MODIFIED FORMALISM FOR THE DESCRIPTION OF MULTIPLE-PULSE NMR EXPERIMENTS FOR SYSTEMS WITH MAGNETIC EQUIVALENCE

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During the last decade, several density operator formalisms[1] have been developed for the description of multiple-pulse NMR experiments with more physical trasparency and easy analysis. Unfortunately, their applications to spin systems with moderate complexity are still cumbrous.

Here we propose a modified formalism for weakly coupled spin 1/2 systems with magnetic equivalence.

Symmetry Adapted Product Operator (SAPO)[2]. For I_n spin system, SAPO is constructed by a permutation symmetric combination of the convensional Cartesian product operators as formula (1), which constitute an irreducible base operator of permutation group Sn.

$$I^{(n)}=(1/2)E_n,\quad I_{\mu}^{(n)}=\sum_i I_{i\mu},\quad I_{\mu\mu}^{(n)}=\sum_{i<j}2I_{i\mu}I_{j\mu},$$
$$I_{\mu\nu}^{(n)}=\sum_{i<j}2(I_{i\mu}I_{j\nu}+I_{i\nu}I_{j\mu}),\quad I_{\mu\mu\mu}^{(n)}=\sum_{i<j<k}4I_{i\mu}I_{j\mu}I_{k\mu},$$
$$I_{\mu\mu\nu}^{(n)}=\sum_{i<j<k}4(I_{i\mu}I_{j\mu}I_{k\nu}+I_{i\mu}I_{j\nu}I_{k\mu}+I_{i\nu}I_{j\mu}I_{k\mu}),$$
$$I_{\mu\nu\omega}^{(n)}=\sum_{i<j<k}4(I_{i\mu}I_{j\nu}I_{k\omega}+I_{i\nu}I_{j\omega}I_{k\mu}+I_{i\omega}I_{j\mu}I_{k\nu}+I_{i\mu}I_{j\omega}I_{k\mu}+I_{i\nu}I_{j\mu}I_{k\omega}+I_{i\omega}I_{j\nu}I_{k\mu})$$
$$\text{etc.}\qquad (1)$$

The main advantage of SAPO is markedly reducing the number of base operators, for instance, 16 to 10 for AX, A_2 and 64 to 20 for AMX, A_3 systems respectively. In addition, general cyclic commutation relations exist among SAPO, which govern the evolution rule of multiple quantum coherences with differen orders. SAPO were used to analyse DEPT etc experiments on A_nX systems[2].

Multiple Quantum Coherence Product Operators (MQCPO). We introduced MQCPO as Hermitia combinations of irreducible tensor operators much like Weitekamp[3], but with the compo site particle spin operators instead of single spin operator:

$$K_{x\pm}^{ij}=I_x^{ij}\pm I_x^{\bar{i}\bar{j}},\qquad K_{y\pm}^{ij}=I_y^{ij}\pm I_y^{\bar{i}\bar{j}},$$
$$K_{z\pm}^{ij}=I_z^{ij}\pm I_z^{\bar{i}\bar{j}},\qquad K_{0\pm}^{ij}=I_0^{ij}\pm I_0^{\bar{i}\bar{j}}.\qquad (2)$$

Evolutions of the operator under the un perturbed weak coupling Hamiltonian are tri vil(cf. Table 1), especially evolution unde $I_z^{(n)}$ is simple. Furthermore it is turned ou that there exist simple linear relationship between SAPO and MQCPO. Taking account of th above facts, an action of rf pulse ma treated by representation transformation t Z-representation via cyclic exchange of coor dinate indexes of SAPO. Concerned using o SAPO and MQCPO made the description of coher ence transfer and evolution terse and easy i multiple-pulse experiments for systems wit magnetic equivalence. The power of this for malism is demonstrated by analysing spin pat tern filtering and heteronuclear spectr editing.

Table 1. Cyclic commutation properties of MQCPO for AnX(InS) systems

$$[I_z^{(n)},K_{x\pm}^{ij}]=ip_{ij}K_{y\pm}^{ij}\ ;\qquad [2I_z^{(n)}S_z,K_{x\pm}^{ij}]=ip_{ij}2K_{y\pm}^{ij}S_z,\qquad [2I_z^{(n)}S_z,2K_{z\pm}^{ii}S_x]=iq_{ij}2K_{z\mp}^{ii}S_y,$$
$$[2I_z^{(n)}S_z,2K_{x\pm}^{ij}S_z]=ip_{ij}K_{y\pm}^{ij}\ ,\quad [2I_z^{(n)}S_z,2K_{x\pm}^{ij}S_x]=iq_{ij}2K_{x\mp}^{ij}S_y\ ,\quad [2I_z^{(n)}S_z,2K_{y\pm}^{ij}S_x]=iq_{ij}2K_{y\mp}^{ij}S_y\ .$$

$p_{ij}=m_i-m_j$, $q_{ij}=m_i+m_j$; $p_{ij}+q_{ij}\geqslant 0$

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