10.3.2.1.6 Properties of spectral apparatus

Spectral purity depends on the ability of an instrument to isolate a wavelength region. It is characterized by the *full width at half maximum* (FWHM), $\delta\lambda_{0.05}$, and the *full width at hundredth maximum*, $\delta\lambda_{0.01}$, of the spectral band. The term *monochromatic radiation* is used only in an approximate and relative sense, depending on the particular context. In reality, strictly monochromatic radiation does not exist as it indicates radiation of infinitely narrow spectral bandwidth.

The (spectral) *instrumental profile* expressed by the *instrument function* describes the distortion of the registered spectrum as well as the spectral purity obtained with a spectral apparatus. Ideally, if the incident radiation were strictly monochromatic, with wavelength λ, the outgoing intensity should be zero if λ_r differs from the wavelength λ_1 to which the spectral apparatus is set. In practice, however, the outgoing radiant power decays more or less smoothly when $|\lambda_1\text{-}\lambda_r|$ is increased. This decay is described by the instrument function $\psi(\lambda_1\text{-}\lambda)$, which is normalized by setting $\psi(0) = 1$. For a spectral absorption filter, for example, the instrumental profile can be related directly to the transmission factor as a function of wavelength. For a prism monochromator, for example, the instrumental profile is determined by dispersion, slit widths, diffraction effects and optical imperfections.

The width of the instrumental profile is a measure of the spectral purity. The *effective spectral width* may be defined by:

$$\Delta\lambda_{\mathrm{eff}} = \int_0^\infty \psi(\lambda_1 - \lambda)\mathrm{d}\lambda$$

This width may be conceived as the width of an imaginary rectangular instrument profile that has the same area as the actual profile.

Stray radiation is that radiation reaching the detector and having wavelengths outside the spectral band defined by the $\delta\lambda_{0.01}$ of its spectral instrument function. This stray radiation may be *heterochromatic* (consisting of many wavelengths). The ratio of the integrated total stray radiation to the selected radiation within the spectral band is called the *stray radiation factor*.

The *exit spectral slit width* is the product of the exit slit width s_{ex} and the reciprocal linear dispersion $\mathrm{d}\lambda/\mathrm{d}x_{\mathrm{ex}}$, i.e.:

$$\Delta\lambda_{\mathrm{ex}} = s_{\mathrm{ex}} \frac{\mathrm{d}\lambda}{\mathrm{d}x_{\mathrm{ex}}}$$

The *entrance spectral slit width* is the product of the entrance slit width and the reciprocal linear dispersion as measured at the entrance slit, if the radiation passes through the instrument in the reverse direction:

$$\Delta\lambda_{\mathrm{en}} = s_{\mathrm{en}} \frac{\mathrm{d}\lambda}{\mathrm{d}x_{\mathrm{en}}}$$

The *resultant spectral slit width* of a dispersive spectral instrument may be illustrated by the case of a monochromator. Here, the resultant spectral exit slit width $\Delta\lambda_{\mathrm{s}}$ is the larger of the two slit widths viz. the entrance spectral slit width $\Delta\lambda_{\mathrm{en}}$ and the exit spectral slit width $\Delta\lambda_{\mathrm{ex}}$ (see Note 1).

The *resolved wavelength distance* is the minimum wavelength distance between two equally intense spectral lines which can be separated clearly, and whose FWHM in the radiation source are small compared with their wavelength distance. They are considered *resolved lines*, when the intensity registered between the lines is $8/\pi^2$ (=81%) of the intensity of two maxima. This is the modified or *second Rayleigh criterion* (see Note 2).

The *theoretical resolution,* $\delta\lambda$, is the calculated wavelength distance between two equally intense lines where the resolution is limited only by diffraction in such a way that the centre of the *diffraction pattern* from one line coincides with the first minimum from the second (also described as the *first Rayleigh criterion* (see Notes 3,4). In these cases it is assumed that the widths of the slits present are sufficiently small.

Note 1 In a subtractive double monochromator the resultant spectral slit width is the smaller of the spectral slit widths of the two single monochromators.

In an additive double monochromator the resultant spectral slit width is the smallest of the three spectral slit widths including the intermediate slit.

Note 2 If the lines do not have the same intensity, the same criterion may be applied approximately, when the recorded local minimum intensity is compared with the recorded maximum of the less intense line.

Note 3 Under these circumstances the resolved wavelength distance is the same as the half-intensity width of the spectral profile. For this reason, the same symbol $\delta_{\mathrm{o}}\lambda$ is used to denote both concepts.

Note 4 Once the theoretical resolving power R_{o} is known, $\delta_{\mathrm{o}}\lambda$ may be derived from the definition of R_{o}, i.e., $R_{\mathrm{o}} = \lambda/\delta_{\mathrm{o}}\lambda$. The calculation of the theoretical resolution of an instrument follows from the theoretical resolving power according to the relation: $\delta\lambda = \lambda/R_{\mathrm{o}}$, or with dispersive instruments, $\delta_{\mathrm{o}}\lambda = s_{\mathrm{o}}(\mathrm{d}\lambda/\mathrm{d}x)$, where s_{o} is the optimal slit width used.

The *practical resolution*, $\delta\lambda$, is the wavelength distance measured under practical conditions conforming to the criterion given above i.e. that intensity between the lines is 81% of the intensity of the two maxima.

Suitable emission line pairs are not always available so that the practical resolution may be obtained from the width of the instrumental profile measured at $4/\pi_2$ i.e., 40.5% of the maximum intensity. For this measurement, a line, narrow with respect to the width of the instrumental profile, can be used.

The *resolving power* is the ratio of (average) wavelength λ to the resolution $\delta_o\lambda$, i.e.

$$R = \frac{\lambda}{\delta_0 \lambda}$$

This relationship holds for both theoretical and practical resolving powers. The theoretical resolving power may be calculated from the instrument specifications according to the appropriate formulae.

The *practical resolving power* is calculated by using the practical resolution, but with the dimensions of the entrance and exit field stops (e.g., slit widths and lengths) of the collimators being specified.

The *optimal slit width* or *optimal slit length* (see Note 5) in a dispersive instrument is equal to the distance between the main (central) maximum and the first minimum of the *virtual diffraction pattern* produced by the entrance aperture stop in the entrance field stop (see Fig. 10.5).

For a rectangular aperture the expressions are:

$$h_0 = \frac{\lambda f_{\text{en}}}{H_{\text{en}}} = \lambda k_{H,\text{en}};$$

$$s_0 = \frac{\lambda f_{\text{en}}}{B_{\text{en}}} = k_{B,\text{en}};$$

Note 5 Optimal is used in terms of theoretical resolution and optical conductance.

For a circular aperture, the *optimal diameter* is:

$$s_0 = h_0 = 1.22\lambda \frac{f_{\text{en}}}{D} = 1.22 l k_{\text{en}}$$

The *optimal entrance field stop* of a Fabry-Perot interferometer and of a Twyman interferometer is a circle of radius r which depends on the focal length of the entrance collimator and the theoretical resolving power:

$$r_0 = \frac{2 f_{\text{en}}}{R_0}$$

From this it follows that the *optimal field angle* w_o is

$$\tan w_0 = \frac{r_0}{f_{\text{en}}}$$

Radiation proceeds from the source to the detector through the optical system. With proper imaging, this process can be described using the concept of *optical conductance*.

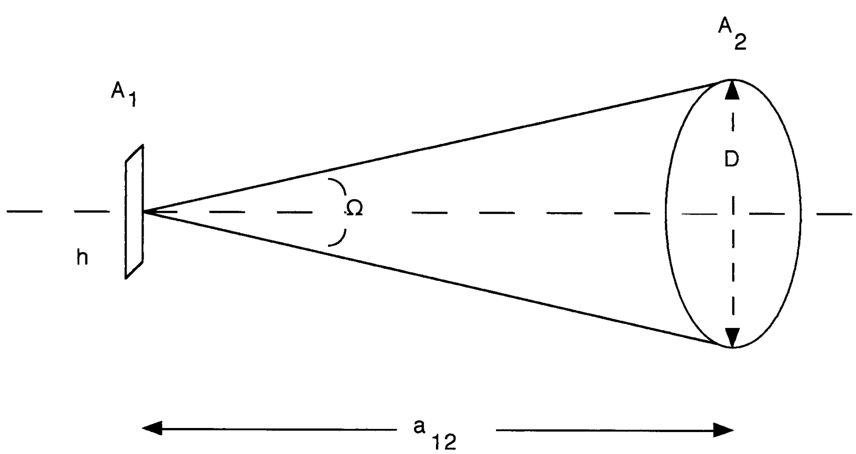

Fig. 10.6 Illustrating the approximate geometrical conductance of a collimator in a spectral apparatus

In the simple case indicated in Fig. 10.6 the *geometrical conductance* G_o of the entrance collimator is defined as the product of the entrance slit area A_1 and the solid angle Ω subtended by the collimator lens measured from the centre of the slit. Defining A_2 as the area of the entrance aperture stop, we have:

$$G_0 = \frac{A_1 A_2}{a_{12}^2}$$

where a_{12} is the distance between A_1 and A_2.

This is an approximation of the correct expression

$$G = \int_{A_1} \int_{A_2} \frac{\cos\alpha_1 \cos\alpha_2}{a_{12}^2} \mathrm{d}a\mathrm{d}a \quad \text{(see Fig.10.7)}$$

where α_1 and α_2 represent the angles between the normals of the surface elements $\mathrm{d}A_1$ and $\mathrm{d}A_2$ to their corresponding connecting straight lines. When the apertures A are small compared to the square of the distance a_{12} and perpendicular to the connecting line, the former equation is obtained.

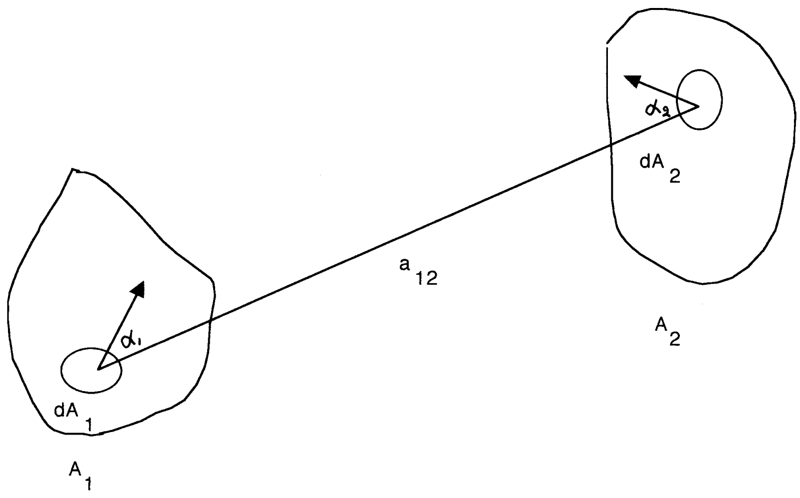

Fig.10.7 General Principles of Geometrical Conductance

The geometrical conductance of a spectral apparatus with a rectangular slit and entrance aperture stop can be expressed by:

$$G_0 = \frac{s_{en} h_{en} B_{en} H_{en}}{f_{en}{}^2} = \frac{\lambda^2 s_{en} h_{en}}{s_0 h_0}$$

The *optical conductance*, G, is the product of the geometrical conductance G_o and the square of the refractive index of the medium between the planes A_1 and A_2:

$$G = G_o n^2.$$

The *effective optical conductance*, G_{eff}, is the product of the transmission factor τ and the optical conductance G:

$$G_{eff} = \tau\, G.$$

It determines the *radiant power* ϕ conducted from a source having the *radiance* L through the instrument:

$$\phi = L\, G_{eff} \qquad \text{(see Note 6)}$$

Note 6 When the various conductances depend on the wavelength, they can be written more precisely $G_o = G_o(\lambda)$, $G = G(\lambda)$ and $G_{eff} = G_{eff}(\lambda)$, respectively.

The *spectral optical conductance of a monochromator*, G_λ, is the quotient of the optical conductance and the resultant spectral width:

$$\lambda = \frac{G}{\Delta\lambda_s}$$

The *effective spectral optical conductance of a monochromator*, $G_{\lambda,\text{eff}}$, is the product of the spectral optical conductance and its transmission factor:

$$G_{\lambda,\text{eff}} = \tau\, G_\lambda$$

The radiant power ϕ_U, with the proper imaging of a *continuum source*, and with a spectral radiance of $L\lambda$ is given by the relationship:

$$\phi_{\lambda U} = L_\lambda\, G_{\lambda,\text{eff}}(\Delta\lambda_s)^2 = L_\lambda\, G_{\text{eff}}\, \Delta\lambda$$

The radiant power, ϕ_L, with the proper imaging of a *spectral line source* with a total radiance:

$$L_0 = \int_0 L_\lambda \mathrm{d}\lambda$$

is given by the relationship:

$$\phi_L = L_o\, G_{\lambda,\text{eff}}\, \Delta\lambda_s\, F(\lambda_L \lambda_{\text{eff}}),$$

in which F denotes (in the plane of the exit slit) the convolution integral, normalized to 1, of the instrument function ψ and the *physical line profile function* of the spectral line $g(x)$, also normalized to 1 by:

$$\int_{\infty}^{-\infty} g(x)dx = 1$$

The complete expression for F is as follows:

$$F(\lambda_L, \delta\lambda_{\text{eff}}) = \int_{1/2\hat{\mathbf{s}}_{\text{ex}}}^{-1/2\hat{\mathbf{s}}_{\text{ex}}} dx \int_{\infty}^{-\infty} \psi(x' - x) g(x') dx'$$

where

$$x = R_0 \frac{\lambda - \lambda_L}{\lambda_L} \quad \text{and} \quad \hat{s}_{\text{ex}} = \frac{s_e}{s_0}$$

are reduced dimensionless variables which are useful for matching different spectral apparatus.