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J HUE and R MAINARD

Faculté des Sciences, Université de Nancy I, France

Abstract. A method is given for resolving the quantum equations of the spin–lattice relaxation for a system of electronic spins. It is shown how the relaxation times may be deduced, for example, from the maxima which occur in the absorption spectra of a modulated radio frequency field and also that, for a generalized spin, more than one maximum may be expected.

1. Introduction

In certain paramagnetic relaxation experiments (for example, Hervé and Pescia 1962, Zueco and Pescia 1965) the spin–lattice relaxation time is measured using an amplitude modulated radio frequency field. If the amplitude of this RF field is taken to be $H^1(1 + d \cos pt)$ the detected signal will have the form

$$S = f_1(p) \sin pt + f_2(p) \cos pt \tag{1}$$

the exact form of S and of the functions $f_1(p)$ and $f_2(p)$ depending on the system of detection chosen.

The first attempts to relate the functions f_1 and f_2 to the relaxation times of the spins have been restricted to a spin $\frac{1}{2}$ and have used either the formalism of Bloembergen *et al* (1948), extended to the electronic case, or the phenomenological equations given by Bloch (1946). Even where Pescia and Bassompierre (1962) have used the density matrix approach, the result could not be generalized to $S > \frac{1}{2}$.

In the present theory we have derived expressions for f_1 and f_2 the *form* of which will be valid for all values of spin (although the detailed calculation is given only for $S = 1$). Further, the theory gives the true relaxation times, rather than the time constants defined phenomenologically, in a form which can be compared directly with experiment.

In effect, the theory consists of three steps. Firstly, following the method of Wangsness and Bloch (1953) (see also Bloch 1956, Willis 1962, Willis and Bergmann 1962) the equation of motion of the spin system is determined in the presence of an RF field and a spin–lattice relaxation coupling. Secondly, it is shown that the spin–lattice coupling can be expressed in terms of a relaxation matrix $[\boldsymbol{\Gamma}]$ and that this matrix can be resolved to yield relatively simple eigenvalues. Finally these eigenvalues are related to the functions f_1 and f_2 of equation (1) when the external RF field is modulated at the frequency p.

2. The equation of motion of the spin system and the relaxation matrix $[\Gamma]$

If it is considered that the spin and lattice Hamiltonians can effectively be written in terms of $\mathcal{H}_s$ the spin Hamiltonian in an external magnetic field, $\mathcal{H}_{ph}$ the Hamiltonian of the lattice phonons, and $\mathcal{H}_c$ the spin–lattice coupling term, the equation of evolution of the density matrix can be written as

$$\dot{\rho} = -\frac{i}{\hbar}[\mathcal{H}_s + \mathcal{H}_{ph} + \mathcal{H}_c, \rho]. \tag{2}$$

The elements of ρ can be written as $\langle mfs|\rho|m'f's'\rangle$ where m and m' represent the spin state quantum numbers, f and f' the frequency states of the lattice which may be treated as a thermostat for the electronic relaxation and s, s' are the degeneracies of the states f, f'. If then we assume that the thermostat is diagonalized we can define a spin density matrix

$$\sigma_{mm'} = \sum_{f,s} \langle mfs|\rho|m'fs\rangle. \tag{3}$$

The equation of motion of this matrix is given from equation (2) using the perturbation theory of Wangsness and Bloch as

$$\dot{\sigma}_{mm'} = -\frac{i}{\hbar}[\mathcal{H}_s, \sigma]_{mm'} + \sum_{\tau} \{2\,e^{-k\tau}\Gamma^{\tau}_{mm'}\sigma_{m+\tau,m'+\tau} - (\Gamma^{\tau}_{mm} + \Gamma^{\tau}_{m'm'})\sigma_{mm'}\} \tag{4}$$

where

$$\Gamma^{\tau}_{mm'} = \pi \sum_{s,s'} \int \eta_s(f)P(f)\eta_{s'}(f+\tau\omega)\langle mfs|\mathcal{H}_c|m+\tau, f+\tau\omega, s'\rangle$$

$$\times \langle m', f+\tau\omega, s'|\mathcal{H}_c|m'fs\rangle \, df$$

with

$$P(f) = \frac{\exp(-\hbar f/k_B T)}{\Sigma_s \int \eta_s(f')\exp(-\hbar f'/k_B T)\,df'}$$

$\eta_s(f)$ being the density of states at the frequency f. The parameter τ takes integral values depending on m, m' such that $(m+\tau)$ and $(m'+\tau)$ run from $-S$ to S. Also

$$\Gamma^{-\tau}_{m'+\tau,m+\tau} = e^{-k\tau}\Gamma^{\tau}_{mm'} \quad \text{and} \quad \Gamma^{\tau}_{m'm} = \Gamma^{\tau*}_{mm'} \quad \text{with} \quad k = \frac{g_{\parallel}\beta H_0}{k_B T}. \tag{5}$$

Although equation (4) was originally derived for nuclear relaxation, Willis and Bergmann (1962) have shown that the same 'algebraic structure' can be obtained by imposing on the relaxation equations a stationary solution in interaction representation, a quite acceptable demand in the field of electronic relaxation. The form of $[\Gamma]$ then appears as a consequence of the conservation of energy. (In particular the existence of time independent relaxation coefficients is justified by the agreement between paramagnetic relaxation experiments and the time independent transition probabilities calculated by Van Vleck (1940) as discussed by Stevens (1967).)

In the experimental situation where a static field H_0 is applied along the axis of symmetry Oz and the rotating RF field H^1 is in the plane perpendicular to H_0, the spin

Hamiltonian will have the form (eg Low 1960)

$$\mathscr{H}_s = \beta\{g_\parallel H_0 S_z + g_\perp(H_x^1 S_x + H_y^1 S_y)\}$$

with $H_x^1 = H^1 \cos \omega t$ and $H_y^1 = H^1 \sin \omega t$. When the equations of motion are transformed to the rotating frame with angular frequency ω, so that operators are changed, say, from $\hat{O}$ to $\bar{O}$ by $\hat{O} = \exp(-i\omega S_z t)\bar{O}\exp(i\omega S_z t)$ the equations (4) will become

$$\dot{\bar{\sigma}}_{mm'} = i[S_z, \bar{\sigma}]_{mm'}(\omega - \omega_0) - i\gamma_\perp H^1[S_x, \bar{\sigma}]_{mm'}$$
$$+ \sum_\tau \{2\,e^{-k\tau}\Gamma_{mm'}^\tau\bar{\sigma}_{m+\tau,m'+\tau} - (\Gamma_{mm}^\tau + \Gamma_{m'm'}^\tau)\bar{\sigma}_{mm'}\} \qquad (6)$$

where

$$\omega_0 = \gamma_\parallel H_0 = \frac{g_\parallel \beta H_0}{\hbar} \quad \text{and} \quad \gamma_\perp = \frac{g_\perp \beta}{\hbar}.$$

In the experimental situation this equation is simplified since the RF field is applied at resonance, that is, $\omega = \omega_0$.
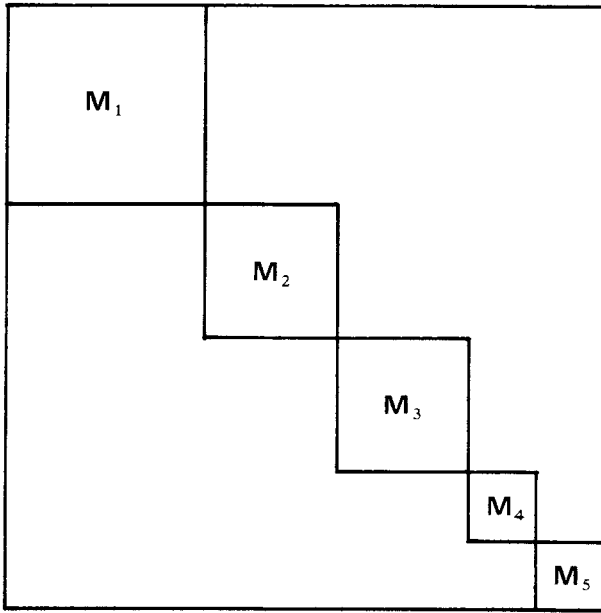
3. The structure of the matrix $[\Gamma]$

Because only those terms which have the same value of $m - m'$ are in fact coupled in the equation (6) it will always be possible to separate the matrix equations into effective submatrices having constant values of $m' - m$. This may be illustrated for the case $S = 1$ by taking the components of the vector $\boldsymbol{\sigma}$ in the order

$$\boldsymbol{\sigma} = \underset{m-m'=0}{[\bar{\sigma}_{11}, \bar{\sigma}_{00}, \bar{\sigma}_{-1-1}]}\underset{m-m'=-1}{[\bar{\sigma}_{01}, \bar{\sigma}_{-10}]}\underset{m-m'=1}{[\bar{\sigma}_{10}, \bar{\sigma}_{0-1}]}\underset{m-m'=-2}{[\bar{\sigma}_{-11}]}\underset{m-m'=2}{[\bar{\sigma}_{1-1}]} \qquad (7)$$

for which the corresponding submatrices of $[\Gamma]$ are

$$\underset{(m'-m=0)}{\mathbf{M}_1 =} \begin{pmatrix} 2\Gamma_{11}^0 - 2(\Gamma_{11}^{-2} + \Gamma_{11}^0 + \Gamma_{11}^{-1}) & 2e^k\Gamma_{11}^{-1} & 2e^{2k}\Gamma_{11}^{-2} \\ 2e^{-k}\Gamma_{00}^1 & 2\Gamma_{00}^0 - 2(\Gamma_{00}^{-1} + \Gamma_{00}^0 + \Gamma_{00}^1) & 2e^k\Gamma_{00}^{-1} \\ 2e^{-2k}\Gamma_{-1-1}^2 & 2e^{-k}\Gamma_{-1-1}^1 & 2\Gamma_{-1-1}^0 - 2(\Gamma_{-1-1}^0 + \Gamma_{-1-1}^1 + \Gamma_{-1-1}^2) \end{pmatrix}$$

$$\underset{(m'-m=1)}{\mathbf{M}_2 =} \begin{pmatrix} 2\Gamma_{01}^0 - (\Gamma_{00}^{-1} + \Gamma_{00}^0 + \Gamma_{11}^{-1} + \Gamma_{11}^0) & 2e^k\Gamma_{01}^{-1} \\ 2e^{-k}\Gamma_{-10}^1 & 2\Gamma_{-10}^0 - (\Gamma_{-1-1}^1 + \Gamma_{-1-1}^0 + \Gamma_{00}^1 + \Gamma_{00}^0) \end{pmatrix}$$

$$\underset{(m'-m=-1)}{\mathbf{M}_3 =} \begin{pmatrix} 2\Gamma_{10}^0 - (\Gamma_{11}^{-1} + \Gamma_{00}^{-1} + \Gamma_{11}^0 + \Gamma_{00}^0) & 2e^k\Gamma_{10}^{-1} \\ 2e^{-k}\Gamma_{0-1}^1 & 2\Gamma_{0-1}^0 - (\Gamma_{00}^0 + \Gamma_{-1-1}^0 + \Gamma_{00}^1 + \Gamma_{-1-1}^1) \end{pmatrix}$$

$$\underset{(m'-m=-2)}{\mathbf{M}_4} = (2\Gamma_{-11}^0 - 2(\Gamma_{-1-1}^0 + \Gamma_{11}^0))$$

$$\underset{(m'-m=2)}{\mathbf{M}_5} = (2\Gamma_{1-1}^0 - 2(\Gamma_{11}^0 + \Gamma_{-1-1}^0)).$$

The $[\Gamma]$ matrix

Because of the symmetry properties of equation (5) it is seen that the matrix $\mathbf{M}_1$ has two lines identical which gives a zero eigenvalue corresponding to the Boltzmann equilibrium while the determinants of the other matrices are nonzero. Further, the matrices $\mathbf{M}_2$ and $\mathbf{M}_3$ can be seen to be identical.

The integration of the relaxation equation

$$\dot{\sigma} = [\Gamma]\sigma$$

gives, in the absence of any external excitation

$$\sigma(t) = \exp([\Gamma]t)\sigma(0) \tag{8}$$

with σ taken from (7). The relaxation times are then the negative of the reciprocals of the eigenvalues of the matrix $[\Gamma]$ (see Lurçat 1956).

4. The equation of motion in the presence of the external excitation

If the commutator $[-iS_x, \bar{\sigma}]$ is developed in equation (6) and the excitation field, applied at the resonance frequency, is modulated as $H^1(1 + d \cos pt)$ the equations of motion become

$$\dot{\sigma} = (\mathbf{A} + b\mathbf{M} \cos pt) \cdot \sigma \tag{9}$$

with

$$\mathbf{A} = [\Gamma] + a\mathbf{M} \qquad a = 2^{-1/2}\gamma_\perp H^1 \qquad b = ad$$

and, in actual experiments, d is appreciably less than one. $\mathbf{M}$ can be divided into sub-matrices in a manner similar to that indicated for $[\Gamma]$ except that the only nonzero elements of $\mathbf{M}$ occur where there are zero elements of $[\Gamma]$. Thus $\mathbf{M}$ and $[\Gamma]$ can be considered, in effect, 'complementary'.

For $S = 1$ the matrix $\mathbf{M}$ is

0	0	0	$-i$	0	i	0	0	0
0	0	0	i	$-i$	$-i$	i	0	0
0	0	0	0	i	0	$-i$	0	0
$-i$	i	0	0	0	0	0	$-i$	0
0	$-i$	i	0	0	0	0	i	0
i	$-i$	0	0	0	0	0	0	i
0	i	$-i$	0	0	0	0	0	$-i$
0	0	0	$-i$	i	0	0	0	0
0	0	0	0	0	i	$-i$	0	0

$$(10)$$

With the modulation small the coefficient b can be considered small and the equation (9) can be linearized. Then

$$\boldsymbol{\sigma} = \boldsymbol{\sigma}_0 + b\boldsymbol{\sigma}_1 \tag{11}$$

and

$$\dot{\boldsymbol{\sigma}}_0 + b\dot{\boldsymbol{\sigma}}_1 = \mathbf{A} \cdot \boldsymbol{\sigma}_0 + b\mathbf{A} \cdot \boldsymbol{\sigma}_1 + b\mathbf{M} \cdot \boldsymbol{\sigma}_0 \cos pt \tag{12}$$

from which

$$\dot{\boldsymbol{\sigma}}_0 = \mathbf{A} \cdot \boldsymbol{\sigma}_0 \tag{13}$$

and

$$\dot{\boldsymbol{\sigma}}_1 - \mathbf{A} \cdot \boldsymbol{\sigma}_1 = \mathbf{M} \cdot \boldsymbol{\sigma}_0 \cos pt. \tag{14}$$

The solution of equation (13) can be taken to be of the form

$$\boldsymbol{\sigma}_0(t) = \exp(\mathbf{A}t)\boldsymbol{\sigma}_0(0) \tag{15}$$

but, provided that the RF field H^1 is not too high, the solution to this zero order expression may be taken, to good approximation, to be the stationary solution in the absence of modulation. This solution corresponds to the case where

$$\mathbf{A} \cdot \boldsymbol{\sigma}_0 = \dot{\boldsymbol{\sigma}}_0 = 0. \tag{16}$$

(That is, $\boldsymbol{\sigma}_0(0)$ is an eigenvector of $\mathbf{A}$ for the eigenvalue zero to the first order in a.) Equation (15) then gives

$$\boldsymbol{\sigma}_0(t) = \left(\mathbf{I} + \mathbf{A}t + \mathbf{A}^2 \frac{t^2}{2!} + \ldots \right) \cdot \boldsymbol{\sigma}_0(0) = \boldsymbol{\sigma}_0(0). \tag{17}$$

Ignoring transient solutions for (14) it is convenient to write

$$\boldsymbol{\sigma}_1 = \boldsymbol{\alpha}_1 \cos pt + \boldsymbol{\beta}_1 \sin pt \tag{18}$$

from which one obtains, on identifying the different terms

$$(\mathbf{A}^2 + p^2\mathbf{I})\boldsymbol{\alpha}_1 = -\mathbf{A} \cdot \mathbf{M} \cdot \boldsymbol{\sigma}_0(0) \quad \text{and} \quad (\mathbf{A}^2 + p^2\mathbf{I})\boldsymbol{\beta}_1 = p\mathbf{M} \cdot \boldsymbol{\sigma}_0(0) \qquad (19)$$

where $\mathbf{I}$ is the unit matrix and $(\mathbf{A}^2 + p^2\mathbf{I})$ is certainly invertible.

The equations (19) now give the coefficients for the solution with modulation as

$$\boldsymbol{\alpha}_1 = -(\mathbf{A}^2 + p^2\mathbf{I})^{-1} \cdot \mathbf{A} \cdot \mathbf{M} \cdot \boldsymbol{\sigma}_0(0) \quad \text{and} \quad \boldsymbol{\beta}_1 = p(\mathbf{A}^2 + p^2\mathbf{I})^{-1} \cdot \mathbf{M} \cdot \boldsymbol{\sigma}_0(0).$$
$$(20)$$

The combination of equations (11), (18), (19) and (20) gives the first order equation of the motion of $\boldsymbol{\sigma}$ under the influence of the modulation as

$$\boldsymbol{\sigma}(t) = \boldsymbol{\sigma}_0(0) - b(\mathbf{A}^2 + p^2\mathbf{I})^{-1} \cdot \mathbf{A} \cdot \mathbf{M} \cdot \boldsymbol{\sigma}_0(0) \cos pt$$
$$+ bp(\mathbf{A}^2 + p^2\mathbf{I})^{-1} \cdot \mathbf{M} \cdot \boldsymbol{\sigma}_0(0) \sin pt. \qquad (21)$$

5. Deduction of the relaxation times

The expression of the coefficients $\boldsymbol{\alpha}_1$ and $\boldsymbol{\beta}_1$ of the equations (20) in a convenient form can be obtained with the aid of the Lagrange interpolation polynomials (see Gantmacher 1959). As is shown in the Appendix it is possible to express any function $f(\mathbf{A})$ of the matrix $\mathbf{A}$ in terms of its eigenvalues A_i and the corresponding matrices $\mathbf{Z}_i$ which are *independent of the form of* $f(\mathbf{A})$. Then $f(\mathbf{A}) = \Sigma_i \mathbf{Z}_i f(A_i)$ and for the present case

$$(\mathbf{A}^2 + p^2\mathbf{I})^{-1} = \sum_i \frac{\mathbf{Z}_i}{A_i^2 + p^2}.$$

$$\boldsymbol{\alpha}_1 = -\sum_i \frac{\mathbf{Z}_i \cdot \mathbf{A} \cdot \mathbf{M}}{A_i^2 + p^2} \cdot \boldsymbol{\sigma}_0(0) \quad \text{and} \quad \boldsymbol{\beta}_1 = p \sum_i \frac{\mathbf{Z}_i \cdot \mathbf{M}}{A_i^2 + p^2} \cdot \boldsymbol{\sigma}_0(0). \qquad (22)$$

Since $\mathbf{A} = [\boldsymbol{\Gamma}] + a\mathbf{M}$ and a is assumed small, the eigenvalues A_i which appear in equation (22) can be derived from those of $[\boldsymbol{\Gamma}]$ by the normal perturbation technique. However, although the degeneracy of $[\boldsymbol{\Gamma}]$ is lifted, the changes in the eigenvalues are found to be of second order in a so that the eigenvalues A_i may be taken to be related directly to the relaxation times as

$$A_i = \frac{1}{T_i} + a^2 C_i. \qquad (23)$$

The measurement of the quantities A_i can be undertaken in a number of ways, each depending in effect on the variation of the z component of the magnetization $\mathscr{M}_z$. Then, since by definition of σ (equation (3))

$$\frac{\mathrm{d}}{\mathrm{d}t}\langle \mathscr{M}_z \rangle = \frac{\mathrm{d}}{\mathrm{d}t}(\mathrm{Tr}\,\sigma \cdot \mathscr{M}_z) = \mathrm{Tr}\left(\mathscr{M}_z \cdot \frac{\mathrm{d}\sigma}{\mathrm{d}t}\right)$$

and $\mathscr{M}_z$ is diagonal, $\langle \mathscr{M}_z \rangle$ will depend only on the diagonal elements of σ (which are the same as those $\bar{\sigma}$), the form of $\langle \mathscr{M}_z \rangle$ can be taken from the appropriate terms of equation (21) to give an expression of the form

$$\langle \dot{\mathscr{M}}_z \rangle = \sum_i \frac{k_i p}{A_i^2 + p^2} \sin pt + \sum_i \frac{l_i p^2}{A_i^2 + p^2} \cos pt \qquad (24)$$

where k_i and l_i will depend on the exact form of $\mathbf{Z}_i$, $\mathbf{A}$ and $\mathbf{M}$ in equation (21). It is thus seen that the dependence of $f_1(p)$ and $f_2(p)$ of equation (1) on p is relatively simple (although, in practice, the coefficients k_i and l_i may be relatively complex).

If now, for example, one detects the component of the signal in quadrature, this component will have an amplitude proportional to

$$y = \sum_i \frac{k_i p}{A_i^2 + p^2} = \sum_i y_i$$

which will vary with the modulation frequency and should show a number of maxima (in general of magnitude decreasing with increasing A_i) one for each value of A_i when $p \simeq A_i$, *provided that these values are well separated*. The variation of p in the vicinity of a frequency A_i will then give the signals as indicated in figure 1. The value found for A_i will vary with the signal amplitude ($a^2 \propto (H^1)^2$) according to equation (23) and the corresponding relaxation time may be found by extrapolation as indicated in figure 2. Similar results may be obtained by detecting the signal in phase, which will be proportional to $\sum_i l_i \{ p^2 / (A_i^2 + p^2) \}$ or the total amplitude of the signal at frequency p which will be proportional to

$$\left\{ \left(\sum_i \frac{k_1 p}{A_i^2 + p^2} \right)^2 + \left(\sum_i \frac{l_i p^2}{A_i^2 + p^2} \right)^2 \right\}^{1/2}$$

although this latter case would only be valuable for comparison (Hervé and Pescia 1962).
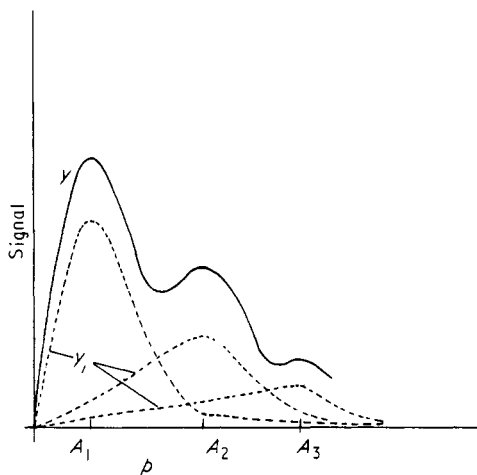

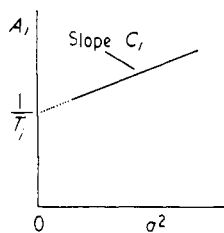**Figure 1.** Variation of signal with frequency p in the vicinity of A_i.

Figure 2. Variation of A_i with signal amplitude.

Conclusion

In conclusion we see that the *method* for the resolution of a Boltzmann quantum equation which is developed here can be used for the determination of relaxation times in paramagnetic electronic relaxation in varying experimental situations.

In the case where the principal Hamiltonian $\mathscr{H}_s^0$ of the spin system does not have the relatively simple form which we have used, the problem is clearly more complicated but the general method remains valid since the key of the method results from the

particular structure of the matrix $[\boldsymbol{\Gamma}]$ which breaks up into diagonal blocks; this particularity which appears here for $S = 1$ as the consequence of equal splitting of the magnetic levels of $\mathcal{H}_s^0$ is, in fact, much more general.

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Appendix. Definition of the matrix $\mathbf{Z}_i$

Consider an $n \times n$ matrix $\mathbf{A}$ with eigenvalues A_i (which for convenience we take to be nondegenerate) and a function $f(\lambda)$ such that the values $f(A_i)$ are defined for all i. If we introduce the interpolation polynomials given by Lagrange as

$$r(\lambda) = \sum_{i=1}^{n} \frac{(\lambda - A_1)(\lambda - A_2) \ldots (\lambda - A_{i-1})(\lambda - A_{i+1}) \ldots (\lambda - A_n)}{(A_i - A_1)(A_i - A_2) \ldots (A_i - A_{i-1})(A_i - A_{i+1}) \ldots (A_i - A_n)} f(A_i)$$

then, since $f(A_i)$ is calculable, the function of the matrix becomes

$$f(\mathbf{A}) = \sum_{i=1}^{n} \mathbf{Z}_i(\mathbf{A}) f(A_i)$$

with

$$\mathbf{Z}_i(\mathbf{A}) = \frac{(\mathbf{A} - A_1\mathbf{I})(\mathbf{A} - A_2\mathbf{I}) \ldots (\mathbf{A} - A_{i-1}\mathbf{I})(\mathbf{A} - A_{i+1}\mathbf{I}) \ldots (\mathbf{A} - A_n\mathbf{I})}{(A_i - A_1)(A_i - A_2) \ldots (A_i - A_{i-1})(A_i - A_{i+1}) \ldots (A_i - A_n)}$$

$\mathbf{I}$ being the unit matrix. We see that, as stated, the matrices $\mathbf{Z}_i$ do not depend on the form of $f(\lambda)$ which, in the present case, is $(\lambda^2 + p^2)^{-1}$ (the method may be extended to the degenerate case by the introduction of the Lagrange–Sylvester polynomials, see Gantmacher 1959, p 102).

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