

## Optical Properties of Materials

### W8.1 Index Ellipsoid and Phase Matching

In the discussions so far<sup>†</sup> the effect of the crystalline lattice has been omitted. The description of light propagation in solids must take account of the breaking of rotational symmetry by the solid. In this section such effects are considered.

Light propagation in an anisotropic medium is often accompanied by birefringence (i.e., a speed of light that depends on the polarization of the light as well as its direction of propagation). In this section it is shown how the concept of the index ellipsoid can be utilized to determine the index of refraction. Then it is demonstrated how, by cleverly making use of birefringence, one may achieve the phase-matching condition, which is necessary for efficient nonlinear optical effects.

Start with Maxwell's equations, Eqs. (W8A.1) to (W8A.4), in a nonmagnetic material and imagine a plane electromagnetic wave, such as that drawn in Fig. 8.1 of the textbook with frequency  $\omega$  and wave vector  $\mathbf{k}$  propagating through it. Assuming that the fields vary as  $\exp[i(\mathbf{k} \cdot \mathbf{r} - \omega t)]$ , the equations become

$$\mathbf{k} \times \mathbf{E} = \omega \mathbf{B}, \quad \frac{1}{\mu_0} \mathbf{k} \times \mathbf{B} = -\omega \mathbf{D}, \quad (\text{W8.1})$$

$$\mathbf{k} \cdot \mathbf{D} = 0, \quad \mathbf{k} \cdot \mathbf{B} = 0. \quad (\text{W8.2})$$

For a linear, anisotropic dielectric

$$\mathbf{D} = \epsilon_0 \vec{\epsilon}_r \cdot \mathbf{E}, \quad (\text{W8.3})$$

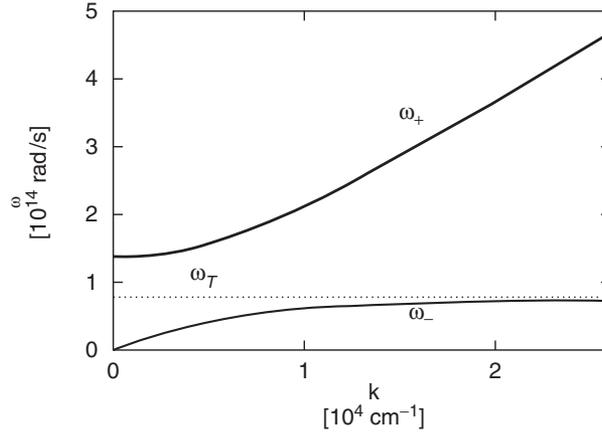
where  $\vec{\epsilon}_r$  is the dielectric tensor. Taking the vector product of Faraday's law with  $\mathbf{k}$  and combining it with the other equations leads to an algebraic form of the wave equation:

$$\mathbf{k} \times (\mathbf{k} \times \mathbf{E}) = \mathbf{k}(\mathbf{k} \cdot \mathbf{E}) - k^2 \mathbf{E} = -\mu_0 \omega^2 \mathbf{D}. \quad (\text{W8.4})$$

Form the scalar product of this equation with  $\mathbf{D}$  to obtain

$$\mathbf{D} \cdot \frac{1}{\vec{\epsilon}_r} \cdot \mathbf{D} = \left(\frac{\omega}{kc}\right)^2 D^2 = \left(\frac{D}{n}\right)^2. \quad (\text{W8.5})$$

<sup>†</sup>The material on this home page is supplemental to *The Physics and Chemistry of Materials* by Joel I. Gersten and Frederick W. Smith. Cross-references to material herein are prefixed by a "W"; cross-references to material in the textbook appear without the "W."



**Figure W8.1.** Polariton branches for MgO, from Eq. (W8.16) using  $\epsilon(0) = 9.8$ ,  $\epsilon(\infty) = 2.95$ , and  $\omega_T = 7.5 \times 10^{13}$  rad/s.

Here  $1/\vec{\epsilon}_r$  is the inverse of the  $\vec{\epsilon}_r$  matrix. The dielectric tensor is symmetric and will therefore be diagonal in some reference frame (called the *principal axis coordinate system*). Choose that frame, defined by the mutually perpendicular unit vectors  $\{\hat{u}_i\}$ , and write, using dyadic notation,

$$\vec{\epsilon}_r = n_1^2 \hat{u}_1 \hat{u}_1 + n_2^2 \hat{u}_2 \hat{u}_2 + n_3^2 \hat{u}_3 \hat{u}_3, \quad (\text{W8.6})$$

where  $n_i = \sqrt{\epsilon_{r_i}}$ . Usually, the set  $\{\hat{u}_i\}$  will coincide with the symmetry axes of the crystal. Thus one finally obtains the pair of equations

$$\sum_i \left( \frac{n \hat{D} \cdot \hat{u}_i}{n_i} \right)^2 = 1, \quad (\text{W8.7})$$

where  $\hat{D} = \mathbf{D}/D$  is the direction of the displacement vector, and

$$\sum_i \hat{D}_i \cdot \hat{u}_i \hat{u}_i \cdot \mathbf{k} = 0. \quad (\text{W8.8})$$

The first formula is the equation of an ellipsoid in  $\mathbf{D}$  space whose axes are aligned with the principal axes and centered at the origin. It is called the *index ellipsoid*. The second equation is that of a plane through the origin in  $\mathbf{D}$  space. The intersection of the plane with the ellipsoid produces the polarization ellipse. The intersection of this ellipse with the unit sphere determines the two pairs of possible directions for polarization of the wave.

Suppose that the vectors  $\mathbf{D}$  and  $\mathbf{k}$  are projected onto the principal axes:

$$\hat{D} = \hat{u}_1 \sin \theta \cos \psi + \hat{u}_2 \sin \theta \sin \psi + \hat{u}_3 \cos \theta, \quad (\text{W8.9})$$

$$\mathbf{k} = k(\hat{u}_1 \sin \alpha \cos \beta + \hat{u}_2 \sin \alpha \sin \beta + \hat{u}_3 \cos \alpha). \quad (\text{W8.10})$$

Then the two conditions become

$$\cos \theta \cos \alpha + \sin \theta \sin \alpha \cos(\beta - \psi) = 0, \quad (\text{W8.11})$$

$$\left(\frac{\sin \theta \cos \psi}{n_1}\right)^2 + \left(\frac{\sin \theta \sin \psi}{n_2}\right)^2 + \left(\frac{\cos \theta}{n_3}\right)^2 = \frac{1}{n^2}. \quad (\text{W8.12})$$

If one were to choose a direction of propagation perpendicular to one of the principal axes (e.g.,  $\hat{u}_3$ ), then  $\alpha = \pi/2$  and  $\sin \theta \cos(\psi - \beta) = 0$ . There are two possibilities:

$$\sin \theta = 0, \quad n = n_3 \equiv n_o, \quad (\text{W8.13a})$$

or

$$|\psi - \beta| = \frac{\pi}{2}, \quad \left(\frac{\sin \theta \sin \beta}{n_1}\right)^2 + \left(\frac{\sin \theta \cos \beta}{n_2}\right)^2 + \left(\frac{\cos \theta}{n_3}\right)^2 \equiv \frac{1}{n_e^2(\theta)}. \quad (\text{W8.13b})$$

Here  $n_o$  is referred to as the *ordinary* index and  $n_e(\theta)$  as the *extraordinary* index.

For crystals, the number of independent indices of refraction depends on the symmetry. For the monoclinic, triclinic, and orthorhombic crystals there are three independent indices. For the hexagonal, tetragonal, and trigonal crystals there are two independent indices. For the cubic class there is only one independent index. For amorphous materials the number of independent elements depends on whether or not there is any remnant orientational or positional order. A glass, which is random on the scale of the wavelength of light, is isotropic and has only one independent element. Liquid crystals may have two independent elements. Quantum-well devices may have two or even three independent elements, depending on the symmetry of the structure. One refers to materials with two independent components as being uniaxially symmetric. In that case, if  $n_1 = n_2$ , the extraordinary index is given by

$$\left(\frac{\sin \theta}{n_1}\right)^2 + \left(\frac{\cos \theta}{n_3}\right)^2 = \frac{1}{n_e^2(\theta)}. \quad (\text{W8.14})$$

A list of indices of refraction for various optical materials is given in Table W8.1. A list of indices of refraction for various semiconductors is given in Table 11.7.

As discussed in Section 8.9, in any nonlinear optical process there are input waves and output waves. One constructs a net input wave by forming the product of the input waves. A similar construct may be formed for the output waves. Associated with these net waves are phases. For the nonlinear process to proceed efficiently, these phases must match each other. There can then be coherent transformation of the net input wave to the output waves over a considerable length in space. The necessity for phase matching occurs in nonlinear optics in processes where photons interact with each other by means of a nonlinear optical material. For example, one may have second-harmonic generation (SHG), where two ordinary wave photons of frequency  $\omega$  and wave vector  $k = \omega n_o(\omega)/c$  combine to form an extraordinary wave photon of frequency  $2\omega$  and wave vector  $2\omega n_e(2\omega, \theta)/c$ . Conservation of momentum then determines the angle  $\theta$  for which phase matching occurs, via  $n_o(\omega) = n_e(2\omega, \theta)$ . Other possibilities exist, such as when an ordinary and an extraordinary photon at frequency  $\omega$  combine to produce an extraordinary photon at  $2\omega$ , where  $n_e(2\omega, \theta) = [n_e(\omega, \theta) + n_o(\omega)]/2$ , and so on.

All nonlinear optical processes make use of phase matching to increase their efficiency. These include third-harmonic generation, three- and four-wave mixing, parametric down-conversion, and stimulated Raman and Brillouin scattering.

**TABLE W8.1** Indices of Refraction for Materials at  $\lambda = 589$  nm (in Vacuum) at  $T = 300$  K

Material	Symmetry	$n_1$	$n_2$	$n_3$
AgCl	Cubic	2.071	—	—
AgBr	Cubic	2.253	—	—
NaCl	Cubic	1.544	—	—
KCl	Cubic	1.490	—	—
ZnSe	Cubic	2.89	—	—
MgO	Cubic	1.736	—	—
C (diamond)	Cubic	2.417	—	—
SrTiO <sub>3</sub>	Cubic	2.403	—	—
Al <sub>2</sub> O <sub>3</sub> (alumina)	Hexagonal	1.768	1.760	—
CaCO <sub>3</sub> (calcite)	Trigonal or hexagonal	1.658	1.486	—
MgF <sub>2</sub>	Tetragonal	1.378	1.390	—
TiO <sub>2</sub> (rutile)	Tetragonal	2.616	2.903	—
As <sub>2</sub> S <sub>3</sub> (orpiment)	Monoclinic	2.40	2.81	3.02
SiO <sub>2</sub> ( $\alpha$ -quartz)	Hexagonal	1.544	1.553	—
SiO <sub>2</sub> (fused silica)	Amorphous	1.458	—	—
SiO <sub>2</sub> (trydimite)	Trigonal	1.469	1.470	1.471
Na <sub>3</sub> AlF <sub>6</sub> (cryolite)	Monoclinic	1.338	1.338	1.339
Cu <sub>2</sub> CO <sub>3</sub> (OH) <sub>2</sub> (malachite)	Monoclinic	1.875	1.655	1.909
KH <sub>2</sub> PO <sub>4</sub>	—	1.510	1.469	—
PMMA	—	1.491	—	—
Polycarbonate	—	1.586	—	—
Polystyrene	—	1.590	—	—

Source: Data from M. J. Weber, *Handbook of Laser Science and Technology*, Vol. III, CRC Press, Boca Raton, Fla., 1986, and other sources.

## W8.2 Polaritons

Infrared radiation propagating through crystals at frequencies close to the optical phonon frequencies propagates as coupled photon–phonon modes, called *polaritons*. Consider, for example, transverse modes. A simple description of these modes follows from combining the optical dispersion formula  $\omega = kc/\sqrt{\epsilon_r(\omega)}$  with a Lorentz oscillator model for the dielectric function introduced in Eqs. (8.23), (8.25), and (8.28). It may be rewritten as

$$\epsilon_r(\omega) = \epsilon_r(0) + \frac{[\epsilon_r(\infty) - \epsilon_r(0)]\omega_T^2}{\omega^2 - \omega_T^2 + i\gamma\omega} \quad (\text{W8.15})$$

for the case of a single oscillator of frequency  $\omega_T$ . Solving the resulting quadratic equation in the variable  $\omega^2$  yields two branches:

$$\omega_{\pm}^2 = \frac{\epsilon_r(0)\omega_T^2 + k^2c^2 \pm \sqrt{(\epsilon_r(0)\omega_T^2 + k^2c^2)^2 - 4\epsilon_r(\infty)(kc\omega_T)^2}}{2\epsilon_r(\infty)}, \quad (\text{W8.16})$$

where  $\gamma \rightarrow 0$ . These branches are plotted in Fig. W8.1 for the case of MgO. The lower branch has long-wavelength behavior given by  $\omega = kc/\sqrt{\epsilon_r(0)}$ , corresponding to a low-frequency photon. The upper branch has the asymptotic behavior  $\omega = kc/\sqrt{\epsilon_r(\infty)}$ , as for a high-frequency photon. The polaritons display the *reststrahl gap*, discussed in Section 8.4, between the frequencies  $\omega_T$  and  $\omega_L = \omega_T\sqrt{\epsilon_r(0)/\epsilon_r(\infty)}$ . The fact that there is no polariton mode between these two frequencies means that propagation of light through the crystal is blocked there and it behaves as a good mirror in that frequency range.

### Appendix W8A: Maxwell's Equations

The laws governing electricity and magnetism are Maxwell's equations. They consist of four equations, which will be presented in SI units:

1. Gauss's law,

$$\nabla \cdot \mathbf{D} = \rho, \quad (\text{W8A.1})$$

where  $\mathbf{D}$  is the electric displacement vector and  $\rho$  is the charge density

2. Gauss's law for magnetism

$$\nabla \cdot \mathbf{B} = 0, \quad (\text{W8A.2})$$

where  $\mathbf{B}$  is the magnetic flux density

3. Faraday's law

$$\nabla \times \mathbf{E} = -\frac{\partial \mathbf{B}}{\partial t}, \quad (\text{W8A.3})$$

where  $\mathbf{E}$  is the electric field

4. Ampère's law, as generalized by Maxwell:

$$\nabla \times \mathbf{H} = \mathbf{J} + \frac{\partial \mathbf{D}}{\partial t}, \quad (\text{W8A.4})$$

where  $\mathbf{H}$  is the magnetic field intensity and  $\mathbf{J}$  is the current density

These equations are supplemented by the constitutive equations

$$\mathbf{D} = \epsilon_0 \mathbf{E} + \mathbf{P}, \quad (\text{W8A.5})$$

where  $\epsilon_0 = 10^7/(4\pi c^2) \approx 8.854 \times 10^{-12} \text{C}^2 \text{N}^{-1} \text{m}^{-2}$  is the permittivity of free space and  $\mathbf{P}$  is the electric polarization vector (the electric dipole moment per unit volume). In addition,

$$\mathbf{B} = \mu_0(\mathbf{H} + \mathbf{M}), \quad (\text{W8A.6})$$

where  $\mu_0 = 4\pi \times 10^{-7} \text{Wb A}^{-1} \text{m}^{-1}$  is the magnetic permeability of free space and  $\mathbf{M}$  is the magnetization vector (the magnetic dipole moment per unit volume).

For linear isotropic materials, one writes Eq. (W8A.5) as

$$\mathbf{D} = \epsilon \mathbf{E} = \epsilon_r \epsilon_0 \mathbf{E}, \quad (\text{W8A.7})$$

where  $\epsilon$  is the permittivity of the material and  $\epsilon_r$  is its dielectric function or *relative permittivity*. The electric susceptibility is defined as  $\chi_e = \epsilon_r - 1$ , so  $\mathbf{P} = \chi_e \epsilon_0 \mathbf{E}$ . Thus  $\epsilon = (1 + \chi_e) \epsilon_0$  and  $\epsilon_r = 1 + \chi_e$ . Also, Eq. (W8A.6) is written as

$$\mathbf{B} = \mu \mathbf{H} = \mu_r \mu_0 \mathbf{H}, \quad (\text{W8A.8})$$

where  $\mu$  is the permeability of the material and  $\mu_r$  is its relative permeability. The magnetic susceptibility is defined as  $\chi_m = \mu_r - 1$ .

Two useful theorems follow from Maxwell's equations. The first is the *continuity equation*, the microscopic form of the law of conservation of charge. Equations (W8A.7) and (W8A.8) will be assumed to apply. Then

$$\nabla \cdot \mathbf{J} + \frac{\partial \rho}{\partial t} = 0, \quad (\text{W8A.9})$$

which follows from taking the divergence of Eq. (W8A.4) and combining it with the time derivative of Eq. (W8A.1), using the identity  $\nabla \cdot \nabla \times \mathbf{H} = 0$ . The second is *Poynting's theorem*, the microscopic form of the law of conservation of energy:

$$\nabla \cdot \mathbf{S} + \frac{\partial u}{\partial t} = -\mathbf{E} \cdot \mathbf{J}, \quad (\text{W8A.10})$$

where  $\mathbf{S}$  is the Poynting vector, whose magnitude is the power per unit area (intensity) carried by the electromagnetic field, defined by

$$\mathbf{S} = \mathbf{E} \times \mathbf{H}, \quad (\text{W8A.11})$$

and  $u$  is the electromagnetic field energy density, given by

$$u = \frac{1}{2} \int (\mathbf{E} \cdot \mathbf{D} + \mathbf{B} \cdot \mathbf{H}) d\mathbf{r}. \quad (\text{W8A.12})$$

The right-hand side of Eq. (W8A.10) gives the work done by the currents on the fields. Equation (W8A.10) follows from taking the scalar product of  $\mathbf{E}$  with Eq. (W8A.4), subtracting the scalar product of  $\mathbf{H}$  with Eq. (W8A.3), and making use of the identity  $\nabla \cdot (\mathbf{E} \times \mathbf{H}) = \mathbf{H} \cdot \nabla \times \mathbf{E} - \mathbf{E} \cdot \nabla \times \mathbf{H}$ .

### Appendix W8B: Nonlocal Dielectric Function

The nonlocal relation between the electric displacement vector and the electric field vector (for linear isotropic materials) is

$$\mathbf{D}(\mathbf{r}, t) = \iint \epsilon(\mathbf{r} - \mathbf{r}', t - t') \mathbf{E}(\mathbf{r}', t') d\mathbf{r}' dt'. \quad (\text{W8B.1})$$

Since the wavelength is much larger than the interatomic spacing, it is reasonable to assume that the dielectric function relating the fields at two points should depend only on the displacement between the two points. The assumption concerning its dependence

on the time difference is valid at frequencies low compared with electronic excitation frequencies. It is an approximation at higher frequencies.

One makes a Fourier expansion of the fields,

$$\mathbf{D}(\mathbf{r}, t) = \iint \mathbf{D}(\mathbf{q}, \omega) e^{i(\mathbf{q}\cdot\mathbf{r} - \omega t)} d\mathbf{q} d\omega, \quad (\text{W8B.2})$$

$$\mathbf{E}(\mathbf{r}, t) = \iint \mathbf{E}(\mathbf{q}, \omega) e^{i(\mathbf{q}\cdot\mathbf{r} - \omega t)} d\mathbf{q} d\omega, \quad (\text{W8B.3})$$

and inserts these expressions in Eq. (W8B.1) to obtain

$$\mathbf{D}(\mathbf{q}, \omega) = \epsilon(\mathbf{q}, \omega) \mathbf{E}(\mathbf{q}, \omega), \quad (\text{W8B.4})$$

where the Fourier-transformed dielectric function is given by

$$\epsilon(\mathbf{q}, \omega) = \int d\mathbf{r} dt \epsilon(\mathbf{r}, t) e^{-i(\mathbf{q}\cdot\mathbf{r} - \omega t)}. \quad (\text{W8B.5})$$

### Appendix W8C: Quantum-Mechanical Derivation of the Dielectric Function

In this appendix the quantum-mechanical derivation of the dielectric function will be given. The Hamiltonian is taken to be

$$H = H_0 - \boldsymbol{\mu} \cdot \mathbf{E}_0 \cos(\omega t) \exp(\alpha t) \equiv H_0 + H_1. \quad (\text{W8C.1})$$

(For technical reasons one introduces a *switching factor*, with parameter  $\alpha \rightarrow 0^+$ , so that the field is turned on slowly from a value of zero at  $t = -\infty$ .) Let the  $n$ th electronic eigenstates of  $H_0$  be denoted by  $|n\rangle$ , where

$$H_0 |n\rangle = \epsilon_n |n\rangle. \quad (\text{W8C.2})$$

To solve the time-dependent Schrödinger equation

$$H |\psi\rangle = i\hbar \frac{\partial}{\partial t} |\psi\rangle, \quad (\text{W8C.3})$$

one writes the wavefunction (approximately) as

$$|\psi\rangle = \exp\left(-\frac{i}{\hbar} E_0 t\right) |0\rangle + \sum_{n>0} a_n(t) \exp\left(-\frac{i}{\hbar} E_n t\right) |n\rangle \quad (\text{W8C.4})$$

and proceeds to solve for the coefficients  $a_n(t)$ . Assuming that the system starts out in state  $|0\rangle$  at  $t = -\infty$ , one obtains

$$a_n(t) = -\frac{i}{\hbar} \int_{-\infty}^t e^{i\omega_n t'} \langle n | H_1 | 0 \rangle dt', \quad (\text{W8C.5})$$

where  $\omega_{n0} = (E_n - E_0)/\hbar$ . The expectation value of the scalar product of the dipole operator with a constant vector  $\mathbf{C}_0$  is

$$\langle \psi | \boldsymbol{\mu} \cdot \mathbf{C}_0 | \psi \rangle = -\frac{1}{2\hbar} \sum_{n>0} \left[ \langle 0 | \boldsymbol{\mu} \cdot \mathbf{C}_0 | n \rangle \langle n | \boldsymbol{\mu} \cdot \mathbf{E}_0 | 0 \rangle \right. \\ \left. \times \left( \frac{e^{-i\omega t}}{\omega - \omega_{n0} + i\alpha} - \frac{e^{i\omega t}}{\omega + \omega_{n0} - i\alpha} \right) + \text{c. c.} \right], \quad (\text{W8C.6})$$

where c.c. means complex conjugate.

The notation is now modified so that the initial state (previously labeled  $|0\rangle$ ) can be any of a set  $\{|m\rangle\}$ , with associated probability  $f_m$ , given by a Fermi factor. Then, by rearranging the indices, one may write

$$\langle \psi | \boldsymbol{\mu} \cdot \mathbf{C}_0 | \psi \rangle = -\frac{1}{2\hbar} \sum_{nm} \left[ \langle n | \boldsymbol{\mu} \cdot \mathbf{C}_0 | m \rangle \langle m | \boldsymbol{\mu} \cdot \mathbf{E}_0 | n \rangle \frac{e^{-i\omega t}}{\omega - \omega_{mn} + i\alpha} (f_n - f_m) + \text{c. c.} \right]. \quad (\text{W8C.7})$$

Dividing by the volume, the expression becomes

$$\frac{1}{V} \langle \psi | \boldsymbol{\mu} \cdot \mathbf{C}_0 | \psi \rangle = \frac{1}{2} \epsilon_0 \mathbf{C}_0 \cdot \tilde{\chi}(\omega) \cdot \mathbf{E}_0 e^{-i\omega t} + \text{c. c.}, \quad (\text{W8C.8})$$

where the dynamic electric susceptibility dyadic is

$$\tilde{\chi}(\omega) = -\frac{1}{\epsilon_0 \hbar V} \sum_{\substack{m,n \\ m \neq n}} \langle n | \boldsymbol{\mu} | m \rangle \langle m | \boldsymbol{\mu} | n \rangle \frac{f_n - f_m}{\omega - \omega_{mn} + i\alpha}. \quad (\text{W8C.9})$$

The dielectric function is

$$\tilde{\epsilon}_r(\omega) = \tilde{I} + \tilde{\chi}(\omega), \quad (\text{W8C.10})$$

where  $\tilde{I}$  is the unit dyadic. In the special case of a crystal, the states are labeled by the quantum numbers  $\{n, \mathbf{k}, s\}$  and the energy eigenvalues are given by  $\epsilon_n(\mathbf{k})$ . Instead of having discrete energy levels, the levels are broadened into bands. The expression for the optical dielectric function becomes

$$\tilde{\epsilon}_r(\omega) = \tilde{I} + \frac{1}{\epsilon_0 V} \sum_{nn'} \sum_{\mathbf{k}\mathbf{k}'} \sum_s \frac{\langle n\mathbf{k} | \boldsymbol{\mu} | n'\mathbf{k}' \rangle \langle n'\mathbf{k}' | \boldsymbol{\mu} | n\mathbf{k} \rangle}{\epsilon_{n'}(\mathbf{k}') - \epsilon_n(\mathbf{k}) - \hbar\omega - i\hbar\alpha} [f_n(\mathbf{k}) - f_{n'}(\mathbf{k}')]. \quad (\text{W8C.11})$$

From Eq. (W8C.11) one sees that the oscillator strengths are determined by the transition matrix elements (i.e., the dipole matrix elements connecting electronic states of the system). Comparing Eqs. (W8C.11) and (8.28), one sees that the resonance frequencies are just the energies of the quantum states divided by Planck's constant.