Effect of Combined Static and Time-Dependent Quadrupole Interactions on Angular Correlation: Asymmetric Electric Field Gradient Case*

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We derive the form of the perturbation factor for the angular correlation of two successive \( \gamma \)-rays when the intermediate state is subject to a non-axially symmetric static electric field gradient plus a small random time-dependent quadrupole perturbation. The Bloch-Wangness-Redfield theory of nuclear relaxation is applied to calculate the evolution of the density matrix, and a general form of the perturbation factor valid for odd and even-\( A \) nuclei is determined.

Determina-se a forma do fator de perturbação da correlação angular de dois raios gama sucessivos quando o estado intermediário está sujeito simultaneamente a um gradiente de campo elétrico estático assimétrico e a uma pequena perturbação aleatória dependente do tempo. Aplica-se a teoria de relaxação nuclear de Bloch-Wangness-Redfield para o cálculo da evolução da matriz densidade que descreve a interação e determina-se uma expressão para o fator de perturbação válida tanto para os núcleos pares como para os ímpares.

1. Introduction

Recently, the Bloch-Wangness-Redfield theory\(^1,2\) of nuclear relaxation has been applied to the calculation of perturbation factors in angular correlations of successive gamma radiations in solids\(^3\). The case of an odd-\( A \) nucleus in the presence of an axially symmetric electric field gradient and a weak time dependent perturbation has been treated. The main feature of the perturbation factor is the presence of a single relaxation exponential for each quadrupole frequency. The theory has been applied to discuss measurements of the time-dependent angular correlations of radiations from \( Hf^{181} \) in the compound \( HfF_7(NH_3)_3 \), giving information about the molecular structure of this compound\(^4\).

The calculation has been extended to the case of an even-\( A \) nucleus\(^5\) but still considering the electric field gradient as axially symmetric. In this

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case the perturbation factor has a combination of exponentials for the relaxation of each frequency. It seems that recent results obtained by Glass and Kliver\(^6\) studying time-dependent angular correlations of radiations from \(Ti^{44}\) in the compound \(BaTiO_3\) can be interpreted by this theory.

In this work we apply the Bloch-Wangness-Redfield theory for nuclear relaxation to determine the main effects on the perturbation factors of the angular correlation in the case of an electric field gradient which is not axially symmetric. In Section 2 we give the basic theory, in Section 3 we derive the expression for the perturbation factors and in Section 4 some comments are made.

2. Basic Theory

The angular correlation function of two successive gamma radiations emitted in directions specified by the wave vectors \(k_1\), \(k_2\), respectively, and separated by a time interval \(t\) during which a perturbation acts on the intermediate state can be written as

\[
W(k_1, k_2, t) = \sum_x \langle x | \rho(k_1, t) | x' \rangle \langle x' | \rho(k_2, 0) | x \rangle ,
\]

where \(\rho(k_1, 0)\) and \(\rho(k_2, 0)\) are the density matrices of the first and second radiation respectively and both are defined in Ref. 7.

If we define \(\rho^*(t)\) such that

\[
\rho_{xx'}(t) = e^{-i\omega_{xx}t} \rho^*_{xx'}(t)e^{i\omega_{xx}t},
\]

Then \(\rho^*(t)\) may be determined from the solution of the relaxation equation given by Redfield

\[
\rho^*_{xx'} = \sum_{\beta\beta'} R_{xx',\beta\beta'} \rho^*_{\beta\beta'},
\]

with

\[
(\omega_{xx} - \omega_{xx'}) = (\omega_{\beta\beta} - \omega_{\beta\beta'}).
\]

In general it is convenient to define operators \(G(t)\) and \(G^*(t)\) such that

\[
\rho_{xx'}(k_1, t) = \sum_{\beta\beta'} \langle xx' | G(t) | \beta\beta' \rangle \rho_{\beta\beta'}(0)
\]

and

\[
\langle xx' | G(t) | \beta\beta' \rangle = \sum_{xx'} e^{-i(\omega_{xx} - \omega_{xx'})t} \langle xx' | G^*(t) | \beta\beta' \rangle.
\]
The conditions for applicability of Eq. (3) and definition of the matrix elements \( R_{\alpha'\beta'} \) in terms of various physical models are discussed in the references (see e.g. Refs. 1 and 2).

The perturbed angular correlation at time \( t \) can be written as

\[
W(k_1k_2t) = 4\pi \sum_{k_1\mu} \sum_{k_2\mu'} A_{k_1} A_{k_2} G_{k_1k_2}^{\mu\mu'}(t) Y_{k_1}^{\mu}(k_1) Y_{k_2}^{\mu'}(k_2),
\]

(6)

where \( G_{k_1k_2}^{\mu\mu'}(t) \) is the perturbation factor.

In the particular case of an axially symmetric static Hamiltonian the labels \( a, a' \), etc. may be taken as the \( m \) quantum numbers for the projection of the angular momentum on the symmetry axis. The expression for the perturbation factors then takes the particularly simple form

\[
G_{k_1k_2}^{\mu\mu'}(t) = 4\pi \sum_{a} \sum_{\beta} \left( I_{\alpha'} I_{\beta'} \right) e^{-i(\omega_{\alpha'} - \omega_{\beta'})t} \langle \alpha\alpha' | G^*(t) | \beta\beta' \rangle.
\]

(7)

The solution of Eq. (3) for this case and the resulting structure for the perturbation factors have been discussed in Refs. 3 and 5.

In the case of a non-axially symmetric static interaction the quadrupole Hamiltonian in the principal axis system of the electric field gradient can be written as

\[
H_0 = A\left[ 3I_z^2 - I(I + 1) + \frac{1}{2}\eta(I_+^2 + I_-^2) \right],
\]

(8)

where

\[
A = \frac{e^2 qQ}{4I(2I - 1)}
\]

and the asymmetry parameter is given by

\[
\eta = \frac{V_{xx} - V_{yy}}{V_{zz}}.
\]

It is customary to choose the coordinate system in such a way that \( |V_{zz}| > |V_{xx}| > |V_{yy}| \), thus allowing values of \( \eta \) between \(-1\) and \(+1\).

As mentioned, when \( \eta = 0 \), the \( z \) axis is a symmetry axis and the eigensta-
tes can be labeled with the $m$ quantum numbers. In this case the eigenvalues are given by

$$E_m = \frac{e^2 q Q}{4I(2I-1)} [3m^2 - I(I + 1)]$$

and are degenerate for $+m$ and $-m$.

When $\eta$ is not zero the situation is somewhat different for odd-A and even-A nuclei. In the odd-A case the levels retain a two-fold degeneracy (Kramers degeneracy), although $m$ is no longer a good quantum number. In the even-A case, on the other hand, the asymmetry will completely remove the degeneracy.

We now discuss the solution of Eq. (3) for these two cases. We note (Ref. 3) that there is a separation of the "diagonal" and "off-diagonal" parts of Eq. (3). The solution of the diagonal part of this system of equations for both cases is identical to the general solution given in Ref. 3.

For even-A nuclei the solution for the off diagonal part of Eq. (3) is particularly simple, since the complete removal of degeneracy implies that the sum in Eq. (3) is in reality restricted to the term with $\beta = a, \beta' = \alpha'$. The resulting equations are of the form

$$\rho_{2a\,'} = R_{2a\,'2a} \rho_{2a\,'}$$

and have as solutions

$$\rho_{2a\,'}(t) = \rho_{2a\,'}(0) e^{-j_{2a\,'}t}.$$ (11)

There is therefore a single exponential associated with each frequency in the perturbed angular correlation spectrum.

For the odd-A nuclei the presence of the degeneracy must be considered. However, a repetition of the arguments given in Ref. 1 demonstrates that when different terms of the perturbing Hamiltonian can be considered incoherent the form of Eq. (10) also applies.

3. Perturbation Factor

The structure of the perturbation factors is somewhat more complex in the asymmetric case.
We write the expansion of the eigenfunctions in angular momentum eigenfunctions as

\[ |I\alpha\rangle = \sum_{m} \langle m|\alpha\rangle |Im\rangle, \]

then we may write the matrix elements of the operator \( G(t) \) defined in Eqs. (4) and (5) as

\[ \langle mm'|G(t)|nn'\rangle = \sum_{\alpha\beta\alpha'\beta'} \langle m|\alpha\rangle \langle m'|\alpha'\rangle^* \langle n|\beta\rangle \langle n'|\beta'\rangle^* \langle \alpha\alpha'|G(t)|\beta\beta'\rangle. \] (12)

The perturbation factors can then be obtained using (12) in the form

\[ \langle mm'|G(t)|nn'\rangle = \sum_{\alpha\beta\alpha'\beta'} \langle m|\alpha\rangle \langle m'|\alpha'\rangle^* \langle n|\beta\rangle \langle n'|\beta'\rangle^* \times \]

\[ \times e^{-i(\omega_\alpha - \omega_\alpha')t} \langle \alpha\alpha'|G^*(t)|\beta\beta'\rangle \] (13)

where the factors \( \langle \alpha\alpha'|G^*(t)|\beta\beta'\rangle \) are to be calculated from the eigensolutions of the diagonal and off-diagonal parts of the Redfield relaxation matrix, Eq. (3).

For the diagonal case one has\(^3\):

\[ \langle \nu|G^*(t)|\mu\rangle = \sum_{r} b_{r\nu} c_{r\mu} e^{-\lambda_{rt}} \] (14)

where \( \nu \) is assigned to the pair of levels \( \alpha\alpha' \), and \( \mu \) to the pair \( \beta\beta' \). For the off-diagonal part one has simply

\[ \langle \alpha\alpha'|G^*(t)|\beta\beta'\rangle = e^{-\lambda_{\alpha\alpha'}t} \delta_{\alpha\beta} \delta_{\alpha'\beta'}. \] (15)

Using the above solution in Eq. (13), the perturbation factor \( G_{k_1k_2}^{\mu\mu'}(t) \) can be written in a general form as:

\[ G_{k_1k_2}^{\mu\mu'}(t) = \sum_{\alpha\beta} \left[ \sum_{m} \sum_{r} \left( \frac{I}{m' - m} \frac{I}{\mu} \right) \left( \frac{I}{n' - n} \frac{I}{\mu'} \right) \times \right. \]

\[ \times b_{r\alpha\beta} c_{r\beta\alpha'} e^{-\lambda_{rt}} \langle m|\alpha\rangle \langle m'|\alpha'\rangle^* \langle n|\beta\rangle \langle n'|\beta'\rangle^* + \]

\[ + \sum_{m} \left( \frac{I}{m' - m} \frac{I}{\mu} \right) \left( \frac{I}{n' - n} \frac{I}{\mu'} \right) e^{-i(\omega_\alpha - \omega_\alpha')t} e^{-\lambda_{\alpha\alpha'}t} \times \]

\[ \times \langle m|\alpha\rangle \langle m'|\alpha'\rangle^* \langle n|\beta\rangle \langle n'|\beta'\rangle^* \left. \right]. \] (16)
Calculation of the coefficients $\langle m | x \rangle$ etc. defined in Eq. (12) above is outlined in Ref. 8. The expression for the perturbation factor (Eq. (16)) can be applied to interpret quadrupole relaxation effects to be expected from some typical relaxation mechanism in solids, such as molecular torsion oscillations and planar and isotropic hindered rotations.

4. Conclusions

The modification of the perturbation factor due to time dependent interactions can be seen to be especially simple for the time dependent parts of the perturbation factors since in the cases treated here each distinct frequency is multiplied by a single exponential.

The relaxation involved with the frequency independent part of the perturbation factor on the other hand will in general be given by a superposition of various exponentials. The parameters involved in the relaxation must in general be obtained numerically from a solution of the Redfield equation.

Angular correlation patterns in the presence of both asymmetry and relaxation may be expected to appear quite complex, since already in the case of a static interaction with asymmetry the spectrum is not periodic. The use of finite Fourier analysis techniques may be of assistance in the interpretation of such spectra.

References