Comment on “Effective field parameters in iron Mössbauer spectroscopy” [J. Chem. Phys. 47, 961 (1967)]

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While the Mössbauer spectrum of a magnetically ordered powder sample can be used to determine the direction of the local hyperfine field \(B_h\) in the coordinate system defined by the electric field gradient (efg) tensor, the spectrum of an oriented single-crystal provides a direct measurement of the principal axis \(B_h\) through the observed line intensities. Several solutions to the general static Mössbauer problem for M1 transitions (relevant for the two most commonly used Mössbauer isotopes: \(^{57}\text{Fe}\) and \(^{119}\text{Sn}\) have been published, and all can be adapted to computer code to fit the relevant experimental variables. Unfortunately there is an error in Eq. (12) from Hoy and Chandra\(^2\) and both the sign of the last term and the sign of the exponent in the last term are incorrect. For single-crystal samples, this leads to a severe mis-calculation of line intensities when the angle \(\gamma\) between \(B_h\) and the principal axis of the efg tensor \((V)\) is non-zero, and so code based on this expression (see, for example, Ref. 4) gives incorrect fits.

Starting from Eq. (11) of Hoy and Chandra\(^2\) for the intensity, \(I(\Lambda^e_1 \leftrightarrow \Lambda^s_1)\), of the transition between the excited state, \(\Lambda^e_1\), and ground state, \(\Lambda^s_1\):

\[
I(\Lambda^e_1 \leftrightarrow \Lambda^s_1) = |a_{11}b_{1j}^+|\left(\frac{1}{2} \frac{1}{2} 1 \frac{1}{2} \frac{1}{2} \frac{1}{2} \frac{1}{2}\right)|\chi^1_1|^2 + a_{22}b_{2j}^+|\frac{1}{2} \frac{1}{2} 0 \frac{1}{2} \frac{1}{2} \frac{1}{2} \frac{1}{2}|\chi^0_1|^2
\]

Defining

\[
A = a_{11}b_{1j}^+ + \frac{1}{\sqrt{3}}a_{22}b_{2j}^+,
\]

\[
B = \frac{1}{\sqrt{3}}(a_{22}b_{1j}^+ + a_{33}b_{2j}^+)
\]

\[
C = a_{44}b_{3j}^+ + \frac{1}{\sqrt{3}}a_{22}b_{2j}^+
\]

then substituting \(A, B, \text{ and } C\) into Eq. (1), and expanding gives

\[
I(\Lambda^e_1 \leftrightarrow \Lambda^s_1) = |A|^2|\chi^1_1|^2 + |B|^2|\chi^0_1|^2 + |C|^2|\chi^{1-1}_1|^2
\]

\[
+ 2Re[AB^*\chi^0_1\chi^{0*}_1] + 2Re[AC^*\chi^{1}_1\chi^{-1*}_1]
\]

\[
+ 2Re[BC^*\chi^0_1\chi^{-1*}_1].
\]

The relevant \(\chi^m_1\) dot products are

\[
|\chi^1_1|^2 = |\chi^{1-1}_1|^2 = 1 + \cos^2 \theta, \quad |\chi^0_1|^2 = 2 \sin^2 \theta,
\]

\[
\chi^0_1 \chi^{0*}_1 = \chi^{1-1}_1 \chi^{-1*}_1 = \sqrt{2} e^{i\phi} \sin \theta \cos \theta,
\]

where \(\theta\) and \(\phi\) denote the polar and azimuthal angles, respectively, of the absorbed \(\gamma\) with respect to the principal axis of the electric field gradient. The error propagating from the original work\(^2\) was introduced in the dot product terms represented by Eq. (6) above. Substituting the \(\chi^m_1\) products into Eq. (3) gives

\[
I(\Lambda^e_1 \leftrightarrow \Lambda^s_1) = (|A|^2 + |C|^2)(1 + \cos^2 \theta) + |B|^2 2 \sin^2 \theta
\]

\[
+ 2Re[AB^*\sqrt{2} e^{i\phi} \sin \theta \cos \theta]
\]

\[
+ 2Re[AC^* e^{2i\phi} \sin^2 \theta]
\]

\[
- 2Re[BC^* \sqrt{2} e^{i\phi} \sin \theta \cos \theta].
\]

This confirms the expression for the intensity from Voyer and Ryan.\(^3\) It should be noted that the powder solution...
provided by Hoy and Chandra\textsuperscript{2} is correct, however single-crystal code developed using the Hoy and Chandra\textsuperscript{2} intensity expression will provide inconsistent values for the hyperfine parameters.

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\textsuperscript{6}For clarity, a common pre-factor of $\frac{1}{16\pi}$ has been omitted from Eqs. (4)–(8).