Basic principles of the Mössbauer spectroscopy

1. Hyperfine Hamiltonian

The hyperfine Hamiltonian in the semi-classical approximation takes on the form:

$$\mathbf{H} = A_Q\,[\,3\mathbf{I}_z^2 - \mathbf{I}^2 + \eta\,(\,\mathbf{I}_x^2 - \mathbf{I}_y^2\,)] + a_M\,[\,\mathbf{I}_z\cos\theta + \sin\theta\,(\,\mathbf{I}_x\cos\varphi + \mathbf{I}_y\sin\varphi\,)] + S\,\mathbf{1}. \tag{1}$$

An electric quadrupole coupling-constant takes on the form $A_Q = \left(\frac{c}{E_0}\right)\left(\frac{eQV_{zz}}{4I(2I-1)}\right)$ with c standing for the speed of light in vacuum, E_0 for the transition energy, and e for positive elementary charge. The symbol Q denotes spectroscopic electric quadrupole moment of the nucleus, V_{zz} stands for the principal component of the electric field gradient (EFG) tensor on the nucleus - along the *z*-axis, and I denotes the nuclear spin. The symbol $0 \le \eta \le 1$ stands for the asymmetry parameter of the EFG tensor defined as $\eta = \frac{V_{xx} - V_{yy}}{V_{zz}}$ with $|V_{xx}| \le |V_{yy}| \le |V_{zz}|$ denoting principal components of the EFG. An electric quadrupole interaction could be observed provided $I \ge 1$. A dipolar magnetic coupling-constant takes on the form $a_M = -\left(\frac{c}{E_0}\right) g\mu_N B$ with g denoting nuclear giro-magnetic factor (eventually corrected for the hyperfine anomaly). The symbol μ_N stands for the nuclear magneton, while the symbol B denotes value of the magnetic induction field (hyperfine field) experienced by the nucleus. Angles θ and φ denote polar and azimuthal angle of the hyperfine field in the main axes of the EFG, respectively. Due to the symmetry constrains they are defined in the range $[0, \pi/2]$. A magnetic dipolar interaction could be observed provided $I \ge \frac{1}{2}$. The symbol S stands for the total spectral shift versus applied single-line (unpolarized) and resonantly thin source. The shift is composed of the isomer shift and second order Doppler (SOD) shift. It is applied to the excited state Hamiltonian i.e. it equals null for the ground state Hamiltonian. Symbols $\mathbf{I}_x$, $\mathbf{I}_y$ and $\mathbf{I}_z$ stand for the nuclear spin projection operators on the respective right-handed Cartesian axes being main axes of the EFG. The symbol $\mathbf{I}^2$ stands for $\mathbf{I}^2 = \mathbf{I}_x^2 + \mathbf{I}_y^2 + \mathbf{I}_z^2$, while the symbol $\mathbf{1}$ denotes unit operator. Solid state parameters V_{zz}, η, B, θ, φ and S are the same in the ground and excited nuclear states. One can introduce the following basically nuclear parameters $Q_R = A_Q^{(1)} / A_Q^{(0)} = (Q_1 / Q_0)\left(\frac{I_0(2I_0-1)}{I_1(2I_1-1)}\right)$ and $G_R = a_M^{(1)} / a_M^{(0)} = g_1 / g_0$ with the indices 1 and 0 referring to the excited and ground nuclear states, respectively. The parameter G_R could account for the eventual hyperfine anomaly. In the case one of the nuclear states is insensitive to the particular non-scalar interaction one has single coupling constant for this interaction referring to the remaining state provided this state is sensitive to this interaction.

2. Matrix element for a transition

The matrix element for a transition from the particular hyperfine ground nuclear state to the particular hyperfine excited nuclear state takes on the form:

$$\langle \lambda_1 \,|\, \mathbf{q}\boldsymbol{\varepsilon}k \,|\, \lambda_0 \rangle = \sum_{LM} \sum_{m_0} \langle \lambda_1 \,|\, I_1 m_1 \rangle \langle I_1 m_1 \,|\, \mathbf{T}_{kM}^{(Lp)}(\mathbf{q}\boldsymbol{\varepsilon}) \,|\, I_0 m_0 \rangle \langle I_0 m_0 \,|\, \lambda_0 \rangle .$$

(2)

Symbols λ_1 and λ_0 denote eigenvalues of the hyperfine Hamiltonians in the excited and ground state, respectively. The symbol $\mathbf{q}$ denotes wave-vector transfer to the nucleus during transition, while the unit vector $\boldsymbol{\varepsilon}$ is perpendicular to the wave-vector transfer and describes polarization of the absorbed photon. The index $k = \pm 1$ stands for the polarization mode of the absorbed radiation. The symbol $|I_1 - I_0| \le L \le I_1 + I_0$ denotes the total angular momentum of the radiation with $M = 0, \pm 1, ..., \pm L$ being the magnetic quantum number of the radiation. Only transitions with $L \ge 1$ are allowed. The following relationship holds $M = m_1 - m_0$ with m_1 and m_0 standing for the magnetic quantum numbers of the respective basal states $|I_1 m_1\rangle$ or $|I_0 m_0\rangle$. Symbols $\langle I_1 m_1 \,|\, \lambda_1 \rangle$ and $\langle I_0 m_0 \,|\, \lambda_0 \rangle$ stand for the respective eigenvector components of the involved Hamiltonians. Finally, the symbol $\mathbf{T}$ stands for the transition operator with $p = 0$ in the case of even transitions (the same parities of both nuclear states) and $p = 1$ in the case of the odd transitions (different parities of the nuclear states involved). The wave-vector transfer could be expressed as $\mathbf{q} = q\boldsymbol{\kappa}$ with $q = \sqrt{\mathbf{q} \bullet \mathbf{q}} > 0$ and $\boldsymbol{\kappa}$ being unit vector. Hence, one can use the following definition of the unit vectors involved:

$$\boldsymbol{\kappa} = \mathbf{R}_\gamma \mathbf{R}_\beta \begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix} = \begin{pmatrix} \kappa_1 \\ \kappa_2 \\ \kappa_3 \end{pmatrix} , \; \boldsymbol{\varepsilon} = \mathbf{R}_\gamma \mathbf{R}_\beta \mathbf{R}_\alpha \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix} = \begin{pmatrix} \varepsilon_1 \\ \varepsilon_2 \\ \varepsilon_3 \end{pmatrix} .$$

(3)

The rotation operators are expressed as follows:

$$\mathbf{R}_\alpha = \begin{pmatrix} \cos\alpha & -\sin\alpha & 0 \\ \sin\alpha & \cos\alpha & 0 \\ 0 & 0 & 1 \end{pmatrix} , \; \mathbf{R}_\beta = \begin{pmatrix} \cos\beta & 0 & \sin\beta \\ 0 & 1 & 0 \\ -\sin\beta & 0 & \cos\beta \end{pmatrix} \text{ and } \mathbf{R}_\gamma = \begin{pmatrix} \cos\gamma & -\sin\gamma & 0 \\ \sin\gamma & \cos\gamma & 0 \\ 0 & 0 & 1 \end{pmatrix} .$$

(4)

Angles $(\alpha\beta\gamma)$ stand for the Eulerian angles of the incoming radiation beam in the quantization co-ordinates. The angle β stands for the polar angle. The angle γ denotes the azimuthal angle, while the angle α is the third Eulerian angle used to describe the radiation polarization. An intensity of the particular transition is obtained as:

$$b(\lambda_1 \lambda_0 \,|\, kk') = w_{\lambda_0} \int_0^{2\pi} d\alpha \int_0^{\pi} d\beta \sin\beta \int_0^{2\pi} d\gamma \, \langle \lambda_1 \,|\, \mathbf{q}\boldsymbol{\varepsilon}k \,|\, \lambda_0 \rangle \langle \lambda_1 \,|\, \mathbf{q}\boldsymbol{\varepsilon}k' \,|\, \lambda_0 \rangle^* \; f(\mathbf{q}) .$$

(5)

The weights w_{λ_0} describe initial (equilibrium) population of the ground nuclear hyperfine states and usually they are equal one another within the whole relevant range (see APPENDIX). The real (positive) function $f(\mathbf{q})$ describes recoilless fraction anisotropy

and/or distribution of the particular reference frames orientation versus incoming beam of the radiation. For unpolarized source this function seldom depends on the vector $\boldsymbol{\varepsilon}$. Hence, due to the orthogonality of the polarization modes one has $b(\lambda_1\lambda_0 \mid kk') \sim \delta_{kk'}$ and $b(\lambda_1\lambda_0 \mid kk') = b(\lambda_1\lambda_0 \mid k)$. Here the symbol $\delta_{kk'}$ stands for the Kronecker's symbol. Furthermore intensities described by equation (5) are normalized to unity:

$$C(\lambda_1\lambda_0 \mid k) = b(\lambda_1\lambda_0 \mid k) / \sum_{k'=\pm 1} \sum_{\lambda_1'\lambda_0'} b(\lambda_1'\lambda_0' \mid k'). \tag{6}$$

For majority of situations absorber has none polarizing properties and one can use simplified approach $C(\lambda_1\lambda_0) = \sum_{k=\pm 1} C(\lambda_1\lambda_0 \mid k)$. A transition operator might involve additional (basically nuclear) parameters called mixing ratios and describing relative amplitudes (real) of the higher angular momentum contributions to the lowest angular momentum transitions. The following transitions are encountered in practice: **E1** (odd), **M1** (even), **M1/E2** (even - mixing ratio required) and **E2** (even). The function $f(\mathbf{q})$ requires some parameterization unless it is isotropic.

A transition operator $\mathbf{T}$ depends on the Eulerian angles via the generalized spherical harmonics i.e. it involves the following terms $\mathrm{e}^{ik\alpha} d^L_{kM}(\beta) \mathrm{e}^{iM\gamma}$ with $d^L_{kM}(\beta)$ being generalized spherical harmonic (real) coupled with the polar angle. Note that above terms are mutually orthogonal i.e. one has $\int_0^{2\pi} d\alpha \int_0^{\pi} d\beta \sin\beta \int_0^{2\pi} d\gamma \, \mathrm{e}^{i(k-k')\alpha} d^L_{kM}(\beta) d^{L'}_{k'M'}(\beta) \mathrm{e}^{i(M-M')\gamma} \sim \delta_{kk'}\delta_{LL'}\delta_{MM'}$. A complete expression for the matrix element of the operator $\mathbf{T}$ takes on the form:

$$\langle I_1 m_1 \mid \mathbf{T}^{(Lp)}_{kM}(\mathbf{q}\boldsymbol{\varepsilon}) \mid I_0 m_0 \rangle = \sqrt{2L+1}\, \chi_{Lkp} A_{Lp}\, C(I_0 m_0\ L-M \mid I_1 m_1)\, \mathrm{e}^{ik\alpha}\, d^L_{kM}(\beta)\, \mathrm{e}^{iM\gamma}. \tag{7}$$

The symbol χ_{Lkp} stands for the kinematic phase factor. Usually one can assume that the reduced matrix element A_{Lp} equals unity for the lowest value of the angular momentum i.e. for $L = L_0$. The symbol $C(I_0 m_0\ L-M \mid I_1 m_1)$ denotes the Clebsch-Gordan (real) coefficient. Integration over directions leads to the following parameterization for unpolarized source and unpolarizing absorber:

$$g^{L_0 LL'}_{MM'} = \frac{\alpha^{LL'}_{MM'}}{\alpha^{L_0 L_0}_{00}} \text{ and}$$

$$\alpha^{LL'}_{MM'} = \left(\frac{\sqrt{(2L+1)(2L'+1)}}{8\pi} \right) \int_0^{2\pi} d\gamma \, \mathrm{e}^{i(M-M')\gamma} \sum_{k=\pm 1} (k)^{L+L'} \int_0^{\pi} d\beta \sin\beta \, d^L_{kM}(\beta)\, d^{L'}_{kM'}(\beta)\, f(\mathbf{q}). \tag{8}$$

Coefficients $g^{L_0 LL'}_{MM'}$ form irreducible completely symmetric traceless tensor of the rank $2L_{\max}$ on the 3-D manifold of the real character, where $L_{\max}$ is the maximum angular momentum of the radiation. Hence, one has five coefficients for dipolar transitions and fourteen for quadrupolar or mixed transitions at most. They could be applied to the unpolarizing medium. For polarizing medium generally one has to apply direct integration over directions, as the

medium has some global anisotropy leading to the variation of the Hamiltonians with respect to the local frame orientation - against the global symmetry-breaking agent.

3. Calculation of the spectrum shape

The spectrum shape (unpolarized source and unpolarizing absorber) is expressed in the transmission geometry by the so-called transmission integral taking on the following form in the simplest situation:

$$B(v) = B_0 \left[1 - \frac{f_s}{\lambda} + \frac{f_s}{\lambda} \int_{-\infty}^{+\infty} d\omega \, \rho(\omega - v) \exp[-t_A \sigma(\omega)] \right]. \tag{9}$$

The symbol B_0 stands for the number of counts per data channel far-off the resonance (base). The symbol f_s (with $0 < f_s < 1$) denotes recoilless fraction of the source (in the beam direction), the parameter $\lambda > 1$ accounts for the background of the detector in the chosen spectral window (windows). The function $\rho(\omega - v)$ stands for the density function of the emitted radiation with ω being ambient velocity and v being applied Doppler shift between source and the absorber. It takes on the form $\rho(\omega - v) = [\Gamma_s / (2\pi)][(\Gamma_s / 2)^2 + (\omega - v)^2]^{-1}$ and it is normalized to unity. The parameter Γ_s stands for the source line-width. The parameter t_A represents effective dimensionless resonant thickness of the absorber and takes on the form $t_A = n \sigma_0 f_A d (\Gamma_0 / \Gamma)$ for flat homogeneous absorber and collimated beam in the narrow geometry. The symbol n stands for the spatial density of the resonant nuclei, the symbol σ_0 denotes resonant cross-section for absorption, f_A denotes recoilless fraction for the absorption (along the incoming beam), while the symbol d stands for the absorber thickness along the beam. The symbol Γ_0 denotes the natural line-width, while the symbol Γ stands for the actual line-width of the absorber (it is assumed that all resonant atoms within the absorber are equivalent). The relative cross-section for absorption takes on the form:

$$\sigma(\omega) = \left(\frac{\Gamma}{2} \right)^2 \sum_{\lambda_1 \lambda_0} C(\lambda_1 \lambda_0) \left[\frac{1 - \left(\frac{2\xi}{\Gamma} \right) [\omega - (\lambda_1 - \lambda_0)]}{(\Gamma / 2)^2 + [\omega - (\lambda_1 - \lambda_0)]^2} \right]. \tag{10}$$

The parameter ξ accounts for the eventual interference of the resonant process with the non-resonant processes. For many transitions it is almost null. Basically it is atomic parameter due to the deep-core electrons. The simplest expression taking into account above interference effects has been applied here.

The situation is much more complex even for the single-line unpolarized and resonantly thin source for the absorber placed in the external magnetic field aligned with the hyperfine field and making some definite angle with respect to the unpolarized beam. For the absorber being in the powder form with some local electric quadrupole interaction angles θ and φ vary across the sample leading to the quasi-continuous distribution of the Hamiltonians eigenvalues and eigenvectors. Hence, the integration of the equation (5) has to be performed

directly with the weights w_{λ_0} being argument of the integral. One can simplify things remembering about orthogonality of the polarization modes and taking into account that the angle between the field and the beam is constant. The simplest situation occurs for the field aligned with the beam. The equation (9) has to be replaced by the following expression:

$$B(v) = B_0 \left[1 - \frac{f_s}{\lambda} + \frac{f_s}{2\lambda} \int_{-\infty}^{+\infty} d\omega \, \rho(\omega - v) \sum_{k=\pm 1} \exp\left[-t_A \sigma_k(\omega) \right] \right]. \tag{11}$$

The symbol $\sigma_k(\omega)$ denotes resonant part of the absorption cross-section dependent on the particular polarization mode $|k\rangle$. The situation is shown below in Fig.1 and Fig.2.

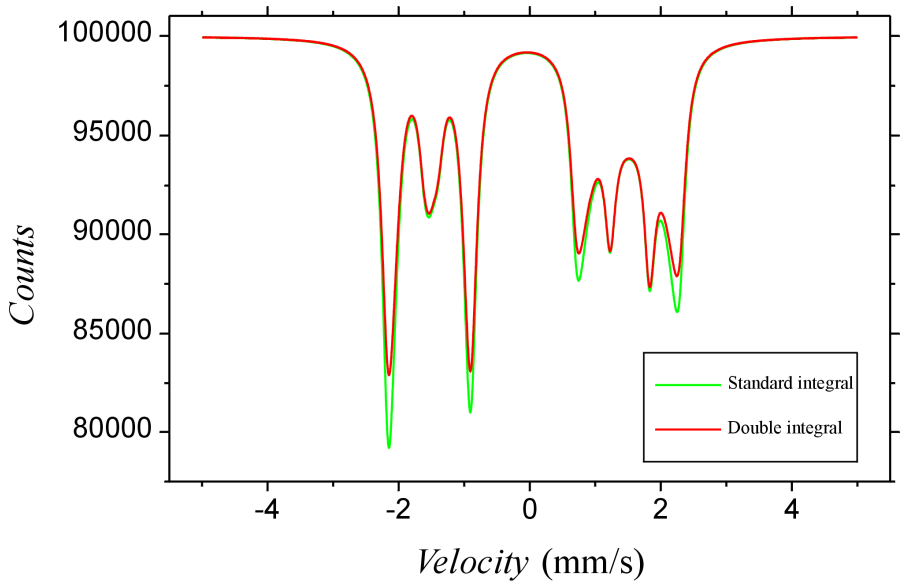

Fig. 1 Spectrum obtained in the external magnetic field aligned with the beam.

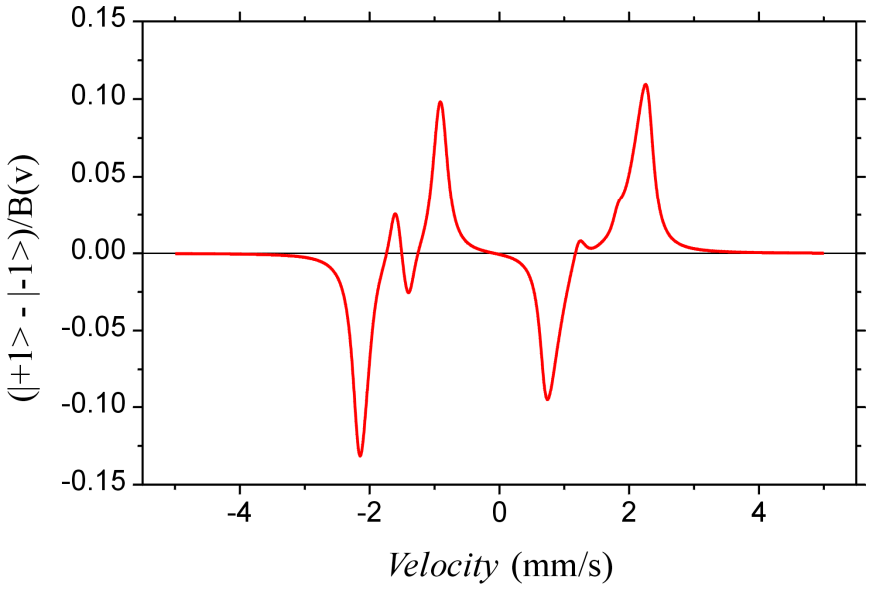

Fig. 2 Relative polarization of the beam as seen far-beyond the absorber. Generally one can assume that the base is velocity independent i.e. $B(v) = B_0$.

APPENDIX

Weights w_{λ_0} obey Boltzmann distribution in for the equilibrium. Hence, one obtains:

$$w_{\lambda_0} = \frac{\exp\left(\frac{-\lambda_0 E_0}{c k_B T}\right)}{\sum_{\lambda_0'} \exp\left(\frac{-\lambda_0' E_0}{c k_B T}\right)}. \tag{A1}$$

The symbol k_B stands for the Boltzmann constant, while the symbol T for the temperature (absolute).

Problem to solve:

The ground state of the stable nucleus ^{197}Au has spin $I_0^{(\pi_0)} = \frac{3}{2}^{(+)}$ (upper index indicates parity of the nuclear state). The spectroscopic electric quadrupole moment for this state amounts to $Q_0 = +0.547\,\mathrm{b}$ [1]. A diamagnetic compound AuCN has single site for gold atoms with the axially symmetric EFG ($\eta = 0$) having the maximum principal component amounting to $V_{zz} = -76.682 \times 10^{21}\ \mathrm{Vm}^{-2}$ on the gold site at low temperatures [1]. What is the occupation of the upper hyperfine level of the Kramers doublet provided sample has temperature $T = 10\,\mathrm{mK}$ and remains at equilibrium. There is neither magnetic field nor pressure applied to the sample. Apply universal physical constants as supplied by NIST.

1. U. D. Wdowik and K. Ruebenbauer, J. Chem. Phys. **129**, 104504 (2008).

Solution: 8.06 %.

Natural extension of the semi-classical Hamiltonian

For isolated paramagnetic atoms or molecules (highly diluted magnetic systems) with the resonant nucleus embedded in the molecule dipolar magnetic hyperfine interaction could be often expressed as:

$$\mathbf{H}_M = \mathbf{S} \bullet \hat{A} \bullet \mathbf{I}. \tag{12}$$

The operator $\mathbf{S}$ stands for the external spin operator having three components, i.e., spin projection operators on subsequent Cartesian axes. The operator $\mathbf{I}$ denotes corresponding nuclear spin operator. Coupling constants form real square matrix in three dimensions, and hence there are up to nine such coupling terms expressed as $\hat{A}_{ij} = -\left(\frac{c}{E_0}\right) g\mu_N B_{ij}$ with the indices enumerating subsequent Cartesian axes and symbols B_{ij} representing some "virtual" magnetic induction fields. Coupling constants account for the possible hyperfine anomaly as well. The Hamiltonian expressed by the equation (1) transforms into the following form:

$$\mathbf{H} = \mathbf{S} \bullet \hat{A} \bullet \mathbf{I} + \delta_{m_s m_s^{'}} \left\{ A_Q [\, 3\mathbf{I}_3^2 - \mathbf{I}^2 + \eta\, (\, \mathbf{I}_1^2 - \mathbf{I}_2^2\,)] + S_0\, \mathbf{1} \right\}. \tag{13}$$

The Hilbert space has dimension $(2S+1)(2I+1)$ with the symbol S standing for the external spin. Previous symbols $\{xyz\}$ are replaced by $\{123\}$, and the total shift is denoted now as S_0 to avoid confusion. Eigenvectors take on the form $\langle I_0 m_0 S m_s \,|\, \lambda_0 \rangle$ and $\langle I_1 m_1 S m_s \,|\, \lambda_1 \rangle$ for the ground and excited nuclear states, respectively. The symbol m_s stands for the magnetic quantum number of the external system. Hence, the expression (2) transforms into the following form:

$$\langle \lambda_1 \,|\, \mathbf{q}\boldsymbol{\varepsilon} k \,|\, \lambda_0 \rangle = \sum_{m_s} \delta_{m_s m_s^{'}} \sum_{LM} \sum_{m_0} \langle \lambda_1 \,|\, S m_s^{'} I_1 m_1 \rangle \langle I_1 m_1 \,|\, \mathbf{T}_{kM}^{(Lp)}(\mathbf{q}\boldsymbol{\varepsilon}) \,|\, I_0 m_0 \rangle \langle I_0 m_0 S m_s \,|\, \lambda_0 \rangle. \tag{14}$$

Terms with $m_s \neq m_s^{'}$ vanish due to the conservation of the angular momentum and the fact that the transition operator does not act on the external spin degrees of freedom. Usually, application of the strong external field restores semi-classical Hamitltonian. For large coupled ensemble one can approximate external spin components by the classical averages: $\mathbf{S}_1 = \langle S_1 \rangle = 0$, $\mathbf{S}_2 = \langle S_2 \rangle = 0$ and $\mathbf{S}_3 = \langle S_3 \rangle$. In such case the third (lowest) row of the matrix $\hat{A}$ survives with the following relationships: $\langle S_3 \rangle B_{31} = B \sin\theta \cos\varphi$, $\langle S_3 \rangle B_{32} = B \sin\theta \sin\varphi$ and $\langle S_3 \rangle B_{33} = B \cos\theta$. Hence, the semi-classical limit is restored again. The simplest system described by the Hamiltonian (12) is the ground state of the hydrogen atom with the interaction between spin of the proton and spin of the electron. The coupling matrix has the form $\hat{A} = A\mathbf{1}$ i.e. it is isotropic. There are four possible eigenstates – three of them degenerate with the same energy.

Time dependent phenomena

For time dependent phenomena, i.e., in the case of fluctuations within the system on the time-scale comparable to the lifetime of the excited state and/or inversed frequencies of the hyperfine interactions one cannot use separate Hilbert spaces for the ground and excited nuclear states. The useful construction is the so-called super-Hamiltonian taking on the form:

$$\langle m_1' m_0' \,|\, \mathbf{H}_n^x \,| m_0 m_1 \rangle = \delta_{m_0 m_0'} \langle m_1' \,|\, \mathbf{H}_1^{(n)} \,|\, m_1 \rangle - \delta_{m_1 m_1'} \langle m_0' \,|\, \mathbf{H}_0^{(n)} \,|\, m_0 \rangle . \tag{15}$$

This is Hermitean operator with eigenvalues being transition energies between the ground and excited nuclear state. Hence, the Hilbert space of this operator has dimension $(2I_1+1)(2I_0+1)$. The index n enumerates various possible super-Hamiltonians due to the fluctuations in the external "world". Hence, the next step is the construction of the so-called super-operator of the form:

$$\langle m_1' m_0' n' | \, \mathbf{R} \,| n m_0 m_1 \rangle = \delta_{m_1 m_1'} \delta_{m_0 m_0'} (n' | \, \mathbf{W} \,| n) + i \delta_{nn'} \langle m_1' m_0' \,|\, \mathbf{H}_n^x \,|\, m_0 m_1 \rangle . \tag{16}$$

The index $n = 1, 2, ..., N$ enumerates all possible external states, and hence the total Hilbert space has dimension $N(2I_1+1)(2I_0+1)$. Matrix elements $(n' | \, \mathbf{W} \,| n) = \left(\frac{\hbar c}{E_0} \right) w_{nn'} \exp(i \Phi_{nn'})$ of the stochastic operator $\mathbf{W}$ contain average jump frequencies $w_{nn'} \geq 0$ from the state $|n)$ to the state $|n')$ and associated phase shifts $\Phi_{nn'}$. Phase shifts are present provided the resonant nucleus physically changes position during the event and it amounts to $\Phi_{nn'} = \mathbf{q} \bullet \mathbf{R}_{nn'}$. The vector $\mathbf{R}_{nn'}$ is the jump vector from the state $|n)$ to the state $|n')$ in the configuration space. The following relationship is satisfied $w_{nn} = -\sum_{n' \neq n} w_{nn'}$ due to the conservation of the fluxes involved. Diagonal elements of the stochastic operator represent decay rates of the particular states. For equilibrium one has $p_n w_{nn'} = p_{n'} w_{n'n}$ with the symbol p_n denoting probability for the occupation of the state $|n)$. Usually, one can assume that the ground hyperfine levels are equally populated for the sample with the significant fluctuations of the environment. The next step is concerned with the diagonalization of the super-operator by solving the set of linear equations $\mathbf{VRU} = \boldsymbol{\lambda}$ with $\mathbf{VU} = \mathbf{1}$. The matrix $\boldsymbol{\lambda}$ is diagonal, but diagonal elements (eigenvalues) are generally complex. Imaginary parts $X_\lambda = \mathrm{Im}(\lambda)$ represent particular transition energies, while the real parts represent particular transition broadening due to the relationship $\Gamma_\lambda = \Gamma - 2\,\mathrm{Re}(\lambda)$. Intensities of the particular transitions could be obtained as follows (usually the medium has no polarizing properties in the case of fluctuations):

$$b_0(\lambda \,|\, \mathbf{q}\boldsymbol{\varepsilon}) = \sum_{nn'} \sum_{kk'=\pm 1} \sum_{LL'} \sum_{MM'} \sum_{m_0 m_0'} \sqrt{p_n p_{n'}} \, V(\lambda \,|\, m_1' m_0' n') \, \langle I_1 m_1' \,|\, \mathbf{T}_{k'M'}^{(L'p)}(\mathbf{q}\boldsymbol{\varepsilon}) \,|\, I_0 m_0' \rangle^* \\ \langle I_1 m_1 \,|\, \mathbf{T}_{kM}^{(Lp)}(\mathbf{q}\boldsymbol{\varepsilon}) \,|\, I_0 m_0 \rangle \, U(\lambda \,|\, m_1 m_0 n) . \tag{17}$$

Symbol p_n denotes equilibrium occupation of the particular stochastic state or initial occupation, otherwise. Symbols $V(\lambda \,|\, m_1' m_0' n')$ and $U(\lambda \,|\, m_1 m_0 n)$ denote components of the left and right eigenvectors, respectively. Furthermore one has to calculate unnormalized

intensities $b(\lambda\,|\,\mathbf{q}\boldsymbol{\varepsilon}) = \sqrt{b_0(\lambda\,|\,\mathbf{q}\boldsymbol{\varepsilon})\, b_0(\lambda\,|\,\mathbf{q}\boldsymbol{\varepsilon})^*}$ and perform integration over directions (it is assumed that the function $f(\mathbf{q})$ is common for all states):

$$b_\lambda = \int_0^{2\pi} d\alpha \int_0^{\pi} d\beta \sin\beta \int_0^{2\pi} d\gamma\, b(\lambda\,|\,\mathbf{q}\boldsymbol{\varepsilon})\; f(\mathbf{q}) \,. \tag{18}$$

For the stochastic operator being dependent on the wave-vector transfer to the sample – see APPENDIX I. Finally, intensities could be normalized as follows:

$$C_\lambda = b_\lambda \,/\, \sum_{\lambda'} b_{\lambda'} \,. \tag{19}$$

The relative cross-section for absorption could be calculated in the following way:

$$\sigma(\omega) = \tfrac{1}{4}\Gamma \sum_\lambda \Gamma_\lambda C_\lambda \left[\frac{1 - \left(\dfrac{2\xi}{\Gamma_\lambda}\right)[\omega - X_\lambda]}{(\Gamma_\lambda / 2)^2 + [\omega - X_\lambda]^2} \right]. \tag{20}$$

More or less standard transmission integral could be used subsequently to calculate the transmission spectrum shape. It is interesting to note that in the case with the resonant atom jumps between various sites eigenvalues and eigenvectors of the super-operator depend on the wave-vector transfer to the system. In particular, a transition broadening is direction dependent. It is worth noticing that for the atom diffusing via equivalent sites arranged on the Bravais lattice the following line-width is obtained:

$$\Gamma_B = \Gamma + 2w_D \left[1 - \int_{-\infty}^{+\infty} d^3 r\; \rho(\mathbf{r}) \cos(\mathbf{q} \bullet \mathbf{r}) \right]. \tag{21}$$

The symbol w_D denotes $w_D = \left(\dfrac{\hbar c}{E_0}\right) w_0$ with $w_0 \geq 0$ being the average event rate leading to the atomic transfer from a given site to another (different) site. The function $\rho(\mathbf{r})$ is a probability density function to reach position $\mathbf{r}$ from the origin during the event. Note that for the Bragg conditions being satisfied there is no broadening due to the normalization of the density function. The function $\rho(\mathbf{r})$ is a discrete function, of course, on the lattice, but above expression for Γ_B is quite general and it could be applied to the continuous motion as well.

APPENDIX I

For the stochastic operator being dependent on the wave-vector transfer to the sample the integration of the equation (18) has to be restricted to:

$$b(\lambda\,|\,\mathbf{q}) = \int_0^{2\pi} d\alpha\, b(\lambda\,|\,\mathbf{q}\boldsymbol{\varepsilon})\; f(\mathbf{q}).$$

(A.I1)

The normalization constant could be obtained as:

$$N_S = \sum_{\lambda} \int_0^{\pi} d\beta \sin\beta \int_0^{2\pi} d\gamma\, b(\lambda\,|\,\mathbf{q}).$$

(A.I2)

Hence, the normalized intensities could be calculated as $C(\lambda\,|\,\mathbf{q}) = N_S^{-1} b(\lambda\,|\,\mathbf{q})$. Due to the fact, that in general one has $\Gamma_\lambda = \Gamma(\lambda\,|\,\mathbf{q})$ and $X_\lambda = X(\lambda\,|\,\mathbf{q})$ the relative cross-section for absorption takes on the form:

$$\sigma(\omega) = \tfrac{1}{4}\Gamma \sum_{\lambda} \int_0^{\pi} d\beta \sin\beta \int_0^{2\pi} d\gamma\, \Gamma(\lambda\,|\,\mathbf{q})\, C(\lambda\,|\,\mathbf{q}) \left[\frac{1 - \left(\dfrac{2\xi}{\Gamma(\lambda\,|\,\mathbf{q})} \right) [\omega - X(\lambda\,|\,\mathbf{q})]}{[\Gamma(\lambda\,|\,\mathbf{q})/2]^2 + [\omega - X(\lambda\,|\,\mathbf{q})]^2} \right].$$

(A.I3)

Problem to solve:

The super-Hamiltonian of the system is scalar and amounts to either $-\varepsilon$ or to $+\varepsilon$ depending on the stochastic state ($\varepsilon > 0$). There are two stochastic states of the equal probabilities to occur and the system remains at equilibrium. Calculate line intensities, positions and line-widths $\Gamma_\lambda = \Gamma - 2\,\mathrm{Re}(\lambda)$ versus jump frequency between stochastic states. The resonant atom remains at the same position in both stochastic states. The symbol $\Gamma > 0$ denotes line-width of the unbroadened line. The super-operator takes on the form:

$$\mathbf{R} = \begin{pmatrix} -w - i\varepsilon & w \\ w & -w + i\varepsilon \end{pmatrix}.$$

(P1)

The symbol $w \geq 0$ denotes here the average jump frequency between stochastic states, and hence the super-Hamiltonian is expressed in the same units.

Solution:

1. $0 \leq w \leq \varepsilon:\ \Gamma_\lambda = \Gamma + 2w;\ X_\lambda = \pm\sqrt{\varepsilon^2 - w^2}\ ;\ C_\lambda = \tfrac{1}{2}$.
2. $w \geq \varepsilon:\ \Gamma_\lambda = \Gamma + 2\left[w \pm \sqrt{w^2 - \varepsilon^2} \right];\ X_\lambda = 0\ ;\ C_\lambda = \tfrac{1}{2}\left[1 \mp \dfrac{\sqrt{w^2 - \varepsilon^2}}{w} \right]$.

Another problem to solve:

The system remains at equilibrium with the super-operator taking on the form:

$$\mathbf{R} = \begin{pmatrix} -w & w\alpha \\ w\alpha^* & -w \end{pmatrix} = w \begin{pmatrix} -1 & \alpha \\ \alpha^* & -1 \end{pmatrix}.$$

(P2)

The symbol $w \geq 0$ denotes jump frequency between two equivalent sites, while the symbol α takes on the form $\alpha = \exp[(i(\mathbf{q} \bullet \mathbf{r})] = \exp(i\phi)$, where the phase angle is expressed as $\phi = \mathbf{q} \bullet \mathbf{r}$ with $\mathbf{r}$ being the jump vector. Calculate eigenvalues and corresponding line intensities.

Solution:

$$\lambda_1 = 0 \qquad : C_1 = \tfrac{1}{2}[1 + \cos\phi];$$
$$\lambda_2 = -2w \qquad : C_2 = \tfrac{1}{2}[1 - \cos\phi].$$

APPENDIX II

Let us consider empty straight chain of equivalent sites separated by the distance $r > 0$. The isolated atom located at one of the sites can jump forward or backward between adjacent sites with equal probabilities. For such case the geometrical factor $\alpha = \alpha(\mathbf{q})$ takes on the form $\alpha(\mathbf{q}) = \frac{1}{2}[\exp(i\phi) + \exp(-i\phi)] = \cos\phi$ with $\phi = \mathbf{q} \bullet \mathbf{r}$ and $r = \sqrt{\mathbf{r} \bullet \mathbf{r}}$. The super-operator takes on the following form:

$$\mathbf{R} = w \begin{pmatrix} -1 & \cos\phi \\ \cos\phi & -1 \end{pmatrix}.$$

(A.II1)

The parameter $w \geq 0$ denotes here the average inverse residence time on the site. The last expression leads to the following relative intensities, line positions and line-widths:

$$C_1 = 1 : X_1 = 0 : \Gamma_1 = \Gamma + \left(\frac{2\hbar c w}{E_0} \right) (1 - \cos\phi);$$
$$C_2 = 0 : X_2 = 0 : \Gamma_2 = \Gamma + \left(\frac{2\hbar c w}{E_0} \right) (1 + \cos\phi).$$

(A.II2)

Hence, only one line is seen without any shift, but with the width depending on the phase angle in a periodic manner. No effect is seen for $\phi = 2n\pi$, where n stands for any integer. The latter condition is called Bragg condition. Note that this example is a special case of the equation (21). Such chain could be considered as a part of the Bravais lattice. For completely random material one has to average line-width over directions applying the following relationship $\phi = \mathbf{q} \bullet \mathbf{r} = qr\cos\vartheta$ with the angle $0 \leq \vartheta \leq \pi$ being the angle between the wave-vector transfer to the system and the jump vector. The proper average takes on the form:

$$\tfrac{1}{2} \int_0^{\pi} d\vartheta \sin\vartheta \cos[qr\cos\vartheta] = \frac{\sin(qr)}{qr}.$$

(A.II3)

Finally, one obtains the following relationship for the line-width:

$$\Gamma_1 = \Gamma + \left(\frac{2\hbar c w}{E_0} \right) \left[1 - \left(\frac{\sin(qr)}{qr} \right) \right].$$

(A.II4)

For the long wave limit ($qr \to +0$) one can use the expression $1 - \dfrac{\sin(qr)}{qr} \approx \frac{1}{6} q^2 r^2 = \frac{1}{6} q^2 \langle r^2 \rangle$. Hence, the line-width takes on the following form in this approximation:

$$\Gamma_1 = \Gamma + \left(\frac{\hbar c w q^2 \langle r^2 \rangle}{3E_0} \right) = \Gamma + \left(\frac{\hbar c}{E_0} \right) q^2 D \text{ with } D = \tfrac{1}{3} w \langle r^2 \rangle .$$

(A.II5)

The symbol $\langle r^2 \rangle$ stands for the mean squared displacement, while the symbol D denotes the scalar (in one dimension) diffusion coefficient.

The situation is quite different for the ensemble of particles diffusing (slowly) within the viscous medium. In such case, one can assume that the particle is unable to rotate significantly during the time period characterized by the lifetime of the excited state and that the particle velocity remains practically constant during this time period. For such situation there is no phase modulation due to the phase break at jump (relaxation), but one has unbroadened Lorentzian shape folded with the velocity distribution being practically described by the Maxwell distribution, i.e., Gaussian along the beam axis. Hence, one obtains the following relationship for the line profile:

$$\sigma_V(\omega) = \left(\frac{\Gamma}{2} \right)^2 \sum_{\lambda_1 \lambda_0} C(\lambda_1 \lambda_0) \int_{-\infty}^{+\infty} du \, \rho(u) \left[\frac{1 - \left(\frac{2\xi}{\Gamma} \right) \left[(\omega - u) - (\lambda_1 - \lambda_0) \right]}{(\Gamma/2)^2 + \left[(\omega - u) - (\lambda_1 - \lambda_0) \right]^2} \right].$$

(A.II6)

A distribution $\rho(u)$ takes on the standard Gaussian form:

$$\rho(u) = \frac{1}{\sqrt{2\pi \langle u^2 \rangle}} \exp \left[\frac{-u^2}{2\langle u^2 \rangle} \right].$$

(A.II7)

The symbol $\langle u^2 \rangle$ stands for $\langle u^2 \rangle = \tfrac{1}{3} \langle v^2 \rangle$ with $\langle v^2 \rangle$ denoting the mean squared velocity of the diffusing particle in the isotropic medium. The profile described by the last two equations is called Voigt profile. It evolves from the Lorentzian shape for the very slow motion to the almost Gaussian shape for the faster motion.

Problem to solve:
Show that expressions (A.II2) apply to the more complex jump model on the Bravais lattice (all sites equivalent with the inversion symmetry) with the geometrical factor of the form:

$$\alpha(\mathbf{q}) = \sum_n W_n \cos(\mathbf{q} \bullet \mathbf{R}_n) \text{ with } \sum_n W_n = 1 \text{ and } W_n \geq 0 : R_n = \sqrt{\mathbf{R}_n \bullet \mathbf{R}_n} > 0 .$$

(P3)

How the expression (A.II4) is going to look now?

Solution:

$$\Gamma_1 = \Gamma + \left(\frac{2\hbar c w}{E_0} \right) \left[1 - \sum_n W_n \left(\frac{\sin(qR_n)}{qR_n} \right) \right].$$

Some other useful information

Matrix elements of the spin projector operators on the Cartesian axes $\{xyz\} \equiv \{1, 2, 3\}$.

$$
\begin{aligned}
&< m \,|\, \mathbf{I}_3 \,|\, m' > = m\, \delta(m, m'),\\
&< m \,|\, \mathbf{I}_1 \,|\, m' > = \tfrac{1}{2} \left(< m \,|\, \mathbf{I}_+ \,|\, m' > + < m \,|\, \mathbf{I}_- \,|\, m' > \right),\\
&< m \,|\, \mathbf{I}_2 \,|\, m' > = \tfrac{i}{2} \left(< m \,|\, \mathbf{I}_- \,|\, m' > - < m \,|\, \mathbf{I}_+ \,|\, m' > \right) \text{ with}\\
&< m \,|\, \mathbf{I}_+ \,|\, m' > = \sqrt{(I - m')\,(I + m' + 1)}\; \delta(m, m + 1) \text{ and}\\
&< m \,|\, \mathbf{I}_- \,|\, m' > = \sqrt{(I + m')\,(I - m' + 1)}\; \delta(m, m - 1):\\
&< m \,|\, \mathbf{I}^2 \,|\, m' > = I\,(I + 1)\, \delta(m, m').
\end{aligned}
$$

Further reading: www.elektron.up.krakow.pl/mosgraf-2009 – see for DEMO (and included HELP files) and for documentation.

Lectures for Ph.D. students – physics: Pedagogical University of Cracow – 10 hours. In order to obtain credit problems are to be solved.

K. Ruebenbauer
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