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Dependence of nuclear quadrupole resonance transitions on the electric field gradient asymmetry parameter for nuclides with half-integer spins

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ABSTRACT

Allowed transition energies and eigenstate expansions have been calculated and tabulated in numerical form as functions of the electric field gradient asymmetry parameter for the zero field Hamiltonian of quadrupolar nuclides with $I = 3/2, 5/2, 7/2$, and $9/2$. These results are essential to interpret nuclear quadrupole resonance (NQR) spectra and extract accurate values of the electric field gradient tensors. Applications of NQR methods to studies of electronic structure in heavy element systems are proposed.

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Contents

1. Introduction

Nuclear quadrupole resonance (NQR) spectroscopy has long been a vital method for studying electronic structure in condensed matter [1,2] and for performing high resolution measurements of nuclear quadrupole moments [3–5]. The key parameter obtained from NQR measurements is the electric field gradient (EFG) tensor at the nuclear coordinates, which is completely determined by two independent variables, viz., the zz component of the field gradient $V_{zz} \equiv \partial^2\phi/\partial z^2$ and the tensor's asymmetry parameter $\eta \equiv (V_{xx} - V_{yy})/V_{zz}$ [2,6].

The dependence of NQR transition frequencies and intensities on the EFG tensor has been numerically mapped [7–11]. Values for η and V_{zz} may be estimated from experimentally measured NQR spectra by referring to data from this previous work. However, the approximation methods used in past calculations did not provide accurate or complete results for many cases of interest, and a more advanced and comprehensive analysis is needed for reliable interpretation of experimental spectra, especially for large η and spin quantum numbers I.

Computational formalisms have recently been described that may be used to characterize the dependence of NQR spectra on η and V_{zz} with substantially improved accuracy and detail [12,13]. The methods are generalizable to arbitrary spin quantum number I, but the majority of nuclei that are of interest for NQR spectroscopy have half-integer spin, i.e., $I = 3/2, 5/2, 7/2$, etc., ^{14}N with $I = 1$ being a notable exception. To demonstrate this approach therefore while providing data of greatest value for the interpretation of NQR experiments, quadrupolar nuclides with half-integral spin are considered exclusively in this paper.

2. Computational method

The zero field spin Hamiltonian of a quadrupolar nuclide in the principal axis system (PAS) of the EFG tensor has the form [2,6]

$$\mathcal{H}_Q = \frac{eQV_{zz}}{4I\,(2I-1)\,h}\left[3I_z^2 - \mathbf{I}^2 + \eta\left(I_x^2 - I_y^2\right)\right] \tag{1a}$$

$$= \frac{eQV_{zz}}{4I\,(2I-1)\,h}\left[3I_z^2 - \mathbf{I}^2 + \frac{\eta}{2}\left(I_+^2 + I_-^2\right)\right]. \tag{1b}$$

For $\eta = 0$, this Hamiltonian has the same eigenstates as the operator I_z; we write these states as $|m\rangle$, with m representing the eigenvalues of I_z, $I \geq m \geq -I$. The eigenstates of $\mathcal{H}_Q$ may be expressed more generally as a linear superposition of the basis states with normalized complex coefficients that are functions of η, namely

$$|\psi_n(\eta)\rangle = \sum_{m=-I}^{I} c_{nm}(\eta)|m\rangle, \tag{2}$$

where $|\psi_n(0)\rangle = |n\rangle$. Similarly, the eigenvalue of $\mathcal{H}_Q$ corresponding to the eigenstate $|\psi_n(\eta)\rangle$ can be written as a function of η, i.e., $\lambda_n(\eta)$. Because of the bilinear I_+^2 and I_-^2 terms in Eq. (1b), the only non-zero coefficients in Eq. (2) will be those with $m = n \pm 2q$, q being an integer.

The mixing of states for non-zero η is embodied by the complex coefficients in the summation in Eq. (2), which can be written

$$c_{nk}(\eta) = \langle k|\psi_n(\eta)\rangle, \tag{3}$$

where $|k\rangle$ is an eigenstate of I_z. A quantitative measure of the superposition of $|m\rangle$ states is the magnitude of $c_{nk}(\eta)$, given by the expression

$$|c_{nk}(\eta)| = \left[c_{nk}(\eta)c_{nk}^*(\eta)\right]^{1/2} = |\langle k|\psi_n(\eta)\rangle|\,. \tag{4}$$

Plots of $|\langle k|\psi_n(\eta)\rangle|$ vs. η thus reveal the extent to which variation of η mixes the basis states in the expansion of $|\psi_n(\eta)\rangle$.

To visualize the dependence of the eigenvalues and eigenstates of $\mathcal{H}_Q$ on η, it is necessary to explicitly solve for $|\psi_n(\eta)\rangle$ and $\lambda_n(\eta)$ for a densely spaced array of η values over the allowed range $1 \geq \eta \geq 0$. Evaluation of the eigenvalues is considerably simplified by observing that the matrix form of $\mathcal{H}_Q$ in the I_z basis can be arranged in a block diagonal form for $I = p/2$, p odd [7,9]. The calculations reported in this paper were performed with the use of linear algebra functions provided within the *Mathematica* programming environment [14].

Numerical diagonalization functions return the $(2I + 1)$ computed eigenvectors of a matrix in an order that may be unpredictable. A procedure must therefore be devised to definitively relate a given eigenvector $|\psi_n(\eta)\rangle$ to its "parent" state $|n\rangle$. Since the eigenvectors are by definition orthonormal, the projection of the kth basis vector onto $|\psi_n(\eta_0)\rangle$, $\eta_0 \sim 0$, should be close to unity only if $n = k$ and zero otherwise, that is

$$|\langle k|\psi_n(\eta_0)\rangle| \approx \delta_{kn}, \tag{5}$$

where δ_{kn} is the Dirac delta function. This procedure may be iterated, beginning with $\eta = 0$ and evaluating the inner products while incrementing the asymmetry parameter in steps of η_0. The criterion for deciding the parent state in the $(p+1)$th iterate in this procedure would be:

$$|\langle\psi_k(p\eta_0)|\psi_n((p+1)\eta_0)\rangle| \approx \delta_{kn}, \tag{6}$$

with p being incremented from 0 to $(\eta_0^{-1} - 1)$. In this way, the eigenstates and eigenvalues of $\mathcal{H}_Q$ can be unambiguously assigned to their parent state for each $p\eta_0$ increment from 0 to 1, even for the pairs of states $|\psi_{\pm n}(\eta)\rangle$, which are degenerate for spins with half integral I. The *Mathematica* codes developed for this work incorporate this procedure to perform the sorting and assignment tasks in an automated fashion.