Pulse sequence editing by symbolic calculation — Sample diagrams

Michael P. Barnett∗and István Pelczer†

January 30, 2010

Construction of Figure 2.1

draw[pulseSeq[HETCOR, refocused] =
{channels[H1, C13], {pulse[90], }, delay[t1/2], {, pulse[180], delay[t1/2],
delay[1/(2J)], pulse[90], delay[1/(3J)], {decouple, acquire}[taq]]}

Figure 2.1. Refocused HETCOR.
Construction of Figure 2.2

draw[pulseSeq[INEPT, gradientAssisted] =
 {channels[H1, C13, Gz], {pulse[90], }, delay[1/(4J)], pulse[180, x],
 delay[1/(4J)], {pulse[90, x]}, gradientPulse[5 s], {, pulse[90, y]},
 {, acquire[taq]}}]

Figure 2.2. Gradient assisted INEPT.

Construction of Figure 2.3

draw[pulseSeq[2D, TOCSY] =
 {channels[H1], pulse[90], delay[t1], spinLock[taum], acquire[t2]})

Figure 2.3. 2D basic TOCSY.
Construction of Figure 2.4

pulseSeq[2D, HSQC, basic] =
{channels[H1, N15], {pulse[90], }, delay[Delta], pulse[180],
delay[Delta], pulse[90], delay[t1/2], {pulse[180], }, delay[t1/2],
pulse[90], delay[Delta], pulse[180], delay[Delta],
{acquire, decouple}[t2]}

drawPulseSequence[2D, HSQC, basic, notes[ "Delta = 1/(4J), J = J[1, NH]"]]

\[\begin{array}{c}
\text{H} \\
90^\circ & \Delta & 180^\circ & \Delta & 90^\circ & \Delta & 180^\circ & \text{t1/2} & 180^\circ & \text{t1/2} & 90^\circ & \Delta & 180^\circ & \Delta & \text{t2} \\
\Delta & \Delta & \Delta & \Delta & \Delta & \Delta & \Delta & \Delta & \Delta & \Delta & \Delta & \Delta & \Delta & \Delta & \Delta & \Delta \\
\text{N} & 180^\circ & 90^\circ & 90^\circ & 180^\circ & \text{decouple} & \phi = x, y, -x, -y; \text{receiver} = -y, x, y, -x \\
\end{array}\]

\[\Delta = 1/(4J), J = J[1, NH]\]

Figure 2.4. 2D basic HSQC.

Phase cycling

phaseList = "phi = x, y, -x, -y; receiver = -y, x, y, -x"

phaseCycled[explanatory] = phaseCycle[phaseList][pulseSeq[short]]

phaseCycled[explanatory] // expand[] =>
{channels[H1], pulse[90, " x"], delay[t], acquire[tq], pulse[90, " y"],
delay[t], acquire[tq], pulse[90, " -x"], delay[t], acquire[tq],
pulse[90, " -y"], delay[t], acquire[tq]}

forCTHSQC = "phi1 = x, -x; phi2 = 8(x), 8(-x); phi3 = 2(x), 2(y), 2(-x), 2(-y); phi4 = 16(y), 16(-y); receiver = 2(x, -x, -x, x), 2(-x, x, x, -x)"

cyclingReplacementRules[forCTHSQC] =>
{(phi1 -> " x", phi2 -> x, phi3 -> x, phi4 -> y, receiver -> x),
{phi1 -> " -x", phi2 -> x, phi3 -> x, phi4 -> y, receiver -> -x},
<<28 cycles >>
{phi1 -> " x", phi2 -> -x, phi3 -> -y, phi4 -> -y, receiver -> x),
{phi1 -> " -x", phi2 -> -x, phi3 -> -y, phi4 -> -y, receiver -> -x})
Construction of Figure 3.1

\[
pulseSeq[2D, HSQC, basic, TOCSY] = pulseSeq[2D, HSQC, basic] // insert[spinLock[tau], on[H1], before[acquire]]
\]

drawPulseSequence[2D, HSQC, basic, TOCSY, notes["Delta = 1/(4J), J = J[1, NH]"]]

\[
1^H \Delta \rightarrow \Delta \rightarrow t_{1/2} \rightarrow t_{1/2} \rightarrow \Delta \rightarrow \Delta \rightarrow \tau_m \rightarrow t_2
\]

\[
15^N \Delta \rightarrow \Delta \rightarrow t_{1/2} \rightarrow t_{1/2} \rightarrow \Delta \rightarrow \Delta
\]

\[
\Delta = 1/(4J), J = J[1, NH]
\]

Figure 3.1. 2D basic HSQC TOCSY.

Construction of Figure 3.2

\[
pulseSeq[2D, HSQC, gradientSelected] = pulseSeq[2D, HSQC, basic] // pipe[
    insert[gradientPulse[10], in[delay[t1/2], 2]],
    insert[gradientPulse[-1], in[delay[Delta], 3]]]
\]

drawPulseSequence[2D, HSQC, gradientSelected, notes["t1/2 > gradient pulse"]]

\[
1^H \Delta \rightarrow \Delta \rightarrow t_{1/2} \rightarrow t_{1/2} \rightarrow \Delta \rightarrow \Delta \rightarrow t_2
\]

\[
15^N \Delta \rightarrow \Delta \rightarrow t_{1/2} \rightarrow t_{1/2} \rightarrow \Delta \rightarrow \Delta
\]

\[
G_z
\]

Figure 3.2. 2D gradient selected HSQC.
Construction of Figure X.1

pulseSeq[2D, HSQC, editedGradientSelected] = pulseSeq[2D, HSQC, basic] //
    pipe[  
        insert[spinEcho, on[N15], after[delay[t1/2], 2]],  
        insert[gradientPulse[10], in[delay[te/2], 2]],  
        insert[gradientPulse[1], in[delay[Delta], 3]]
    ]

drawPulseSequence[2D, HSQC, editedGradientSelected,  
    notes["te/2 >gradient pulse duration"]];

Figure X.1. 2D edited gradient selected HSQC.
Construction of Figure X.2

pulseSeq[2D, HSQC, gradientEnhanced] = pulseSeq[2D, HSQC, basic] // pipe[insert[gradientChannel], numberThePulses, pulse[3][_] -> Sequence[{pulse[90], }, gradientPulse[7s], {, pulse[90]}], pulse[5][_] -> Sequence[{, pulse[90]}, gradientPulse[10], {pulse[90], }, gradientPulse[-1]], unnumberThePulses]
drawPulseSequence[2D, HSQC, gradientEnhanced]

Figure X.2. 2D gradient enhanced HSQC.

Composite pulses

RRRbRb = {R} // attachCopy // attachInverse => {R, R, -R, -R}
waltz4 = RRRbRb /. R -> {1, -2, 3} // Flatten => {1, -2, 3, 1, -2, 3, -1, 2, -3, -1, 2, -3}
waltz8 = Rp // attachInverse => {-2, 4, -2, 3, -1, 2, -4, 2, -3, 1, -2, 4, -2, 3, -1}
waltz16 = waltz8 // RotateRight // attachInverse // coalesce => {-3, 4, -2, 3, -1, 2, -4, 2, -3, 3, -4, 2, -3, 1, -2, 4, -2, 3, 3, -4, 2, -3, 1, -2, 4, -2, 3}
**Construction of Figures 4.1, X3, X4**

adaptAssignmentOfPulse[2D, HSQC, basic, TOCSY, by[basic -> gradientSelected]]

This produces the following intermediate result, and the statement after it produces Figure 4.1.

{channels[H1, N15, Gz], {pulse[90], Null}, delay[Delta], pulse[180], delay[Delta], pulse[90], delay[t1/2], {pulse[180], Null},
{delay, delay, gradientPulse[10]}[t1/2], pulse[90],
{delay, delay, gradientPulse[-1]}[Delta], pulse[180], delay[Delta],
{spinLock, Null, Null}[taum], {acquire, decouple}[t2]}

drawPulseSequence[2D, HSQC, gradientSelected, TOCSY]

---

**Figure 4.1.** 2D gradient selected HSQC TOCSY.

Reconstruct Figure 4.1 and construct Figures X.3, X.4:

(adaptAssignmentOfPulse[2D, HSQC, basic, TOCSY, by[basic -> #]];
drawPulseSequence[2D, HSQC, #, TOCSY])&
{gradientSelected, editedGradientSelected, gradientEnhanced};

---

**Figure X.3.** 2D edited gradient selected HSQC TOCSY.
See nmr.dta for the intermediate expressions that reconstruct Figure 4.1, and (re)construct the further diagrams in this note.

Figure X.4. 2D gradient enhanced HSQC TOCSY.

**Construction of Figures 4.2, X.5, X.6, X.7**

```math
hsqcList = 
{basic, gradientSelected, editedGradientSelected, gradientEnhanced}

(pulseSeq[2D, TOCSY, HSQC, #] =
 pulseSeq[2D, HSQC, #] //
           insert[spinLock[taum], on[H1], before[delay[Delta], 1] ];
 drawPulseSequence[2D, TOCSY, HSQC, #]) & @ hsqcList
```

Figure 4.2. 2D basic TOCSY HSQC.
Figure X.5. 2D gradient selected TOCSY HSQC.

Figure X.6. 2D edited gradient selected TOCSY HSQC.

Figure X.7. 2D gradient enhanced TOCSY HSQC.
Construction of Figures 4.3, X8, X9, X10

\[
\text{list} = \text{pulseSeq}(\text{3D, HSQC, TOCSY}) = \text{pulseSeq}(2D, \text{HSQC, TOCSY}) /\!
\text{pipe} \left[ \text{insert} \left[ \text{spinEcho, on} \left[ N_{15} \right], \text{before} \left[ \text{spinLock} \right] \right], t_2 \rightarrow t_3, te \rightarrow t_2 \right]; \text{drawPulseSequence}(\text{3D, HSQC, TOCSY}) & /\!
\text{hsqcList}
\]

Figure 4.3. Basic 3D HSQC TOCSY.

Figure X.8. 3D gradient selected HSQC TOCSY.

Figure X.9. 3D edited gradient selected HSQC TOCSY.
Construction of Figures 4.4, X11, X12, X13

list[3D, TOCSY, HSQC] = adaptAssignmentOf[ list[3D, HSQC, TOCSY],
  by[sequence[HSQC, #, TOCSY] -> sequence[TOCSY, HSQC, #]] ]

=>
list[3D, TOCSY, HSQC] =
(pulseSeq[3D, TOCSY, #, HSQC] = pulseSeq[2D, TOCSY, #, HSQC] //
  pipe[insert[spinEcho, on[N15], before[spinLock]], t2 -> t3, te -> t2];
drawPulseSequence[3D, TOCSY, #, HSQC])& /@ hsqcList

Figure 4.4. 3D basic TOCSY HSQC.

Figure X.10. 3D gradient enhanced HSQC TOCSY.

Figure X.11. 3D gradient selected TOCSY HSQC.
Figure X.12. 3D edited gradient selected TOCSY HSQC.

Figure X.13. 3D gradient enhanced TOCSY HSQC.

Acknowledgements

This work could not have been done without the expertise and patience of the computer experts to whom the authors have turned on an almost daily basis. In particular, we thank Dan Nordlund in the Chemistry Department, Neal Bituin, Greg Blaha, Tom Byrne, Dan Candeto, Mark Giannullo, Tom McStravock, Jesse Saunders, Eric Swingle, Donna Sy and Brad Wells in the Help Desk team of the Office of Information Technology, accessible 24/7, and Tom Francais, Becky Goodman, Paula Hulick and Mark Talarick, in other OIT groups.