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描述自旋体系密度算符演化的新方法

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提出一种描述自旋体系密度算符演化的新方法，可统一处理核磁共振波谱学中强、弱偶合自旋体系及弱射频场存在下密度算符的演化. 具体分析一些核磁共振实验：自旋轻扰、自旋锁定、偶极耦合作用、强耦合 AB 和 ABX 自旋体系的演化.

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一、引　　言

脉冲技术大大推动了核磁共振(NWR)波谱学的发展. 在设计和分析新的脉冲技术时，通常采用三种方法来描述自旋体系的演化. 第一种方法是经典或半径典矢量模型，简单直观，但不能描述涉及多量子相干和二维谱等复杂实验. 第二种方法是密度矩阵方法，能正确描述任何复杂脉冲实验，但由于涉及繁复的计算，物理含义不直观. 第三种方法是密度算符方法，既能处理复杂的脉冲实验，又保留有一定的象经典或半经典矢量模型方法的直观性. 目前普遍采用密度算符方法来描述脉冲 NWR 实验.

积算符方法[1]是最常用的描述非选择性脉冲实验的密度算符方法，可以很方便地计算自旋为 1/2 的弱耦合体系密度算符的演化. 但对强耦合体系，由于体系哈密顿量中各项并非都对易，乘积基算符方法是不适用的. 即使是弱耦合体系，在弱射频场如选择性脉冲的存在下，乘积基算符方法应用起来也是非常困难的.

为解决强耦合自旋体系问题，Kay[2]采用球谐张量基[3]方法来处理 AB 和 ABX 体系，但不涉及弱射频场的作用问题. Chandrakumar[4]应用 L öwdin 投影算符[5]把哈密顿演化传播子(propagator)指数算符展开成算符多项式，来考察自旋体系的演化过程. 投影算符方法的不足之处是构造具体的投影算符时首先要求出哈密顿量的本征值，而复杂自旋体系以及含射频场作用的自旋体系哈密顿量之本征值是不易得到或具体表达出来的，而且如果本征值有多个，则投影算符表达式是很复杂的，当用于计算密度算符的演化时是很繁复和困难的. 譬如，这种方法就难于处理强耦合自旋体系.

本文提出一种新方法来计算密度算符的演化，不需要计算哈密顿量的本征值，也不涉及表象变换问题，由算符演化分析表达式，结合合适选择的基算符及其对易关系，计算密度算符的演化. 可统一处理强、弱耦合自旋体系和弱射频场存在下的自旋体系的演化，而且应用起来较为方便.

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二、理 论

1. 算符演化公式

任一算符 $\hat{A}$ 在哈密顿量 $\hat{\mathscr{H}}$ 作用下的演化遵循 Hausdorff 公式[6]

$$\exp(-\mathrm{i}\hat{\mathscr{H}}t)\hat{A}\exp(\mathrm{i}\hat{\mathscr{H}}t) = \hat{A} + (-\mathrm{i}t)[\hat{\mathscr{H}},\hat{A}] + \frac{(-\mathrm{i}t)^2}{2!}[\hat{\mathscr{H}},[\hat{\mathscr{H}},\hat{A}]] + \frac{(-\mathrm{i}t)^3}{3!}[\hat{\mathscr{H}},[\hat{\mathscr{H}},[\hat{\mathscr{H}},\hat{A}]]] + \cdots \tag{1}$$

如果 $[\hat{\mathscr{H}},\hat{A}] = C\hat{A}$，则

$$\exp(-\mathrm{i}\hat{\mathscr{H}}t)\hat{A}\exp(\mathrm{i}\hat{\mathscr{H}}t) = \hat{A}\exp(-\mathrm{i}Ct). \tag{2}$$

简记为

$$\hat{A} \xrightarrow{\hat{\mathscr{H}}t} \hat{A}\exp(-\mathrm{i}Ct).$$

如果 $[\hat{\mathscr{H}},\hat{A}] = C_1\hat{A} + C_2\hat{B}, [\hat{\mathscr{H}},\hat{B}] = D_1\hat{A} + D_2\hat{B}$，则

$$\hat{A} \xrightarrow{\hat{\mathscr{H}}t} \hat{A}\exp(-\mathrm{i}Gt)\cos(Qt) - \frac{\mathrm{i}}{Q}\mathrm{esp}(-\mathrm{i}Ct)$$

$$[\frac{1}{2}(C_1 - D_2)\hat{A} + C_2\hat{B}]\sin(Qt), \tag{3}$$

其中 $G = (C_1 + D_2)/2$， $Q = [(C_1 - D_2)^2/4 + C_2D_1]^{1/2}$.

Banwell 和 Primas[7]最先推导出(3)式.(2)式是(3)式的特殊情况.

2. 基算符

基算符的选择是密度算符方法的关键，不同的密度算符方法采用不同的基算符.对自旋为 1/2 的二核体系，下面定义的这套基算符是合适的.

如以球谐张量基 $\hat{I}^{\pm} = \hat{I}_x \pm \mathrm{i}\hat{I}_y, \hat{I}^0 = \hat{I}_z$ 表示，以相干级 m 分类：

$m = 0$， $\hat{S}_0 = \frac{1}{2}$， $\hat{S}_1 = \frac{\mathrm{i}}{2}(\hat{I}_1^+\hat{I}_2^- - \hat{I}_1^-\hat{I}_2^+)$，

$\hat{S}_2 = \frac{1}{2}(\hat{I}_1^+\hat{I}_2^- + \hat{I}_1^-\hat{I}_2^+)$， $\hat{S}_3 = \frac{1}{2}(\hat{I}_1^0 - \hat{I}_2^0)$，

$\hat{S}_4 = \frac{1}{2}(\hat{I}_1^0 + \hat{I}_2^0)$， $\hat{S}_5 = \hat{I}_1^0\hat{I}_2^0$；

$m = 1$， $\hat{S}_6 = \hat{I}_1^+(\hat{I}_2^0 + \frac{1}{2})$， $\hat{S}_7 = (\hat{I}_1^0 + \frac{1}{2})\hat{I}_2^+$，

$\hat{S}_8 = \hat{I}_1^+(\hat{I}_2^0 - \frac{1}{2})$， $\hat{S}_9 = (\hat{I}_1^0 - \frac{1}{2})\hat{I}_2^+$；

$m = -1$， $\hat{S}_{10} = \hat{I}_1^-(\hat{I}_2^0 + \frac{1}{2})$， $\hat{S}_{11} = (\hat{I}_1^0 + \frac{1}{2})\hat{I}_2^-$，

$\hat{S}_{12} = \hat{I}_1^-(\hat{I}_2^0 - \frac{1}{2})$， $\hat{S}_{13} = (\hat{I}_1^0 - \frac{1}{2})\hat{I}_2^-$；

$m = 2$， $\hat{S}_{14} = \hat{I}_1^+\hat{I}_2^+$；

$m = -2$， $\hat{S}_{15} = \hat{I}_1^-\hat{I}_2^-$.

正交基算符定义为[8]

$$\hat{E}_{ik} = |i\rangle\langle k|, \qquad i,k = 1-4.$$

其矩阵形式为

$$\begin{array}{cc} & \quad k \\ i & \begin{bmatrix} & \vdots & \\ \cdots & \boxed{1} & \cdots \\ & \vdots & \end{bmatrix} \end{array}$$

即矩阵中只有 (i,k) 元素为 1，其余元素均为零，是单位元矩阵.

可以在无耦合表象中考察这两套基算符的关系. 选择基函数 $|1\rangle = 22, |2\rangle = 2\beta, |3\rangle = \beta\alpha, |4\rangle = \beta\beta$，求出 $\{\hat{S}_l\}$　$(l = 0-15)$ 的矩阵，与 $\hat{E}_{ik}$ 关系

$$\hat{S}_6 = \hat{E}_{13}, \quad \hat{S}_7 = \hat{E}_{12}, \quad \hat{S}_8 = \hat{E}_{24}, \quad \hat{S}_9 = \hat{E}_{34},$$
$$\hat{S}_{10} = \hat{E}_{31}, \quad \hat{S}_{11} = \hat{E}_{21}, \quad \hat{S}_{12} = \hat{E}_{42}, \quad \hat{S}_{13} = \hat{E}_{43},$$
$$\hat{S}_{14} = \hat{E}_{14}, \quad \hat{S}_{15} = \hat{E}_{41}.$$

$\hat{S}_{6\text{-}15}$ 都是单位元矩阵，其不为零的矩阵元在 4×4 维矩阵中位置见图 1.

	s_7	s_6	s_{14}
s_{11}			s_8
s_{10}			s_9
s_{15}	s_{12}	s_{13}	

图 1

$$\hat{S}_0 = \frac{1}{2}(\hat{E}_{11} + \hat{E}_{22} + \hat{E}_{33} + \hat{E}_{44}), \qquad \hat{S}_1 = \frac{i}{2}(\hat{E}_{23} - \hat{E}_{32}),$$

$$\hat{S}_2 = \frac{1}{2}(\hat{E}_{23} + \hat{E}_{32}), \qquad \hat{S}_3 = \frac{1}{2}(\hat{E}_{22} - \hat{E}_{33})$$

$$\hat{S}_4 = \frac{1}{2}(\hat{E}_{11} - \hat{E}_{44}), \qquad \hat{S}_5 = \frac{1}{4}(\hat{E}_{11} - \hat{E}_{22} - \hat{E}_{33} + \hat{E}_{44}).$$

$\hat{S}_{0-5}$不是单位元矩阵.

可以证明(见附录 A)：基算符 $\{\hat{S}_l\}$　$(l = 0-15)$ 是相互正交归一的完备集，可用来展开自旋体系的密度算符，也可用来表示乘积基算符[1]和升降算符.

这些基算符之间的对易关系 $[\hat{x},\hat{y}] = \hat{x}\hat{y} - \hat{y}\hat{x}$ 列于表 1. 利用表 1 及(3)式可计算自旋为 1/2 的二核体系的密度算符的演化.

三、应　　用

1. 自旋轻扰实验[9]

考虑自旋 1/2 的同核弱耦合二核体系 IS，选择性辐照 S 核双线中的低频分量(设 $J > 0$)，在旋转坐标系中，体系哈密顿量为[4]

$$\hat{\mathscr{H}} = \Delta I_z + \frac{J}{2}(1 + 2\hat{I}_z)\hat{S}_z + \frac{1}{2}\omega_1(1 - 2\hat{I}_z\hat{S}_x). \tag{4}$$

上式等号右端第一项描述 I 自旋的偏共根，第二项描述 IS 弱耦合及 S 自旋的偏共振，第三项描述弱射频场照射 S 核的一个跃迁产生的效应.

记 $\hat{\mathscr{H}}_1 = \Delta\hat{I}_z$，

$$\hat{\mathscr{H}}_2 = \frac{J}{2}(1 + 2\hat{I}_z)\hat{S}_z + \frac{1}{2}\omega_1(1 - 2\hat{I}_z\hat{S}_x) \tag{5}$$

由于 $\hat{\mathscr{H}}_2$,$\hat{\mathscr{H}}_2$ 对易，其作用次序可任意，本文着重研究 $\hat{\mathscr{H}}_2$ 作用下的演化.

由表 1 及(3)式得基算符演化式

$$\hat{S}_6 \xrightarrow{\hat{\mathscr{H}}_2 t} \hat{S}_6\exp(-\mathrm{i}\,\frac{J}{2}t)\cos(\frac{\omega_1}{2}t) + \mathrm{i}\hat{S}_{14}\exp(-\mathrm{i}\,\frac{J}{2}t)\sin(\frac{\omega_1}{2}t),$$

$$\hat{S}_{10} \xrightarrow{\hat{\mathscr{H}}_2 t} \hat{S}_{10}\exp(\mathrm{i}\,\frac{J}{2}t)\cos(\frac{\omega_1}{2}t) - \mathrm{i}\hat{S}_{15}\exp(\mathrm{i}\,\frac{J}{2}t)\sin(\frac{\omega_1}{2}t),$$

$$\hat{S}_8 \xrightarrow{\hat{\mathscr{H}}_2 t} \hat{S}_8\exp(\mathrm{i}\,\frac{J}{2}t)\cos(\frac{\omega_1}{2}t) - \mathrm{i}(-\mathrm{i}\hat{S}_1 + \hat{S}_2)\exp(\mathrm{i}\,\frac{J}{2}t)\sin(\frac{\omega_1}{2}t),$$

$$\hat{S}_{12} \xrightarrow{\hat{\mathscr{H}}_2 t} \hat{S}_{12}\exp(-\mathrm{i}\,\frac{J}{2}t)\cos(\frac{\omega_1}{2}t) + \mathrm{i}(\mathrm{i}\hat{S}_1 + \hat{S}_2)\exp(-\mathrm{i}\,\frac{J}{2}t)\sin(\frac{\omega_1}{2}t).$$

由

$$\hat{I}y = \frac{\mathrm{i}}{2}(\hat{S}_8 - \hat{S}_6 + \hat{S}_{10} - \hat{S}_{12}), \tag{6}$$

$$\hat{\sigma}(t) = \exp(-\mathrm{i}\hat{\mathscr{H}}_2 t)\hat{I}_y\exp(\mathrm{i}\hat{\mathscr{H}}_2 t), \tag{7}$$

得到谱线强度

$$S(t) = \frac{1}{2}\mathrm{Tr}\{\hat{I}y\hat{\sigma}(t)\} = \frac{1}{2}\left[\cos\left(\frac{J+\omega_1}{2}t\right) + \cos\left(\frac{J-\omega_1}{2}t\right)\right]. \tag{8}$$

即 I 自旋每条谱线都分裂成等强度同相的双线，裂距为 ω_1.

$$\hat{\sigma}(t) = \frac{1}{2}\hat{I}_y\left[\cos\left(\frac{J+\omega_1}{2}t\right) + \cos\left(\frac{J-\omega_1}{2}t\right)\right] - \hat{I}_x\hat{S}_z\left[\sin\left(\frac{J+\omega_1}{2}t\right) + \sin\left(\frac{J-\omega_1}{2}t\right)\right]$$
$$+ \hat{I}_x\hat{S}_y\left[\cos\left(\frac{J-\omega_1}{2}t\right) - \cos\left(\frac{J+\omega_1}{2}t\right)\right] + \hat{I}_x\hat{S}_x\left[\sin\left(\frac{J+\omega_1}{2}t\right) - \sin\left(\frac{J-\omega_1}{2}t\right)\right]. \tag{9}$$

表 1　基算符对易关系

$x \backslash y$	$\hat S_0$	$\hat S_1$	$\hat S_2$	$\hat S_3$	$\hat S_4$	$\hat S_5$	$\hat S_6$	$\hat S_7$	$\hat S_8$	$\hat S_9$	$\hat S_{10}$	$\hat S_{11}$	$\hat S_{12}$	$\hat S_{13}$	$\hat S_{14}$	$\hat S_{15}$
$\hat S_0$	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
$\hat S_1$	0	0	$i\hat S_3$	$-i\hat S_2$	0	0	$\frac{i}{2}\hat S_7$	$-\frac{i}{2}\hat S_6$	$-\frac{i}{2}\hat S_9$	$\frac{i}{2}\hat S_8$	$\frac{i}{2}\hat S_{11}$	$-\frac{i}{2}\hat S_{10}$	$-\frac{i}{2}\hat S_{13}$	$\frac{i}{2}\hat S_{12}$	0	0
$\hat S_2$	0	$-i\hat S_3$	0	$i\hat S_1$	0	0	$-\frac{1}{2}\hat S_7$	$-\frac{1}{2}\hat S_6$	$\frac{1}{2}\hat S_9$	$\frac{1}{2}\hat S_8$	$\frac{1}{2}\hat S_{11}$	$\frac{1}{2}\hat S_{10}$	$-\frac{1}{2}\hat S_{13}$	$-\frac{1}{2}\hat S_{12}$	0	0
$\hat S_3$	0	$i\hat S_2$	$-i\hat S_1$	0	0	0	$\frac{1}{2}\hat S_6$	$-\frac{1}{2}\hat S_7$	$\frac{1}{2}\hat S_8$	$-\frac{1}{2}\hat S_9$	$-\frac{1}{2}\hat S_{10}$	$\frac{1}{2}\hat S_{11}$	$-\frac{1}{2}\hat S_{12}$	$\frac{1}{2}\hat S_{13}$	0	0
$\hat S_4$	0	0	0	0	0	0	$\frac{1}{2}\hat S_6$	$\frac{1}{2}\hat S_7$	$\frac{1}{2}\hat S_8$	$\frac{1}{2}\hat S_9$	$-\frac{1}{2}\hat S_{10}$	$-\frac{1}{2}\hat S_{11}$	$-\frac{1}{2}\hat S_{12}$	$-\frac{1}{2}\hat S_{13}$	$\hat S_{14}$	$-\hat S_{15}$
$\hat S_5$	0	0	0	0	0	0	$\frac{1}{2}\hat S_6$	$\frac{1}{2}\hat S_7$	$-\frac{1}{2}\hat S_8$	$-\frac{1}{2}\hat S_9$	$-\frac{1}{2}\hat S_{10}$	$-\frac{1}{2}\hat S_{11}$	$\frac{1}{2}\hat S_{12}$	$\frac{1}{2}\hat S_{13}$	0	0
$\hat S_6$	0	$-\frac{i}{2}\hat S_7$	$\frac{1}{2}\hat S_7$	$-\frac{1}{2}\hat S_6$	$-\frac{1}{2}\hat S_6$	$-\frac{1}{2}\hat S_6$	0	0	0	$-\hat S_{14}$	$\hat S_3+\hat S_4+2\hat S_5$	$i\hat S_1-\hat S_2$	$\hat S_3+\hat S_4$	0	0	$\hat S_{13}$
$\hat S_7$	0	$\frac{i}{2}\hat S_6$	$\frac{1}{2}\hat S_6$	$\frac{1}{2}\hat S_7$	$-\frac{1}{2}\hat S_7$	$-\frac{1}{2}\hat S_7$	0	0	$-\hat S_{14}$	0	$-i\hat S_1-\hat S_2$	$-\hat S_3+\hat S_4+2\hat S_5$	0	$-\hat S_3+\hat S_4$	0	$\hat S_{12}$
$\hat S_8$	0	$\frac{i}{2}\hat S_9$	$-\frac{1}{2}\hat S_9$	$-\frac{1}{2}\hat S_8$	$-\frac{1}{2}\hat S_8$	$\frac{1}{2}\hat S_8$	0	$\hat S_{14}$	0	0	$\hat S_3+\hat S_4$	0	$\hat S_3+\hat S_4-2\hat S_5$	$-i\hat S_1+\hat S_2$	0	$-\hat S_{11}$
$\hat S_9$	0	$-\frac{i}{2}\hat S_8$	$-\frac{1}{2}\hat S_8$	$\frac{1}{2}\hat S_9$	$-\frac{1}{2}\hat S_9$	$\frac{1}{2}\hat S_9$	$\hat S_{14}$	0	0	0	0	$-\hat S_3+\hat S_4$	$i\hat S_1+\hat S_2$	$-\hat S_3+\hat S_4-2\hat S_5$	0	$-\hat S_{10}$
$\hat S_{10}$	0	$-\frac{i}{2}\hat S_{11}$	$-\frac{1}{2}\hat S_{11}$	$\frac{1}{2}\hat S_{10}$	$\frac{1}{2}\hat S_{10}$	$\frac{1}{2}\hat S_{10}$	$-\hat S_3-\hat S_4-2\hat S_5$	$i\hat S_1+\hat S_2$	$-\hat S_3-\hat S_4$	0	0	0	0	$\hat S_{15}$	$-\hat S_9$	0
$\hat S_{11}$	0	$\frac{i}{2}\hat S_{10}$	$-\frac{1}{2}\hat S_{10}$	$-\frac{1}{2}\hat S_{11}$	$\frac{1}{2}\hat S_{11}$	$\frac{1}{2}\hat S_{11}$	$-i\hat S_1+\hat S_2$	$\hat S_3-\hat S_4-2\hat S_5$	0	$\hat S_3-\hat S_4$	0	0	$\hat S_{15}$	0	$-\hat S_8$	0
$\hat S_{12}$	0	$\frac{i}{2}\hat S_{13}$	$\frac{1}{2}\hat S_{13}$	$\frac{1}{2}\hat S_{12}$	$\frac{1}{2}\hat S_{12}$	$-\frac{1}{2}\hat S_{12}$	$-\hat S_3-\hat S_4$	0	$-\hat S_3-\hat S_4+2\hat S_5$	$-i\hat S_1-\hat S_2$	0	$-\hat S_{15}$	0	0	$\hat S_7$	0
$\hat S_{13}$	0	$-\frac{i}{2}\hat S_{12}$	$\frac{1}{2}\hat S_{12}$	$-\frac{1}{2}\hat S_{13}$	$\frac{1}{2}\hat S_{13}$	$-\frac{1}{2}\hat S_{13}$	0	$\hat S_3-\hat S_4$	$i\hat S_1-\hat S_2$	$\hat S_3-\hat S_4+2\hat S_5$	$-\hat S_{15}$	0	0	0	$\hat S_6$	0
$\hat S_{14}$	0	0	0	0	$-\hat S_{14}$	0	0	0	0	0	$\hat S_9$	$\hat S_8$	$-\hat S_7$	$-\hat S_6$	0	$2\hat S_4$
$\hat S_{15}$	0	0	0	0	$\hat S_{15}$	0	$-\hat S_{13}$	$-\hat S_{12}$	$\hat S_{11}$	$\hat S_{10}$	0	0	0	0	$-2\hat S_4$	0

2. **自旋锁定实验**

同核 IS 体系在共振或 Hartmann-Hahn 匹配的偏共振自旋锁定实验的哈密顿量为[10-12]

$$\hat{\mathscr{H}} = J\hat{I}\cdot\hat{S} = J(\hat{S}_2 + \hat{S}_5). \tag{10}$$

由

$$\hat{I}x = \frac{1}{2}(\hat{S}_6 - \hat{S}_8 + \hat{S}_{10} - \hat{S}_{12}), \tag{11}$$

$$\hat{S}_6 \xrightarrow{\hat{\mathscr{H}}t} \hat{S}_6\exp(-\mathrm{i}\frac{J}{2}t)\cos(\frac{J}{2}t) + \mathrm{i}\hat{S}_7\exp(-\mathrm{i}\frac{J}{2}t)\sin(\frac{J}{2}t),$$

$$\hat{S}_8 \xrightarrow{\hat{\mathscr{H}}t} \hat{S}_8\exp(\mathrm{i}\frac{J}{2}t)\cos(\frac{J}{2}t) - \mathrm{i}\hat{S}_9\exp(\mathrm{i}\frac{J}{2}t)\sin(\frac{J}{2}t),$$

$$\hat{S}_{10} \xrightarrow{\hat{\mathscr{H}}t} \hat{S}_{10}\exp(\mathrm{i}\frac{J}{2}t)\cos(\frac{J}{2}t) - \mathrm{i}\hat{S}_{11}\exp(\mathrm{i}\frac{J}{2}t)\sin(\frac{J}{2}t),$$

$$\hat{S}_{12} \xrightarrow{\hat{\mathscr{H}}t} \hat{S}_{12}\exp(-\mathrm{i}\frac{J}{2}t)\cos(\frac{J}{2}t) + \mathrm{i}\hat{S}_{13}\exp(-\mathrm{i}\frac{J}{2}t)\sin(\frac{J}{2}t),$$

得到自旋为 1/2 的二核体系的演化式：

$$\hat{I}_x \xrightarrow{\hat{\mathscr{H}}t} \frac{1}{2}\hat{I}_x[1 + \cos(Jt)] + \frac{1}{2}\hat{S}_x[1 - \cos(Jt)] + (\hat{I}_y\hat{S}_z - \hat{I}_z\hat{S}_y)\sin(Jt). \tag{12}$$

3. **偶极耦合作用**

在旋转坐标系中，自旋为 1/2 的二核 IS 体系偶极耦合作用哈密顿量为

$$\hat{\mathscr{H}}_d = \frac{\gamma^2 h}{4\pi r_{IS}^3}(1 - 3\cos^2\theta)(3\hat{I}_z\hat{S}_z - \hat{I}\cdot\hat{S}), \tag{13}$$

记

$$C = \frac{\gamma^2 h}{4\pi r_{IS}^3}(1 - 3\cos^2\theta),$$

$$\hat{\mathscr{H}}_d = C(3\hat{I}_z\hat{S}_z - \hat{I}\cdot\hat{S}) = C(2\hat{S}_5 - \hat{S}_2). \tag{14}$$

由

$$\hat{S}_6 \xrightarrow{\hat{\mathscr{H}}dt} \hat{S}_6\exp(-\mathrm{i}Ct)\cos(\frac{C}{2}t) - \mathrm{i}\hat{S}_7\exp(-\mathrm{i}Ct)\sin(\frac{C}{2}t),$$

$$\hat{S}_8 \xrightarrow{\hat{\mathscr{H}}dt} \hat{S}_8\exp(\mathrm{i}Ct)\cos(\frac{C}{2}t) + \mathrm{i}\hat{S}_9\exp(\mathrm{i}Ct)\sin(\frac{C}{2}t),$$

$$\hat{S}_{10} \xrightarrow{\hat{\mathscr{H}}dt} \hat{S}_{10}\exp(\mathrm{i}Ct)\cos(\frac{C}{2}t) + \mathrm{i}\hat{S}_{11}\exp(\mathrm{i}Ct)\sin(\frac{C}{2}t),$$

$$\hat{S}_{12} \xrightarrow{\hat{\mathscr{H}}dt} \hat{S}_{12}\exp(-\mathrm{i}Ct)\cos(\frac{C}{2}t) - \mathrm{i}\hat{S}_{13}\exp(-\mathrm{i}Ct)\sin(\frac{C}{2}t),$$

$$\hat{I}_x \xrightarrow{\hat{\mathscr{H}}dt} \frac{1}{2}\hat{I}_x[\cos(\frac{3}{2}Ct) + \cos(\frac{1}{2}Ct)] + \frac{1}{2}\hat{S}_x[\cos(\frac{3}{2}Ct) - \cos(\frac{1}{2}Ct)]$$
$$+ I_y\hat{S}_z[\sin(\frac{3}{2}Ct) + \sin(\frac{1}{2}Ct)] + \hat{I}_z\hat{S}_y[\sin(\frac{3}{2}Ct) - \sin(\frac{1}{2}Ct)] \tag{15}$$

以上列举的三个例子,Chandrakumar 曾用投影算符方法[4]分析过,结果与本文一致.但对强耦合自旋体系,投影算符方法就难于应用.

4. 自旋为 1/2 的强耦合二核 AB 体系

AB 体系哈密顿量为

$$\mathscr{H} = \Omega_A \hat{A}_Z + \Omega_B \hat{B}_Z + J(\hat{A}_x \hat{B}_x + \hat{A}_y \hat{B}_y + \hat{A}_z \hat{B}_z). \tag{16}$$

令 $\Omega_0 = \Omega_A + \Omega_B$, $\Delta = \Omega_A - \Omega_B$, 则

$$\mathscr{H} = \Omega_0 \hat{S}_4 + \Delta \hat{S}_3 + J(\hat{S}_5 + \hat{S}_2),$$

$$\hat{F}^- = \hat{A}^- + \hat{B}^- = \hat{S}_{10} + \hat{S}_{11} - \hat{S}_{12} - \hat{S}_{13}.$$

记

$$\rho_1 = \frac{1}{2}(\Omega_0 + J),$$

$$\rho_2 = \frac{1}{2}(\Omega_0 - J),$$

$$\lambda = \frac{1}{2}(J^2 + \Delta^2)^{1/2} = \frac{1}{2}R,$$

$$\begin{aligned}\hat{F}^- \xrightarrow{\mathscr{H}t} & (\hat{S}_{10} + \hat{S}_{11})\exp(i\rho_1 t)\cos(\lambda t) - (\hat{S}_{12} + \hat{S}_{13})\exp(i\rho_2 t)\cos(\lambda t) \\ & - \frac{i}{\lambda}\exp(i\rho_1 t)[-\frac{\Delta}{2}(\hat{S}_{10} - \hat{S}_{11}) + \frac{J}{2}(\hat{S}_{10} + \hat{S}_{11})]\sin(\lambda t) \\ & + \frac{i}{\lambda}\exp(i\rho_2 t)[-\frac{\Delta}{2}(\hat{S}_{12} - \hat{S}_{13}) - \frac{J}{2}(\hat{S}_{12} + \hat{S}_{13})]\sin(\lambda t).\end{aligned} \tag{17}$$

谱线强度为

$$\begin{aligned}S(t) = & \frac{1}{4}(1 - \frac{J}{2\lambda})\{\exp[\frac{i}{2}(\Omega_0 + J + R)] + \exp[\frac{i}{2}(\Omega_0 - J - R)]\} \\ & + \frac{1}{4}(1 + \frac{J}{2\lambda})\{\exp[\frac{i}{2}(\Omega_0 + J - R)] + \exp[\frac{i}{2}(\Omega_0 - J + R)]\}.\end{aligned} \tag{18}$$

表明同核 AB 体系在 $\pi/2$ 脉冲作用后有四条谱线(见表 2)

表 2

频率	$(\Omega_0+J+R)/2$	$(\Omega_0+J-R)/2$	$(\Omega_0-J+R)/2$	$(\Omega_0-J-R)/2$
强度	$1-J/2\lambda$	$1+J/2\lambda$	$1+J/2\lambda$	$1-J/2\lambda$

这与用量子力学处理 AB 体系的能量本征值问题得到的结果[13]一致.

类似地,可求出乘积基算符方法所采用的乘积基算符 $\hat{A}_x, \hat{A}_y, \hat{A}_z, 2\hat{A}_x\hat{B}_z, 2\hat{A}_y\hat{B}_z$ 等之演化表式,如

$$\begin{aligned}\hat{A}_x \xrightarrow{\mathscr{H}t} & \hat{A}_x a_1 C + \hat{A}_y a_2 C - 2\hat{A}_x\hat{B}_z a_2 S + 2\hat{A}_y\hat{B}_z a_1 S \\ & + 2\hat{A}_z\hat{B}_x a_3 C - 2\hat{A}_z\hat{B}_y a_4 C + \hat{B}_x a_4 S + \hat{B}_y a_3 S,\end{aligned} \tag{19}$$

$$\begin{aligned}2\hat{A}_x\hat{B}_z \xrightarrow{\mathscr{H}t} & 2\hat{A}_x\hat{B}_z a_1 C - \hat{A}_x a_2 S + \hat{A}_y a_1 S + 2\hat{A}_y\hat{B}_z a_2 C \\ & + 2\hat{A}_z\hat{B}_y a_3 S + 2\hat{A}_z\hat{B}_x a_4 S + \hat{B}_x a_3 C - \hat{B}_y a_4 C,\end{aligned} \tag{20}$$

其中

$$a_1(t)=\cos(\frac{\Omega_0}{2}t)\cos(\lambda t)-\frac{\Delta}{2\lambda}\sin(\frac{\Omega_0}{2}t)\sin(\lambda t),$$

$$a_2(t)=\sin(\frac{\Omega_0}{2}t)\cos(\lambda t)+\frac{\Delta}{2\lambda}\cos(\frac{\Omega_0}{2}t)\sin(\lambda t),$$

$$a_3(t)=\frac{J}{2\lambda}\sin(\frac{\Omega_0}{2}t)\sin(\lambda t),$$

$$a_4(t)=\frac{J}{2\lambda}\cos(\frac{\Omega_0}{2}t)\sin(\lambda t),$$

$$C(t)=\cos(\frac{J}{2}t),$$

$$S(t)=\sin(\frac{J}{2}t).$$

(19),(20)式在 $\Delta\gg J$ 时化为

$$\hat{A}_x\xrightarrow{\hat{\mathscr{H}}t}\hat{A}_xa_1C+\hat{A}_ya_2C-2\hat{A}_x\hat{B}_za_2S+2\hat{A}_y\hat{B}_za_1S, \tag{21}$$

$$2\hat{A}_x\hat{B}_z\xrightarrow{\hat{\mathscr{H}}t}2\hat{A}_x\hat{B}_za_1C-\hat{A}_xa_2S+\hat{A}_ya_1S+2\hat{A}_y\hat{B}_za_2C. \tag{22}$$

这正是用乘积基算符方法[1]处理自旋为 1/2 的弱耦合 AB 体系的结果.

5. 自旋为 1/2 的强耦合三核 ABX 体系

ABX 体系哈密顿量为

$$\hat{\mathscr{H}}=\Omega_A\hat{A}_z+\Omega_B\hat{B}_Z+\Omega_x\hat{X}_z+J_{AB}\hat{A}\cdot\hat{B}+J_{AX}\hat{A}_z\hat{X}_Z+J_{BX}\hat{B}_Z\hat{X}_Z. \tag{23}$$

令 $\Omega_0=\Omega_A-\Omega_B,\Delta=\Omega_A-\Omega_B,\bar{J}=J_{AX}+J_{BX},\delta J=J_{AX}-J_{BX},$

则

$$\hat{\mathscr{H}}=(\Omega_0+\bar{J}\hat{X}_z)\hat{S}_4+(\Delta+\delta J\hat{X}_z)\hat{S}_3+J_{AB}(\hat{S}_2+\hat{S}_5)+\Omega_X\hat{X}_z. \tag{24}$$

再令 $\rho_1^{\pm}=(\Omega_0+J_{AB})/2\pm\bar{J}/4,\quad \rho_2^{\pm}=(\Omega_0-J_{AB})/2\pm\bar{J}/4,$

$\lambda^{\pm}=\frac{1}{2}[J_{AB}^2+(\Delta\pm\frac{1}{2}\delta J)^2]^{1/2}=\frac{1}{2}R^{\pm},$

由

$$(\hat{S}_{10}+\hat{S}_{11})(1\pm2\hat{X}_Z)\xrightarrow{\hat{\mathscr{H}}t}(\hat{S}_{10}+\hat{S}_{11})(1\pm2\hat{X}_Z)\exp(\mathrm{i}\rho_1^{\pm}t)\cos(\lambda^{\pm}t)-\frac{\mathrm{i}}{2\lambda^{\pm}}$$

$$\exp(\mathrm{i}\rho_1^{\pm}t)[-(\Delta\pm\frac{1}{2}\delta J)(\hat{S}_{10}-\hat{S}_{11})+J_{AB}(\hat{S}_{10}+\hat{S}_{11})](1\pm2\hat{X}_Z)\sin(\lambda^{\pm}t),$$

$$(\hat{S}_{12}+\hat{S}_{13})(1\pm2\hat{X}_Z)\xrightarrow{\hat{\mathscr{H}}t}(\hat{S}_{12}+\hat{S}_{13})(1\pm2\hat{X}_Z)\exp(\mathrm{i}\rho_2^{\pm}t)\cos(\lambda^{\pm}t)$$

$$-\frac{\mathrm{i}}{2\lambda^{\pm}}\exp(\mathrm{i}\rho_2^{\pm}t)[-(\Delta\pm\frac{1}{2}\delta J)(\hat{S}_{12}-\hat{S}_{13})-J_{AB}(\hat{S}_{12}+\hat{S}_{13})](1\pm2\hat{X}_Z)\sin(\lambda^{\pm}t)$$

和
$$\hat{F}_{AB}^{-} = \hat{S}_{10} + \hat{S}_{11} - \hat{S}_{12} - \hat{S}_{13}, \tag{25}$$
得 ABX 体系中 AB 子体系的密度算符为

$$\begin{aligned}
\hat{\sigma}_{AB}(t) &= \exp(-\mathrm{i}\hat{\mathscr{H}}t)\hat{F}_{AB}^{-}\exp(\mathrm{i}\hat{\mathscr{H}}t) \\
&= (\hat{S}_{10} + \hat{S}_{11})(1 + 2\hat{X}_Z)\exp(\mathrm{i}\rho_1^{+}t)\cos(\lambda^{+} t) + (\hat{S}_{10} + \hat{S}_{11})(1 - 2\hat{X}_Z) \\
&\quad \times \exp(\mathrm{i}\rho_1^{-}t)\cos(\lambda^{-} t) - (\hat{S}_{12} + \hat{S}_{13})(1 + 2\hat{X}_Z)\exp(\mathrm{i}\rho_2^{+}t)\cos(\lambda^{+} t) \\
&\quad - (\hat{S}_{12} + \hat{S}_{13})(1 - 2\hat{X}_Z)\exp(\mathrm{i}\rho_2^{-}t)\cos(\lambda^{-} t) \\
&\quad - \frac{\mathrm{i}}{2\lambda^{+}}\exp(\mathrm{i}\rho_1^{+}t)[-(\Delta + \frac{1}{2}\delta J)(\hat{S}_{10} - \hat{S}_{11}) + J_{AB}(\hat{S}_{10} + \hat{S}_{11})](1 + 2\hat{X}_Z)\sin(\lambda^{+} t) \\
&\quad - \frac{\mathrm{i}}{2\lambda^{-}}\exp(\mathrm{i}\rho_1^{-}t)[-(\Delta - \frac{1}{2}\delta J)(\hat{S}_{10} - \hat{S}_{11}) + J_{AB}(\hat{S}_{10} + \hat{S}_{11})](1 - 2\hat{X}_Z)\sin(\lambda^{-} t) \\
&\quad + \frac{\mathrm{i}}{2\lambda^{+}}\exp(\mathrm{i}\rho_2^{+}t)[-(\Delta + \frac{1}{2}\delta J)(\hat{S}_{12} - \hat{S}_{13}) - J_{AB}(\hat{S}_{12} + \hat{S}_{13})](1 + 2\hat{X}_Z)\sin(\lambda^{+} t) \\
&\quad + \frac{\mathrm{i}}{2\lambda^{-}}\exp(\mathrm{i}\rho_2^{-}t)[-(\Delta - \frac{1}{2}\delta J)(\hat{S}_{12} - \hat{S}_{13}) - J_{AB}(\hat{S}_{12} + \hat{S}_{13})](1 - 2\hat{X}_Z)\sin(\lambda^{-} t).
\end{aligned} \tag{26}$$

自由感应衰减信号为

$$\begin{aligned}
S_{AB}(t) &= \frac{1}{8}Tr\{\hat{F}_{AB}^{+}\hat{\sigma}_{AB}(t)\} \\
&= \frac{1}{8}(1 - \frac{J_{AB}}{2\lambda^{+}})\{\exp[\mathrm{i}(\Omega_0 + \bar{J}/2 + J_{AB} + R^{+})/2] + \exp[\mathrm{i}(\Omega_0 + \bar{J}/2 - J_{AB} - R^{+})/2]\} \\
&\quad + \frac{1}{8}(1 + \frac{J_{AB}}{2\lambda^{+}})\{\exp[\mathrm{i}(\Omega_0 + \bar{J}/2 + J_{AB} - R^{+})/2] + \exp[\mathrm{i}(\Omega_0 + \bar{J}/2 - J_{AB} + R^{+})/2]\} \\
&\quad + \frac{1}{8}(1 - \frac{J_{AB}}{2\lambda^{-}})\{\exp[\mathrm{i}(\Omega_0 - \bar{J}/2 + J_{AB} + R^{-})/2] + \exp[\mathrm{i}(\Omega_0 - \bar{J}/2 - J_{AB} - R^{-})/2]\} \\
&\quad + \frac{1}{8}(1 + \frac{J_{AB}}{2\lambda^{-}})\{\exp[\mathrm{i}(\Omega_0 - \bar{J}/2 + J_{AB} - R^{-})/2] + \exp[\mathrm{i}(\Omega_0 - \bar{J}/2 - J_{AB} + R^{-})/2]\}
\end{aligned} \tag{27}$$

表明 ABX 体系中同核强耦合 AB 子体系在 $\pi/2$ 脉冲作用后有 8 条谱线(见表 3).

表 3

频　率	强　度
$(\Omega_0+\bar{J}/2+J_{AB}+R^{+})/2$	$1-J_{AB}/2\lambda^{+}$
$(\Omega_0+\bar{J}/2-J_{AB}+R^{+})/2$	$1+J_{AB}/2\lambda^{+}$
$(\Omega_0+\bar{J}/2+J_{AB}-R^{+})/2$	$1+J_{AB}/2\lambda^{+}$
$(\Omega_0+\bar{J}/2-J_{AB}-R^{+})/2$	$1-J_{AB}/2\lambda^{+}$
$(\Omega_0-\bar{J}/2+J_{AB}+R^{-})/2$	$1-J_{AB}/2\lambda^{-}$
$(\Omega_0-\bar{J}/2-J_{AB}+R^{-})/2$	$1+J_{AB}/2\lambda^{-}$
$(\Omega_0-\bar{J}/2+J_{AB}-R^{-})/2$	$1+J_{AB}/2\lambda^{-}$
$(\Omega_0-\bar{J}/2-J_{AB}-R^{-})/2$	$1-J_{AB}/2\lambda^{-}$

这与用量子力学解 ABX 体系的能量本征值问题而得到 AB 子体系的谱线频率位置和强度[13]一致. X 核的演化较为复杂,这里略去.

类似可求出乘积基算符的演化式,如

$$\begin{aligned}\hat{A}_x \xrightarrow{\mathscr{H}t} & \hat{A}_x h_1^+ C + \hat{A}_y h_2^+ C + \hat{B}_x h_4^+ S + \hat{B}_y h_3^+ S - 2\hat{A}_x \hat{B}_Z h_2^+ S + 2\hat{A}_y \hat{B}_Z h_1^+ S \\ & + 2\hat{A}_z \hat{B}_x h_3^+ C - 2\hat{A}_z \hat{B}_y h_4^+ C + 2\hat{A}_x \hat{X}_Z h_1^- C + 2\hat{A}_y \hat{X}_Z h_2^- C \\ & + 2\hat{B}_x \hat{X}_Z h_4^- S + 2\hat{B}_y \hat{X}_Z h_3^- S - 4\hat{A}_x \hat{B}_Z \hat{X}_Z h_2^- S + 4\hat{A}_y \hat{B}_Z \hat{X}_Z h_1^- S \\ & + 4\hat{A}_Z \hat{B}_x \hat{X}_Z h_3^- C - 4\hat{A}_Z \hat{B}_y \hat{X}_Z h_4^- C \end{aligned} \tag{28}$$

其中 $h_i^{\pm} = (a_i^+ \pm a_i^-)/2 \quad (i = 1 - 4)$,

$$\Omega_0^{\pm} = \Omega_0 \pm J_{AB}, \Delta^{\pm} = \Delta \pm \frac{1}{2}\delta J,$$

$$a_1^{\pm}(t) = \cos(\frac{\Omega_0^{\pm}}{2}t)\cos(\lambda^{\pm} t) - \frac{\Delta^{\pm}}{2\lambda^{\pm}}\sin(\frac{\Omega_0^{\pm}}{2}t)\sin(\lambda^{\pm} t),$$

$$a_2^{\pm}(t) = \sin(\frac{\Omega_0^{\pm}}{2}t)\cos(\lambda^{\pm} t) + \frac{\Delta^{\pm}}{2\lambda^{\pm}}\cos(\frac{\Omega_0^{\pm}}{2}t)\sin(\lambda^{\pm} t),$$

$$a_3^{\pm}(t) = \frac{J_{AB}}{2\lambda^{\pm}}\sin(\frac{\Omega_0^{\pm}}{2}t)\sin(\lambda^{\pm} t),$$

$$a_4^{\pm}(t) = \frac{J_{AB}}{2\lambda^{\pm}}\cos(\frac{\Omega_0^{\pm}}{2}t)\sin(\lambda^{\pm} t),$$

$$C(t) = \cos(\frac{J_{AB}}{2}t), \qquad S(t) = \sin(\frac{J_{AB}}{2}t).$$

上面几个例子表明本文提出的描述自旋体系密度算符演化的方法是成功的,可方便地计算弱射频场存在下自旋体系的演化,统一处理自旋为 1/2 的强、弱耦合体系的演化. 值得一提的是,本文提出的这种密度算符方法,还可用来描述强耦合 AB 体系在偏共振的自旋锁定实验(如旋转坐标系的 ROESY 实验)和 J 交叉极化实验(如 JCP,RJCP 实验)中的演化,计算其理论谱,这方面的工作将另文介绍.

附 录 A

证明 $\{s_l\}(l = 0 - 15)$ 是正交归一的基算符完备集

1. $\hat{S}_l(l = 6 - 15)$ 相互正交归一

$\hat{S}_{6-15}$ 是单位元矩阵,等于相应的正交基算符 $\hat{E}_{ik}$,易证 $\hat{E}_{ik}$ 是正交归一的,

$$\begin{aligned}(\hat{E}_{ik}, \hat{E}_{lm}) &= \mathrm{Tr}\{\hat{E}_{ik}\hat{E}_{lm}\} \\ &= \sum_p \langle p|\hat{E}_{ik}{}^+ \hat{E}_{lm}|p\rangle \\ &= \sum_p \langle p|k\rangle\langle i|l\rangle\langle m|p\rangle \\ &= \sum_p \delta_{ik}\delta_{il}\delta_{pm} \\ &= \delta_{il}\delta_{km}.\end{aligned}$$

得证 $\hat{E}_{ik}$ 是正交归一的,从而得证 $\hat{S}_{6-15}$ 也是正交归一的.

2. $\hat{S}_l(l = 0 - 5)$ 相互正交归一

用 $\hat{S}_{0-5}$ 与 $\hat{E}_{ik}$ 的关系式很容易证明,如

$$(\hat{S}_0, \hat{S}_1) = \frac{i}{4}(\hat{E}_{11} + \hat{E}_{22} + \hat{E}_{33} + \hat{E}_{44}, \hat{E}_{23} - \hat{E}_{32}) = 0,$$

$$(\hat{S}_1,\hat{S}_1)=\frac{1}{4}(\hat{E}_{23}-\hat{E}_{32},\hat{E}_{23}-\hat{E}_{32})=1.$$

同理可证明其它的 $(\hat{S}_i,\hat{S}_j)=\delta_{ij}(i,j=0-5)$.

3. $\hat{S}_l(l=0-5)$ 与 $\hat{S}_l(l=6-15)$ 正交

$\hat{S}_{0-5}$ 是 $\hat{E}_{11},\hat{E}_{22},\hat{E}_{33},\hat{E}_{44},\hat{E}_{23},\hat{E}_{32}$ 的线性组合,而 $\hat{S}_{6-15}$ 分别等于 $\hat{E}_{13},\hat{E}_{12},\hat{E}_{24},\hat{E}_{34},\hat{E}_{31},\hat{E}_{21},\hat{E}_{42},\hat{E}_{43},\hat{E}_{14},\hat{E}_{41}$,由 $\hat{E}_{ik}$ 的正交性知 $\hat{S}_{0-5}$ 与 $\hat{S}_{6-15}$ 正交.

以上证明了 $\{\hat{S}_l\}(l=0-15)$ 是正交归一的.

4. $\{\hat{S}_l\}(l=0-15)$ 是完备集.

$\{\hat{E}_{ik}\}$ 是正交归一的完备集,而 $\{\hat{S}_l\}$ 都可化为 $\{\hat{E}_{ik}\}$ 的线性组合,或者反过来讲 $\{\hat{E}_{ik}\}$ 都可化为 $\{\hat{S}_l\}$ 的线性组合,因此 $\{\hat{S}_l\}$ 也是完备集,可以用来展开密度算符.

采用 $\{\hat{S}_l\}$ 这一套基算符的好处是能简洁地表示体系的哈密顿量,并容易满足算符演化公式即(3)式的条件.

[1] O. W. Sorensen, G. W. Eich, M. H. Levitt, G. Bodenhausen and R. R. Ernst, *Prog. NMR Spectrosc.*, **16** (1983), 163.

[2] L. E. Kay, *J. Magn. Reson.*, **77**(1988), 258.

[3] T. T. Nakashima and R. E. D. McClung, *J. Magn. Reson.*, **70**(1986), 187.

[4] N. Chandrakumar, *J. Magn. Reson.*, **88**(1990), 86.

[5] P. O. Lowdin, *Rev. Mod. Phys.*, **34**(1962), 520.

[6] F. Hausdorff and Leipzig. Ber. Ges. Wiss, *Math. Phys.*, **58**(1906), 19.

[7] C. N. Banwell and H. Primas, *Mol. Phys.*, **6**(1963), 225.

[8] R. R. Ernst, G. Bodenhausen and A. Wokaun, Principles of Nuclear Magnetic Resonance in One and Two Dimensions (Clarendon Press, Oxford, 1987), pp. 9-43.

[9] W. A. Anderson and R. Freeman, *J. Chem. Phys.*, **37**(1962), 85. R. Freeman and W. A. Anderson. *J. Chem. Phys.*, **37**(1962), 2053.

[10] L. Braunschweiler and R. R. Ernst, *J. Magn. Reson.*, **53**(1983), 521.

[11] N. Chandrakumar and S. Subramanian, *J. Magn. Reson.*, **62**(1985), 346.

[12] N. Chandrakumar, *J. Magn. Reson.*, **71**(1987), 322.

[13] 裘祖文、裴奉奎,核磁共振波谱(科学出版社,北京,1989),112—137 页.

A NEW FORMALISM FOR DESCRIBING THE EVOLUTION OF DENSITY OPERATORS

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ABSTRACT

A new formalism for describing the evolution of density operators was proposed. It can evaluate the evolution of density operators of strongly and weakly coupled spin systems in a unified way, and describe the experiments involving weak RF pluse. Some problems were explicitly treated including spin tickling, isotropic mixing in systems of two coupled nuclei ($I=1/2$), dipolar evolution and strongly coupled AB and ABX spin systems.

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