Mössbauer Spectrum in a fluctuating Environment

February 28, 2016

1 The inversion solution decomposed

The original solution of M. Blume and J.A. Tjon (1976)[1] of the "Mössbauer spectrum in a fluctuating environment" ends up with an inversion of a matrix for each velocity point. Later (1970) M.J. Clauser [2] published the paper " Relaxation Effects in Spectra: Eigenvalue treatment of Superoperators". In that paper it is shown, that the spectrum is a sum of resonance lines. For a special case of $\pm H$ fluctuation of the the hyperfine field the solution of Blume & Tjon is decomposed (partial fraction decomposition) to a sum of resonance lines. The result gives some insight in the origion of lineshifts and broadening, especially the condition of the collaps of resonance lines.

2 Appendix B of M. Blume and J.A. Tjon[1]

The emission probabilty W

$$W = \frac{2}{\Gamma} Re \sum_{m_0 m_1} \frac{1}{4} \left| \langle I_0 m_0 | H^{(+)} | I_1 m_1 \rangle \right|^2 \sum_{ij} p_i (j | [\widetilde{A}^{-1}(p) + 3Q^2 \eta^2 \widetilde{B}(p)]^{-1} | i) \tag{1}$$

Performing the matrix inversion (decomposes to 2x2 matrices) the sum is written as the ratio

$$\sum_{ij} p_i (j | [\widetilde{A}^{-1}(p) + 3Q^2 \eta^2 \widetilde{B}(p)]^{-1} | i) = N/D \tag{2}$$

where

$$\begin{aligned} N &= d(p + i\beta + 2w) + 3Q^2\eta^2(p - i\beta) \qquad (3)\\ D &= d[(p + i(\beta - C_1 + C_0) + w)(p + i(\beta + C_1 - C_0) + w) - w^2] \\ &\quad +3Q^2\eta^2[(p + i(\beta + C_1 - C_0) + w)(p - i(\beta - C_1' + C_0) + w) \\ &\quad +(p + i(\beta - C_1 + C_0) + w)(p - i(\beta + C_1' - C_0) + w) + 2w^2 + 3Q^2\eta^2] \end{aligned}$$

and d

$$d = (p - i\beta)^2 + (C_1' - C_0)^2 + 2w(p - i\beta) \tag{4}$$

$p_i = 1/2$ and $w = w_{+-} = w_{-+}$ were used. Further on

$$\begin{aligned} p &= -i(\omega - \omega_0) + \frac{1}{2}\Gamma \\ C_1 &= g_1 m_1 \mu h \\ C_1' &= g_1(m_1 \pm 2)\mu h \\ C_0 &= g_0 m_0 \mu h h \\ \beta &= Q(3m_1^2 - 15/4) \end{aligned} \tag{5}$$

Here the simple case Q=0 is considered such that N/D reduces to

$$\begin{aligned} N/D &= \frac{(p+2w)}{(p - i(C_1 - C_0) + w)(p + i(C_1 - C_0) + w) - w^2} \\ &= \frac{(p+2w)}{p^2 + \omega_n^2 + 2pw} \\ \omega_n &= (C_1 - C_0) = (g_1 m_1 - g_0 m_0)\mu h \end{aligned} \tag{6}$$

N/D shall be written as a sum of 2 Lorentz curves such the the number of Lorentzians is 2 times the number of allowed (by the Clebsch Gordon coefficients) m_1, m_0 pairs. The partial fraction decomposition determines the constants δ, ζ for the nominators, $\Gamma_\delta, \Gamma_\zeta$ for the linewidth and $\omega_\delta, \omega_\zeta$ for the positions of the Lorentzians.

$$\frac{(p+2w)}{p^2 + \omega_n^2 + 2pw} = \frac{\delta}{i(\omega - \omega_\delta) + \frac{\Gamma_\delta}{2}} + \frac{\zeta}{i(\omega - \omega_\zeta) + \frac{\Gamma_\zeta}{2}} \tag{7}$$

This equality for all ω is obtained with

$$\omega_\delta = \sqrt{\omega_n^2 - w^2}, \qquad \Gamma_\delta = \Gamma + 2w, \qquad \delta = \frac{1}{2}\left(1 - i\frac{w}{\omega_\delta}\right) \tag{8}$$

and $\Gamma_\zeta = \Gamma_\delta$, $\omega_\zeta = -\omega_\delta$, $\zeta = \delta^*$

$$\frac{(p+2w)}{p^2 + \omega_n^2 + 2pw} = \frac{-i}{2}\left[\frac{1 - i\frac{w}{\omega_\delta}}{(\omega - \omega_\delta) - i\frac{\Gamma_\delta}{2}} + \frac{1 + i\frac{w}{\omega_\delta}}{(\omega + \omega_\delta) - i\frac{\Gamma_\delta}{2}}\right] \tag{9}$$

If $w = 0$ (no fluctuation) there are 2 Lorentzians at positions $\pm\omega_n$. With increasing w the positions move to $\omega_\delta = 0$ and the linewidth increases by w. The lineshape has contibutions of squared Lorentzians by the w/ω_δ term in the nominator. For the spezial case $w = \omega_n$ where $\omega_\delta = 0$ the real part of equation 6 becomes

$$Re\{N/D\} = \frac{\frac{\Gamma}{2}}{\omega^2 + \left(\frac{\Gamma}{2} + \omega_n\right)^2} + \frac{2\omega_n\left(\frac{\Gamma}{2} + \omega_n\right)^2}{\left(\omega^2 + \left(\frac{\Gamma}{2} + \omega_n\right)^2\right)^2} \tag{10}$$

If w increases $w > \omega_n$ the position parameter ω_δ becomes imaginary (eq. 8) so that the denominators of equation 9 stay at position zero and ω_δ contributes to the linewidth. The situation becomes more complicate if the "relaxation matrix" does not rearange quasidiagonally to 2x2 matrices. The general case is much more effectively handled by diagonalisation of the"relaxation matrix" instead of diagonalization (M. J. Clauser [2]).

3 Eigenvalue Treatment of Superoperators [2]

The forward scattering amplitude is written as follows using the definitions given in the article of M. Blume and O.C. Kistner [3] and [4] concerning the tensors V.

$$\begin{aligned} F_{pq} &= -2\pi\frac{2I_e+1}{2I_g+1}\sum_{LL\beta' e' g'\alpha e g}\gamma_\beta\cdot i^L V_{Lp}^{e'g'*}(M_L^*-ipE_L^*) \\ &\quad [\Omega - i\Pi + H^x]^{-1}_{\beta g'e',\alpha g e}(-i)^{L'}V_{L'q}^{eg}(M_{L'}+ipE_{L'}) \end{aligned} \tag{11}$$

$$\begin{aligned} \sigma &= \frac{2\pi}{k^2}\frac{2I_e+1}{2I_g+1}\frac{1}{1+\alpha} \\ \Gamma_\gamma &= 8\pi\left(|M_L|^2+|E_{L+1}|^2\right), \qquad \gamma - width \\ \Gamma &= \Gamma_\gamma+\Gamma_\alpha = \Gamma_\gamma(1+\alpha), \qquad total\ width \\ \delta &= \frac{M_1}{E_2}, \qquad real\ value \\ \Omega &= E + i\frac{\Gamma}{2} \end{aligned} \tag{12}$$

Only L=1,2 dipole and quadrupole transitions are of interest.

$$\begin{aligned} F_{pq} &= -\frac{k}{2\pi}\sigma_0\frac{1}{1+\delta^2} \\ &\quad \sum_{\beta e' g'\alpha e g}\gamma_\beta\cdot\frac{1}{2}\left[V_{1p}^{e'g'*}V_{1q}^{eg}+pq\delta^2V_{2p}^{e'g'*}V_{2q}^{eg}-\delta\left(pV_{2p}^{e'g'*}V_{1q}^{eg}+qV_{1p}^{e'g'*}V_{2q}^{eg}\right)\right] \\ &\quad \frac{\Gamma}{2}\left[\Omega\cdot 1 - i\Pi + H^x\right]^{-1}_{\beta g'e',\alpha g e} \end{aligned} \tag{13}$$

$$\begin{aligned} [\Omega\cdot 1 - i\Pi + H^x]_{\beta g'e',\alpha g e} &= \Omega\cdot\delta_{g'g}\delta_{e'e}\delta_{\alpha\beta} - i\Pi_{\alpha\beta}\delta_{g'g}\delta_{e'e} \\ &\quad + \left(H^{\beta *}_{g'g}\delta_{e'e} - H^{\beta}_{e'e}\delta_{g'g}\right)\delta_{\alpha\beta} \end{aligned} \tag{14}$$

The matrix $-i\Pi + H^x$ is non-Hermitian and is diagonalized by left and right eigenvectors. (subroutine jacCmplx16(N,fOUT,A,V,W,nrot) in mth_routine.f90: VAW=diagonal) The left eigenvectors are the rows of V and the right one the columns of W.

$$\begin{aligned} V(\Omega\cdot 1 - i\Pi + H^x)W &= \Omega\cdot 1 + V(-i\Pi + H^x)W \\ &= \Omega\cdot 1 + D, \qquad diagonal\ matrix \\ \left[V^{-1}V(\Omega\cdot 1 - i\Pi + H^x)W\cdot W^{-1}\right]^{-1} &= W\left[V(\Omega\cdot 1 - i\Pi + H^x)W\right]^{-1}\cdot V \\ &= W\left[\Omega\cdot 1 + D\right]^{-1}\cdot V \end{aligned} \tag{15}$$

The invers of a diagonal martrix is the invers of its diagonal elements $D_{jj} = Dr_{jj} + iDi_{jj}$ such that

$$\frac{\Gamma}{2}(\Omega + D_{jj})^{-1} = \frac{\frac{\Gamma}{2}}{E + Dr_{jj} + i\left(\frac{\Gamma}{2} + Di_{jj}\right)} \tag{16}$$

A sum over Lorentzians at positions $-Dr_{jj}$ and width $(\Gamma/2 + Di_{jj})$ are obtained. The broadening Di_{jj} is decribed by the parameter w_Lorentz defined as $Di_{jj}/(\Gamma/2)$ (gamnat=Γ).

This type of Lorentzian is coded in the routines:
subroutine LORGAU(gamnat,e_xsi,srw,w_Lorentz,w_Gauss,iflag_Voigt,ipos,nLG)
cLORGAU(gamnat,e_xsi,srw,w_Lorentz,w_Gauss,nLG,cLG) and
aLORGAU(Eagd,gamnat,e_xsi,srw,w_Lorentz,w_Gauss,iflag_Voigt,nLG,cLG)
contained in tpg_lorgau.f90.

The matrices W and V are multiplied by the matrices V_{Lp}^{eg} such that products of the following type are obtained (L,L'=1,2).

$$\left(W\,[\Omega\cdot 1+D]^{-1}\cdot V\right)_{\beta\alpha} \;=\; \sum_{e'g'j,egj} V_{Lp}^{e'g'} W_{\beta e'g',j}\,[\Omega\cdot 1+D]^{-1}_{j,j}\,V_{j,\alpha eg}V_{L'q}^{eg} \qquad (17)$$

The index j stands for three indices $j := \beta'', e'', g''$. The matrices

$$\begin{aligned}()_{\beta Lpj} &= \sum_{e'g'} V_{Lp}^{e'g'} W_{\beta e'g',j} \\ ()_{\alpha L'qj} &= \sum_{eg} V_{j,\alpha eg} V_{L'q}^{eg}\end{aligned} \qquad (18)$$

are calculated only once and then multiplied to the Lorentz curves of Eq.16. According to Eq.13 the sum L,L' and α,β can be elaborated with population γ_β of the different nuclear Hamiltonians so that three indices (p,q,j) are left. The subroutines:
subroutine intJgJeRELAX2(itr,icase,r_QUDI,amueg,amuee,QgdQe,cTms,je,jg,jge,
shift12,pop1,fsx1,fsx2,w12,hv1,efg1,hv2,efg2,Eagd,VV)
and subroutine hintJgJeRELAX2() provide the energies Eagd($=Dr_{jj}$) and the matrix $VV(p,q,j)$ for integral and halfintegral nuclear spin, respectively. The sum over all Lorentzcurves at energies Eagd(j) is done by the subroutine:
subroutine th_22indexRELAXsad(isubthe,icase,iput,iget,info)
which calculates the index of refraction at all energies seperated by a stepwidth srw. The array of the index of refraction is called by the subroutine:
subroutine mossbauer_tmre(b_total,info) which is part of the file pg_mossbauer.f90.

References

[1] M. Blume and J. A. Tjon, Phys. Rev. **165**, 446–456 (1968).

[2] M. J. Clauser, Phys. Rev. B **3**, 3748–3753 (1971).

[3] M. Blume and O.C. Kistner, Phys. Rev. **171**, 417 (1968).

[4] H. Spiering, *Mössbauer Spectroscopy Applied to Inorganic Chemistry*, chapter The Electric field Gradient and the quadrupole interaction, (PLenum Press, New York and London, 1984).