

## APPENDIX D: PROPERTIES OF PRODUCT OPERATORS

A system of  $m$  spin 1/2 nuclei has  $N = 2^m$  states. The basis set for this system consists of  $N^2$  product operators (PO) which are  $N \times N$  hermitian matrices. We summarize here the most significant features of these matrices.

1. There is only one nonvanishing element per row. As a consequence, any PO has only  $N$  nonvanishing elements out of  $N^2$  elements.

2. There is also only one nonvanishing element per column. Properties 1 and 2 are found in the matrices representing angular momentum components  $I_x, I_y, I_z$  (see Appendix C). A product of two matrices having these properties inherits them.

3. The nonvanishing elements of a PO are either  $\pm 1$  or  $\pm i$ .

4. If  $P_j$  and  $P_k$  are two product operators from the basis set, the trace (sum of diagonal elements) of their product is

$$\text{Tr}(P_j P_k) = N \delta_{jk} \quad (\text{D1})$$

where  $\delta_{jk}$  (the Kronecker delta) has the value

$$\begin{aligned} \delta_{jk} &= 0 & \text{if } j \neq k \\ \delta_{jk} &= 1 & \text{if } j = k \end{aligned}$$

The property (D1) illustrates the *orthogonality* of the PO's. The product of two different PO's is traceless. The square of a given PO is equal to the unit matrix, therefore its trace is equal to  $N$ .

### Expressing a given matrix in terms of PO's

Since the basis set is a complete set, any  $N \times N$  matrix can be expressed as a linear combination of PO's :

$$D = c_1 P_1 + c_2 P_2 + \dots + c_L P_L \quad \text{where} \quad L = N^2 \quad (\text{D2})$$

Given the matrix  $D$ , the coefficients  $c_j$  can be determined using the orthogonality relation (D1).

$$\text{Tr}(DP_j) = \sum_{k=1}^m c_k \text{Tr}(P_k P_j) = \sum_{k=1}^m c_k N \delta_{kj} = N c_j \quad (\text{D3})$$

Therefore 
$$c_j = \frac{1}{N} \text{Tr}(DP_j) \quad (\text{D4})$$

In the PO treatment of NMR sequences we do not have to go through the routine described above since we start with the density matrix expressed in terms of PO's and we have rules for any rotation or evolution which give the new density matrix also expressed in terms of PO's. For the same reason, we do not need to know the PO's in their matrix form in order to operate with them.

The complete basis set for  $m = 2$  ( $N = 4$ ) is given in table II.1. We give in the following pages a few examples of PO's in matrix form for  $m = 3$  ( $N = 8$ ) and for  $m = 4$  ( $N = 16$ ). At the end of this appendix a computer program can be found (written in BASIC) which can help generate all the product operators for  $n = 2, 3$ , or 4.

In all the matrices given below as examples, the dots represent zeros.

$$\begin{aligned}
 [111] &= \begin{bmatrix} 1 & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & 1 & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & 1 & \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & 1 & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & 1 & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & 1 & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & 1 & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & 1 \end{bmatrix} &
 [11y] &= \begin{bmatrix} \cdot & \cdot & \cdot & \cdot & -i & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & -i & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & -i & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & -i \\ i & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & i & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & i & \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & i & \cdot & \cdot & \cdot & \cdot \end{bmatrix} \\
 [z11] &= \begin{bmatrix} 1 & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & -1 & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & 1 & \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & -1 & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & 1 & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & -1 & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & 1 & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & -1 \end{bmatrix} &
 [1y1] &= \begin{bmatrix} \cdot & \cdot & -i & \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & -i & \cdot & \cdot & \cdot & \cdot \\ i & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & i & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & -i & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & -i \\ \cdot & \cdot & \cdot & \cdot & i & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & i & \cdot & \cdot \end{bmatrix}
 \end{aligned}$$









```

118 PRINT " X - Exit MENU"
120 M%=14
125 FOR I%=1 TO M% : PRINT : NEXT I%
130 INPUT MENU$
135 IF MENU$="A" THEN GOSUB 4050
137 IF MENU$="B" THEN GOSUB 4000
139 IF MENU$="C" THEN GOSUB 4050
141 IF MENU$="D" THEN GOSUB 4000
143 IF MENU$="E" THEN GOSUB 4500
145 IF MENU$="F" THEN GOSUB 4500
170 PRINT " Do you want to join the MENU again ? (Y or N)"
175 INPUT A$
180 IF A$="Y" THEN 75
935 END
940 REM- Subroutine 940-3650 to calculate all PO for given NN%
945 REM- Zero order product operator (unit matrix)
950 FOR M%=1 TO NS%
955 N%(0,M%)=M%
960 D%(0,M%)=1
965 MEXT M%
970 F%(0)=0
975 REM- First order product operators Ix, Iy, Iz
980 FOR K%=1 TO NN%
985 K1%=2^(K%-1) : K2%=K1%*K1%
990 F%(K2%)=0 : F%(2*K2%)=1 : F%(3*K2%)=0
995 M%=1 : SG%=1
1000 FOR C%=1 TO K1%
1010 N%(K2%,M%)=M%+SG%*K1%
1020 N%(2*K2%,M%)=M%+SG%*K1%
1030 N%(3*K2%,M%)=M%
1040 D%(K2%,M%)=1
1050 D%(2*K2%,M%)=-SG%
1060 D%(3*K2%,M%)=SG%
1070 M%=M%+1
1080 NEXT C%
1090 SG%=-SG%
1100 IF M%<=NS% THEN 1000
1100 NEXT K%
2000 REM- Second order base operators (Two factor PO's)
2010 FOR KA%=1 TO NN%-1
2020 FOR KB%=KA%+1 TO NN%
2030 FOR JA%=1 TO 3
2040 FOR JB%=1 TO 4
2050 K2A%=4^(KA%-1)
2060 K2B%=4^(KB%-1)
2070 SA%=JA%*K2A% : SB%=JB%*K2B%
2080 GOSUB 5000
2090 NEXT JB%
2100 NEXT JA%

```

154 Appendix D

```
2110 NEXT KB%
2120 NEXT KA%
3000 REM- Three factor product operators
3010 IF NN%<3 THEN 3625
3020 FOR KC%=1 TO NN%-2
3030 FOR KD%=KC%+1 TO NN%-1
3040 FOR KB%=KD%+1 TO NN%
3050 FOR JC%=1 TO 3
3060 FOR JD%=1 TO 3
3070 FOR JB%=1 TO 3
3080 K2C%=4^(KC%-1) : K2D%=4^(KD%-1) : K2B%=4^(KB%-1)
3090 SC%=JC%*K2C% : SD%=JD%*K2D% : SB%=JB%*K2B%
3100 SA%=SC%+SD%
3100 GOSUB 5000
3120 NEXT JB%
3130 NEXT JD%
3140 NEXT JC%
3150 NEXTKB%
3160 NEXT KD%
3170 NEXT KC%
3500 REM- Four factor product operators
3510 IF NN%<4 THEN 3625
3520 FOR JC%=1 TO 3
3530 FOR JD%=1 TO 3
3540 FOR JE%=1 TO 3
3550 FOR JB%=1 TO 3
3560 SA%=JC%+4*JD%+16*JE%
3570 SB%=64*JB%
3580 GOSUB 5000
3590 NEXT JB%
3600 NEXT JE%
3610 NEXT JD%
3620 NEXT JC%
3625 REM- Operator labeling
3630 FOR S%=0 TO NS%^2-1
3635 GOSUB 3900
3637 NEXT S%
3640 REM- All product operators are now calculated and labeled
3641 REM- Arrays d(s,m), n(s,m), F(s) and B$(s) are filled
3650 RETURN
3900 REM- Subroutine 3900-3045 generates label, given s
3901 B$="[ "
3904 R%=S%
3908 FOR I%=1 TO NN%
3912 J%(I%)=R%-4*INT(R%/4)
3916 R%=INT(R%/4)
3920 IF J%(I%)=0 THEN JS(I%)="1"
3924 IF J%(I%)=1 THEN JS(I%)="x"
3928 IF J%(I%)=2 THEN JS(I%)="y"
```



```

3932 IF J%(I%)=3 THEN J$(I%)="z"
3936 B$=B$+J$(I%)
3940 NEXT I%
3943 B$=B$+"J"
3945 RETURN
3950 REM- Subroutine 3950-3995 generates s, given label
3952 P=0 : S%=0
3955 FOR I%=1 TO NN%
3960 IF J$(I%)="1" THEN J%(I%)=0 GOTO 3985
3965 IF J$(I%)="X" THEN J%(I%)=1 GOTO 3985
3970 IF J$(I%)="Y" THEN J%(I%)=2 GOTO 3985
3975 IF J$(I%)="Z" THEN J%(I%)=3 GOTO 3985
3980 P=1 : GOTO 3995
3985 S%=S%+4^(I%-1)*J%(I%)
3990 NEXT I%
3995 RETURN
4000 REM- Subroutine 4000-4040 to output all product operators
4005 IF MENU$="D" THEN MENU$="C"
4010 FOR S%=0 TO NS%^2-1
4020 GOSUB 4155
4030 NEXT S%
4040 RETURN
4050 REM- Subroutine 4050-4110 to output one specified PO
4051 PRINT "Please label desired product operator, e.g. ";
4052 IF NN%=2 THEN B$="X,Y or 1,Z etc."
4053 IF NN%=3 THEN B$="X,Y,Z or 1,X,Y etc."
4054 IF NN%=4 THEN B$="X,Y,X,Z or X,Y,Z,1 etc."
4055 PRINT B$
4056 PRINT " then press RETURN"
4060 IF NN%=2 THEN INPUT J$(1),J$(2)
4070 IF NN%=3 THEN INPUT J$(1),J$(2),J$(3)
4080 IF NN%=4 THEN INPUT J$(1),J$(2),J$(3),J$(4)
4090 GOSUB 3950
4095 IF P>0 THEN 4105
4100 GOSUB 4155 : GOTO 4107
4105 PRINT : PRINT : PRINT "Please try again "
4107 PRINT "Do you want another ? (Y or N)"
4108 INPUT A$ : IF A$="Y" THEN 4050
4110 RETURN
4155 REM- Subroutine 4155-4275 to display or print on PO, given s
4160 PRINT : PRINT B$(S%)+ " = " : PRINT
4166 IF MENU$="C" THEN 4167 ELSE 4170
4167 LPRINT : LPRINT B$(S%)+ " = " : LPRINT
4170 FOR M%=1 TO NS%
4180 FOR I%=1 TO N%(S%,M%)-1
4190 PRINT " . ";
4195 IF MENU$="C" THEN 4196 ELSE 4200
4196 LPRINT " . ";
4200 NEXT I%

```

156 Appendix D

```

4210 D%=D%(S%,M%)
4220 GOSUB 5300
4230 PRINT D$;
4235 IF MENU$="C" THEN 4236 ELSE 4240
4236 LPRINT D$;
4240 FOR I%=N%(S%,M%)=1 TO NS%
4250 PRINT " .";
4255 IF MENU$="C" THEN 4256 ELSE 4260
4256 LPRINT " .";
4260 NEXT I%
4265 PRINT
4266 IF MENU$="C" THEN LPRINT ELSE 4270
4270 NEXT M% : PRINT : PRINT
4272 IF MENU$="C" THEN 4273 ELSE 4275
4273 LPRINT : LPRINT
4275 RETURN
4400 PRINT "Do you want another ? (Y or N)" : INPUT H$
4410 IF H$="Y" THEN 4002
4500 REM- Subroutine 4500-4790 to express a given matrix
4501 REM- in terms of product operators
4530 FOR M%=0 TO NS% : FOR N%=0 TO NS%
4540 A(M%,N%)=0 : B(M%,N%)=0
4550 NEXT N% : NEXT M%
4555 PRINT "How many nonvanishing elements in the matrix ?"
4556 INPUT N
4560 PRINT "For every nonvanishing element in your matrix"
4561 PRINT "      d(m,n) = a + i*b"
4562 PRINT "please enter: m, n, a, b then press RETURN"
4569 FOR I%=1 TO N
4570 INPUT M%,N%,A,B
4580 A(M%,N%)=A : B(M%,N%)=B
4590 NEXT I%
4600 T$="Your matrix has the following non-zero elements"
4601 PRINT T$
4601 IF MENU$="F" THEN LPRINT T$
4610 FOR M%=1 TO NS% : FOR N%=1 TO NS%
4620 IF A(M%,N%)=0 THEN IF B(M%,N%)=0 THEN 4640
4625 B$="+i*" : B=B(M%,N%)
4626 IF B<0 THEN B=-B : B$="-i*"
4630 PRINT "d("M%","N%")=", A(M%,N%),B$;B
4635 IF NEMU$="F" THEN 4636 ELSE 4640
4636 LPRINT "d("M%","N%")=", A(M%,N%),B$;B
4640 NEXT N% : NEXT M%
4645 PRINT : PRINT : PRINT "Your matrix ="
4646 IF MENU$="F" THEN 4647 ELSE 4650
4647 LPRINT : LPRINT : LPRINT "Your matrix ="
4650 FOR S%=0 TO NS%^2-1
4660 R%=1-F%(S%)
4665 CR=0 : CI=0

```

```

4670 FOR M%=1 TO NS%
4680 N%=N%(S%,M%)
4690 CR=CR+(A(M%,N%)*R%+B(M%,N%)*F%(S%))*D%(S%,M%)
4700 CI=CI+(B(M%,N%)*R%-A(M%,N%)*F%(S%))*D%(S%,M%)
4710 NEXT M%
4720 CR=CR/2 : CI=CI/2
4730 IF CR=0 THEN IF CI=0 THEN 4780
4735 B$="+i" : B=CI
4736 IF CI<0 THEN B=-B : B$="-i*"
4740 PRINT "("CR,B$;B;)"*"$B$(S$)
4745 IF MENU$="F" THEN 4746 ELSE 4780
4746 LPRINT "("CR,B$;B;)"*"$B$(S$)
4780 NEXT S%
4781 PRINT : PRINT
4790 RETURN
5000 REM- Subroutine 5000-5090 special matrix multiplication
5010 S%=SA%+SB%
5020 FOR M%=1 TO NS%
5030 MB%=N%(SA%,M%)
5040 N%(S%,M%)=N%(SB%,MB%)
5050 D%(S%,M%)=D%(SA%,M%)*D%(SB%,MB%)5060 NEXT M%
5070 F%(S%)=F%(SA%)+F%(SB%)
5080 IF F%(S%)>1 THEN GOSUB 5100
5090 RETURN
5100 F%(S%)=0
5110 FOR M%=1 TO NS%
5120 D%(S%,M%)=-D%(S%,M%)
5122 NEXT M%
5130 RETURN

```