

Comments on the problem

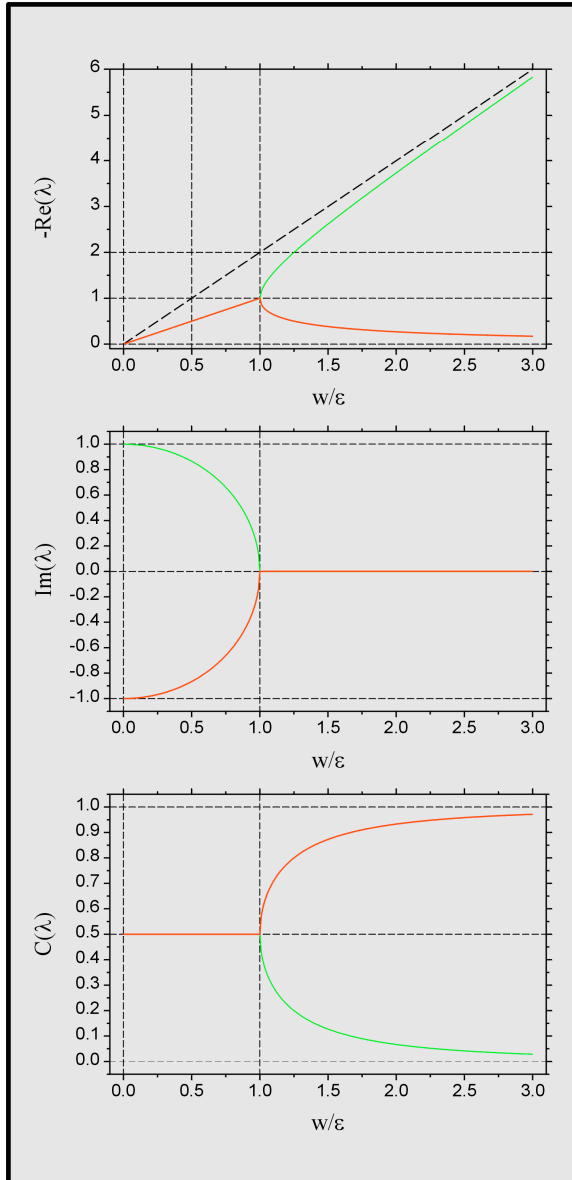
The relaxation operator has the form:

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

It describes relaxation between two isomer shift states having equal probability to occur. States are separated by the energy $2\varepsilon > 0$, and the relaxation occurs at the average rate of $w \geq 0$. System remains at equilibrium with the energy origin set in the midpoint of the respective shifts. The eigensolutions [$\det(\mathbf{R} - \lambda) = 0$, $\mathbf{VRU} = \lambda$ with $\mathbf{VU} = \mathbf{UV} = \mathbf{1}$ and λ being diagonal complex matrix] are as follows:

$$\lambda = -w \pm i\sqrt{\varepsilon^2 - w^2} : C(\lambda) = \frac{1}{2} \text{ for } 0 \leq w \leq \varepsilon \text{ and } :$$

$$\lambda = -w \pm \sqrt{w^2 - \varepsilon^2} : C(\lambda) = \frac{1}{2} \left[1 \pm \frac{\sqrt{w^2 - \varepsilon^2}}{w} \right] \text{ for } w \geq \varepsilon.$$



Note that both solutions merge for $w = \varepsilon$. Eigenvalues λ and relative intensities $C(\lambda)$ are plotted (at the side) versus w/ε . Relative intensities are calculated here as $C(\lambda) = b_\lambda / \sum_{\lambda'} b_{\lambda'}$, with:

$$b_\lambda = \sqrt{\left(\sum_{jk} V_{\lambda j} U_{k\lambda} \right) \left(\sum_{jk} V_{\lambda j} U_{k\lambda} \right)^*}.$$

This is typical example of the so-called motional narrowing process.

How to proceed

The first step is to find eigenvalues applying equation $\det(\mathbf{R} - \lambda) = 0$. There are two complex eigenvalues, i.e., four parameters to find. There are separate solutions in the slow relaxation limit ($0 \leq w \leq \varepsilon$) and fast relaxation limit ($w \geq \varepsilon$). Solutions are obtained as solutions of the following equation in the complex domain:

$$(-w - i\varepsilon - \lambda)(-w + i\varepsilon - \lambda) - w^2 = 0.$$

The matrix \mathbf{U} contains four complex elements (eigenvectors are columns), i.e., eight parameters to establish. The same statement

applies to the matrix \mathbf{V} with eigenvectors as rows. Hence, one has to find sixteen parameters separately in the slow and fast relaxation limits. The equation $\mathbf{VRU} = \lambda$ yields eight equations for real parameters, while the equation $\mathbf{VU} = \mathbf{1}$ yields another eight equations of the same type (the symbol $\mathbf{1}$ stands for the unit matrix). Hence, one can find all elements of the left (\mathbf{V}) and right (\mathbf{U}) eigenvectors and calculate respective relative line intensities in both relaxation limits. Note that the parameters $C(\lambda)$ have to satisfy the following relationships for any physically meaningful value of the argument, i.e., for $w/\varepsilon \geq 0$: $C(\lambda) \geq 0$ and $\sum_{\lambda} C(\lambda) = 1$.

K. Ruebenbauer
December 1st 2012