda)e^{-2\alpha_3(\lambda)d_3}}{1-R_{32}(\lambda) + \frac{T_{32}(\lambda)R_{21}(\lambda)T_{23}(\lambda)e^{-2\alpha_2(\lambda)d_2}}{1-R_{32}(\lambda)R_{21}(\lambda)e^{-2\alpha_2(\lambda)d_2}} R_{34}(\lambda)e^{-2\alpha_3(\lambda)d_3}} \quad (A23)$$

The  $R_{123}(\lambda)$ - and  $R_{321}(\lambda)$ - formulas are *unlike but under strict conditions*, while  $T_{123}(\lambda) = T_{321}(\lambda)$  if layers 1 and 3 are transparent whether layer 2 is absorbing or not. If light waves travelling in layer 1 hit its interface to coherent thin layer 2, multiple internal reflections inside it and their interference are significant. Part of waves will be reflected back into layer 1 and the other will be transmitted to incoherent thick layer 3, where multiple internal reflections occur with no interference, before emerging out to layer 4 without *back reflections*. Inspection of the  $R_{1234}(\lambda)$ - and  $T_{1234}(\lambda)$ - equations (A22) and (A23) of this four-layered system ensures the need, in addition to  $R_{123}(\lambda)$ - and  $T_{123}(\lambda)$ - equations (A12) and (A13), derived for the case when light waves are travelling from layer 1 to layer 2, then to layer 3 (123-route), the formulas of  $R_{321}(\lambda)$  and  $T_{321}(\lambda)$  given in equations (A14) and (A15), derived for the case when light plane waves are passing from layer 3 to layer 2 to layer 1 (321-route). This is of key importance as light waves propagating through the incoherent thick layer 3 execute multiple reflections at its interfaces to layers 2 and 4, so that light is travelling in layer 3 in both forward and backward directions- that is, 123- and 321- routes, for which  $R_{123}(\lambda) \neq R_{321}(\lambda)$  and  $T_{123}(\lambda) \neq T_{321}(\lambda)$ .

For an air-supported {thin layer 2/thick layer 3}-stacking,  $n_1 = n_4 = 1$ ,  $\kappa_1 = \kappa_4 = 0$ , and the complex indices of refraction of layers 2 and 3 are  $\hat{n}_2 \equiv n_2 + j\kappa_2$  and  $\hat{n}_3 \equiv n_3 + j\kappa_3$ , respectively. The intensity reflection  $R_{34}(\lambda)$  and transmission  $T_{34}(\lambda)$  coefficients at the interface of thick layer 3 with the semi-infinite layer 4 can be found in terms of their indices of refraction; however, to be consistent with the formulas of  $R_{123}(\lambda)$ ,  $T_{123}(\lambda)$ ,  $R_{321}(\lambda)$  and  $T_{321}(\lambda)$ , we will use the real scalar reflection and transmission coefficients  $\rho_{34}$  and  $\tau_{34}$  that are related to complex Fresnel reflection and transmission coefficients  $\hat{r}_{34}$  and  $\hat{t}_{34}$  at interface of layer 3-layer 4 (34-interface) by  $\hat{r}_{34} \equiv \rho_{34} \exp(j\phi_{34})$  and  $\hat{t}_{34} \equiv \tau_{34} \exp(j\chi_{34})$ , where  $\phi_{34}$  and  $\chi_{34}$  are the phase-change angles produced upon reflection and transmission at this interface. In effect, the normal-incidence intensity reflection and transmission coefficients at the 34-interface are given by

$$R_{34} = \rho_{34}^2 \quad \text{and} \quad T_{34} = \frac{1}{n_3} \tau_{34}^2 \quad (A24)$$

The  $T_{1234}(\lambda)$ -equation (A23) that describes spectral *normal-incidence* specular transmittance of an ideal four-layered structure of the {air/coherent thin film/incoherent thick substrate/air}-stacking can be written, with the wavelength dependence of its parameters implicit, in terms of optical absorption coefficients  $\alpha_2$  and  $\alpha_3$  of its film and substrate, respectively, and of the various *scalar* reflection and transmission coefficients  $\rho_{ll'}$  and  $\tau_{ll'}$  at the different interfaces of its adjacent  $l-l'$  layers in a general form as illustrated below

$$T_{1234}(\lambda) = \frac{(\tau_{12}^2 \tau_{23}^2 e^{-\alpha_2 d_2})(\tau_{34}^2 e^{-\alpha_3 d_3})}{1 - \frac{\rho_{23}^2 + \rho_{12}^2 e^{-2\alpha_2 d_2} + 2\rho_{12}\rho_{23} e^{-\alpha_2 d_2} \cos(2\delta_2' + \phi_{12} - \phi_{23})}{1 + \rho_{12}^2 \rho_{23}^2 e^{-2\alpha_2 d_2} + 2\rho_{12}\rho_{23} e^{-\alpha_2 d_2} \cos(2\delta_2' + \phi_{12} + \phi_{23})} (\rho_{34}^2 e^{-2\alpha_3 d_3})} \quad (A25)$$

One can derive an expression for the specular reflectance  $R_{1234}(\lambda)$ , which is much more unwieldy and with which we are not here interested. To analyze the  $T_{\text{exp}}(\lambda) - \lambda$  data of an air-supported four-layered stack, scalar reflection and transmission coefficients  $\rho_{12}$ ,  $\rho_{23}$ ,  $\rho_{34}$ ,  $\tau_{12}$ ,  $\tau_{23}$ , and  $\tau_{34}$  at interfaces of adjacent layers and phase-change angles in  $T_{1234}(\lambda)$ -equation (A25) had to be expressed in terms of real and imaginary parts of their complex indices of refraction  $n_2$ ,  $\kappa_2$ ,  $n_3$ , and  $\kappa_3$ , using equations (A10) and (A11). So, the  $T_{1234}(\lambda)$ -formula cannot be used in algebraic handling of  $T_{\text{exp}}(\lambda)$  data at a wavelength  $\lambda$ , but the  $T_{\text{exp}}(\lambda) - \lambda$  spectrum can be curve-fitted to this  $T_{1234}(\lambda)$ -formula, with the effect of absorption in film and substrate being taken into account. As optical constants of a sample may vary with  $\lambda$ , the problem is much tortuous because one must insert in the transmittance formula a proper dispersion relation.

### A.3.3 Normal-Incidence Transmittance of {Air/Thin Film/Thick Transparent Substrate/Air}-Stacks

For an {air/thin layer 2/thick transparent layer 3/air}-stack at which light is incident *normally*, the  $T_{1234}(\lambda)$ -equation (A25) becomes simpler as  $n_1 = n_4 = 1$ ,  $\kappa_1 = \kappa_4 = 0$ ,  $\kappa_3 = \alpha_3 = 0$ . This is the case of a material thin film grown on a dielectric substrate whose absorption edge is below the strong absorption region of the film. Equation (A25) reduces to an expression that describes spectral normal-incidence specular transmittance

$T_{1234}(\lambda) = T\{\lambda; n(\lambda), \kappa(\lambda), d, n_s(\lambda)\}$ , which can be employed in both algebraic and curve-fitting techniques, the miniature details of its mathematical derivation has been carried out elsewhere (Jafar, 2013). The symbols  $d$ ,  $n$ ,  $\kappa$ ,  $\alpha$ , and  $n_s$  are used instead of  $d_2$ ,  $n_2$ ,  $\kappa_2$ ,  $\alpha_2$ , and  $n_3$ , respectively, so the normal-incidence  $T(\lambda; n, \kappa, d, n_s)$ -expression can be written, with their  $\lambda$ -dependence being omitted for clarity, in a final compact form (for  $n > n_s$ ) as (Swanepoel, 1983; Jafar, 2013)

$$T(\lambda; n, \kappa, d, n_s) = \frac{A' x}{B' - C' x + D' x^2} \quad (\text{A26})$$

The absorbance parameter  $x \equiv \exp(-\alpha d)$ , where  $\alpha \equiv 4 \pi \kappa / \lambda$ , with the constants  $A'$ ,  $B'$ ,  $C'$  and  $D'$  being written in terms of  $n_s$ ,  $n$  and  $\kappa$  via the expressions given below

$$A' = 16 n_s (n^2 + \kappa^2) \quad (\text{A26} - a)$$

$$B' = [(n+1)^2 + \kappa^2] * [(n+1) * (n + n_s^2) + \kappa^2] \quad (\text{A26} - b)$$

$$C' = \{(n^2 - 1 + \kappa^2) * (n^2 - n_s^2 + \kappa^2) - 2 \kappa^2 (n_s^2 + 1)\} * (2 \cos \varphi) - \kappa \{2 (n^2 - n_s^2 + \kappa^2) + (n_s^2 + 1) * (n^2 - 1 + \kappa^2)\} * (2 \sin \varphi) \quad (\text{A26} - c)$$

$$D' = [(n-1)^2 + \kappa^2] * [(n-1) * (n - n_s^2) + \kappa^2] \quad (\text{A26} - d)$$

Here,  $\varphi (\equiv 4 \pi n d / \lambda)$  is the interference phase-change angle produced upon a *double normal-incidence traversal* of light waves inside the coherent thin film of this air-supported {film/substrate}-stack, with equation (A26) can be used in numeric analysis of its measured transmittance using curve-fitting programs with dispersion models for the optical constants of its film and substrate, and in numeric analysis based on the Pointwise Unconstraint Minimization Approach (PUMA) software, where no dispersion relations are needed in prior (Birgin et al., 1999). To perform algebraic analysis of transmittance of air-supported {thin film/thick transparent substrate}-structures, equation (A26) has been simplified further by proposing some justified assumptions and reasonable model approximations to get a  $T(\lambda)$ -formula that enables one to cognize their optical behavior and gain important conclusions from their observed transmittance spectra. If  $\kappa_s(\lambda) = \alpha_s(\lambda) = 0$  and  $n_s(\lambda) = n_s$  at wavelengths above the substrate's absorption edge, and  $\kappa^2 \ll n^2$  and  $\kappa \sim 0$  in the transparent and weakly absorbing regions of the film, the specular transmittance of such a four-layered stack can be described by a  $T(\lambda; n, \kappa, d, n_s)$ -formula that is usually quoted in a neat form (for  $n > n_s$ ) as (Swanepoel, 1983; Jafar, 2013)

$$T(\lambda; n, \kappa, d, n_s) = \frac{A x}{B - C x \cos \varphi + D x^2} \quad (\text{A27})$$

$$A = 16 n^2 n_s \quad (\text{A27} - a)$$

$$B = (n+1)^3 * (n + n_s^2) \quad (\text{A27} - b)$$

$$C = 2 (n^2 - 1) * (n^2 - n_s^2) \quad (\text{A27} - c)$$

$$D = (n-1)^3 * (n - n_s^2) \quad (\text{A27} - d)$$

Equation (A27) forms the rigorous basis for the analytical envelope method developed by Swanepoel for partially-absorbing uniform films deposited onto thick transparent substrates, whether their indices of refraction were taken to be constant (non-dispersive) or dispersive. Putting  $\cos \varphi = \pm 1$  in equation (A27), it reduces to two independent equations that describe the maximum  $T_{M0}$  and minimum  $T_{m0}$  values of its normal-incidence transmittance  $T(\lambda; n, \kappa, d, n_s)$  which are often described by the forms (Swanepoel, 1983; Jafar, 2013)

$$T_{M0} = \frac{A x}{B - C x + D x^2} \quad \text{and} \quad T_{m0} = \frac{A x}{B + C x + D x^2} \quad (\text{A28})$$

When interference-fringe maxima and minima are superimposed on the as-measured normal-incidence transmittance spectrum of an air-supported {film/substrate}-stack,  $T_{M0}$  and  $T_{m0}$  represent the  $T$ -values at the *tangent* points to these maxima and minima, respectively (Swanepoel, 1983). Equation (A28) forms the basis of the analytical procedures of the envelope method, where one has to construct two reliable continuous curve-like functions in  $\lambda$  from the as-measured tangent  $T_{M0}$ - and  $T_{m0}$ - values that prudently bound observed transmittance extremes. The normal-incidence specular transmittance  $T_s(\lambda)$  and reflectance  $R_s(\lambda)$  of an incoherent thick transparent substrate standing freely in air can be shown, using Equations (A10), (A11), (A16), (A17), and (A24), to be related to its index of refraction  $n_s$  as (Swanepoel, 1983; Jafar, 2013)

$$R_s(\lambda) = \frac{(n_s-1)^2}{n_s^2+1} \quad \text{and} \quad T_s(\lambda) = 1 - R_s(\lambda) = \frac{2n_s}{n_s^2+1} \quad (\text{A29})$$

$$n_s(\lambda) = \frac{1}{T_s(\lambda)} + \left( \frac{1}{[T_s(\lambda)]^2} - 1 \right)^{1/2} = \frac{1 + \{R_s(\lambda)[2 - R_s(\lambda)]\}^{1/2}}{1 - R_s(\lambda)} \quad (\text{A30})$$

In the transparent region of an ideal air-supported {film/substrate}-stack,  $\alpha = 0$  ( $x = 1$ ) and  $T_{M0}$ -expression is equal to  $T_s(\lambda)$ -equation (A29)- that is, transmittances of film and its substrate coincide. For small SBW, the deviation of as-measured film's transmittance maxima from  $T_s$  with decreasing wavelength denotes onset of optical absorption in the film (Swanepoel, 1983; Swanepoel, 1984). If the film is non-uniform or suffers from surface roughness, its  $T(\lambda)$ -formula can be re-formulated, but handling its spectra is not easily skilled. In transparent or weakly-absorbing region of this film, Equations (A27) and (A28) can be modified to account for small film non-uniformity and analytical methods can be used to treat its optical response (Swanepoel, 1984).

## Appendix B

### *Dielectric Behavior and Optical Absorption of Material Solid Layers*

All material media consist of atoms, composed of atomic nuclei and bound electrons, which can be affected by the presence of an electric field such that the positive and negative charged particles are pushed apart in opposite directions by the force caused by the applied electric field. In pure dielectrics, valence electrons are tightly bound to atoms and will be displaced, relative to respective nuclei, slightly in a *weak static* electric field. A *net* electric field is thus created in the solid and the restoring forces set up by the change in atomic charge arrangement will limit these field-induced shifts. The distorted charge distribution around atoms of a solid can be approximated by a collection of atomic dipoles and it is said to be polarized. Molecules in a polar solid form *intrinsic* electric dipoles that are more or less free to rotate and oriented in the solid under thermal agitations and applied electric fields, resulting in a net permanent electric dipole moment. In ionic non-polar solids, electric dipoles result from shifts in the positions of *oppositely charged ions* in the presence of an electric field. Field-induced distortions of electronic charge distribution around atoms in an ionic or a polar solid also result in nonvanishing dipole moments. However, when a conductor (metal) exposed to a *static* electric field, its *nearly* free electrons will screen the induced static field inside it. When an electromagnetic field is, however, imposed to a metal or dielectric solid, its permanent electric dipoles, ion-pairs, bound-electrons, free electrons will oscillate in response as the ensuing oscillating electric fields acting at their sites and its electric response is totally different from its electrostatic behavior (Christman, 1988; Rogalski & Palmer, 2000; Palik, 1998; Dressel & Grüner, 2002; Reitz et al., 1993). Both reflection and refraction of light in a solid are associated with oscillations of microscopic dipoles, as are its absorption and dispersion of its optical constants. We shall address optical behavior of linear, isotropic, and non-magnetic solids exposed to weak electromagnetic radiation with ultraviolet frequencies and below. Thus, their wavelengths are much larger than interatomic spacing so diffraction features are not important, and a macroscopic classical description of its ensuing dielectric and optical response is quite adequate and comparable to the results obtained from a rigorous quantum-mechanical treatment (Rogalski & Palmer, 2000; Palik, 1998; Dressel & Grüner, 2002; Reitz et al., 1993).

#### *B.1 Relations Between Electric Quantities for Static and Time-Dependent Electric Fields*

Macroscopically, the overall effect of an electromagnetic field interacting with a substance can be pictured, instead of treating each of its field-induced electric dipoles, as a displacement of its *entire* positive charge relative to negative charge, which creates its own electric field outside and inside it (Reitz et al., 1993). In general, the *macroscopic* electric field  $\mathbf{E}_{\text{mac}}$  inside a polarized sample differs from *local* electric field  $\mathbf{E}_{\text{loc}}$  acting at the site of a dipole inside it, which determines moments of its electric dipoles and their alignments. Each electric dipole  $\ell$  will have a *nonvanishing* average dipole moment  $\mathbf{p}_\ell$ , with the vector sum  $\sum \mathbf{p}_\ell$  of all dipole moments gives a *net macroscopic electric polarization vector*  $\mathbf{P}(\mathbf{r})$  inside the polarized sample, defined as the *total electric dipole moment per unit volume of the sample*, which depends on  $\mathbf{E}_{\text{mac}}$  inside it, with part of it being produced by the polarized sample itself (Reitz et al., 1993). A relation between  $\mathbf{E}_{\text{loc}}$  and  $\mathbf{E}_{\text{mac}}$  in a polarized sample is only wanted to link interactions of its electric dipoles with electromagnetic field to its resulting macroscopic dielectric behavior, related to  $\mathbf{P}(\mathbf{r})$ . so to describe the optical response of a sample to an applied weak electromagnetic field, no need to do explicit calculations of its electric dipole moments, but their connection to the applied field and the formulas of its microscopic electric response will suffice.

The electric polarization of a solid depends not only on the total electric field  $\mathbf{E}_{\text{mac}}(\mathbf{r}')$  inside it, but also on its constituents. Macroscopically, the dielectric behavior of a material in response to  $\mathbf{E}_{\text{mac}}(\mathbf{r}')$  is identified by a *point*

relationship, called the *constitutive equation*  $\mathbf{P}(\mathbf{r}') = \mathbf{P}[\mathbf{E}_{\text{mac}}(\mathbf{r}')]$ , so if  $\mathbf{E}_{\text{mac}}(\mathbf{r}')$  varies from one point  $\mathbf{r}'$  to another inside it, then  $\mathbf{P}(\mathbf{r}')$  will vary accordingly. For materials with *no permanent electric polarization* (Rogalski & Palmer, 2000; Palik, 1998; Dressel & Grüner, 2002; Reitz et al., 1993),  $\mathbf{P}(\mathbf{r}')$  vanishes for  $\mathbf{E}_{\text{mac}}(\mathbf{r}') = 0$ , and if a material is *isotropic* with alike properties in all directions, then its polarization vector has the same direction as the electric field causing it. Many polycrystalline and amorphous solids are *isotropic*, but few substances may be electrically polarized easier in certain directions than along others (*anisotropic*) (Reitz et al., 1993). If sample properties do not vary with its composition or position, it is called *homogeneous*. The static polarization of a linear, isotropic, and homogeneous material is proportional to an applied weak *static* electric field, with *constant of proportionality is field-independent* and only typical of the material, via a *linear constitutive equation* between  $\mathbf{E}_{\text{mac}}$  and its macroscopic polarization  $\mathbf{P}$  (Christman, 1988; Rogalski & Palmer, 2000; Palik, 1998; Dressel & Grüner, 2002; Reitz et al., 1993; Jackson, 1998)

$$\mathbf{P} \equiv \epsilon_0 \chi \mathbf{E}_{\text{mac}} \quad (\text{B1})$$

where  $\epsilon_0$  is the free-space electric permittivity. The *dimensionless* constant of proportionality  $\chi$  is called the *static macroscopic electric susceptibility* of the substance, which depends on its microscopic structure and experimental conditions such as ambient temperature. Another constitutive equation is that relating  $\mathbf{E}_{\text{mac}}$  inside a linear, isotropic, and homogenous substance to the macroscopic electric displacement vector  $\mathbf{D}$ , viz. (Christman, 1988; Rogalski & Palmer, 2000; Palik, 1998; Dressel & Grüner, 2002; Reitz et al., 1993; Jackson, 1998)

$$\mathbf{D} \equiv \epsilon_0 \mathbf{E}_{\text{mac}} + \mathbf{P} \equiv \epsilon_0 (1 + \chi) \mathbf{E}_{\text{mac}} \equiv \epsilon_0 \epsilon \mathbf{E}_{\text{mac}} \quad (\text{B2})$$

The *dimensionless* constant of proportionality  $\epsilon$  is the *static macroscopic relative electric permittivity (dielectric constant)* of the substance, which do not convey any information *not* available in its susceptibility  $\chi$ . In equation (B1),  $\mathbf{E}_{\text{mac}}$  is in part due external charges added to a dielectric sample and in part due to electric polarization of itself; thus, if an external electrostatic field  $\mathbf{E}_{\text{app}}$  is imposed on it, we cannot compute  $\mathbf{P}$  directly from equation (B1), as this external field will polarize the sample, and this polarization will produce its own internal electric field, which then contributes to the total electric field inside it, and this in turn modifies the polarization, and so on- that is, we seem to be in a bind. An explicit mathematical formulation for  $\mathbf{P}$  or  $\mathbf{E}_{\text{mac}}$  inside a polarized sample is, however, not required for studying its dielectric behavior, but in general a connection between its macroscopic electric susceptibility and *microscopic structure* is required, and this demands a connection between the *actual (local)* electric field  $\mathbf{E}_{\text{loc}}(\mathbf{r})$  responsible for inducing electric dipoles at the point  $\mathbf{r}$  inside it and  $\mathbf{E}_{\text{mac}}(\mathbf{r})$  that is related to its macroscopic electric polarization  $\mathbf{P}(\mathbf{r})$ . The linear constitutive equations relating  $\mathbf{P}(\mathbf{r})$  and  $\mathbf{D}(\mathbf{r})$  to  $\mathbf{E}_{\text{mac}}(\mathbf{r})$  in a linear, isotropic polarized sample via a proportionality constant are only valid for weak *electrostatics* or *slowly time-varying* fields, but *not* for *general time-varying* electric fields, where the local and macroscopic electric fields will also of same time dependency. The time-dependent  $\mathbf{P}(\mathbf{r}, t)$  is *not* linearly related to  $\mathbf{E}_{\text{mac}}(\mathbf{r}, t)$  via a proportionality constant, but involves in an algebraic relation between  $\mathbf{E}_{\text{loc}}(\mathbf{r}, t)$  and  $\mathbf{E}_{\text{mac}}(\mathbf{r}, t)$  at point  $\mathbf{r}$  inside the polarized solid that facilitates linking its *microscopic* and *macroscopic* dielectric functions; however, calculation of  $\mathbf{E}_{\text{loc}}(\mathbf{r}, t)$  at the site of an electric dipole in a polarized solid is quite difficult, but for some solids there is an *approximate* formula that links  $\mathbf{P}(\mathbf{r}, t)$ ,  $\mathbf{E}_{\text{loc}}(\mathbf{r}, t)$  and  $\mathbf{E}_{\text{mac}}(\mathbf{r}, t)$ , which, for *linear* and *isotropic* cubic crystalline or *highly-symmetric amorphous* solids, is given by (Reitz et al., 1993; Jackson, 1998)

$$\mathbf{E}_{\text{loc}}(\mathbf{r}, t) \cong \mathbf{E}_{\text{mac}}(\mathbf{r}, t) + \eta \mathbf{P}(\mathbf{r}, t) / \epsilon_0 \quad (\text{B3})$$

where  $\eta$  is a *local-field correction factor* accounting for mutual interactions among all electric dipoles in a solid, with  $\eta = 0$  for metals and  $\eta = 1/3$  (*Lorentz local-field correction*) for isotropic, nonpolar dielectrics (Reitz et al., 1993).

## B.2 Physical Origin of Dispersion Phenomena and Loss Mechanisms in Solids

An optical constant of a linear material sample is its index of refraction  $n(\lambda)$  that may vary with spectral wavelength  $\lambda$  of light incident on it, a phenomenon called *dispersion*. Most materials behave as nonmagnetic ( $\mu \cong \mu_0$ ) at optical frequencies as their magnetic properties are significant in other frequency regions. In addition to dispersion, a light wave may experience attenuation upon interacting with the solid and a change in its properties may occur via a variety of loss mechanisms, some of them are active at wavelengths above a threshold wavelength  $\lambda_c$  typifying its fundamental absorption edge, while few dominate below  $\lambda_c$ ; thus, we often characterize such a dispersive, non-magnetic, and lossy substance by a complex index of refraction  $\hat{n}(\lambda) \equiv n(\lambda) + j \kappa(\lambda)$ , where  $n(\lambda)$  is its index of refraction and  $\kappa(\lambda)$  its extinction coefficient, which determines its absorption that can also be described by the so-called absorption coefficient  $\alpha(\lambda)$ , inter-related to  $\kappa(\lambda)$  as  $\alpha(\lambda) \equiv 4\pi\kappa(\lambda)/\lambda$  or, in terms of angular frequency  $\omega$  ( $\equiv 2\pi c/\lambda$ ) of the monochromatic light incident on the sample,  $\alpha(\omega) \equiv 2\omega\kappa(\omega)/c$ , where  $c$  is the speed of light in free space.



Loss in energy of light interacting with a solid at frequencies below its  $\lambda_c$  may arise from absorption by lattice vibrations (phonons) and *electronic transitions* among its narrow-gaped valence bands (Christman, 1988). Absorption by excess charge carriers bounded to defects, electrons (holes) of donors (acceptors), and free carriers (*intraband* electronic transitions) are also effective in some solids at long wavelengths in the infrared, while energy loss by oscillating permanent dipoles in dipolar solids is sizable (at microwave frequencies and below) and absorptions by oscillating ion-pairs in ionic solids contribute up to an infrared frequency (Christman, 1988). Absorption arising from localized bandgap tailing energy states occurs in structurally-disordered films at wavelengths longer than  $\lambda_c$ , transitions to energy states of *bound electron-hole pairs* (*excitons*) are observed at low temperatures (Christman, 1988), while optical loss by light scattering is important in inhomogeneous and rough samples. Loss and dispersion dominating optical behavior of a solid beyond its absorption edge are mainly due to valence-band to conduction-band (*interband*) electronic transitions, which can also result, to less extent, from excitations of core electrons by deep ultraviolet and X-ray frequencies (Christman, 1988). Optical and dielectric responses of a linear, isotropic, and non-magnetic sample are often addressed by the dependence of its *macroscopic optical constants*  $n(\lambda)$  and  $\kappa(\lambda)$  on spectral wavelength  $\lambda$  (angular frequency  $\omega$ ) or by the  $\omega$ -dependency of the real part  $\epsilon'(\omega)$  and imaginary part  $\epsilon''(\omega)$  of its *macroscopic complex dielectric constant*  $\hat{\epsilon}(\omega) \equiv \epsilon'(\omega) + j\epsilon''(\omega)$  or the real  $\chi'(\omega)$  and imaginary  $\chi''(\omega)$  parts of its *macroscopic complex electric susceptibility*  $\hat{\chi}(\omega) \equiv \chi'(\omega) + j\chi''(\omega) \equiv \hat{\epsilon}(\omega) - 1 \equiv [\epsilon'(\omega) - 1] + j\epsilon''(\omega)$ . Since  $(\epsilon', \epsilon'') - \omega$  and  $(n, \kappa) - \lambda$  presentations depict the same optical (dielectric) response of a substance to electromagnetic radiation interacting with it, there must be an algebraic link between its  $\hat{\epsilon}$  or  $\hat{\chi}$  and its  $\hat{n}(\lambda)$ , which are occasionally called optical or dielectric functions. Regardless of the physical mechanism responsible for polarization and absorption phenomena in a solid, this link is given, for a linear, isotropic, nonmagnetic, and lossy substance, by formula

$$\hat{n}(\lambda) \equiv \sqrt{\hat{\epsilon}(\lambda)} = \sqrt{\hat{\chi}(\lambda) + 1} \quad (B4)$$

Equation (B4) can be simplified to give inter-relations between optical constants  $n$  and  $\kappa$  or  $\alpha$  of a sample and its dielectric functions  $\epsilon'$  and  $\epsilon''$  that are depicted, with their dependence on  $\lambda$  or  $\omega$  being implicit, as

$$\epsilon' \equiv n^2 - \kappa^2; \quad \epsilon'' \equiv 2n\kappa; \quad \alpha \equiv \omega\epsilon''/nc \quad (B5)$$

$$n(\lambda) = \left( \frac{\epsilon' + \sqrt{\epsilon'^2 + \epsilon''^2}}{2} \right)^{1/2}; \quad \kappa(\lambda) = \left( \frac{\sqrt{\epsilon'^2 + \epsilon''^2} - \epsilon'}{2} \right)^{1/2} \quad (B6)$$

### B.3 Link Between Microscopic Electric Polarizability and Macroscopic Dielectric Functions

To clarify the nature of dispersion and absorption mechanisms responsible for spectral dependence of optical functions of a substance, formulations that describe them in different wavelength ranges are needed. Empirical formulas were used to depict  $\lambda$ -dependence of its  $n(\lambda)$  and  $\kappa(\lambda)$  like the Cauchy and Sellmeier dispersion relations, which work well for some substances in certain spectral regions (Tan, 2006; Tan et al., 2007; Tan et al., 2006; Christman, 1988; Reitz et al., 1993). Yet, theoretical models based on the physics of electric polarization and optical absorption in a substance upon its interaction with electromagnetic fields are more informative and these models usually yield formulas for the frequency dependency of its  $\epsilon''(\omega)$  and  $\epsilon'(\omega)$  dielectric functions, the derivation of which demands a link between its microscopic and macroscopic electrical quantities, and may require a quantum-mechanical treatment of the problem and the fundamental Kramers-Kronig relations (Reitz et al., 1993; Jackson, 1998). Microscopic response of a linear, lossy sample to a time-varying electric field is often expressed in terms of a collective effect of *microscopic complex electric polarizabilities*  $\hat{\alpha}_p^{(i)} \equiv \alpha_p'^{(i)} + j\alpha_p''^{(i)}$  of each field-induced electric dipole of type  $i$  in its primitive unit cell, with  $\alpha_p'^{(i)}$  and  $\alpha_p''^{(i)}$  being its real and imaginary parts, respectively, with  $\alpha_p''^{(i)} = 0$  when it is exposed to *electrostatic* or *slowly time-varying* electric fields, where its *macroscopic* dielectric functions are constants and coupled to the sum of electric polarizabilities of all its microscopic electric dipoles by the *Clausius-Mossotti* relation (Christman, 1988; Rogalski & Palmer, 2000; Palik, 1998; Dressel & Grüner, 2002; Reitz et al., 1993; Jackson, 1998); however, if the substance is excited by *rapidly time-varying* electric fields, this relation can be generalized to account for the complex-functional behavior of macroscopic and microscopic electric functions and their frequency dependency. The formulation of  $\hat{\alpha}_p^{(i)}(\omega)$  of a field-induced dipole in a substance exposed to time-dependent electric fields can be developed by hypothetical *microscopic* models for electric polarization and loss mechanisms (Christman, 1988; Rogalski & Palmer, 2000; Palik, 1998; Dressel & Grüner, 2002; Reitz et al., 1993; Jackson, 1998). If each basis of type  $i$  has a concentration per unit volume  $N_i$  in a primitive unit cell of a polarized substance where  $\mathcal{E}_{loc}(t)$  is different from  $\mathcal{E}_{mac}(t)$  inside it, its  $\hat{\epsilon}(\omega)$  can be linked to  $\hat{\alpha}_p^{(i)}(\omega)$  as (Christman, 1988; Rogalski & Palmer, 2000; Palik, 1998; Dressel & Grüner, 2002; Reitz et al., 1993; Jackson, 1998)

$$\frac{\hat{\epsilon}(\omega)-1}{1+\eta[\hat{\epsilon}(\omega)-1]} = \frac{1}{\epsilon_0} \sum_i N_i \hat{\alpha}_p^{(i)}(\omega) \quad (B7)$$

On the other hand, for the *Lorentz local-field correction*  $\eta = 1/3$ , equation (B7) reduces to the frequency-dependent generalized form of the *Clausius-Mossotti* equation cited below (Christman, 1988; Rogalski & Palmer, 2000; Palik, 1998; Dressel & Grüner, 2002; Reitz et al., 1993; Jackson, 1998)

$$\frac{\hat{\epsilon}(\omega)-1}{\hat{\epsilon}(\omega)+2} = \frac{1}{3\epsilon_0} \sum_i N_i \hat{\alpha}_p^{(i)}(\omega) \quad (B8)$$

As the optical index of refraction  $n = \sqrt{\epsilon'}$  for a linear, nonmagnetic dielectric, the *Clausius-Mossotti* relation reduces, for *one atom in a primitive basis*, to the so-called *Lorentz-Lorenz equation* (Christman, 1988; Rogalski & Palmer, 2000; Palik, 1998; Dressel & Grüner, 2002; Reitz et al., 1993; Jackson, 1998)

$$\frac{(n^2-1)}{(n^2+2)} \cong \frac{N\alpha_p}{3\epsilon_0} \quad (B9)$$

Neglecting the difference between local and macroscopic electric fields ( $\eta = 0$ ) in a polarized sample with only *one basis atom* in its primitive cell, equation (B7) simplifies to approximate forms for  $\epsilon'(\omega)$  and  $\epsilon''(\omega)$  as

$$\epsilon'(\omega) \equiv 1 + N \alpha_p'(\omega)/\epsilon_0 \quad \text{and} \quad \epsilon''(\omega) \equiv N \alpha_p''(\omega)/\epsilon_0$$

#### B.4 Basic Formulations for Frequency Response of Linear, Dispersive, and Lossy Media

For optical response of a linear, isotropic, nonmagnetic, and lossy sample exposed to time-dependent weak electric fields, there is no *linear constitutive relation* between the macroscopic electric field and field-induced electric polarization via a *time-dependent constant of proportionality* as that described in Equation (B1) for the electrostatic case- that is, a relation of the form  $\mathbf{P}(t) \equiv \epsilon_0 \chi(t) \mathbf{E}_{\text{mac}}(t)$  is not applicable. Also, the derivation of Equation (B7) or (B8) is not straightforward as in the *static case*. In fact, the microscopic electric polarizability  $\hat{\alpha}_p^{(i)}(\omega)$  of a field-induced electric dipole in such a substance and its macroscopic dielectric constant  $\hat{\epsilon}(\omega)$  exhibit *frequency dependency*, the actual form of which is not simple and is material dependent. We shall adopt an approach that is based on the concepts of *linearity and causality of optical response of dispersive media* excited by *oscillatory electromagnetic fields* to accomplish expedient linear relations in *frequency domain* (not in *time domain*) between these driving (input) fields and their dielectric response functions (Reitz et al., 1993). Let a monochromatic electromagnetic radiation wave of an angular frequency  $\omega$  whose electric field vector  $\mathbf{E}(\mathbf{r}, t)$ , at position  $\mathbf{r}$ , varies sinusoidally in time  $t$  to travel in a *linear, isotropic, dispersive, and lossy* substance, whose optical response is not affected by the electromagnetic field vector  $\mathbf{B}(\mathbf{r}, t)$ . There is seldom a notable overlap in the frequency range where optical and magnetic responses of a substance to electromagnetic fields are strongly frequency dependent; thus, its optical response can be treated as if it is nonmagnetic ( $\mu \cong \mu_0$ ). A real dispersive medium is said to be *linear* if its response (output)  $\mathcal{O}(t)$  at time  $t$  to an external *time-dependent* excitation (input or driving force)  $\mathcal{I}(t)$  is described by an expression that carries with it a *nonlocal time connection* between  $\mathcal{O}(t)$  and  $\mathcal{I}(t)$  such that  $\mathcal{O}(t)$  at the time  $t$  depends on the excitation agent  $\mathcal{I}(t')$  at times *other* than  $t$  and the input  $\mathcal{I}(t)$  must not produce an output  $\mathcal{O}(t)$  for times less (earlier) than  $t$ , viz. (Reitz et al., 1993)

$$\mathcal{O}(t) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} \mathcal{R}(t'') \mathcal{I}(t - t'') dt'' \quad (B11)$$

where  $\mathcal{R}(t)$  is called its *response function* that is *independent of the strength* of the input  $\mathcal{I}(t)$ ; otherwise, terms containing higher orders of the applied input may be important and the medium is *nonlinear*. Equation (B11) is a *linear relation* between an output  $\mathcal{O}(t)$  and input  $\mathcal{I}(t)$  in the sense that if  $\mathcal{I}(t)$  is multiplied by a constant,  $\mathcal{O}(t)$  is multiplied by that constant, and if two inputs are applied concurrently the output is the sum of the two outputs produced by these inputs separately. Also, this linearity aspect helps one to use the superposition principle to get the results of applying several simultaneous inputs to such a linear medium, or to determine its response to a complicated input by decomposing it into simpler excitations and adding the resulting individual responses.

For a real *linear and dispersive system*, however, the applicability of Equation (B11) is limited, because of *causality*, to cases where  $\mathcal{R}(t'') = 0$  for  $t'' < 0$ , with a *finite input* produces only a *finite output* and an input at time  $t' = t - t''$  yields an output at time  $t$  that decreases steadily at large values of  $t''$ , so that  $\mathcal{R}(t)$  is *square integrable* in the time interval  $-\infty < t < \infty$ . Its linearity leads to two consequences. First, the Fourier inverse transform functions of the time-varying functions  $\mathcal{O}(t)$ ,  $\mathcal{R}(t)$ , and  $\mathcal{I}(t)$ , denoted by the complex frequency-dependent quantities  $\hat{\mathcal{O}}(\omega)$ ,  $\hat{\mathcal{R}}(\omega)$ , and  $\hat{\mathcal{I}}(\omega)$ , respectively, are linearly linked together via a

frequency-dependent proportionality constant, the Fourier inverse transform response function  $\hat{\mathcal{R}}(\omega)$  as (Reitz et al., 1993; Jackson, 1998)

$$\hat{\mathcal{O}}(\omega) = \hat{\mathcal{R}}(\omega) \hat{\mathcal{I}}(\omega) \quad (\text{B12})$$

The second consequence of the linear Equation (B11) is that the time-dependent input  $\mathcal{I}(t)$  and output (response)  $\mathcal{O}(t)$  of a linear, dispersive medium are related by a time-dependent *ordinary linear differential equation of degree  $M$  with a set of constant coefficients  $a_m$*  of the form (Reitz et al., 1993)

$$\sum_{m=0}^M a_m \frac{d^m}{dt^m} \{\mathcal{O}(t)\} = \mathcal{I}(t) \quad (\text{B13})$$

with the number  $M$  of the *constant coefficients*  $a_m$  is determined by the physical mechanisms typifying the medium. This  $M$ th-degree differential equation reduces to a formula that linearly relates the complex Fourier inverse transform functions  $\hat{\mathcal{O}}(\omega)$  and  $\hat{\mathcal{I}}(\omega)$  of the input and output functions  $\mathcal{O}(t)$  and  $\mathcal{I}(t)$  as (Reitz et al., 1993)

$$\sum_{m=0}^M a_m (-j\omega)^m \hat{\mathcal{O}}(\omega) = \hat{\mathcal{I}}(\omega) \quad (\text{B14})$$

Combine Equations (B12) and (B14) to get a *complex frequency-dependent* Fourier inverse transform response function  $\hat{\mathcal{R}}(\omega)$  of the *time-dependent* response function  $\mathcal{R}(t)$  of a linear, dispersive medium as

$$\hat{\mathcal{R}}(\omega) = [\sum_{m=0}^M a_m (-j\omega)^m]^{-1} \quad (\text{B15})$$

As  $\mathcal{R}(t) = 0$  for  $t < 0$ ,  $\mathcal{R}(t)$  is physically meaningful for  $t > 0$  only, and boundedness condition underlying its *square integrability* in the time-domain interval  $-\infty < t < \infty$  implies that its Fourier transform inverse response function  $\hat{\mathcal{R}}(\omega) \equiv \mathcal{R}'(\omega) + j\mathcal{R}''(\omega)$  is *also square integrable* in the frequency-domain  $-\infty < \omega < \infty$ , where  $\mathcal{R}'(\omega)$  and  $\mathcal{R}''(\omega)$  are its real and imaginary parts, respectively. Also, a *real* physical input produces a *real* output and  $\mathcal{R}(t)$  must be *real* for all real values of  $t$  even if the functions  $\mathcal{O}(t)$  and  $\mathcal{I}(t)$  are not real; thus, a physical linear dispersive system with a real, square-integrable, and causal time-dependent response function  $\mathcal{R}(t)$  imposes a time-reversal symmetry condition on its Fourier inverse transform response function  $\hat{\mathcal{R}}(\omega)$  and its *conjugate*  $\hat{\mathcal{R}}^*(\omega)$  such that (Reitz et al., 1993; Jackson, 1998)

$$\hat{\mathcal{R}}^*(\omega) = \hat{\mathcal{R}}(-\omega) \quad \text{or} \quad \mathcal{R}'(-\omega) = \mathcal{R}'(\omega) \quad \text{and} \quad \mathcal{R}''(-\omega) = -\mathcal{R}''(\omega) \quad (\text{B16})$$

Equation (B16) implies that the real  $\mathcal{R}'(\omega)$  and imaginary  $\mathcal{R}''(\omega)$  parts of  $\hat{\mathcal{R}}(\omega)$  at *negative* values of  $\omega$  are related to their values at *positive*  $\omega$ -values, so *only positive* frequencies are used in formulas of response functions  $\mathcal{R}'(\omega)$  and  $\mathcal{R}''(\omega)$  of a linear, dispersive, and lossy system, which are related by the Cauchy principal pair of integrals (Reitz et al., 1993; Jackson, 1998)

$$\mathcal{R}'(\omega) = \frac{2}{\pi} \mathcal{P} \int_0^\infty \frac{\omega' \mathcal{R}''(\omega')}{\omega'^2 - \omega^2} d\omega' \quad (\text{B17})$$

$$\mathcal{R}''(\omega) = -\frac{2\omega}{\pi} \mathcal{P} \int_0^\infty \frac{\mathcal{R}'(\omega')}{\omega'^2 - \omega^2} d\omega' \quad (\text{B18})$$

The Cauchy principal pair of integrals in Equations (B17) and (B18) do not depend on what kind of linear system is considered; it can be mechanical, quantum mechanical, electrical circuitry, dispersive substance, or otherwise, so long as a real, square-integrable and causality time-dependent linear response function  $\mathcal{R}(t)$  and its complex frequency-dependent Fourier inverse transform response function  $\hat{\mathcal{R}}(\omega)$  are allocated to this system.

#### B.4.1 Electric Response Functions for Linear, Isotropic, Non-Magnetic, Dispersive, and Lossy Substances Exposed to Weak Electromagnetic Fields

Linearity and causality formulations described above can now be applied to electromagnetic fields interacting with a linear, isotropic, homogeneous, non-magnetic, and dispersive medium with losses. The input in the linearity Equation (B11) is a *time-varying* electric field vector  $\mathbf{E}(\mathbf{r}, t)$  associated with an electromagnetic wave at time  $t$  and position  $\mathbf{r}$  in the medium, with its output can be the spatially- and time- dependent macroscopic electric displacement  $\mathbf{D}(\mathbf{r}, t) \equiv \epsilon_0 \mathbf{E}(\mathbf{r}, t) + \mathbf{P}(\mathbf{r}, t)$ , polarization  $\mathbf{P}(\mathbf{r}, t)$ , or current density  $\mathbf{J}(\mathbf{r}, t)$ . The time-dependent *macroscopic electric* polarization  $\mathbf{P}(\mathbf{r}, t)$  inside medium is linearly related to  $\mathbf{E}(\mathbf{r}, t)$  via a time-dependent response function  $\mathcal{R}_P(\mathbf{r}, t)$  as

$$\mathbf{P}(\mathbf{r}, t) = \frac{1}{\sqrt{2\pi}} \int_0^\infty \mathcal{R}_P(\mathbf{r}, t') \mathbf{E}(\mathbf{r}, t - t') dt' \quad (\text{B19})$$

There is a *spatial local connection* between input electric field  $\mathbf{E}(\mathbf{r}, t)$  and output electric polarization  $\mathbf{P}(\mathbf{r}, t)$ , but they are *nonlocally* connected in the time domain, with their spatial dependencies being negligible for a sample with minor inhomogeneity, so its macroscopic properties do not vary significantly with position; thus, in terms of their *time-dependent* components  $E(t)$  and  $P(t)$ , Equation (B19) reduces to the causality time-dependent linearity formalism

$$P(t) = \frac{1}{\sqrt{2\pi}} \int_0^\infty \mathcal{R}_p(t') E(t - t') dt' \quad (\text{B20})$$

The electric response function  $\mathcal{R}_p(t)$  *does not depend explicitly on exciting electric field  $E(t)$* , it is *real for all times  $t$* , so  $\mathcal{R}_p(t') = 0$  for  $t' < 0$ , and is *square-integrable* in the time interval  $0 < t < \infty$ . Equation (B20) tells us that  $P(t)$  depends *not just* on the value of  $E(t)$  at time  $t$ , *but on the value of  $E$  at all past times*; there is *no* simple quantity that can properly be called the *electric susceptibility* of a linear lossy substance exposed to electromagnetic fields in the *time domain*; *electric susceptibility is, however, a frequency domain concept*. Yet, the frequency-dependent complex Fourier inverse transforms  $\hat{E}(\omega)$  and  $\hat{P}(\omega)$  of the time-dependent electric input field  $E(t)$  and output polarization  $P(t)$  can be related via their respective Fourier inverse transform integrals (Reitz et al., 1993; Jackson, 1998) to get a linear relation as that of Equation (B12), with the complex Fourier inverse transform response function  $\hat{\mathcal{R}}_p(\omega)$  of the time-dependent response function  $\mathcal{R}_p(t)$  is now a scalar proportionality constant at a certain frequency  $\omega$  - that is,  $\hat{P}(\omega) = \hat{\mathcal{R}}_p(\omega) \hat{E}(\omega)$ , with  $\hat{\mathcal{R}}_p(\omega) \equiv \mathcal{R}'_p(\omega) + j \mathcal{R}''_p(\omega)$  whose real and imaginary parts  $\mathcal{R}'_p(\omega)$  and  $\mathcal{R}''_p(\omega)$  satisfy reality and causality Equation (B16).

The electric response of a linear, isotropic, dispersive, non-magnetic lossy substance to a time-dependent weak electric field  $E(t)$  can be envisaged using the electric response functions  $\mathcal{R}_p(t)$ ,  $\mathcal{R}_D(t)$ , and  $\mathcal{R}_J(t)$  associated with the electric polarization  $P(t)$ , displacement  $D(t)$ , and current density  $J(t)$  outputs. The respective complex Fourier inverse transform response functions  $\hat{\mathcal{R}}_p(\omega)$ ,  $\hat{\mathcal{R}}_D(\omega)$ , and  $\hat{\mathcal{R}}_J(\omega)$  of this substance are correlated to each other and to its electric and dielectric functions, whose real and imaginary parts are linked together by the Cauchy principal integrals of Equations (B17) and (B18) or the fundamental *Kramers-Kronig (KK) dispersion relations*. The complex Fourier inverse transform polarization response function  $\hat{\mathcal{R}}_p(\omega)$  of a sample is related to its  $\hat{\chi}(\omega) \equiv \chi'(\omega) + j\chi''(\omega)$  as  $\hat{\mathcal{R}}_p(\omega) \equiv \epsilon_0 \hat{\chi}(\omega)$ , with  $\chi'(\omega) \equiv \epsilon'(\omega) - 1$  and  $\chi''(\omega) \equiv \epsilon''(\omega)$  are connected by the KK-integral relations (Reitz et al., 1993; Jackson, 1998)

$$\chi'(\omega) = \frac{2}{\pi} \mathcal{P} \int_0^\infty \frac{\omega' \chi''(\omega')}{\omega'^2 - \omega^2} d\omega' \quad \chi''(\omega) = -\frac{2\omega}{\pi} \mathcal{P} \int_0^\infty \frac{\chi'(\omega')}{\omega'^2 - \omega^2} d\omega' \quad (\text{B21})$$

$$\epsilon'(\omega) = 1 + \frac{2}{\pi} \mathcal{P} \int_0^\infty \frac{\omega' \epsilon''(\omega')}{\omega'^2 - \omega^2} d\omega' \quad \epsilon''(\omega) = -\frac{2\omega}{\pi} \mathcal{P} \int_0^\infty \frac{\omega' [\epsilon'(\omega') - 1]}{\omega'^2 - \omega^2} d\omega' \quad (\text{B22})$$

For a conducting substance, where free electrons contribute to its dc conduction, the electric susceptibility exhibits singularity at  $\omega = 0$  and though this problem can be overcome, its frequency response to a *weak* exciting time-dependent electric field  $E(t)$  is usually formulated in terms of its electrical conductivity to avoid problems with singularities (Reitz et al., 1993). Here, the time-dependent conduction current density  $J(t)$  is taken to be the response (output) to the input  $E(t)$  and its electrical conductivity  $\sigma_c(t)$  is the response function. The corresponding dispersion relations can be derived using our linearity-causality approach in terms of a Fourier inverse transform response function pictured by a macroscopic complex electrical conductivity  $\hat{\sigma}_c(\omega) \equiv \sigma'(\omega) + j\sigma''(\omega) \equiv -j\omega\epsilon_0 \hat{\chi}(\omega)$  satisfying the linear relation  $\hat{J}(\omega) = \hat{\sigma}_c(\omega) \hat{E}(\omega)$ , with the results hold for conductors as well as insulators, since  $\hat{\sigma}_c(\omega)$  has no singularity at  $\omega = 0$ . The real and imaginary parts  $\sigma'(\omega)$  and  $\sigma''(\omega)$  of  $\hat{\sigma}_c(\omega)$  are interrelated by the KK-integral relations (Reitz et al., 1993)

$$\sigma'(\omega) = \frac{2}{\pi} \mathcal{P} \int_0^\infty \frac{\omega' \sigma''(\omega')}{\omega'^2 - \omega^2} d\omega' \quad \sigma''(\omega) = -\frac{2\omega}{\pi} \mathcal{P} \int_0^\infty \frac{\sigma'(\omega')}{\omega'^2 - \omega^2} d\omega' \quad (\text{B23})$$

The very general validity of fundamental Kramers-Kronig dispersion integrals stems from the fact that if, for example, the real part  $\chi'(\omega)$  of the complex electric susceptibility  $\hat{\chi}(\omega)$  of a linear dielectric substance is known for *all real* values of exciting frequencies in the range  $0 \leq \omega \leq \infty$ , then its imaginary part  $\chi''(\omega)$  can be calculated from the second KK-integral relation given in Equation (B21), and conversely. Further, it deserves to note here that the KK integrals of the real and imaginary parts of the macroscopic electric and dielectric functions of a linear, dispersive substance with losses as well as those of the real and imaginary parts of its respective macroscopic optical functions yield some general relations, called sum rules (Reitz et al., 1993; Jackson, 1998), that can be utilized to test consistency of approximations adopted in computation and measurements.

#### B.4.2 Classical Forced-Damped Harmonic Oscillator (Lorentz) Dispersion Model

There is no single dispersion function that describes the optical and dielectric response of an excited solid in the entire frequency range as these loss mechanisms contribute differently to its electric polarization and in diverse frequency regions. The actual form of contributions of individual dispersion functions is quite unwieldy and in real world is difficult to realize. However, most of the physics of dispersion and loss in a solid exposed to weak electromagnetic fields can be understood from a simple classical model that accounts for its electric response to such fields in the presence of internal interactions that retard the motions of the field-induced electric dipoles. In practice, a linear combination of different simple models is often adopted to describe the overall dispersion and loss of a substance over a wide frequency range of the electromagnetic spectrum.

An intuitive guide to find electric response function of a linear dispersive sample exposed to an oscillating weak electric field  $E(\mathbf{r}, t)$  is to treat an electric dipole as a classical *forced-damped harmonic oscillator* and solve an *ordinary linear differential equation* describing its motion (Christman, 1988). In a dielectric, each electron of an atom having  $Z$  bound electrons, each of charge  $-e$  and mass  $m$ , around its nucleus, is often pictured as a charged particle vibrating (oscillating) relative to an equilibrium position  $\mathbf{r}_0$  under the action of a linear restoring force proportional to its displacement  $\mathbf{r}(t)$  from  $\mathbf{r}_0$  and a linear resistive force proportional to its instantaneous velocity  $\mathbf{v}(\mathbf{r}, t) \equiv d\mathbf{r}(t)/dt$ . The charged oscillator under the action of restoring forces only executes indefinite sinusoidal oscillations with the same amplitude and same natural frequency  $\omega_0$ , which is determined by several repulsive and attractive physical interactions between ingredients of the substance (Christman, 1988; Rogalski & Palmer, 2000; Palik, 1998; Dressel & Grüner, 2002). The resistive forces retards the dipole motion and cause energy dissipation, signified by a damping coefficient  $\gamma$ , which, in a real substance, originate from interactions of dipoles with phonons, defects, and impurities. The energy of a charged-particle oscillator under the action of restoring and retarding forces only diminishes in time, so its motion will eventually cease (die out)- that is, a *damped oscillator*. When a solid is excited by electromagnetic radiation of angular frequency  $\omega$ , the electromagnetic fields  $\mathbf{E}(\mathbf{r}, t)$  and  $\mathbf{B}(\mathbf{r}, t)$  interact with its electric dipoles via *Lorentz force*  $\mathbf{F}_L(\mathbf{r}, t) \equiv Q[\mathbf{E}(\mathbf{r}, t) + \mathbf{v}(\mathbf{r}, t) \times \mathbf{B}(\mathbf{r}, t)]$ , but the effect of  $\mathbf{B}(\mathbf{r}, t)$  is neglected so the oscillator is chiefly driven by  $\mathbf{E}(\mathbf{r}, t)$ . The macroscopic electric functions of the charged-particle oscillator model do not depend on the magnitude of  $\mathbf{E}(\mathbf{r}, t)$ , but depend on the frequency  $\omega$  of its electromagnetic wave, with each of its microscopic electric dipoles being treated as a classical forced-damped harmonic oscillator whose motion is described by a second order linear differential equation (SOLDE), where the effect of restoring and damping forces are both included. In principle, quantum mechanics must be applied for atomic electrons, but the results based on the solution of classical SOLDE are analogous to those found from a quantum-mechanics solution (Rogalski & Palmer, 2000). The actual local electric field  $\mathbf{E}_{\text{loc}}(\mathbf{r}, t)$  at the site  $\mathbf{r}$  of a dipole in a collection of electric dipoles in a linear, isotropic sample differs from the applied field  $\mathbf{E}(\mathbf{r}, t) \equiv \mathbf{E}_{\text{mac}}(\mathbf{r}, t)$  such that  $\mathbf{E}_{\text{loc}}(\mathbf{r}, t) \equiv \mathbf{E}(\mathbf{r}, t) + \eta \mathbf{P}(\mathbf{r}, t)/\epsilon_0$ , where the local-field correction factor  $\eta$  is introduced to take account of mutual interactions among all of its particles. If the amplitude of oscillations of dipoles is small enough for spatial variation of  $\mathbf{E}_{\text{loc}}(\mathbf{r}, t)$  over twice this amplitude to be minor, it is reasonable to neglect it over the distance between peaks of oscillating dipole and permit electric-field evaluation at the dipole average position (Reitz et al., 1993; Jackson, 1998). If there are  $N$  atoms per unit volume in the sample, then  $\mathbf{P}(t) = N\mathbf{p}(t) = Ne\mathbf{r}(t)$  is, with spatial dependence implicit, described by the SOLDE (Reitz et al., 1993)

$$\left(\frac{1}{\epsilon_0 \omega_p^2}\right) \frac{d^2 P(t)}{dt^2} + \left(\frac{\gamma}{\epsilon_0 \omega_p^2}\right) \frac{dP(t)}{dt} + \frac{1}{\epsilon_0} \left(\frac{\omega_0^2}{\omega_p^2} - \eta\right) P(t) = E(t) \quad (\text{B24})$$

Equation (B24) has the form of Equation (B13) with three *constant coefficients*:  $a_0 = [(\omega_0^2/\omega_p^2) - \eta]/\epsilon_0$ ,  $a_1 = (\gamma/\epsilon_0 \omega_p^2)$ , and  $a_2 = (1/\epsilon_0 \omega_p^2)$ , where  $\omega_p (\equiv \sqrt{Ne^2/\epsilon_0 m})$ , with its solution fulfills the linearity Equation (B20) such that  $P(t)$  is the response (output) of the substance related to the applied (input) field  $E(t)$  via the response function  $\mathcal{R}_p(t)$ , with the complex Fourier inverse transforms  $\hat{E}(\omega)$  and  $\hat{P}(\omega)$  are *linearly* related as  $\hat{P}(\omega) \equiv \hat{\mathcal{R}}_p(\omega)\hat{E}(\omega) \equiv \epsilon_0 \hat{\chi}(\omega)\hat{E}(\omega)$ . The dispersion formula of the *complex* electric susceptibility  $\hat{\chi}(\omega)$  of a collection of  $N$  *microscopic forced-damped* oscillating dipoles driven by a weak electromagnetic field of frequency  $\omega$  can be found by inserting the constant coefficients  $a_0$ ,  $a_1$ , and  $a_2$  into Equation (B15), viz.

$$\frac{\hat{\chi}(\omega)}{1 + \eta \hat{\chi}(\omega)} = \frac{\hat{\epsilon}(\omega) - 1}{1 + \eta [\hat{\epsilon}(\omega) - 1]} = \frac{\omega_p^2}{\omega_0^2 - \omega^2 - j\gamma\omega} \quad \text{or} \quad \hat{\chi}(\omega) = \frac{\omega_p^2}{(\omega_0^2 - \eta\omega_p^2) - \omega^2 - j\gamma\omega} \quad (\text{B25})$$

with  $\hat{\chi}(\omega)$  fulfills Equation (B16) as long as  $\gamma > 0$  and is square integrable in the frequency range  $0 \leq \omega \leq \infty$ ; thus, satisfying all requirements for a real response function of a linear, isotropic, dispersive, and lossy medium, with Equation (B25) gives a relation between its complex *macroscopic* dielectric function  $\hat{\chi}(\omega)$  and *microscopic* features of its electric dipoles. By a simple generalization, its applicability can be extended to a real materials, in

which seldom do all of its charged particles have the same dielectric behavior in different frequency regions; they may divide into electrons and ions, as in ionic substances, or into electrons and permanent electric dipoles exist in molecular materials, or into electrons in different inner (core) and outer (valence) orbits of an atom. If there are  $N_i$  identical particles, each of charge  $e_i$ , mass  $m_i$ , natural frequency  $\omega_{0i}$ , and damping frequency  $\gamma_i$ , in a linear, dispersive substance with losses, the formula of its  $\hat{\epsilon}(\omega)$  arising from polarizability  $\hat{\alpha}_p^{(i)}(\omega)$  contributions of all electric dipoles would have the form

$$\frac{\hat{\epsilon}(\omega)-1}{1+\eta[\hat{\epsilon}(\omega)-1]} = \frac{\hat{\chi}(\omega)}{1+\eta\hat{\chi}(\omega)} = \sum_i \frac{\omega_{pi}^2}{\omega_{0i}^2 - \omega^2 - j\gamma_i\omega} = \frac{1}{\epsilon_0} \sum_i N_i \hat{\alpha}_p^{(i)}(\omega) \quad (\text{B26})$$

Since  $\omega_{pi}^2$  is proportional to  $N_i$  as  $\omega_{pi}^2 \equiv N_i e^2 / m_i \epsilon_0$  for each collection of identical particles of type  $i$ , each of a complex electric polarizability  $\hat{\alpha}_p^{(i)}(\omega)$ , Equation (B26) resembles Equations (B7) and (B8), the generalized frequency-dependent *Clausius-Mossotti formula*, with  $\hat{\epsilon}(\omega)$  being dimensionless, the MKS units of  $\hat{\alpha}_p^{(i)}(\omega)$  and  $N_i$  are  $\text{F.m}^2$  and  $\text{m}^{-3}$ , respectively, with  $\omega$  in rad/s. The mass  $m$  in this dispersion relation depends on the nature of electric dipole and is the *reduced mass*  $\mu = (m_+ m_-) / (m_+ + m_-)$  of its charges. In ionic solids the charge  $Q$  is less than  $ze$  on an isolated ion of valence  $z$ , because charged electron-cloud distributions around neighboring ions overlap somewhat in a solid (Christman, 1988). At optical frequencies where one of the resonance peaks of Equation (B26) dominates all others, then Equation (B25) describes a single-resonance peak with an *effective resonance frequency*  $\omega_{\text{eff}} = (\omega_0^2 - \eta\omega_p^2)^{1/2}$ . Dissimilar loss mechanisms rarely contribute to dielectric behavior in the same frequency region, so the frequency dependence of  $\hat{\epsilon}(\omega)$  or  $\hat{\chi}(\omega)$  can be pictured by a harmonic oscillator (Lorentz) model of a *shifted resonance frequency*  $\omega_{\text{eff}}$ . This can be applied to many practical problems where electric polarizability of various origins (electronic, or ionic, or dipolar) can be described by a harmonic-oscillator dispersion formula

$$\hat{\chi}(\omega) \equiv \chi'(\omega) + j\chi''(\omega) = \left[ \frac{\omega_p^2 (\omega_{\text{eff}}^2 - \omega^2)}{(\omega_{\text{eff}}^2 - \omega^2)^2 + (\gamma\omega)^2} \right] + j \left[ \frac{\gamma\omega\omega_p^2}{(\omega_{\text{eff}}^2 - \omega^2)^2 + (\gamma\omega)^2} \right]$$

The  $\epsilon'(\omega) = \chi'(\omega) + 1$  and  $\epsilon''(\omega) = \chi''(\omega)$  in Equation (B27) can then be inserted into Equation (B6) to get explicit frequency-dependent expressions for the substance optical constants  $n(\omega)$  and  $\kappa(\omega)$ ; however, the results are unwieldy to reveal analytical features of the dispersion phenomena, unless simplifying assumptions are used, but this is not a nuisance problem in numerical iterative curve-fitting optical analysis.

#### B.4.2.1 Electronic Contribution to Dielectric Behavior of Linear, Dispersive Media With Losses

Let all charged particles to have the same charge  $e$  and mass  $m$ , as if there are  $N$  identical atoms per unit volume, each of  $Z$  electrons distributed over its different orbits. In an oscillating electric field, orbital atomic electrons oscillate relative to their respective nuclei, with the center of mass of the electron charge distribution in an atomic orbit at any time  $t$  being at the position vector  $\mathbf{r}_-(t)$  around its nucleus at  $\mathbf{r}_+(t)$ . Each of the field-induced orbital atomic dipoles has a moment  $\mathbf{p}(t) = e [\mathbf{r}_+(t) - \mathbf{r}_-(t)]$  and their oscillatory motions are governed by different damping and restoring forces (bindings). So, in view of classical forced-damped harmonic oscillator model, there are, instead of a single natural (resonance) frequency for all electrons,  $f_i$  bound orbital electrons ( $f_i$  oscillators of type  $i$ ) per atom, with their own resonance frequency  $\omega_{0i}$  and damping frequency  $\gamma_i$ . The resulting polarizabilities due to all these differently-bounded  $NZ$  electrons lead to a dispersion relation for  $\hat{\chi}(\omega)$  having the form of Equation (B26), viz. (Reitz et al., 1993; Jackson, 1998)

$$\frac{\hat{\chi}(\omega)}{1+\eta\hat{\chi}(\omega)} = \omega_p^2 \sum_i \frac{f_i}{\omega_{0i}^2 - \omega^2 - j\gamma_i\omega} = \omega_p^2 \sum_i f_i \frac{\omega_{0i}^2 - \omega^2 + j\gamma_i\omega}{(\omega_{0i}^2 - \omega^2)^2 + (\gamma_i\omega)^2} \quad (\text{B28})$$

where  $\omega_p = \sqrt{Ne^2/\epsilon_0 m}$  is the plasma frequency for a collection of  $N$  atoms per unit volume, different from the *plasma frequency*  $\Lambda_p \equiv \sqrt{NZe^2/\epsilon_0 m}$  of a solid due to its *total number*  $NZ$  of bound electrons per unit volume, where  $m$  had to be replaced by the *effective mass*  $m^*$  of the electron (hole) in the solid (Christman, 1988; Rogalski & Palmer, 2000; Palik, 1998). As mentioned above, quantum mechanics must be used to get accurate picture of electronic polarizability due to the atomic electron system oscillating under the influence of an oscillatory electric field at an atom site, which causes distortion (perturbation) of the wave functions of its electrons, resulting in oscillating electric dipole moments. The average values of these time-dependent dipoles can be calculated using the standard quantum-mechanics time-dependent perturbation theory, which are related to the local electric field via a tensor-like constant of proportionality, the electronic polarizability tensor (Rogalski & Palmer, 2000). The solution of classical model, where electrons are pictured as particles bounded to their fixed atomic sites by elastic Coulombic forces, yields the same accurate quantum description of the contribution of time-dependent perturbed bound electron clouds around atoms to the medium susceptibility, but with different

definitions of  $\omega_{0i}$ ,  $\gamma_i$ , and  $f_i$ . Classically, the fraction of classical oscillators of type  $i$  out of the total number of oscillators is  $f_i$ , while in quantum mechanics,  $f_i$  is the *oscillator strength*, which is characteristic of resonance atomic transitions satisfying a relation called the Thomas-Kuhn sum or *f-sum rule* ( $\sum_i f_i = Z$ ) (Jackson, 1998). In quantum mechanics description, maximum absorption (resonance) corresponds to an electron transition from one quantized energy level (state) to another and occurs when the exciting photon energy  $\hbar\omega$  matches the difference in energy  $\Delta E$  between the two energy states of the electron system involved in the electron transition taking place upon a photon absorption- that is,  $\Delta E = \hbar\omega_{0i} = \hbar\omega$ . Many electron resonances (transitions) contribute to the overall polarizability of the solid and we must sum their contributions, but since the wave functions associated with different transitions between occupied and unoccupied states are unlike, electron resonances do not contribute equally; thus a different factor (the oscillator strength  $f_i$ ) must multiply each term of this sum. Equation (B28) reduces to equation (B27) if  $\eta = 0$  or, for any  $\eta$ , if transitions of only outer valence orbital electrons of the same  $f$ ,  $\omega_0$ , and  $\gamma$  are involved in the absorption (resonance) process, with a shifted resonance frequency  $\omega_{0\text{eff}}$ , a situation that is justified in practice as oscillator strengths of atomic tightly-bound and core-core electrons are relatively small (Christman, 1988).

For pure crystalline insulator or semiconductor the resonance region begins when conditions are right for an electron to absorb a photon and jump the energy-band gap of the solid between the valence band (VB) and conduction band (CB)- that is, a *band-to-band (interband)* electronic transition takes place. The corresponding photon energy (frequency  $\omega_0$ ) is known as the fundamental absorption edge, which is, for parabolic valence and conduction bands, is the band-gap energy  $E_{g0}$  or the separation, in  $\mathbf{k}$ -space, between CB-minimum and VB-maxima at  $\mathbf{k} = 0$  (Christman, 1988). Electromagnetic radiation of photon frequencies equal to or larger than the fundamental absorption edge can excite electrons from occupied energy states  $E_v(\mathbf{k})$  having the wavevector  $\mathbf{k}$  in a lower VB to unoccupied energy states  $E_c(\mathbf{k})$  in an upper empty CB. Crystal momentum as well as energy should be conserved in an absorption (resonance) electronic process. If  $\hbar\mathbf{k}_f$  is the crystal momentum of the final electron state,  $\hbar\mathbf{k}_i$  is the crystal momentum of the initial electron state, and  $\mathbf{s}$  is the propagation vector of the electromagnetic radiation wave, then the corresponding oscillator strength vanishes unless  $\mathbf{k}_f = \mathbf{k}_i + \mathbf{s}$ . Since  $\mathbf{s}$  for frequencies in the infrared, visible, and ultraviolet spectral regions is much shorter than any Brillouin zone dimension, we may neglect it and take  $\mathbf{k}_f \cong \mathbf{k}_i$ . A vertical line connects the initial and final electron states in the conduction and valence bands on a reduced Brillouin zone (BZ) band diagram and the electronic transition is called vertical (*direct band-to-band (interband) transition*), which takes place in a crystal with its conduction and valence band states at the same  $\mathbf{k}$ -point in BZ, so  $E_{g0} = E_c(\mathbf{k} = 0) - E_v(\mathbf{k} = 0)$ , the lowest interband resonance frequency  $\omega_0 \equiv E_{g0}/\hbar$ . For some insulators,  $E_{g0}$  is as large as 10 eV wide, corresponding to an angular frequency  $\omega_0$  up to  $10^{16}$  rad/s or wavenumber  $\bar{\nu} \cong 8 \times 10^4 \text{ cm}^{-1}$ , lying deep in the ultraviolet. For crystalline semiconductors,  $E_{g0}$  ranges from a small fraction of eV up to few eV; for silicon (Si) and germanium (Ge),  $E_{g0}$  lies in the near infrared (IR), while for selenium (Se)  $E_{g0} \sim 2 \text{ eV}$ , equivalent to a visible-light frequency of  $3 \times 10^{15}$  rad/s ( $\bar{\nu} \cong 1.6 \times 10^4 \text{ cm}^{-1}$ ).

Amorphous semiconductors, however, do not have definite and sharp band-energy structures with abrupt band edges like perfectly crystalline ones, but have smeared band edges as tailing energy states are formed throughout the forbidden bandgap, and hence narrowing the bandgap and modifying their optical absorption features. Some crystalline and amorphous semiconductors have complicated band structures with many valleys and hills for valence and conduction bands, with the minima in conduction band being located in at  $\mathbf{k}$ -points different from that of the maxima in the valence band; thus, yielding complicated dispersion and absorption spectra. More details on the various types of *interband* electronic transitions that may take place between occupied and empty energy states lying in the valence and conduction bands as well as in band tails of crystalline and amorphous insulating and undoped semiconducting solids and the associated dispersion and absorption phenomena occurring in these solids will be given later.

Field-induced electronic transitions can occur between energy states within a partially-filled energy band (*intraband transitions*) of a substance exposed to certain electromagnetic radiations, leading to the so-called *quasi-free carrier effects*, the contribution of which to its dielectric and optical behavior is often exemplified by a dispersion formulation describing its macroscopic complex electrical conductivity  $\hat{\sigma}_c(\omega)$  that can be found by the use of the relaxation-time approximation approach (Christman, 1988) or linearity-causality approach (Reitz et al., 1993; Jackson, 1998). The dispersion and optical formulations related to *intraband* electronic transitions in an electrically-excited solid are usually underlined in the classical Drude and modified Drude-like dielectric functions, which are particularly employed in the analysis of optical behavior of highly-conducting substances (e.g., metals and doped semiconductors) excited by monochromatic electromagnetic radiations having spectral wavelengths in the infrared and microwave regions of the spectrum (Christman, 1988; Reitz et al., 1993; Jackson, 1998).

#### B.4.2.2 Dielectric Functions in Spectral Regions Near and Far From the Resonance of a Lorentz Oscillator

To exemplify the nature and frequency-range of bound-charge contribution to the dielectric response of solids, let us apply the results of the preceding section to a system of bound charges in materials which do not conduct direct electric currents- that is, to perfect insulators of *zero* static (dc) electric conductivity. This can be achieved if one has reasonable estimations for values of the natural resonance frequency  $\omega_0$ , plasma frequency  $\omega_p$ , and damping constant  $\gamma$  for the bound outer-shell (valence) and inner-shell (core) electrons of an atom having a total number of electrons  $Z$ , as well as of the oscillator strength  $f_i$  of different interband transitions- that is, the probability for transitions of bound charges (valence or core) in atomic orbits to occur upon exciting the solid with electromagnetic radiations. Depending on type and size of atom in the solid, electron resonance frequencies around  $\omega_0 \lesssim 6 \times 10^{15}$  rad/s, corresponding to wavelengths in air  $\lambda_0 \gtrsim 315$  nm, spanning spectral ranges from UV-side near visible region down to lowest UV, where, however, oscillator strengths of electronic transitions are negligible (Reitz et al., 1993). For closely-packed collection of atoms in highly-dense substances,  $\omega_p^2/\omega_0^2 \gtrsim 1$ , but reasonable values for  $\gamma$  are more difficult to estimate as the physical origin of loss and damping mechanisms in a real substance are not known for certain. There are few physical processes responsible for damping mechanisms that lead to a loss of energy of an oscillating electric dipole in a real sample arising from mutual interactions among phonons (lattice vibrations), impurities and defects in the solid, where  $(\gamma/\omega_0) \ll 1$  is valid for practical dispersion cases of interest.

Examining the forced-damped harmonic-oscillator dispersion model when  $\gamma = 0$  (no damping) is sometimes informative, but it is unphysical for revealing interesting features of the dielectric and optical responses of a real linear, dielectric substance exposed to electromagnetic radiation of a wide range of frequencies. Therefore, it is more realistic to examine its dispersion and loss behavior in the presence of small damping such that  $\gamma > 0$  and  $\gamma^2 \ll \omega_{0e}^2 = \omega_0^2 - (\omega_p^2/3)$ , in the spectral regions far from and near the effective absorption (resonance) frequency  $\omega_{0e}$ . The single-resonance absorption curves for real  $\epsilon'(\omega)$  and imaginary  $\epsilon''(\omega)$  parts of the *complex dielectric constant*  $\hat{\epsilon}(\omega)$  of a real sample is complicated as damping (loss) effects is not accurately known or large. The average time rate of energy loss  $\langle dW/dt \rangle_t$  from electromagnetic radiation of angular frequency  $\omega$  and electric-field amplitude  $\mathcal{E}_0$  to a linear, isotropic, non-magnetic and lossy solid pictured by a single forced-damped harmonic oscillator dispersion model is given in terms of  $\epsilon''(\omega)$  by (Christman, 1988; Jackson, 1998)

$$\langle dW/dt \rangle_t = \frac{1}{2} \epsilon_0 \omega \epsilon''(\omega) \mathcal{E}_0^2 = \frac{(\frac{1}{2} \epsilon_0 \gamma \omega_p^2 \mathcal{E}_0^2) \omega^2}{(\omega_{0e}^2 - \omega^2)^2 + (\gamma \omega)^2} \quad (\text{B29})$$

The response of a single-resonance Lorentz dispersion model for exciting frequencies near  $\omega \rightarrow 0$  and  $\omega \rightarrow \infty$  can be realized from Equation (B27) when  $\gamma > 0$ ,  $\gamma \ll \omega_{0e}$ , and  $(\omega_p^2/\omega_{0e}^2) \gtrsim 1$ . At exciting frequencies far less than  $\omega_{0e}$  and near  $\omega = 0$  (dc case), where the dc conductivity of pure dielectrics and dissipation are vanishing, the bound-electron zero-frequency asymptotic real part  $\epsilon'(\omega \rightarrow 0)$  of the complex dielectric constant is sizable with values greater than 1, while the magnitude of its zero-frequency *asymptotic* imaginary part  $\epsilon''(\omega \rightarrow 0)$  tends to zero. For small damping and very high frequencies far above  $\omega_{0e}$ ,  $\epsilon'(\omega \rightarrow \infty)$  approaches 1 and  $\epsilon''(\omega \rightarrow \infty)$  tends to zero, as if the dielectric were vacuum, in the sense  $\epsilon''(\omega) \equiv \chi''(\omega) \cong (\gamma \omega_p^2/\omega^3)$  and  $\epsilon'(\omega) \equiv 1 + \chi'(\omega) \cong 1 - (\omega_p^2/\omega^2)$ . In addition to modifying microscopic and macroscopic dielectric functions of a substance, the damping mechanisms remove singularities expected in zero-damping dielectric behavior (Reitz et al., 1993). For exciting frequencies in the neighborhood of  $\omega_{0e}$  ( $\omega = \omega_{0e} \pm 3\gamma$ ), the dielectric and optical behavior of a single harmonic oscillator dispersion model with small damping ( $\gamma > 0$  and  $\gamma \ll \omega_{0e}$ ) can be described by the  $\epsilon'(\omega)$ - $\omega$  and  $\epsilon''(\omega)$ - $\omega$  dependencies given by (Reitz et al., 1993)

$$\epsilon'(\omega) - 1 = M \left( \frac{(\frac{\gamma}{2})(\omega_{0e} - \omega)}{(\omega_{0e} - \omega)^2 + (\frac{\gamma}{2})^2} \right) \quad \text{and} \quad \epsilon''(\omega) = M \left( \frac{(\frac{\gamma}{2})^2}{(\omega_{0e} - \omega)^2 + (\frac{\gamma}{2})^2} \right) \quad (\text{B30})$$

where  $M = (\omega_p^2/\omega_{0e}^2) \cdot (\omega_{0e}/\gamma)$  is the maximum value (amplitude) of  $\epsilon''(\omega)$  at a frequency  $\omega$  that matches  $\omega_{0e}$ . The dispersion behavior has the *Lorentzian* line shape which embodies a variety of properties of the  $[\epsilon'(\omega) - 1]$ - and  $\epsilon''(\omega)$ - functions. The  $\epsilon''(\omega)$  function is *even* with respect to  $(\omega_{0e} - \omega)$  and  $[\epsilon'(\omega) - 1]$  function is *odd* and vanishes at  $\omega = \omega_{0e}$ . The  $\epsilon''(\omega) - \omega$  curve (absorption line) has a full width at half maximum (FWHM) equals to  $\gamma$  and the frequencies at which  $\epsilon''(\omega)$  is  $M/2$  are  $\omega_{\pm} = \omega_{0e} \pm (\gamma/2)$ , where the extremes ( $= \pm M/2$ ) of the  $[\epsilon'(\omega) - 1]$  function occur. Depending on relative magnitudes of resonance, plasma, and damping frequencies in a dielectric, the  $\epsilon''(\omega)$ -amplitude is somewhat large that gives a real electric conductivity  $\sigma'_c(\omega) \equiv \omega \epsilon_0 \epsilon''(\omega)$  at resonance comparable with the dc conductivity of a metal.



### B.4.2.3 Optical Constants in the Normal Dispersion Region in View of the Lorentz-Oscillator Model

The frequency dependence of the real and imaginary parts  $n(\omega)$  and  $\kappa(\omega)$  of the complex optical constant  $\hat{n}(\omega) \equiv n(\omega) + j\kappa(\omega)$  in a single-resonance damped harmonic-oscillator dispersion model can be found from the dispersion function of  $\hat{\epsilon}(\omega)$  given in Equation (B25), which describes a linear, dispersive lossy dielectric, even if free charges are absent ( $\sigma_c = 0$ ). If the electron-system plasma frequency  $\omega_p$  is small enough for the absolute value of the complex quantity on the right-hand side of Equation (B25) to be small when compared to unity, for all frequencies, so that we may justify the approximation in the binomial expansion given below

$$\hat{n}(\omega) \equiv n(\omega) + j\kappa(\omega) = \left(1 + \frac{\omega_p^2}{\omega_{0e}^2 - \omega^2 - j\gamma\omega}\right)^{\frac{1}{2}} \cong 1 + \frac{1}{2} \frac{\omega_p^2}{\omega_{0e}^2 - \omega^2 - j\gamma\omega} \quad (\text{B31})$$

Equation (B31) yields approximate formulas for  $n(\omega)$  and  $\kappa(\omega)$  or  $\alpha(\omega) \equiv 2\omega\kappa(\omega)/c$  given by (Rogalski & Palmer, 2000; Reitz et al., 1993)

$$n(\omega) \cong 1 + \frac{1}{2} \frac{\omega_p^2(\omega_{0e}^2 - \omega^2)}{(\omega_{0e}^2 - \omega^2)^2 + (\gamma\omega)^2} \quad (\text{B32})$$

$$\kappa(\omega) \cong \frac{1}{2} \frac{\gamma\omega_p^2\omega}{(\omega_{0e}^2 - \omega^2)^2 + (\gamma\omega)^2} \quad \text{or} \quad \alpha(\omega) \cong \frac{(\gamma/c)\omega_p^2\omega^2}{(\omega_{0e}^2 - \omega^2)^2 + (\gamma\omega)^2} \quad (\text{B33})$$

Accurate but involved  $n(\omega)$ - and  $\kappa(\omega)$ - formulas for a Lorentz dispersion model can be found by putting  $\epsilon'(\omega)$  and  $\epsilon''(\omega)$  of Equation (B27) into Equation (B6), which are in numerical calculations of  $n(\omega)$  and  $\kappa(\omega)$ . In the *optically transparent region*, where  $\omega$  is well below  $\omega_{0e}$  and  $(\omega_{0e}^2 - \omega^2)^2 \gg (\gamma\omega)^2$ , Equations (B32) and (B33) reduce to

$$n(\omega) \cong 1 + \frac{1}{2} \frac{\omega_p^2}{\omega_{0e}^2 - \omega^2} \quad \kappa(\omega) \cong \frac{1}{2} \frac{\gamma\omega_p^2\omega}{(\omega_{0e}^2 - \omega^2)^2} \rightarrow 0 \quad \text{or} \quad \alpha(\omega) \cong \frac{(\gamma/c)\omega_p^2\omega^2}{(\omega_{0e}^2 - \omega^2)^2} \rightarrow 0 \quad (\text{B34})$$

Equation (B34) tells us that the index of refraction  $n(\omega \ll \omega_{0e})$  of a real linear, non-magnetic dielectric substance in its optically transparent region is greater than unity and is dispersive such that it increases with increasing frequency up to a certain frequency  $\omega$  ( $< \omega_{0e}$ )- that is,  $[\partial n(\omega)/\partial \omega] > 0$ , before starting to drop sharply in the vicinity of  $\omega_{0e}$ . Such a frequency-dependent behavior of  $n(\omega)$ , which is characteristics of dielectric materials in spectral regions below resonance as well as of ionic and molecular crystals in visible region of the spectrum, is called *normal dispersion*, where  $\kappa(\omega) \rightarrow 0$  and  $\alpha(\omega) \rightarrow 0$  as  $\omega \rightarrow 0$  -that is, optical absorption increasingly ceases with decreasing frequency in the optically transparent region of such substances. In the optically transparent (normal-dispersion) region, where  $(\omega/\omega_{0e}) \ll 1$ , the  $n(\omega)$ -formula given in Equation (B34) can be expanded in the form of a Taylor's series to obtain a simple formula for the variation of  $n(\omega)$  with the exciting frequency  $\omega$  as described below

$$n(\omega) \cong 1 + \frac{1}{2} \left(\frac{\omega_p}{\omega_{0e}}\right)^2 \left[1 + \left(\frac{\omega}{\omega_{0e}}\right)^2 + \left(\frac{\omega}{\omega_{0e}}\right)^4 + \left(\frac{\omega}{\omega_{0e}}\right)^6 + \dots\right] \quad (\text{B35})$$

In terms of spectral wavelength  $\lambda \equiv 2\pi c/\omega$  and defining a plasma wavelength  $\lambda_p \equiv 2\pi c/\omega_p$  and a resonance wavelength  $\lambda_{0e} \equiv 2\pi c/\omega_{0e}$ , Equation (B35) becomes an even function of  $\lambda$  of the form

$$n(\lambda) \cong 1 + \frac{1}{2} \left(\frac{\lambda_{0e}}{\lambda_p}\right)^2 \left[1 + \left(\frac{\lambda_{0e}}{\lambda}\right)^2 + \left(\frac{\lambda_{0e}}{\lambda}\right)^4 + \left(\frac{\lambda_{0e}}{\lambda}\right)^6 + \dots\right] = A_0 + \frac{A_2}{\lambda^2} + \frac{A_4}{\lambda^4} + \dots = \sum_{n=0} \frac{A_n}{\lambda^{2n}} \quad (\text{B36})$$

Equation (B36) resembles a *multi-term Cauchy dispersion relation* with constant coefficients  $A_0$ ,  $A_2$ ,  $A_4$ , etc. The Cauchy relation is an *empirical* dispersion formula often quoted with its first few terms for use in curve-fitting of experimental data of the index of refraction of transparent materials to determine its adjustable constants. The empirical relation  $\kappa(\lambda) = \sum_{k=0} (B_k/\lambda^{2k})$  has been suggested to model dispersion of the extinction coefficient  $\kappa(\lambda)$  of transparent substances (Poelman & Smet, 2003). However, at the *low-frequency (long-wavelength)* side of the transparent region where Equation (B34) is valid, a multi-term  $\kappa(\lambda)$ -dispersion expression in  $\lambda$  can be attained, with the result being given below

$$\kappa(\lambda) \cong \frac{B_1}{\lambda} + \frac{B_3}{\lambda^3} + \frac{B_5}{\lambda^5} + \dots = \sum_{k=0} \frac{B_k}{\lambda^{2k+1}} \quad (\text{B37})$$

If there are several kinds of elastically bound electrons with the  $\hat{\epsilon}(\omega)$ -function of a linear, non-magnetic dielectric sample being described by Equation (B28), then Equation (B31) may be re-written in the approximate form (Rogalski & Palmer, 2000)

$$\hat{n}(\omega) \equiv n(\omega) + j\kappa(\omega) \cong 1 + \frac{1}{2}\omega_p^2 \sum_i \frac{f_i}{\omega_{0i}^2 - \omega^2 - j\gamma_i\omega} = \frac{1}{2}\omega_p^2 \sum_i f_i \frac{\omega_{0i}^2 - \omega^2 + j\gamma_i\omega}{(\omega_{0i}^2 - \omega^2)^2 + (\gamma_i\omega)^2} \quad (\text{B38})$$

Equation (B38) can be shown to give an approximate  $n(\omega)$ - $\omega$  relation for transparent dielectric substances and undoped semiconductors that may be valid in the infrared region of the spectrum as depicted below (Rogalski & Palmer, 2000)

$$n(\lambda) = 1 + \frac{1}{2}\omega_p^2 \sum_i \frac{f_i}{\omega_{0i}^2 - \omega^2} = 1 + \sum_i \left( \frac{f_i \lambda_{0i}^2}{2\lambda_p^2} \right) \frac{\lambda^2}{\lambda^2 - \lambda_{0i}^2} = 1 + S_1 \frac{\lambda^2}{\lambda^2 - \lambda_{01}^2} + S_2 \frac{\lambda^2}{\lambda^2 - \lambda_{02}^2} + \dots \quad (\text{B39})$$

Equation (B39) with the constants  $S_1$ ,  $S_2$ , etc. is known as the *multi-term Sellmeier-like dispersion relation*, which can also be used for experimental curve-fitting of measured values of  $n(\lambda)$  in the transparent region of a dielectric material. At very low frequencies close to  $\omega = 0$  (*static regime*), Equation (B39) reduces to the so-called Maxwell relation for the *static* index of refraction  $n_0$  of transparent media, given by (Rogalski & Palmer, 2000)

$$n_0 = 1 + \frac{1}{2}\omega_p^2 \sum_i \frac{f_i}{\omega_{0i}^2} = 1 + \frac{1}{2\lambda_p^2} \sum_i f_i \lambda_{0i}^2 \quad (\text{B40})$$

A *three-constant* Sellmeier-like dispersion formula that is most commonly used to describe spectral dependence of  $n(\lambda)$  ( $= \sqrt{\epsilon'(\omega)}$ ) of a dielectric in its *transparency region far above its fundamental absorption edge* can be found from Equation (B31). This is often termed as the *first-order* Sellmeier-like dispersion relation, which can be written in terms of the spectral wavelength  $\lambda$  and three constants: a threshold bandgap wavelength  $\lambda_0$  ( $\ll \lambda$ ),  $c_0$  ( $> 1$ ), which is equal to *unity* in original Sellmeier equation, and  $c_1$  ( $> 0$ ), viz.

$$[n(\lambda)]^2 = c_0 + \frac{c_1 \lambda^2}{\lambda^2 - \lambda_0^2} \quad (\text{B41})$$

The constant parameter  $c_0$  in the Sellmeier-like relation given in Equation (B41) can be taken to account for a constant electronic contribution to the dielectric constant that is considered to approach a limiting value at long spectral wavelengths ( $\lambda \rightarrow \infty$ ). An equivalent relation to the Sellmeier-like dispersion relation given in Equation (B41) is often expressed in terms of the light photon energy  $E \equiv \hbar\omega$  to get the familiar Wemple-DiDomenico (WDD) dispersion relation underlying a single-effective-oscillator model (Wemple & DiDomenico, 1971), which is valid in the transparency region above the absorption edge of an undoped semiconductor, commonly written in an analytical energy-dependent form

$$\epsilon'(\hbar\omega) = [n(\hbar\omega)]^2 = 1 + \frac{E_0 E_d}{E_0^2 - (\hbar\omega)^2} \quad (\text{B42})$$

The physically significant dispersion parameters  $E_0$  ( $\gg \hbar\omega$ ) or the single-oscillator resonance energy, and  $E_d$ , the dispersion energy or single-oscillator energy strength, which is a measure of the strength of interband optical transitions, are constants that relate to the structural and material properties (Wemple & DiDomenico, 1971). At very low frequencies where  $\omega \rightarrow 0$  ( $\lambda \rightarrow \infty$ ), the corresponding *static dielectric constant*  $\epsilon_s = \epsilon'(\omega = 0)$  and *static index of refraction*  $n_0 = n(\lambda = \infty)$  are expressed as  $n_0 = \sqrt{\epsilon'(\omega = 0)} = \sqrt{1 + (E_d/E_0)}$ , which is equivalent to  $n_0 = \sqrt{c_0 + c_1}$  in the framework of Sellmeier dispersion relation described in Equation (B41). The parameter  $E_0$  is an “average” gap energy whose actual value depends on the material and is connected to differently defined bandgap energies in more or less an empirical way (Wemple & DiDomenico, 1971). To a good approximation,  $E_0$  varies in proportion to Tauc (optical) bandgap energy  $E_g^{\text{opt}}$  and is frequently quoted as  $E_0 \approx 2E_g^{\text{opt}}$  (Wemple & DiDomenico, 1971), or to the *lowest direct bandgap energy*  $E_g$  ( $= E_{\text{ph}} > E_g^{\text{opt}}$ ), a *threshold photon energy for photogeneration of free charge carriers in substance* with  $E_0 \cong 1.5E_g$ , as quoted for many materials (Wemple & DiDomenico, 1971). For pure (undoped) amorphous selenium (*a*-Se),  $E_{\text{ph}} \cong 2.53$  eV, or a photon wavelength  $\lambda_{\text{ph}} \sim 490$  nm, at which  $\epsilon''$  is supposed to exhibit a maximum amplitude (Adachi & Kao 1980). The parameter  $E_d$  obeys an empirical relation  $E_d(\text{eV}) = \beta N_c Z_a N_e$ , which is applied to several glasses and amorphous semiconductors, where  $\beta$  is a constant that takes values between 0.26 (ionic materials) and 0.37 (covalent substances),  $N_c$  is the *coordination number* of the cation nearest-neighbor to the anion,  $Z_a$  is the formal chemical valence of the anion, and  $N_e$  is the *effective* number of valence electrons (cores excluded) per anion (Wemple & DiDomenico, 1971).

#### B.4.2.4. Anomalous Dispersion and Absorption in Dielectrics Near a Lorentz-Oscillator Resonance

The shape of  $n(\omega)$ - $\omega$  and  $\kappa(\omega)$ - $\omega$  curves in the neighborhood of a resonance frequency  $\omega_{0e}$  related to the Lorentzian dielectric functions  $\epsilon'(\omega)$  and  $\epsilon''(\omega)$  depicted in Equation (B30) depends on the  $\epsilon''(\omega)$ -amplitude. Equations (B32) and (B33) can be used to get a couple of  $n(\omega)$  and  $\kappa(\omega)$  formulas in the region near resonance of a Lorentz harmonic oscillator, with  $\omega_p$  and  $\gamma$  being taken to be small compared to  $\omega_{0e}$ , viz. (Rogalski & Palmer, 2000; Reitz et al., 1993)

$$n(\omega \approx \omega_{0e}) \cong 1 + \left( \frac{\omega_p^2}{4\omega_{0e}^2} \right) \frac{(\omega_{0e} - \omega)}{(\omega_{0e} - \omega)^2 + (\gamma/2)^2} \quad (\text{B43})$$

$$\kappa(\omega \approx \omega_{0e}) \cong \left( \frac{\omega_p^2}{4\omega_{0e}^2} \right) \frac{(\gamma/2)\omega}{(\omega_{0e} - \omega)^2 + (\gamma/2)^2} \quad (\text{B44})$$

In the immediate neighborhood of a resonance of a Lorentz harmonic oscillator in a dielectric, both  $n(\omega)$  and  $\kappa(\omega)$  depend on frequency, with some interesting features can be concluded from the  $\omega$ -dependency of  $n(\omega)$  and  $\kappa(\omega)$  close to resonance. The frequency range  $\omega = \omega_{0e} \pm (\gamma/2)$  over which  $\kappa(\omega)$  is non-zero is called the *absorption region*, where  $n(\omega)$  reaches a maximum ( $= 1 - [\omega_p^2/4\omega_{0e}^2]$ ) for the frequency  $\omega = \omega_{0e} - (\gamma/2)$  and then falls sharply to a minimum ( $= 1 - [\omega_p^2/4\omega_{0e}^2]$ ) at  $\omega = \omega_{0e} + (\gamma/2)$ . In other words, the  $n(\omega)$ - $\omega$  curve in the region of the  $\kappa(\omega)$ -peak always has a region of a negative slope such that  $[\partial n(\omega)/\partial \omega] < 0$  and the substance may be opaque in this frequency range, where the electrons are being driven at their resonating frequency; thus, the amplitude of their oscillation is relatively large, and a correspondingly large amount of energy is dissipated by the damping mechanism, as seen from the  $\langle dW/dt \rangle_t$ -formula given in Equation (B39). This  $n(\omega)$ - $\omega$  behavior is atypical and is called *anomalous dispersion*, where  $n(\omega)$  runs below 1 above the resonance, but contributions of other terms in the sum described in Equation (B38) add a relatively constant index of refraction  $n_0$  that keeps  $n > 1$  on both sides of the resonance.

The simple forced-damped harmonic motion of electrons (ions) in a non-conducting (ionic) material can account for the frequency dependence of its index of refraction  $n(\omega)$  and it explains why  $n(\omega)$  is ordinarily a slowly increasing function of  $\omega$  (normal dispersion), with occasional *anomalous dispersion regions where it swiftly drops*. It also clarifies that the resonant frequency  $\omega_0$  of electronic (ionic) contribution to relative permittivity is shifted when electrons (ions) are bound to a crystal lattice rather than to isolated atoms (ions)- that is, resonances will occur at different effective frequencies  $\omega_{0\text{eff}}$  given by  $\omega_{0\text{eff}}^2 = \omega_0^2 - (\Omega_p^2/3)$ , where  $\Omega_p$  is a plasma frequency. The connection between absorption and dispersion of a linear material is contained in the fundamental Kramers-Kronig integrals. If damping is *not small*, none of the foregoing simple relations would hold quantitatively, but a qualitative behavior of  $\hat{\epsilon}(\omega)$  and  $\hat{n}(\omega)$  is supposed to be still similar (Reitz et al., 1993). A single Lorentz harmonic oscillator dispersion model is not at all times suitable for explaining experimental dispersion and optical absorption spectra of real substances, mainly the disordered non-crystalline ones, over a broad range of spectral wavelengths, including those lying nearby the absorption edge region, where other rigorous dielectric models seem to be more applicable, as will be briefed in next sections.

#### B.5. Full Parameterization of Dielectric and Optical Functions of Insulating and Undoped Semiconducting Substances in the Interband Transition and Sub-Band Spectral Regions

Optical absorption and reflection spectra of a dielectric or undoped semiconducting substance are in general related to its band-energy structure, quality, and crystallinity. Under certain experimental conditions, the as-measured optical data of a substance often mimic immaculately many of its structural features in its absorption edge and nearby spectral regions, which can be assisted by a quantitative analysis of the spectral dependence of its dielectric and optical parameters. A compelling parameterized dispersion model that is consistent with the principle of causality (Kramers-Kronig relations) and that works appropriately in the band-to-band (interband) transition region of a substance and in faraway sub-bandgap spectral regimes is, however, demanding. Theoretical and empirical models that are mostly used for discussing dielectric and optical functions of crystalline and amorphous semiconductors will be presented below.

##### B.5.1 Lorentz-Like Oscillator and Drude-Like Dispersion Models

In some cases, parameterization of dielectric and optical functions of a semiconductor or dielectric of  $N$  atoms, each having  $Z$  bound electrons, as a function of angular frequency  $\omega$  (wavelength  $\lambda$ ) of the light incident on a sample can be managed on the basis of the forced-damped harmonic (Lorentz) oscillator model. A sum of two or more Lorentz oscillators with diverse resonance frequencies  $\omega_{0i}$ , quantum-mechanical strengths  $f_{0i}$  ( $\sim \omega_{0i}$ ), with  $\sum_i f_{0i} = Z$ , and damping frequencies (broadening linewidths)  $\gamma_i$  may be adequate to describe the complex

dielectric constant function  $\hat{\epsilon}(\omega)$  of a dielectric sample in ultraviolet, visible, and near infrared spectral regions. A common form of an oscillator-like formulation for a collection of  $N$  non-interacting atoms in a substance (zero Lorentz field-correction factor) that is frequently adopted in literature is given by the expression (Reitz et al., 1993; Jackson, 1998)

$$\hat{\epsilon}(\omega) = \epsilon'(\omega) + j\epsilon''(\omega) = \epsilon_{\infty} + \sum_i \frac{\omega_{p0i}^2 f_{oi}}{\omega_{0i}^2 - \omega^2 - j\gamma_i \omega} \quad (\text{B45})$$

The plasma frequency  $\omega_p = \sqrt{Ne^2/m^* \epsilon_0}$ ,  $e$  is the magnitude of electronic charge and  $m^*$  is the effective mass of the electron in the substance. The parameter  $\epsilon_{\infty}$  ( $= n_{\infty}^2$ ) represents a constant dielectric function at *infinite photon energy* or *zero wavelength*, which is often introduced, instead of 1 often written in standard forms of Lorentz oscillator model, as a fitting parameter to account for the dielectric function at spectral wavelengths much smaller than measured (Poelman & Smet, 2003), where  $n_{\infty}$  is the corresponding zero-wavelength index of refraction. For a linear, isotropic and non-magnetic lossy dielectric, the optical constants  $n(\lambda)$  and  $\kappa(\lambda)$  can be evaluated from the values of  $\epsilon'(\omega) = n^2 - \kappa^2$  and  $\epsilon''(\omega) = 2n\kappa$  by making use of Equations (B4) to (B6). Recall that the set of coupled Lorentz-like oscillator formulas of the macroscopic dielectric functions  $\epsilon'(\omega)$  and  $\epsilon''(\omega)$  or of the optical constants  $n(\lambda)$  and  $\kappa(\lambda)$  of a substance are consistent with the fundamental Kramers-Kronig (KK) relations (Jackson, 1998), in contrary to the empirical Cauchy-like and Sellmeier-like dispersion relations, usually utilized in computational curve-fitting analysis of optical data in the transparency region of a material. In disordered substances, the simple Lorentz oscillator model is sometimes modified to account for distribution of resonance frequencies (*Brendel oscillator* (Theiss, 2012)) or for a frequency dependence of the damping constant by introducing a parameter  $\sigma_k$ , called Gauss-Lorentz switch, with  $\sigma_k = 0$  (Gaussian-line) and  $\sigma_k > 5$  (Lorentzian-line) in dispersion functions, as in *Kim oscillator* (Theiss, 2012) that is useful when one works with many oscillators. Further, when optical response of a metallic-like sample or a layer made from doped semiconducting materials, where a significant number of free charge carriers supplied from their impurity donors or acceptors, is investigated over a wide spectral range, including the infrared region of the spectrum, it may be obligatory to combine oscillator-like dispersion formulations with formulas of classical and extended Drude dielectric models (Theiss, 2012) to describe its measured optical data as contributions of electronic transitions due to *intraband absorption* (free-carrier effects) to its dielectric and optical functions turn out to be significant. No further details will be given here on Drude-like dielectric functions as free-carrier contribution is supposed to be irrelevant in an undoped *a*-Se film when its optical response is studied at wavelengths much below those conforming to intraband absorption.

A combined dispersion formulation that integrates multi-Lorentz oscillators would be in reality unsatisfactory to account for the observed optical behavior of a crystalline or non-crystalline undoped semiconducting substance in the region of its absorption edge, since all energy states in valence and conduction bands separated in energy by the exciting photon energy  $\hbar\omega$  are involved in radiation-induced electronic transitions and many fitting parameters are required in a comprehensive optical analysis. So, one needs dispersion models which takes into consideration most of possible contributions to dielectric response and optical absorption of a substance over a wide range of photon energies that cover both of its band-to-band (interband) and sub-bandgap regions. Further, these models should have closed analytical forms that will be virtually convenient and computationally feasible for analyzing its experimental optical data, but with few parameters of physical significance, as briefed below.

#### B.5.2 Dielectric Functions in the Band-To-Band (Interband) Transition Region

There are at present several physical dispersion models that could be used for interpreting the dependency of index of refraction and extinction coefficient of solid substances on the spectral wavelength (or photon energy) in the band-to-band (interband) absorption region. The single- or multi-term Forouhi-Bloomer (FB-) set of  $n(\lambda)$  and  $\kappa(\lambda)$  formulations (Forouhi & Bloomer, 1986; Forouhi & Bloomer, 1988), also consistent with the fundamental Kramers-Kronig relations, and their modifications were proposed to model optical absorption in crystalline and amorphous materials in the interband transition region. Although the FB-like dispersion formulations were adopted by a number of workers to fit experimental  $n(\lambda)$  and  $\kappa(\lambda)$  data sets in the interband and sub-bandgap energy regions of some amorphous materials, they suffer from few physical limitations (Jellison & Modine, 1996) as, for example, they are not apposite to model optical behavior in the sub-bandgap or normal dispersion regions (Jellison & Modine, 1996). Interband transition models are quite asymmetric and are not easy to formulate theoretically without model approximations, as numerous electronic transitions between occupied and empty energy states of valence and conduction bands of a substance overlap each other, giving rise to convoluted dispersion and absorption spectra, so, it may be difficult to resolve different contributions using a single interband transition model. Quantum-mechanical interband transition models yield an expression for only the imaginary part

$\epsilon''(\omega)$  of the sample's complex dielectric function or absorption coefficient  $\alpha(\omega) \equiv \omega\epsilon''(\omega)/n(\omega)c$ , a viable form of which cannot be found unless structures of its energy bands involved in electronic transitions are known. The KK  $\epsilon''(\omega)$ -integral is then used to construct an analytical expression for real part  $\epsilon'(\omega)$  of its dielectric function, which is either intricate or unwieldy. An  $\epsilon'(\omega)$ -spectrum of a sample can be computed via the KK  $\epsilon'(\omega)$ -integral from a large amount of accurate numeric  $\epsilon''(\omega)$ -data measured at all frequencies from 0 to  $\infty$ , and we may run into severe difficulties with spectral resolution in the infrared, a flaw that is not met when KK relations are used to describe interband transitions in ultraviolet and visible regions. Spectrophotometric data, which yield indirectly  $\epsilon'(\lambda)$  and  $\epsilon''(\lambda)$ -data, over an infinitely wide range of spectral wavelengths cannot easily be acquired and are in practice limited in the range 0.2 – 3.5  $\mu\text{m}$ , shortcomings that may not be encountered in spectroscopic ellipsometry, where both  $\epsilon'(\lambda)$  and  $\epsilon''(\lambda)$  data is calculated directly from measured macroscopic quantities over a range of photon energies  $\hbar\omega (\lesssim E_g)$ , though taking ellipsometric data is not always feasible at certain experimental conditions (Adachi & Kao1980; Innami et al., 1999).

#### B.5.2.1 Quantum-Mechanical Direct and Indirect Interband Dielectric Models for Crystalline Substances

If a crystalline semiconductor is illuminated with electromagnetic radiation of an angular frequency  $\omega$  equal to or larger than its absorption edge, the radiation will be partially absorbed, mainly due to induced band-to-band (interband) electronic transitions. Quantum mechanical time-dependent perturbation theory of interband transitions Rogalski & Palmer, 2000; Bassani & Parravicini, 1975; Sólyom, 2009) elucidates that the material's absorption coefficient  $\alpha(\omega)$  at a certain  $\omega$  is governed by the probability  $\mathcal{P}_{if}$  of transition of electrons from an initial energy state  $|i\rangle$  to a final energy state  $|f\rangle$  and by both of the density of energy states  $N_i$  in the initial  $|i\rangle$ -states in the valence band and the density of empty energy states  $N_f$  in the final  $|f\rangle$ -states lying in an upper conduction band, including all occupied and empty energy states in lower valence and upper conduction bands separated by an energy equals to the exciting photon energy  $\hbar\omega$ . Interactions between electrons in a solid and monochromatic electromagnetic field  $\mathbf{E}(\mathbf{r}, t)$  (electron-photon interactions) can be treated as a slight time-dependent perturbed Hamiltonian in the dipole approximation, where effects of the electromagnetic field  $\mathbf{B}(\mathbf{r}, t)$  are neglected, or as a small time-dependent perturbed Hamiltonian via specifying the electromagnetic field by a magnetic vector potential  $\mathbf{A}(\mathbf{r}, t) = \hat{\mathbf{e}}A_0 \exp [j(\mathbf{k}_{ph} \cdot \mathbf{r} - \omega t)] + \text{c.c.}$ , where  $\omega$  and  $\mathbf{k}_{ph}$  are the angular frequency and wavevector of the radiation field, respectively, where  $\hat{\mathbf{e}}$  is a real photon polarization unit vector in the direction of  $\mathbf{E}(\mathbf{r}, t)$  and the first term gives rise to the absorption of photons, with the c.c.-term being the complex conjugate of the first term corresponding to emission of photons. A time-depending oscillating electric field  $\mathbf{E}(\mathbf{r}, t)$  of monochromatic electromagnetic radiation of an angular frequency  $\omega$  and photon wavevector  $\mathbf{k}_{ph}$  may cause interband electronic transitions from all conceivable initial occupied valence-band energy states, each is characterized by the wavevector  $\mathbf{v}\mathbf{k}_i$ , spin state indexed by  $s_i$ , wavefunction  $\psi_{\mathbf{v}\mathbf{k}_i}$ , and energy eigenvalue  $E_i$ , to all available (empty) final conduction-band energy states, each is characterized by the wavevector  $\mathbf{c}\mathbf{k}_f$ , spin state indexed by  $s_f$ , wavefunction  $\psi_{\mathbf{c}\mathbf{k}_f}$ , and energy eigenvalue  $E_f$ . The corresponding transition probability  $\mathcal{P}_{\mathbf{v}\mathbf{k}_i s_i \rightarrow \mathbf{c}\mathbf{k}_f s_f}$  per unit time, taking all possible electronic transitions between occupied initial and empty final energy states, separated by an energy  $E_f - E_i = \hbar\omega$ , can be described in the adiabatic and one-electron approximation within the first-order time-dependent perturbation theory (Fermi's Golden Rule) by the following general expression (Bassani & Parravicini, 1975)

$$\mathcal{P}_{\mathbf{v}\mathbf{k}_i s_i \rightarrow \mathbf{c}\mathbf{k}_f s_f} = \left(\frac{1}{\hbar}\right) \left(\frac{eA_0}{m_e^*}\right)^2 \delta_{s_i s_f} \left| \left\langle \psi_{\mathbf{c}\mathbf{k}_f} \left| e^{j(\mathbf{k}_{ph} \cdot \mathbf{r})} \hat{\mathbf{e}} \cdot \hat{\mathbf{p}} \right| \psi_{\mathbf{v}\mathbf{k}_i} \right\rangle \right|^2 \delta(E_f - E_i - \hbar\omega) \quad (\text{B46})$$

Note that the transition probability is only non-vanishing if  $E_f - E_i = \hbar\omega$  and that  $m_e^*$  is the effective mass of the charge carriers (electrons), excited from valence-band energy states to conduction-band energy states. Further, one can argue that equation (B46) is one of the basic quantum-mechanical formulations for computing dielectric and optical constants of a substance in the frequency region of its interband electronic transitions, with  $\delta_{s_i s_f}$  and  $\delta(E_f - E_i - \hbar\omega)$  being, respectively, the Kronecker and Dirac delta functions. The quantity  $\left| \left\langle \psi_{\mathbf{c}\mathbf{k}_f} \left| e^{j(\mathbf{k}_{ph} \cdot \mathbf{r})} \hat{\mathbf{e}} \cdot \hat{\mathbf{p}} \right| \psi_{\mathbf{v}\mathbf{k}_i} \right\rangle \right|^2$  represents the single-electron momentum matrix element for an electronic transition from a valence-band state  $\mathbf{v}\mathbf{k}_i$  to an empty conduction-band state  $\mathbf{c}\mathbf{k}_f$ , with the vector  $\hat{\mathbf{p}}$  being the corresponding single-electron momentum vector operator  $-j\hbar\nabla_{\mathbf{cv}}$ . In a quantum mechanical transition with non-vanishing matrix element, both total energy and momentum (wavevector) of the electron-photon system involved in field-induced electronic transitions in a periodic crystalline lattice are conserved, often written in terms of selection (conservation) rules specified by the relations (Bassani & Parravicini, 1975)

$$E_f - E_i - \hbar\omega = 0 \quad \Delta\mathbf{k} = \mathbf{k}_f - \mathbf{k}_i - \mathbf{k}_{ph} - \mathbf{G} = 0 \quad (\text{B47})$$

where  $\mathbf{G}$  is any reciprocal lattice vector in first Brillouin zone. For photons in the ultraviolet, visible, and infrared regions of the spectrum,  $\mathbf{k}_{ph} \ll \mathbf{k}_i$  or  $\mathbf{k}_f$ , the range of their variation in a solid of lattice constant  $a$  of the order of a few angstroms is  $2\pi/a$ - that is within the width of the first Brillouin zone of the respective band; thus, for the so-called “vertical” (direct) interband transitions induced by the electromagnetic radiation field of angular frequency  $\omega$  between occupied valence-band states of energy  $E_v(\mathbf{k})$  and empty conduction-band states of energy  $E_c(\mathbf{k})$ , separated by  $\hbar\omega$ , we may write  $\mathbf{k}_{ph} \cong 0$  and  $\mathbf{k}_f \cong \mathbf{k}_i$ . Direct interband transitions are observed in a crystalline substance where the top  $\mathbf{k}$ -point in its valence band has the same wavevector as the bottom  $\mathbf{k}$ -point in its conduction band and this substance is referred to as a *direct bandgap material*. The transition probability per unit time can be written in a simpler form as

$$P_{vks \rightarrow cks} = \left(\frac{1}{\hbar}\right) \left(\frac{eA_0}{m_e^*}\right)^2 |\hat{\mathbf{e}} \cdot \mathbf{M}_{cv}(\mathbf{k})|^2 \delta(E_c(\mathbf{k}) - E_v(\mathbf{k}) - \hbar\omega) \quad (B48)$$

The single-electron momentum matrix element  $\mathbf{M}_{cv}(\mathbf{k})$  of the field-induced transition can be evaluated from an integral, which when is carried out over three-dimensional (3D) crystal volume  $= \int d^3\mathbf{r}$ , is given by

$$\hat{\mathbf{e}} \cdot \mathbf{M}_{cv}(\mathbf{k}) = \langle \psi_{ck} | \hat{\mathbf{e}} \cdot \mathbf{p} | \psi_{vk} \rangle = \langle \psi_{ck} | \hat{\mathbf{e}} \cdot (-j\hbar \nabla_{\mathbf{k}}) | \psi_{vk} \rangle = \hat{\mathbf{e}} \cdot \int \psi_c^*(\mathbf{k}, \mathbf{r}) (-j\hbar \nabla_{\mathbf{r}}) \psi_v(\mathbf{k}, \mathbf{r}) d^3\mathbf{r} \quad (B49)$$

To get the number of electronic transitions  $W_{cv}(\omega)$  per unit time per unit volume induced by light of frequency  $\omega$ , Equation (B48) is summed over all possible energy states per unit volume- that is, over  $\mathbf{k}$ , the spin variable  $s$ , and energy band states indexed by  $v$  (occupied) and  $c$  (empty). Since the allowed wavevectors  $\mathbf{k}$  in a 3D crystalline solid of geometrical volume  $V$  are distributed equally-spaced in a Brillouin zone with a density of states (in  $\mathbf{k}$ -space) equals to  $V/(2\pi)^3$ ,  $W_{cv}(\omega)$  can be expressed by the following general form (Bassani & Parravicini, 1975)

$$W_{cv}(\omega) = \left(\frac{1}{\hbar}\right) \left(\frac{eA_0}{m_e^*}\right)^2 \sum_{v,c} \int \frac{2d^3\mathbf{k}}{(2\pi)^3} |\hat{\mathbf{e}} \cdot \mathbf{M}_{cv}(\mathbf{k})|^2 \delta(E_c(\mathbf{k}) - E_v(\mathbf{k}) - \hbar\omega) \quad (B50)$$

The integral extends over the first Brillouin zones of energy bands involved in electronic transitions and the factor 2 arises from the contribution of the two possible electron spins (spin up and spin down) in each  $\mathbf{k}$ -state. Now, a closed analytical form of the sought-for dielectric (or optical) function of a linear, isotropic, non-magnetic crystalline dielectric or semiconducting solid can be found by combining the  $W_{cv}(\omega)$ -expression given in Equation (B50) and the time-average energy density  $\langle u \rangle_t$  of monochromatic electromagnetic radiation of angular frequency  $\omega$  propagating through solid. The expression for the electromagnetic energy density  $\langle u \rangle_t$  in a solid can be written in terms of its index of refraction  $n(\omega)$  and amplitude of the magnetic vector potential  $A_0$ , by making use of the relation  $\mathbf{E}(\mathbf{r}, t) = -\partial \mathbf{A}(\mathbf{r}, t)/\partial t$  and the above-defined  $\mathbf{A}(\mathbf{r}, t)$ -formula, as (Bassani & Parravicini, 1975)

$$\langle u \rangle_t = \epsilon_0 [n(\omega)]^2 A_0^2 \omega^2 \quad (B51)$$

The absorption coefficient  $\alpha(\omega)$  of a sample at a frequency  $\omega$  is by definition equal to the total electromagnetic energy absorbed inside it per unit time per unit volume- that is,  $\hbar\omega W_{cv}(\omega)$ , divided by the product of the average energy density  $\langle u \rangle_t$  of the electromagnetic radiation and its wave propagation velocity inside the solid- that is, the energy of incident electromagnetic radiation per unit time per unit area (radiation energy flux), viz.

$$\alpha(\omega) \equiv \frac{\hbar\omega W_{cv}(\omega)}{\langle u \rangle_t (c/n)} = \left(\frac{e^2}{\epsilon_0 c n(\omega) m_e^* \omega}\right) \sum_{v,c} \int \frac{2d^3\mathbf{k}}{(2\pi)^3} |\hat{\mathbf{e}} \cdot \mathbf{M}_{cv}(\mathbf{k})|^2 \delta(E_c(\mathbf{k}) - E_v(\mathbf{k}) - \hbar\omega) \quad (B52)$$

The imaginary part  $\epsilon''(\omega)$  of the complex dielectric constant of the solid can then be described by the formula

$$\epsilon''(\omega) \equiv \frac{c n(\omega) \alpha(\omega)}{\omega} = \frac{e^2}{\epsilon_0 m_e^* \omega^2} \sum_{v,c} \int \frac{2d^3\mathbf{k}}{(2\pi)^3} |\hat{\mathbf{e}} \cdot \mathbf{M}_{cv}(\mathbf{k})|^2 \delta(E_c(\mathbf{k}) - E_v(\mathbf{k}) - \hbar\omega) \quad (B53)$$

The  $\epsilon''(\omega)$ -formula given in Equation (B53) does *not* depend on the index of refraction  $n(\omega)$  of the substance, and hence eliminating the effect of the variation of  $n(\omega)$  with  $\omega$  on its  $\epsilon''(\omega)$ , and is alleged to be the basic formulation that connects its band energy structure with its optical properties. The corresponding  $\epsilon'(\omega)$ -formula can now be found from the Kramers-Kronig  $\epsilon'(\omega)$ -integral relation given in equation (B22) using the  $\epsilon''(\omega)$ -formula of Equation (B53) and making use of the features of Dirac delta function formalism (Bassani & Parravicini, 1975), viz.

$$\epsilon'(\omega) = 1 + \frac{2e^2}{\pi \epsilon_0 m_e^* \omega^2} \sum_{v,c} \int \frac{2d^3\mathbf{k}}{(2\pi)^3} \frac{|\hat{\mathbf{e}} \cdot \mathbf{M}_{cv}(\mathbf{k})|^2}{\{[E_c(\mathbf{k}) - E_v(\mathbf{k})]/\hbar\} * \{[E_c(\mathbf{k}) - E_v(\mathbf{k})]^2/\hbar^2 - \omega^2\}} \quad (B54)$$

The dielectric and optical functions satisfy some general relations, called the sum rules, which are often used to test the consistency of the approximations involved in their computation. The dipole transition matrix elements  $|\hat{\mathbf{e}} \cdot \mathbf{M}_{cv}(\mathbf{k})|^2$  between valence and conduction bands can be taken to be smooth slowly functions of  $\mathbf{k}$  and one can then presume that  $\hat{\mathbf{e}} \cdot \mathbf{M}_{cv}(\mathbf{k})$  is a *constant*, independent of  $|\mathbf{k}|$  of such energy states; so, the contribution to the dielectric function  $\epsilon''(\omega)$  from electronic transitions between a pair of energy bands will be proportional to  $1/\omega^2$  and to a quantity  $J_{cv}(\hbar\omega)$  called the *joint density of states* (JDOS), which is a combined density of pair of states involved in the transition- one occupied and the other empty, separated by an energy  $\hbar\omega$ , that is described by the expression (Bassani & Parravicini, 1975)

$$J_{cv}(\hbar\omega) \equiv \int \frac{2d^3\mathbf{k}}{(2\pi)^3} \delta(E_c(\mathbf{k}) - E_v(\mathbf{k}) - \hbar\omega) \quad (\text{B55})$$

In order to calculate the JDOS, one needs to integrate Equation (B55) over all possible transition channels in the entire first Brillouin zone, which can be made for a given band structure, in terms of which the integral of Equation (B55) can be expressed explicitly via making use of the properties of Dirac delta function given by

$$\int_a^b g(x) \delta[f(x)] dx = \sum_{x_0} g(x_0) \left| \frac{df(x)}{dx} \right|_{x=x_0}^{-1} \quad (\text{B56})$$

The parameter  $x_0$  represents a zero of the function  $f(x)$  contained in the interval  $(a, b)$ . In *three dimensions*, the  $J_{cv}$ -expression of Equation (B55) reduces to the more workable integral-type formula given below (Bassani & Parravicini, 1975; Sólyom, 2009)

$$J_{cv}(\hbar\omega) \equiv \frac{2}{(2\pi)^3} \int \frac{dS_{\mathbf{k}}}{|\nabla_{\mathbf{k}}[E_c(\mathbf{k}) - E_v(\mathbf{k})]|} \quad (\text{B57})$$

where  $dS_{\mathbf{k}}$  represents an infinitesimal areal element in  $\mathbf{k}$ -space for all possible optical transitions on the constant-energy surface defined by the equation  $E_c(\mathbf{k}) - E_v(\mathbf{k}) = E$ . The joint density of states for the interband transitions in a crystalline solid as a function of the energy  $E$  ( $= \hbar\omega$ ) shows strong variations in the neighborhood of certain values of  $E$ , called critical-point energies, where singularities in the JDOS (van-Hove singularities) occur when  $\nabla_{\mathbf{k}} E_c(\mathbf{k}) - \nabla_{\mathbf{k}} E_v(\mathbf{k}) = 0$  at any  $\mathbf{k}$  vector (Bassani & Parravicini, 1975; Sólyom, 2009). In terms of the JDOS  $J_{cv}(\hbar\omega)$  and the dipole transition matrix elements  $|\hat{\mathbf{e}} \cdot \mathbf{M}_{cv}(\mathbf{k})|^2$  between energy states in valence and conduction bands, we can re-write Equation (B53) to get a closed analytical form for the imaginary part  $\epsilon''(\omega)$  of the transverse complex dielectric constant of a crystalline semiconducting substance, which determines the optical absorption in its interband transition region, as (Sólyom, 2009)

$$\epsilon''(\omega) = \frac{e^2}{\epsilon_0 m_e^* \omega^2} \sum_{v,c} |\hat{\mathbf{e}} \cdot \mathbf{M}_{cv}(\mathbf{k})|^2 J_{cv}(\hbar\omega) = \frac{e^2 \hbar^2}{\epsilon_0 m_e^* \omega^2} \sum_{v,c} |\langle c, \mathbf{k} | \hat{\mathbf{e}} \cdot \nabla_{\mathbf{k}} | v, \mathbf{k} \rangle|^2 J_{cv}(\hbar\omega) \quad (\text{B58})$$

To evaluate the closed analytical form for the frequency dependency of  $\epsilon''(\omega)$  corresponding to *direct-band optical absorption* in a crystalline solid, one needs to calculate the momentum matrix element  $\hat{\mathbf{e}} \cdot \mathbf{M}_{cv}(\mathbf{k})$  of the electron-photon interaction Hamiltonian, taken to be independent of radiation frequency  $\omega$  and wavevectors  $\mathbf{k}$  of energies states in its bands, and to find the frequency dependence of the JDOS function  $J_{cv}(\hbar\omega)$ , both of which are dependent on the detailed structure of its valence and conduction energy bands involved in electronic transitions between their energy states, separated by the energy  $\hbar\omega$ . For simple parabolic-like conduction and valence energy bands of an isotropic crystalline solid, in which electrons and holes have the effective masses  $m_e^*$  and  $m_h^*$ , respectively, the lowest energy separation is  $E_c(\mathbf{k}=0) - E_v(\mathbf{k}=0) = E_{g0}$  and the energies of their states having  $|\mathbf{k}|$ -values near  $\mathbf{k}=0$  vary, relative to the valence-band energy  $E_v(\mathbf{k}=0)$ , with  $k$  ( $|\mathbf{k}|$ ) as

$$E_c(\mathbf{k}) = E_v(\mathbf{k}=0) + E_{g0} + \frac{\hbar^2 k^2}{2m_e^*} \quad E_v(\mathbf{k}) = E_v(\mathbf{k}=0) - \frac{\hbar^2 k^2}{2m_h^*}; \quad (\text{B59})$$

The difference in energy  $E_c(\mathbf{k}) - E_v(\mathbf{k})$  of states separated by  $E = \hbar\omega$  can be written in terms of a *reduced* effective mass  $\mu_{eh}^*$  of the exciting electron-hole (e-h) pair as (Christman, 1988)

$$E_c(\mathbf{k}) - E_v(\mathbf{k}) = E_{g0} + \frac{\hbar^2 k^2}{2} \left( \frac{1}{m_e^*} + \frac{1}{m_h^*} \right) = E_{g0} + \frac{\hbar^2 k^2}{2\mu_{eh}^*} \quad (\text{B60})$$

The frequency dependence of the joint-density-of-states  $\mathcal{J}_{cv}(\omega)$  corresponding to the allowed direct interband electronic transitions in a linear, isotropic crystalline solid can now be found from Equation (B57) by integrating over a spherical constant-energy surface of a constant wavevector  $k = (2\mu_{eh}^*/\hbar^2)^{1/2}(\hbar\omega - E_{g0})^{1/2}$ , viz.

$$\mathcal{J}_{cv}(\hbar\omega) = \begin{cases} 0 & \hbar\omega < E_{g0} \\ \frac{1}{2\pi^2} \left( \frac{2\mu_{eh}^*}{\hbar^2} \right)^{3/2} (\hbar\omega - E_{g0})^{1/2} & \hbar\omega \geq E_{g0} \end{cases} \quad (B61)$$

When electromagnetic radiation of photon energies  $\hbar\omega$  smaller than the fundamental absorption edge  $E_{g0}$  of a linear, isotropic crystalline dielectric or semiconducting sample deficient of lattice imperfections and defects, no allowed direct interband electronic transitions (optical absorption) will take place in such a sample and hence the corresponding imaginary part  $\epsilon''(\omega)$  of its complex dielectric constant will be zero, and the sample is said to be transparent; however, for  $\hbar\omega \geq E_{g0}$ , its  $\epsilon''(\omega)$  and absorption coefficient  $\alpha(\omega) \equiv (\omega\epsilon''(\omega)/n(\omega)c)$  due to allowed direct interband transitions are described by, assuming the momentum matrix element  $\hat{\mathbf{e}} \cdot \mathbf{M}_{cv}(\mathbf{k})$  of the electron-photon interaction is frequency and  $|\mathbf{k}|$  independent, the following expressions (Bassani & Parravicini, 1975)

$$\epsilon''(\omega) = \left\{ \frac{e^2}{\epsilon_0 m_e^* \omega^2} \frac{1}{2\pi^2} \left( \frac{2\mu_{eh}^*}{\hbar^2} \right)^{3/2} \sum_{v,c} |\hat{\mathbf{e}} \cdot \mathbf{M}_{cv}(\mathbf{k})|^2 \right\} (\hbar\omega - E_{g0})^{1/2} = A_\epsilon \frac{(\hbar\omega - E_{g0})^{1/2}}{(\hbar\omega)^2} \quad (B62)$$

$$\alpha(\omega) = \left\{ \frac{e^2 \hbar}{\epsilon_0 n(\omega) c m_e^* \omega^2} \frac{1}{2\pi^2} \left( \frac{2\mu_{eh}^*}{\hbar^2} \right)^{3/2} \sum_{v,c} |\hat{\mathbf{e}} \cdot \mathbf{M}_{cv}(\mathbf{k})|^2 \right\} * \frac{(\hbar\omega - E_{g0})^{1/2}}{\hbar\omega} = A_\alpha * \frac{(\hbar\omega - E_{g0})^{1/2}}{n(\omega)\hbar\omega} \quad (B63)$$

The pre-factors  $A_\epsilon$  and  $A_\alpha$  are frequency-independent constants of the material itself. When analyzing variation of  $\alpha(\hbar\omega)$  with photon energy  $\hbar\omega$  in the region of the absorption edge of a crystalline substance, the index of refraction  $n(\omega)$  is often taken to be a slowly-varying function of frequency- that is, treated as a constant value. The contribution of allowed direct interband transitions to the dispersion of the real part  $\epsilon'(\omega)$  of the complex dielectric constant of a defect-free crystalline sample near its absorption edge can be obtained by making use of Equations (B54) and (B60) or by inserting the  $\epsilon''(\omega)$ -expression described in Equation (B62) into the KK  $\epsilon'(\omega)$ -integral given in Equation (B22). The final result can be described by the following expression

$$\epsilon'(\omega) = 1 + \frac{1}{\omega^2} \left\{ \frac{e^2}{\epsilon_0 m_e^* \omega^2} \frac{1}{2\pi^2} \left( \frac{2\mu_{eh}^*}{\hbar^2} \right)^{3/2} \sum_{v,c} |\hat{\mathbf{e}} \cdot \mathbf{M}_{cv}(\mathbf{k})|^2 \right\} \left\{ 2E_{g0} - \sqrt{E_{g0}}(E_{g0} + \hbar\omega)^{1/2} - \sqrt{E_{g0}}(E_{g0} - \hbar\omega)^{1/2} \Theta\{E_{g0} - \hbar\omega\} \right\} \quad (B64)$$

The Heaviside step function  $\Theta\{z\}$  is often defined by the identity (Jackson, 1998)

$$\Theta\{x - x'\} = \begin{cases} 1 & \text{if } x > x' \\ 0 & \text{if } x < x' \end{cases} \quad (B65)$$

Plots of  $\epsilon'(\omega)$ - $\omega$  and  $\epsilon''(\omega)$ - $\omega$  show that  $\epsilon'(\omega)$  displays a maximum at  $\omega_{g0} = E_{g0}/\hbar$  and falls off as  $(E_{g0} - \hbar\omega)^{1/2}$  at frequencies right below  $\omega_{g0}$ . In a direct bandgap crystalline solid there are small changes in the wavevector  $\mathbf{k}$  near absorption edge at  $\mathbf{k} = 0$ , which may originate from scattering of electrons with phonons or other scatterers in solid. Due to scattering processes, *forbidden direct interband* transitions among energy states in valence and conduction bands of slightly different  $\mathbf{k}$  are possible. The transition matrix element probability of *forbidden direct interband transitions* is proportional to  $|\mathbf{k}|^2 \propto (\hbar\omega - E_{g0})$ , giving rise to additional energy dependency for  $\alpha(\omega)$  of a functional form that differs from that governs allowed direct interband absorption processes, viz.

$$\alpha(\omega) = C_\alpha \frac{(\hbar\omega - E_{g0})^{3/2}}{n(\omega)\hbar\omega} \quad (B66)$$

where  $C_\alpha$  is frequency-independent constant of the material and its  $n(\omega)$  is presumed to vary slightly with  $\omega$ .

Now, consider an *indirect bandgap* crystalline material with the empty energy states near the bottom point (minimum) in its conduction band have wavevectors  $c\mathbf{k}$  quite different from the wavevectors  $v\mathbf{k}$  of occupied energy states near the top point (maximum) in a lower valence band. Then electronic transitions induced directly across the absorption-edge bandgap by an electromagnetic field of wavevector  $\mathbf{k}_{ph}$  ( $\ll \mathbf{k}_i, \mathbf{k}_f$ ) are *not allowed* (forbidden) in view of the dipole-approximation momentum conservation (selection) rule of Equation (B47),



which is only applied to direct interband transitions taking place at  $\mathbf{k}_i = \mathbf{k}_f \cong 0$ ; yet, optical transitions between valence-band and conduction-band extrema lying at quite different wavevectors  $\mathbf{v}\mathbf{k}_i$  and  $\mathbf{c}\mathbf{k}_f$  are still possible in an indirect bandgap crystalline substance, albeit they are much weaker than the direct interband transitions. Electronic transitions between extrema (maxima and minima) energy states in the valence and conduction bands of dissimilar wavevectors are usually referred to as *indirect interband transitions*, which only take place via the participation of normal-mode lattice vibrations (phonons), each of which is specified by the wavevector  $\mathbf{q}$ , dispersive frequency  $\omega_{\mathbf{q}}$ , and quantized energy  $\hbar\omega_{\mathbf{q}}$  (Bassani & Parravicini, 1975). The interaction of phonons with radiation-induced electrons (electron-phonon-photon interaction) or one-photon phonon-assisted electronic transition is only possible under energy and momentum conservations (selection rules) given by

$$\hbar\omega - E_g \pm \hbar\omega_{\mathbf{q}} = 0 \quad \mathbf{k}_{ph} + \mathbf{v}\mathbf{k}_i \pm \mathbf{q} = \mathbf{c}\mathbf{k}_f \quad (\text{B67})$$

The energy  $E_g$  corresponds to the energy difference  $E_c(\mathbf{c}\mathbf{k}_f) - E_v(\mathbf{v}\mathbf{k}_i)$  between energy states at the maximum of the valence band having wavevectors  $\mathbf{v}\mathbf{k}_i$  and energy states lying at the minimum of the conduction band having wavevectors  $\mathbf{c}\mathbf{k}_f \neq 0$  ( $\neq \mathbf{v}\mathbf{k}_i$ ). For indirect bandgap materials, this bandgap energy is usually referred to as *indirect bandgap energy*  $E_g^{\text{ind}}$  ( $< E_{g0} = E_c(\mathbf{k} = 0) - E_v(\mathbf{k} = 0)$ , the *direct bandgap energy* of the solid). The  $\pm$  sign in Equation (B67) shows that for electrons in the upper valence-band states to get to energy states at the minimum of the conduction band, *indirect interband transitions* take place by absorption (+) or emission (−) of phonons when the crystal is illuminated with photons of energy  $\hbar\omega < E_g$  or  $\hbar\omega > E_g$ . The formal calculation of the transition probability  $\mathcal{P}_{\mathbf{v}\mathbf{k}_i \rightarrow \mathbf{c}\mathbf{k}_f}$  of indirect band-to-band electronic transitions is too involved and awkward (Bassani & Parravicini, 1975), in addition to that it is of no primary concern in the present work. Therefore, we shall only quote here the final forms for the non-vanishing indirect-band absorption coefficients  $\alpha_{\pm}^{\text{ind}}(\omega)$  for  $\hbar\omega > E_g \mp E_{\text{phon}}$  resulting from absorption (+) and emission (−) of phonons with a quantized energy  $E_{\text{phon}} = k_B\theta = \hbar\omega_{\mathbf{q}_0}$ , the energy of the phonon of wavevector  $\mathbf{q}_0$  that connects extrema of valence and conduction bands involved in allowed indirect interband electronic transitions. The optical absorption spectra accompanying radiation-induced indirect interband transitions are, in contrast to the temperature-independent direct interband transitions, strongly dependent on the absolute sample's temperature  $T$  via the Boltzmann energy factor  $e^{E/k_B T}$  in the Planck's (statistical Bose-Einstein) distribution law describing the average occupation number of phonons (bosons) of energy  $E$  at the temperature  $T$ , where  $k_B$  is the Boltzmann constant (Christman, 1988). The final functional forms of the dependency of  $\alpha_{\pm}^{\text{ind}}(\omega)$  on the photon frequency  $\omega$  are often written as (Bassani & Parravicini, 1975)

$$\alpha_+^{\text{ind}}(\omega) = B \frac{(\hbar\omega - E_g + E_{\text{phon}})^2}{\hbar\omega n(\omega) [e^{+(\hbar\omega_{\mathbf{q}_0}/k_B T)} - 1]}; \quad \alpha_-^{\text{ind}}(\omega) = B \frac{(\hbar\omega - E_g - E_{\text{phon}})^2}{\hbar\omega n(\omega) [1 - e^{-(\hbar\omega_{\mathbf{q}_0}/k_B T)}]} \quad (\text{B68})$$

Experimentally, however, one usually observes the contribution of both of the absorption and emission of phonons involved in allowed indirect electronic transitions in a crystalline solid, giving rise to a total absorption coefficient  $\alpha_{\text{tot}}^{\text{ind}}(\omega) = \alpha_+^{\text{ind}}(\omega) + \alpha_-^{\text{ind}}(\omega)$  that can be described by a compact expression of the form

$$\alpha_{\text{tot}}^{\text{ind}} = \frac{B}{\hbar\omega n(\omega)} \left\{ \frac{(\hbar\omega - E_g + E_{\text{phon}})^2}{[e^{+(\hbar\omega_{\mathbf{q}_0}/k_B T)} - 1]} + \frac{(\hbar\omega - E_g - E_{\text{phon}})^2}{[1 - e^{-(\hbar\omega_{\mathbf{q}_0}/k_B T)}]} \right\} \quad (\text{B69})$$

To a good degree of approximation, the pre-factor  $B$  does not depend on wavevectors in conduction and valence bands and is a constant of the material. The total absorption coefficient  $\alpha_{\text{tot}}^{\text{ind}}(\omega)$  due to allowed indirect interband transitions in a crystalline sample depends quadratically on  $\hbar\omega$  and, for a wavevector  $\mathbf{q}_0$ , both absorbed and emitted phonons can participate in optical transitions. When absorption coefficient of an indirect crystalline sample is plotted against  $\hbar\omega$ , two linear regimes would be obtained for phonon-assisted indirect interband transitions (Bassani & Parravicini, 1975) and their crossings with the  $\hbar\omega$ -axis yield two threshold frequencies (energies):  $\omega_1$  satisfies  $\hbar\omega_1 = E_g - E_{\text{phon}}$ , corresponding to an indirect interband transitions involving absorption of phonons of energy  $\hbar\omega_{\mathbf{q}_0}$  and  $\omega_2$  given by  $\hbar\omega_2 = E_g + E_{\text{phon}}$  related to an indirect interband transition process where phonons of energy  $\hbar\omega_{\mathbf{q}_0}$  are emitted, so,  $\hbar\omega_2 - \hbar\omega_1 = 2E_{\text{phon}} = 2\hbar\omega_{\mathbf{q}_0}$ . The absorption edge frequency  $\omega_g$  (indirect bandgap energy  $E_g = \hbar\omega_g$ ) is  $\omega_g = (\omega_1 + \omega_2)/2$ , while the frequency  $\omega_{\mathbf{q}_0}$  of phonons is  $\omega_{\mathbf{q}_0} = (\omega_2 - \omega_1)/2$ . At a low ambient temperature  $T$ , there are *no phonons to be absorbed* and only  $\alpha_-^{\text{ind}}(\omega)$  due to phonon emission is observed, but upon increasing temperature, contribution of  $\alpha_+^{\text{ind}}(\omega)$  comes in with relative intensity governed by the Boltzmann factor  $e^{\pm(\hbar\omega_{\mathbf{q}_0}/k_B T)}$ . *Forbidden indirect* interband electronic transitions are also possible in an indirect bandgap sample, the variation of its absorption coefficient with the exciting photon energy  $\hbar\omega$  is analogous to that of allowed indirect interband electronic transitions, but with a stronger power-law frequency dependency of the form  $\alpha_{\pm}^{\text{ind}}(\omega) \propto (\hbar\omega - E_g \pm E_{\text{phon}})^3 / \hbar\omega n(\omega)$ ,

however, with much smaller probability of transition compared to that of the allowed indirect band-to-band electronic transitions.

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