

An Analytical Expression for Fractional Absorption in Mössbauer Spectroscopy

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Removing the restriction that the line widths (Γ_s and Γ_a) of a source and an absorber be equal, we have obtained an exact analytical expression for the fractional intensity of absorbed γ -rays in Mössbauer spectroscopy. This expression is compact and consists of three terms; the first two are known in the literature for the case $\Gamma_s = \Gamma_a$, and the third term contains a simple sum of higher-order terms arising from $\Gamma_s \neq \Gamma_a$. We provide quantitative analyses and a discussion of the contribution from this third term and its effect on the fractional absorption of a Mössbauer spectral line.

Index Terms—Bessel functions, gamma-ray absorption, Mössbauer spectroscopy, spectral analysis, transmission integral.

I. INTRODUCTION

MÖSSBAUER spectroscopy is a well-established methodology for characterizing magnetic materials and studying hyperfine interactions. In Mössbauer effect studies, ⁵⁷Fe is the most widely used isotope, followed by several rare-earth elements, all of which are commonly found in magnetic materials. Mössbauer spectra can therefore provide a wealth of information related to magnetic properties of materials, including alloys, ceramics, iron-oxides, and nanostructured composites. As Mössbauer spectra can be recorded more and more accurately, the desire for a better determination of spectral parameters also increases. In this work, we have obtained an exact analytical expression for the fractional intensity of absorbed gamma-rays, without the assumption that the line widths (Γ_s and Γ_a) of a source and an absorber be equal. This expression is compact and consists of three terms; the first two are known in the literature for the case $\Gamma_s = \Gamma_a$, and the third contains a simple sum of higher order terms arising from $\Gamma_s \neq \Gamma_a$. We also provide quantitative analyses and a discussion of the contribution from this third term and its effect on a Mössbauer absorption line.

In Mössbauer spectroscopy, a spread of resonance energies is always observed, even in a spectrum with a single-line source and single-line absorber. This inherent line width arises not only from the natural widths of the emission and absorption processes, but also from further broadening by any small variations in local isomer shift and other hyperfine interactions. In addition, it can be caused by possible lattice defects in the sample, by slight imperfections in the velocity modulation of the spectrometer, etc. Therefore, both the emission line width of the source (Γ_s) and the absorption line width of the absorber (Γ_a) may be larger than the corresponding natural line width (Γ_n) associated with the nuclear transition. More importantly, Γ_s and Γ_a are not guaranteed to be the same but may differ significantly from each other.

The simplest Mössbauer spectrum in transmission geometry is from a single-line source with a single-line absorber. The

spectral line shape of such absorption can be theoretically predicted. Assuming Lorentzian energy profiles for both emission and absorption, researchers have developed a line-shape theory using a convolution integral between emission and absorption. Several results of the convolution integral (also known as transmission integral, line-shape function, or absorption curve) have been obtained; some are approximate; others are accurate. Early efforts on calculating the convolution integral were limited to the degenerate case of $\Gamma_s = \Gamma_a$ and aimed at a simple and exact expression, an example of which is the pioneering work by Ruby and Hicks [1]. However, the need for a general expression in the case of $\Gamma_s \neq \Gamma_a$ was soon recognized. The approaches to this problem have been mainly within two categories, using approximations or using infinite series. For example, O'Connor [2] calculated the convolution with two separate approximations, one for thin absorbers and the other for thick ones, and spliced the two regions together. Using the method of infinite series, Cleveland [3] obtained an exact expression in the form of a rapidly converging series where the terms were generated by a recursive relation. Mullen *et al.* [4] derived expressions for the area under the absorption curve and the resonance peak height using Fourier transform, and Flores-Llamas [5] used Chebyshev polynomials to express the single-line convolution integral. However, these results are mathematically cumbersome and difficult to apply because of the infinite series. In 1995, Capaccioli *et al.* [6] used a set of ingenious substitutions in the integral and arrived at a relatively condensed expression of the line shape for the general case $\Gamma_s \neq \Gamma_a$.

In this paper, we have evaluated Capaccioli's result at the resonance peak, which allowed us to carry out further simplifications, and we obtained an analytical expression which is exact, compact, and explicitly depends on Γ_s and Γ_a . This expression also allows us to discuss the impact on the spectral analysis when the restriction of $\Gamma_s = \Gamma_a$ is relaxed in the line-shape theory.

II. RESULTS

In transmission Mössbauer spectroscopy, radiation from a source is perpendicularly incident upon an absorber of uniform thickness d . The gamma-ray energy E_0 is modulated by a Doppler velocity v and becomes $E_0 + E_0v/c$. In a transmission Mössbauer spectrum, an absorption peak is indicated by the on-resonance counting rate $I(v)$ as a function of the source velocity v (Fig. 1). $I(v)$ is reduced from the off-resonance

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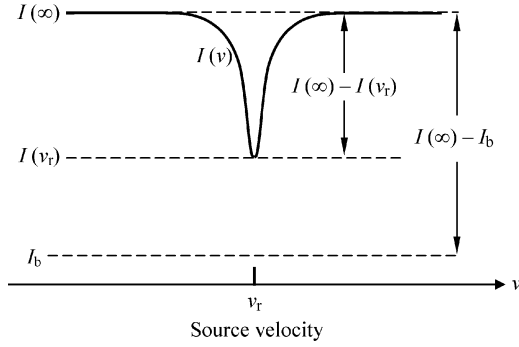


Fig. 1. Definitions of counting rates: on-resonance $I(v)$, off-resonance $I(\infty)$, and background I_b . The ratio between $I(\infty) - I(v)$ and $I(\infty) - I_b$ is defined as the fractional absorption $\varepsilon(v)$. The maximum fractional absorption $\varepsilon(v_r)$ occurs at $v = v_r$.

counting rate $I(\infty)$ corresponding to source and absorber completely out of resonance.

If we use I_b to represent the background counting rate, then the fractional absorption can be experimentally measured as

$$\varepsilon(v) = \frac{I(\infty) - I(v)}{I(\infty) - I_b}. \quad (1)$$

Theoretically, we assume that the source emission spectrum is a normalized Lorentzian

$$L\left(E - E_0 - E_0 \frac{v}{c}, \Gamma_s\right) = \frac{\Gamma_s/2\pi}{(E - E_0 - E_0 v/c)^2 + (\Gamma_s/2)^2} \quad (2)$$

centered at E_0 with a full-width at half-maximum Γ_s and modulated by v . Similarly, we assume that the absorption cross-section is also a Lorentzian

$$S(E - E'_0, \Gamma_a) = \frac{(\Gamma_a/2)^2}{(E - E'_0)^2 + (\Gamma_a/2)^2} \quad (3)$$

centered at E'_0 with a line width Γ_a . The spectral line shape is theoretically calculated by the following convolution integral [6]:

$$\varepsilon(v) = f_s \int_{-\infty}^{+\infty} L(E - E_0 - E_0 v/c, \Gamma_s) \times \{1 - \exp[-t_a S(E - E'_0, \Gamma_a)]\} dE \quad (4)$$

where t_a is the effective thickness of the absorber and f_s is the recoilless fraction of the source. The effective thickness t_a is a dimensionless parameter defined as $t_a = n_a f_a \sigma_0 d$, where n_a is the number of Mössbauer nuclei per gram, f_a is the recoilless fraction, σ_0 is the maximum cross-section (cm^2), and d is the thickness (g/cm^2), all quantities pertaining to the absorber [7].

To calculate this convolution integral, Capaccioli *et al.* [6] devised a series of substitutions

$$\begin{aligned} y &= \frac{2(E_0 + E_0 v/c - E'_0)}{\Gamma_a} \\ \xi &= \frac{\Gamma_s}{\Gamma_a} \\ \rho \cos \theta &= \frac{y^2 + \xi^2 - 1}{y^2 + \xi^2 + 1} \\ \rho \sin \theta &= \frac{-2y}{y^2 + \xi^2 + 1} \end{aligned}$$

and obtained an expression in terms of the modified Bessel functions $I_n(x)$

$$\frac{\varepsilon(v)}{f_s} = 1 - e^{-t_a/2} \left\{ I_0\left(\frac{t_a}{2}\right) + \sum_{n=1}^{\infty} \left[\left(\frac{1 - \sqrt{1 - \rho^2}}{\rho} e^{i\theta} \right)^n + \left(\frac{1 - \sqrt{1 - \rho^2}}{\rho} e^{-i\theta} \right)^n \right] I_n\left(\frac{t_a}{2}\right) \right\} \quad (5)$$

where each of the parameters ρ and θ is a function of the source velocity v and the ratio ξ . At maximum absorption $v = v_r$, the modulated source energy ($E_0 + E_0 v_r/c$) matches the absorber's center energy E'_0 , and it is easy to see that

$$y = 0 \quad \theta = 0 \quad \rho = \frac{\xi^2 - 1}{\xi^2 + 1}. \quad (6)$$

The quantity $\varepsilon(v_r)$ represents the maximum fractional absorption of a Mössbauer line, or the peak height of the resonance absorption curve. Obviously, it is one of the important parameters in the quantitative analysis of any Mössbauer spectrum.

We now describe our present work of evaluating (5) to obtain fractional absorption $\varepsilon(v_r)$ at the resonance peak and converting it analytically to a more compact and useful formula. By introducing a new quantity

$$\alpha = \frac{1 - \sqrt{1 - \rho^2}}{\rho} \quad (7)$$

and using $\theta = 0$, (5) can be written as

$$\frac{\varepsilon(v_r)}{f_s} = 1 - e^{-t_a/2} \left\{ I_0\left(\frac{t_a}{2}\right) + 2 \sum_{n=1}^{\infty} \alpha^n I_n\left(\frac{t_a}{2}\right) \right\}. \quad (8)$$

We have discovered that α can be drastically reduced, and it has a surprisingly simple dependence on ξ . From (6), we have

$$\begin{aligned} \sqrt{1 - \rho^2} &= \sqrt{(1 - \rho)(1 + \rho)} = \sqrt{\left(\frac{2}{\xi^2 + 1}\right) \left(\frac{2\xi^2}{\xi^2 + 1}\right)} \\ &= \frac{2\xi}{\xi^2 + 1} \end{aligned}$$

and (7) becomes

$$\begin{aligned} \alpha &= \frac{1}{\rho} (1 - \sqrt{1 - \rho^2}) = \frac{\xi^2 + 1}{\xi^2 - 1} \left(1 - \frac{2\xi}{\xi^2 + 1}\right) \\ &= \frac{\xi^2 - 2\xi + 1}{\xi^2 - 1} = \frac{(\xi - 1)^2}{(\xi + 1)(\xi - 1)} = \frac{\xi - 1}{\xi + 1}. \end{aligned} \quad (9)$$

Substituting this relationship into (8), the fractional absorption of a Mössbauer spectral line can now be written explicitly in terms of the ratio ξ

$$\frac{\varepsilon(v_r)}{f_s} = 1 - e^{-t_a/2} I_0\left(\frac{t_a}{2}\right) - 2e^{-t_a/2} \sum_{n=1}^{\infty} \left(\frac{\xi - 1}{\xi + 1}\right)^n I_n\left(\frac{t_a}{2}\right). \quad (10)$$

This result provides an exact expression for the dependence of $\varepsilon(v_r)$ on the three important physical parameters, t_a , Γ_s , and Γ_a for the general case of $\Gamma_s \neq \Gamma_a$. It is also mathematically straightforward, because the modified Bessel functions can be easily calculated by the following fast converging series:

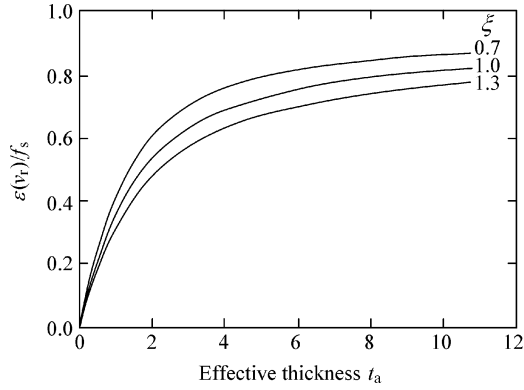


Fig. 2. Fractional absorption $\varepsilon(v_r)/f_s$ as a function of effective thickness t_a for $\xi = 0.7, 1.0$, and 1.3 .

$$I_n(x) = \left(\frac{x}{2}\right)^n \sum_{k=0}^{\infty} \frac{(x/2)^{2k}}{k!(k+n)!}, \quad (n = 0, 1, 2, 3, \dots) \tag{11}$$

III. DISCUSSION

In the literature, a well-known result [1] for fractional absorption (assuming $\Gamma_s = \Gamma_a$) is

$$\frac{\varepsilon(v_r)}{f_s} = 1 - e^{-t_a/2} I_0\left(\frac{t_a}{2}\right) \tag{12}$$

which can be identified as the first two terms in our result (10), as well as in Capaccioli’s result (5). But in (10) it is much easier to see how restricting $\Gamma_s = \Gamma_a$ (i.e., $\xi = 1$) would make all high-order terms vanish, which is not immediately discernible in (5). Therefore, the first two terms in our result are consistent with the literature, and the third term

$$\varepsilon_3 = -2e^{-t_a/2} \sum_{n=1}^{\infty} \left(\frac{\xi - 1}{\xi + 1}\right)^n I_n\left(\frac{t_a}{2}\right) \tag{13}$$

represents an additional contribution when ξ deviates from unity. It should be noted that not only does this correctional term ε_3 depend on ξ , it is also a function of the effective thickness t_a of the absorber. We now discuss how ξ and t_a affect ε_3 and therefore influence the fractional absorption $\varepsilon(v_r)$.

The known properties of the modified Bessel functions $I_n(x)$ allowed us to carry out several specific analyses. The dependence of $\varepsilon(v_r)/f_s$ on t_a for three different ξ -values is plotted in Fig. 2. The curve corresponding to $\xi = 1.0$ is completely consistent with that given in [1]. Because $I_n(t_a/2)$ is always positive, the sign of ε_3 is solely determined by the factor $(\xi - 1)/(\xi + 1)$. It follows that, when $\xi > 1$, $\varepsilon(v_r)/f_s$ becomes smaller, and when $\xi < 1$, $\varepsilon(v_r)/f_s$ is larger. A Mössbauer source is usually carefully manufactured from the best possible crystalline material. Consequently, the line width of the source (Γ_s) is minimized, but the line width of the absorber (Γ_a) may not be as ideal; therefore, one usually encounters the case $\Gamma_s < \Gamma_a$ (i.e., $\xi < 1$), giving higher fractional absorption than in the case of $\Gamma_s = \Gamma_a$.

Our result in (13) represents a correction that needs to be added to (12) when the line widths of the source and absorber are different, $\Gamma_s \neq \Gamma_a$. This contribution ε_3 is plotted against t_a

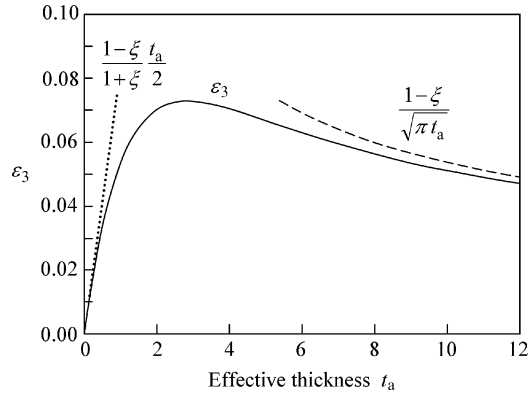


Fig. 3. (Solid curve) The correctional term ε_3 as a function of t_a for $\xi = 0.7$. (Dotted line) The initial linear growth $\varepsilon_3 \approx [(1 - \xi)/(1 + \xi)](t_a/2)$ for small t_a . (Dashed curve) The asymptotic behavior $\varepsilon_3 \approx (1 - \xi)(\pi t_a)^{-1/2}$ for large t_a .

for $\xi = 0.7$ in Fig. 3. After an initial linear growth, ε_3 quickly reaches its maximum and then decreases gradually. For a particular ξ , ε_3 is a product of two functions: one decreases exponentially as $\exp(-t_a/2)$, and the other increases according to a polynomial of t_a . A maximum value of ε_3 is expected near where these two functions intersect. Our calculation using terms up to $n = 15$ shows that ε_3 reaches its maximum at $t_a = 2.8$ when $\xi = 0.7$. For a practical absorber with an effective thickness of $t_a = 1$, ε_3 is 0.054, and (10) gives $\varepsilon(v_r)/f_s = 0.409$ (for $\xi = 0.7$). Compared to $\varepsilon(v_r)/f_s = 0.355$ assuming $\xi = 1$ and according to (12), the correctional term causes an increase of 15%, which is definitely not negligible.

For a very small t_a (thin absorber limit), we may make a first-order approximation $I_1(t_a/2) \approx t_a/4$ and neglect all higher order terms in (13), resulting in

$$\varepsilon_3 \approx \frac{1 - \xi t_a}{1 + \xi 2}. \tag{14}$$

This small contribution from ε_3 has a simple dependence on ξ , and it is linear with respect to t_a . As indicated in Fig. 3, ε_3 initially grows linearly with t_a , at a rate dictated mainly by how much ξ deviates from 1.

For large t_a -values (thick absorbers), these Bessel functions become approximately independent of n

$$I_n\left(\frac{t_a}{2}\right) \approx \frac{1}{\sqrt{\pi t_a}} e^{t_a/2}, \quad (n = 1, 2, 3, \dots) \tag{15}$$

and the summation in (13) becomes a geometric series

$$\varepsilon_3 \approx -\frac{2}{\sqrt{\pi t_a}} \sum_{n=1}^{\infty} \left(\frac{\xi - 1}{\xi + 1}\right)^n = -\frac{2}{\sqrt{\pi t_a}} \frac{\xi - 1}{2} = \frac{1 - \xi}{\sqrt{\pi t_a}}. \tag{16}$$

Evidently, it is a linear function of ξ and only weakly dependent on t_a . This behavior is indicated in Fig. 3 by the dashed curve, and it asymptotically approaches the exact ε_3 .

IV. CONCLUSION

Our result in this work provides an analytical expression of the fractional absorption $\varepsilon(v_r)$ for a more accurate and convenient determination of spectral parameters. This formula is exact, compact, and explicit in its dependence on the ratio $\xi = \Gamma_s/\Gamma_a$. It can be used to calculate the absorption peak height

and carry out accurate spectral simulations, even when the absorber line width differs significantly from the source line width. More importantly, the explicit dependence on ξ provides us the opportunity to gain a better understanding of the spectral behavior for different ξ -values and for different absorber thicknesses. Specifically, our analytical result allows us to conclude that: 1) the high-order terms usually have a positive contribution and thus increase the fractional absorption at resonance; 2) for $t_a = 1$, such increase is about 15% when $\xi = 0.7$; and 3) a maximum increase occurs near $t_a = 2.8$ and thereafter only declines slightly.

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