Operators For The Calculation Of EPR Transition Probabilities

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Forbidden hyperfine transitions ($\Delta M = 1$, $\Delta m \neq 0$; $\Delta M \neq 1$, $\Delta m \neq 0$) arise due to the admixing of nuclear states corresponding to different m values. A procedure is described that enable one to calculate easily the intensities of EPR transitions by the use of operators; one needs only to evaluate the matrix elements of the operators between the zero-order eigenstates corresponding to the (perturbed) levels participating in the resonance.

The following spin-Hamiltonian is considered:

$$\mathcal{H} = \mu_B \vec{S}^T \cdot \tilde{g} \cdot \vec{B} + \sum_k \sum_{q=-k}^{k} \{B_k^q\}\{O_k^q\} + \vec{S}^T \cdot \tilde{A} \cdot \vec{I}. \qquad (1)$$

The various terms in eq.(1) have their usual meaning. The second-order normalized perturbed eigenfunctions, $|M,m\rangle$, of Hamiltonian (1) can be written in terms of the zero-order eigenvectors, $|M,m\rangle^0$, of the zero-order Hamiltonian as :

$$|M,m\rangle = (1 + a^{M,m}_{M\pm N,\, m\pm n})|M,m\rangle^0 + \sum_{N,n}{}' c^{M,m}_{M\pm N,\, m\pm n} |M\pm n, m\pm n\rangle^0, \qquad (2)$$

Using the usual raising and lowering operators, eq. (2) can be rewritten as :

$$|M,m\rangle = \mathcal{J}_{M,m}|M,m\rangle^0 , \qquad (3)$$

The intensity, $I_{M,m;M',m'}$, of the transition between the perturbed states $|M',m'\rangle$ and $|M,m\rangle$ is proportional to the square of the absolute value of the matrix element of the perturbing Hamiltonian

$$\mathcal{H}_{exc} = \mu_B \vec{S}^T . \tilde{g} . \vec{B}_1 . \qquad (4)$$

where $\vec{B}_1$ is the excitation field, i.e.,

$$\langle M',m'|\mathcal{H}_{exc}|M,m\rangle = {}^0\langle M',m'|\mathcal{J}^{\dagger}_{M',m'}\mathcal{H}_{exc}\mathcal{J}_{M,m}|M,m\rangle^0 . \qquad (5)$$

The calculation of the intensity thus reduces to the evaluation of the matrix elements of the operator given by eq.(5), which involves the evaluation of $\mathcal{J}^{\dagger}_{M',m'}$, $S_\alpha \mathcal{J}_{M,m}$; α = +, - and z.

In order to compare the present results with those published previously, intensities were calculated for the various transitions for the case the Zeeman and excitation fields were perpendicular to one another and assuming coincident principal axes for $\tilde{g}$, $\tilde{D}$ and $\tilde{A}$. It was found that the present results differ from Golding et al (1,2) for the $\Delta M = 1$, $\Delta m = 2$; $\Delta M = 2$, $\Delta m = 0, \pm 1$ transitions; from Mialhe (3,4) for the $\Delta M = 1$, $\Delta m = 0$ transition.

[1] R.M. Golding, R.H. Newman, A.D. Rae and W.C. Tennant J. Chem. Phys. 57 1912 (1972)

[2] R.M. Golding and W.C. Tennant Mol. Phys. 28 167 (1974)

[3] P. Mialhe and A. Erbeia Phys. Rev B7 4061 (1973)

[4] P. Mialhe and P. Quedec Phys. Rev. B14 2757 (1976)