NMR Double Quantum Transitions Using the Direct Method

BO GESTBLOM and OLA HARTMANN

Institute of Physics, University of Uppsala, Uppsala, Sweden

The transition frequencies in an NMR spectrum are usually derived as differences between the eigenvalues of the Hamiltonian operator matrix, and the intensities are then calculated from the corresponding eigenfunctions. An alternative way of deriving an NMR spectrum is given by the so-called direct method.[1] In this method the transition frequencies are obtained directly as eigenvalues to the Hamiltonian derivation superoperator.

The NMR spectrum in the presence of a strong r.f. field, such as the double quantum spectrum, may be derived by a transformation to the rotating frame. In the indirect method the eigenvalues and eigenfunctions to the rotating frame Hamiltonian must be calculated, and the double quantum transition frequencies are then obtained from the criterion of near-degeneracy of the corresponding eigenvalues.[2,3]

It is the purpose of this paper to show that double quantum spectra may be derived using the direct method without going the roundabout way of solving the eigenvalue problem of the rotating frame Hamiltonian.

Theory. The nuclear spin Hamiltonian operator in the frame rotating with the angular frequency ω of the perturbing r.f. field H_1 is given by

$$V = H^0 + \omega I^z - \gamma H_1 I^x \qquad (1)$$

Here H^0 is the spin Hamiltonian in the laboratory frame, γ is the gyromagnetic ratio of the nuclei, I^z and I^x are the Cartesian components of the spin angular momentum operator I. The energies in eqn. (1) are expressed in angular frequency units. Let us call the derivation superoperators corresponding to the three different contributions to V for A^0, A^z and A^x. The total derivation superoperator corresponding to V is called A.

Since H^0 commutes with I^z so do the derivation superoperators A^0 and A^z. This means that the matrix representation of $A^0 + A^z$ can be made blockwise diagonal, by choosing the basis operators as eigen-

operators to the A^z derivation superoperator with eigenvalues $\omega\mu$ with $\mu = 0, \pm 1, \pm 2$, etc. Basis operators with this property[4] are the shift operators R^0_{jk} which transform one eigenstate k of the spin Hamiltonian H^0 into another eigenstate j.

The transition frequencies are given by the eigenvalues of the A^0 matrix; the single quantum transitions are found from the eigenvalues in the $|\mu| = 1$ blocks, while the double quantum transitions are found from the eigenvalues in the $|\mu| = 2$ blocks, etc. Alternatively it may be said that the transitions are found at frequencies ω for which we have singularities in the different blocks of the matrix $A^0 + A^z$. This is true if we neglect the influence of the strong perturbing r.f. field H_1. If we include A^x, we will no longer obtain singularities in the strict sense within the $\mu \neq 0$ blocks, instead the resonances are found at frequencies ω for which we have local minima in the eigenvalues of the derivation superoperator A.

The derivation superoperator matrix can be evaluated without specifying the basis operators, by using a basis function representation.[4,5] The matrix elements are

$$A_{jklm} = \delta_{km} \langle j | V | l \rangle - \delta_{jl} \langle m | V | k \rangle \qquad (2)$$

This is a matrix where the two indices jk determine the row and the indices lm determine the column. If we choose the basis functions j, k ... as eigenfunctions to H^0, the $A^0 + A^z$ matrix will be diagonal with elements

$$(A^0 + A^z)_{jkjk} = E_j - E_k + \omega(M_j - M_k) \qquad (3)$$

E_j, E_k are the eigenvalues of H^0 belonging to the states j and k, and M_j, M_k are the corresponding magnetic quantum numbers. The A^x matrix is given by

$$A^x_{jklm} = -\delta_{km}\,\gamma H_1 \langle j | I^x | l \rangle + \delta_{jl}\,\gamma H_1 \langle m | I^x | k \rangle \qquad (4)$$

Double quantum transition frequency. Now consider the double quantum transition ω_{sq} between states q and s with magnetic quantum numbers $M_q = M_s + 2$. The corresponding diagonal elements of the derivation superoperator are given by

$$(A^0 + A^z)_{sqsq} = E_s - E_q - 2\omega \qquad (5\text{ a})$$

within the $\mu = -2$ block and

$$(A^0 + A^z)_{qsqs} = E_q - E_s + 2\omega \qquad (5\text{ b})$$

within the $\mu = 2$ block. It is clear that vanishing eigenvalues within these block are obtained at the frequency

$$\omega = (E_s - E_q)/2$$

The influence of H_1 can now be obtained by including A^x and evaluating the eigenvalues of A. If the diagonal elements of the matrix are large compared to the off-diagonal elements, the eigenvalues may be obtained from perturbation theory. Physically this means that the double quantum transition we study is well removed from all other transitions with which it has an off-diagonal element in the A matrix.

At the double quantum frequency the two diagonal elements $(A^0 + A^z)_{sqsq}$ and $(A^0 + A^z)_{qsqs}$ are degenerate, and the eigenvalues have to be found from a form of perturbation theory which is based on a transformation of the basis operators, which will introduce off-diagonal elements to second order in the diagonal elements of the derivation superoperator.[3,6] The transformation will also introduce a new A'_{sqqs} off-diagonal element, which is of second order in the perturbation. The new diagonal elements to second order in A^x are

$$A'_{sqsq} = E_s - E_q - 2\,\omega +$$
$$\sum_{uv} \frac{A^x_{squv}{}^2}{E_s - E_q - 2\,\omega - E_u + E_v - \omega(M_u - M_v)} \quad (6a)$$

and

$$A'_{qsqs} = E_q - E_s + 2\,\omega +$$
$$\sum_{uv} \frac{A^x_{qsuv}{}^2}{E_q - E_s + 2\,\omega - E_u + E_v - \omega(M_u - M_v)} \quad (6b)$$

The eigenvalues have to be found from a diagonalization of the corresponding 2×2 matrix, since the A'_{sqqs} element will ensure a strong mixing of the basis operators. We need not perform this diagonalization, however, since it is evident that the eigenvalues will show a minimum when the A'_{sqsq} and A'_{qsqs} elements become degenerate and equal to zero.

This occurs when

$$\omega = \frac{E_s - E_q}{2} + \tfrac{1}{2} \sum_{uv} \frac{A^x_{squv}{}^2}{E_v - E_u - \omega(M_u - M_v)} \quad (7)$$

In eqn. (7) the term $E_s - E_q - 2\,\omega$ has been dropped in the denominator, since this term is very small. Using the definition of A^x_{squv} in eqn. (4) and the relations $2\,\omega \approx E_s - E_q$ and $M_q = M_s + 2$ this can be rewritten as

$$\omega = \frac{E_s - E_q}{2} + \tfrac{1}{2}\,(\gamma H_1)^2$$

$$\left\{ \sum_u \frac{\langle s | I^x | u \rangle^2}{E_s - E_u + \omega\,(M_s - M_u)} \right.$$

$$\left. - \sum_v \frac{\langle q | I^x | v \rangle^2}{E_q - E_v + \omega\,(M_q - M_v)} \right\} \quad (8)$$

This is the same double quantum transition frequency as derived from the indirect method.[2]

Double quantum intensity. The relative intensity of a transition in the direct method is given by [1,4]
$\sum_p | T_r\,(I^y\,R_p)|^2$ where R_p are the eigenoperators corresponding to the local minima of the derivation superoperator A. To evaluate the intensity of the double quantum transition ω_{sq} we therefore need the corresponding eigenoperators.

The basis operators, $R_{jk}{}^0$ of the derivation superoperator $A^0 + A^x$ as given in eqns. (2) and (3) have the important property of annihilating all other eigenstates of H^0 except the k state which is transformed into the j state.[4]

The transformation of basis operators used in the perturbation treatment, will to first order in the perturbation A^x give the new basis operators

$$R_{sq}{}' = R_{sq}{}^0 + R_{sq}{}^P$$

and

$$R_{qs}{}' = R_{qs}{}^0 + R_{qs}{}^P$$

where $R_{sq}{}^P = \sum_{\substack{uv \\ \neq sq}} R_{uv}{}^0$ \quad (9a)

$$\frac{A^x_{squv}}{E_s - E_q - 2\,\omega - E_u + E_v - \omega(M_u - M_v)}$$

and $R_{qs}{}^P = \sum_{\substack{uv \\ \neq qs}} R_{uv}{}^0$ \quad (9b)

$$\frac{A^x_{qsuv}}{E_q - E_s + 2\,\omega - E_u + E_v - \omega(M_u - M_v)}$$

The terms $E_s - E_q - 2\,\omega$ may be dropped in the denominators of these expressions.

The complete mixing of the $R_{sq}{}'$ and $R_{qs}{}'$ basis operators at the double quantum frequency will on diagonalization of the 2×2 matrix give the new operators

$$R_{sq} = (R_{sq}' + R_{qs}')/\sqrt{2} \qquad (10a)$$

$$R_{qs} = (-R_{sq}' + R_{qs}')/\sqrt{2} \qquad (10b)$$

R_{sq} and R_{qs} are the eigenoperators of the derivation superoperator Λ to first order in the perturbation Λ^x, and are the operators to be used in evaluation of the intensity of the double quantum transition ω_{sq}.

$$I_{sq} \propto (\gamma H_1)\{|\,\mathrm{Tr}(I^y R_{sq})|^2 +$$

$$|\,\mathrm{Tr}(I^y R_{qs})|^2\} \qquad (11)$$

The trace in eqn. (11) can be evaluated in any basis, however the most favourable choice in this case is a basis of eigenfunctions to H^0.

In evaluation of the traces we will consider the contributions to the R_{sq} operators one at a time.

The shift operators $R_{sq}{}^0$ and $R_{qs}{}^0$ will not contribute to the double quantum intensity. This follows from the fact that the $R_{sq}{}^0$ operator will annihilate all basis functions in the trace except the q state, which is transformed into the s state (or *vice versa* for the $R_{qs}{}^0$ operator), however, $\langle q\,|\,I^y\,|\,s\rangle = 0$ since $M_q = M_s + 2$. Then consider the contribution from $R_{sq}{}^P$.

$$\mathrm{Tr}\,\{I^y R_{sq}{}^P\} = \gamma H_1$$

$$\mathrm{Tr}\left\{I^y\left(\sum_{v \neq q} R_{sv}{}^0 \frac{\langle v\,|\,I^x\,|\,q\rangle}{E_v - E_s - \omega(M_s - M_v)}\right.\right. \qquad (12)$$

$$\left.\left. - \sum_{u \neq s} R_{uq}{}^0 \frac{\langle s\,|\,I^x\,|\,u\rangle}{E_q - E_u - \omega(M_u - M_q)}\right)\right\}$$

Using the annihilating property of the shift operators eqn. (12) can be rewritten as

$$\mathrm{Tr}\,\{I^y R_{sq}{}^P\} = \gamma H_1\left\{\sum_{v \neq q} \frac{\langle v\,|\,I^y\,|\,s\rangle\langle v\,|\,I^y\,|\,q\rangle}{E_v - E_s - \omega(M_s - M_v)}\right.$$

$$\left. - \sum_{u \neq s} \frac{\langle q\,|\,I^y\,|\,u\rangle\,\langle s\,|\,I^x\,|\,u\rangle}{E_q - E_u - \omega\,(M_u - M_q)}\right\} \qquad (13)$$

Non-vanishing contributions to the sums in eqn. (13) are only obtained from states v and u with magnetic quantum numbers $M_u = M_v = M_q - 1 = M_s + 1$, since the I^x, I^y operators only connect states differing by unity in their magnetic quantum numbers. If we change the summation index in eqn. (19) to r $(M_r = M_q - 1)$ and use the relations $2\,\omega \simeq E_s - E_q$ and $\langle q\,|\,I^y\,|\,r\rangle = \langle r\,|\,I^y\,|\,q\rangle$ this can be rewritten as

$$|\,\mathrm{Tr}\{I^y R_{sq}{}^P\}| = |\,2\,\gamma H_1$$

$$\sum_r \frac{\langle s\,|\,I^x\,|\,r\rangle\langle r\,|\,I^x\,|\,q\rangle}{\omega - E_s + E_r}| \qquad (14)$$

since $|\,\langle s\,|\,I^x\,|\,r\rangle| = |\,\langle s\,|\,I^y\,|\,r\rangle|$.

A similar calculation shows that

$$\mathrm{Tr}\{I^y R_{qs}{}^P\} = -\,\mathrm{Tr}\{I^y R_{sq}{}^P\} \qquad (15)$$

From eqns. (11), (14), and (15) we obtain the intensity of the double quantum transition

$$I_{sq} \propto (\gamma\,H_1)^3 \sum_r \frac{\langle s\,|\,I^x\,|\,r\rangle\,\langle r\,|\,I^x\,|\,q\rangle}{\omega - E_s + E_r} \qquad (16)$$

This is the same formula as derived by the indirect method.[2]

Conclusion. The previous analysis shows that the direct method may be used to evaluate the transition frequencies also in the presence of a strong r.f. field, including the appearance of double quantum transitions. The method is applicable also in the derivation of double resonance spectra, where a similar transformation to the rotating frame is made. Although the computational advantages seem to be very limited in treating the double quantum spectra, the method has the virtue of incorporating the influence of the strong r.f. field on the transition frequencies in a straight-forward manner.

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