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Technology Report

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A Coin-Flipping Analogy and Web App for Teaching Spin–Spin Splitting in ^{1}H NMR Spectroscopy

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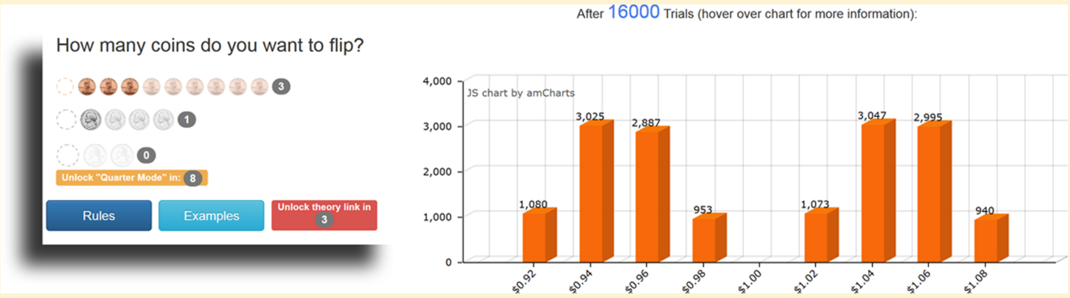
Ⓢ *Supporting Information*



How many coins do you want to flip?

After 16000 Trials (hover over chart for more information):

ABSTRACT: A coin-flipping analogy and free corresponding web app have been developed to facilitate student understanding of the origins of spin–spin splitting. First-order splitting patterns can easily be derived and understood. "Complex" splitting patterns (e.g., doublet of quartets), are easily incorporated into the analogy. A study of the efficacy of the analogy/web app vs traditional lecture showed that the analogy worked as well as traditional lecture for overall NMR analysis, and better than traditional lecture for understanding the origins of splitting and why a signal has a given shape and peak-height ratio. The web app is freely available online, as discussed in the report.

KEYWORDS: *Second-Year Undergraduate, Organic Chemistry, Analogies/Transfer, Internet/Web-Based Learning, NMR Spectroscopy*

Mastering ^{1}H NMR analysis and understanding why ^{1}H NMR signals arise are two different cognitive abilities. Understanding can be difficult for students,[1] especially if they have not enrolled in a physics course. In particular, understanding why spin–spin splitting (or coupling, or multiplicity) occurs can be a confusing subject for students.[2]

One difficulty encountered with the explanation of spin–spin splitting and NMR spectroscopy as a whole is the introduction of a large amount of new vocabulary[3] in a short period of time ("chemical shift", "up(down)field", "(de)shielded", "*J* value", etc.). Many of the new vocabulary terms have colloquial definitions which may be dramatically different than their usage within the context of NMR spectroscopy ("resonance", "integration", "with(against) the field", etc.). Furthermore, the same concept may be described by more than one new vocabulary word ("splitting/multiplicity/coupling", "peak/signal", "*J* value/coupling constant").

Understanding the origins of spin–spin splitting can be additionally complicated for students, because the introduction of this abstract concept uses new vocabulary in similar yet slightly different and nuanced ways. Discussion of the "observed (or resonating) proton(s)" vs the "neighboring proton(s)," or the "external magnetic field" vs the "effective magnetic field" which the observed proton(s) "feel" can lead to one of two pedagogical approaches, one instructor-centered, one student-centered. If the instructor truly wants students to have conceptual understanding, the first approach involves the instructor delving deeper into the underlying physics. This can be problematic if students have not taken a physics course. When the first technique fails, this can lead to the second approach: students memorizing the "n+1" rule for the correlation between "neighboring protons" and the number of peaks within the signal.

The memorizing technique suffers from two shortcomings. (1) Students can have considerable trouble transferring the "n+1" rule to "complex splitting patterns" such as doublet of doublets, and (2) a student who memorizes does not understand why splitting patterns arise and will not benefit from long-term retention.

Many articles in this journal focus on helping students analyze and interpret spectra,[4−6] including incorporating NMR analysis into laboratory courses[7−10] or earlier in the lecture course—even at the general chemistry level.[11,12] But few offer better ways to improve student understanding of why the NMR spectra appear the way they do.

One such article suggests introducing NMR spectroscopy on the first day of organic chemistry, starting with ^{13}C DEPT NMR spectra, continuing with more examples to introduce structure, isomerism, unsaturation, aromaticity, and chirality in the first three lectures.[13] Another suggests using computer-

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aided molecular modeling to illustrate magnetic anisotropy, inductive deshielding, and long-range coupling.[14]

Few articles focus on spin−spin splitting specifically, and those that do typically focus on interpreting the signals,[15−17] or using "Pascal-like" triangles for determining the peak height ratio for nuclei with any spin number,[18−21] rather than understanding the origin of spin−spin splitting. To help students understand the origins of spin−spin splitting, one article proposes using computational chemistry as a guide.[22] Another study uses navigational compasses and a homemade permanent magnet to work through the physics of NMR spectroscopy, including the effect of "neighboring" compasses on the "observed" compass.[23]

In considering various teaching strategies, analogies can be employed to help students understand various components of NMR spectroscopy. One letter proposes a telescope analogy to explain difference in resolution between chemical shift and coupling constants.[24] One article offers a cinematographic analogy for understanding the reciprocity of spin−spin splitting: each actor's facial expressions are a result of interactions with his interlocutor.[25] The analogy serves well in a general sense, but stops short of explaining the derivation of the peak height ratios.

■ PURPOSE

This report offers a relatable, concrete coin-flipping analogy and associated free web app for teaching the origins of spin−spin splitting. Students can understand why a signal is split into multiple peaks, why the "n+1" rule holds, and why the peak height ratios are predictable. Perhaps most useful is the ease with which different *J* values can be incorporated into the analogy. A doublet of quartets simply becomes another case, rather than a dramatically different scenario requiring an entirely new explanation. The free web app[26] includes scenarios corresponding to the analogy, allowing additional practice and explanation at home.

■ DESCRIPTION OF ANALOGY

To introduce the analogy, the students are told that they work at a casino which pays them \$1/day, and every day they may gamble the value of their daily wage by flipping one penny when they clock in. If the penny lands obverse-side up ("heads"), the daily wage is increased by \$0.01, but landing reverse-side up ("tails") decreases the daily wage by \$0.01. Each day they start over with a new \$1 daily wage. The students predict the outcomes (distribution and frequency) over one month of working at the casino. See the Supporting Information for an example narrative.

Depending on time constraints, students can physically flip coins to generate results themselves. This example demonstrates that the "spin-state" of the penny influences the ultimate value of that day's wage. Flipping one penny generates two possible outcomes, \$0.99 or \$1.01, in a 1:1 distribution called a doublet. It follows that flipping one nickel would similarly yield two outcomes, \$0.95 or \$1.05 in a 1:1 ratio, where only the distance between outcomes (the "*J* value") changes.

Students are guided through more examples with more than one penny. They are told that during the second month of employment, they may flip two pennies per day. Flipping two pennies derives a triplet with outcomes of either \$0.98, \$1.00, or \$1.02 (with the same \$0.02 "*J* value" as the doublet) in a 1:2:1 ratio. Flipping more pennies derives the remaining simple splitting patterns. The analogy can be related back to the physical and theoretical basis of NMR spectroscopy using the terminology already applied. Just as the value of the day's wage was influenced by the random spin state of a collection of pennies, the chemical shift value of a proton is influenced by the random spin state of the neighboring protons. Further, some combinations are more probable; thus, some outcomes are more abundant. By closing the loop back to the physical and theoretical basis of spin−spin splitting, the students will understand not only the statistical reasoning but also the physical basis for the phenomenon.

With the context firmly grounded, students can imagine flipping a penny and a nickel, or a nickel and two pennies, and students understand why complex splitting patterns adopt the shape and peak-height ratio they do. Working backward, the analogy allows students to understand how to draw molecular fragments for structures giving rise to a doublet of quartets, for example, the vinyl *β*-proton of methyl crotonate, by having flipped 1 nickel and 3 pennies, Figure 1.

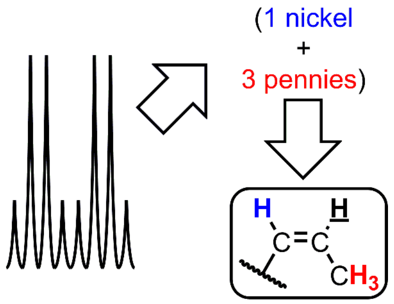


Figure 1. Using the coin-flip analogy to analyze a doublet of quartets.

■ FREE WEB APP

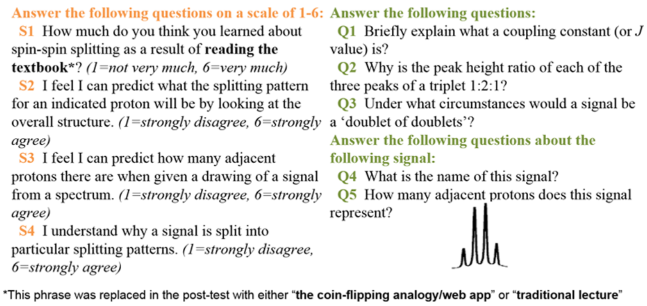
To accompany the coin-flipping analogy, a free web app[26] was developed for students to interact with the analogy outside of class. Students may select a collection of pennies or nickels, and the web app simulates the flipping of these coins thousands of times. The result is graphed and takes the shape of a regular splitting pattern. This web app benefits students by providing immediate feedback and the ability to simulate relatively complex splitting patterns instantaneously. The frequency of each outcome is also plotted on each graph, showing the relative peak height ratio for each splitting pattern. The web app includes an explanation page for further reinforcement of the concepts. Students also have the ability to unlock "Quarter Mode" to introduce a third *J* value.

■ METHODS

The participants in this two-year study consisted of a control classroom and an intervention classroom taught by different instructors (due to constraints in the scheduling of classes at the institution). A total of 182 students were enrolled among both classes (68 in the intervention classroom, 91 in the control classroom during spring 2013, summer 2013, and spring 2014). Informed consent was received, and a brief pre/post-test assessment was given.

The night before spin−spin splitting was discussed, students in both classrooms were assigned to read the section of the textbook covering spin−spin splitting.[27] The students completed identical unannounced pretests the following day. The students in the control classroom received typical, lecture-based instruction on spin−spin splitting, while students in the intervention classroom were led through the coin-flipping analogy and introduced to the web app. Students in the intervention classroom were instructed to practice predicting spin−spin splitting using the web app overnight. The day following completion of either the coin-flipping intervention or the control lectures, students completed identical unannounced post-tests (identical to each other and to the pretest). The web app was freely available to all students for the remainder of the semester.

The pre/post-test consisted of four Likert scale questions (Figure 2, survey questions S1−S4) and five content questions (Figure 2, quiz questions Q1−Q5). The Likert scale responses (survey questions S1−S4) ranged from 1 (low confidence) to 6 (high confidence) and content questions (quiz questions Q1−Q5) were graded on a 0−2 scale. The maximum confidence score for the Likert scale was 24, and the maximum aptitude score for the content questions was 10. After completion of both quizzes, the assessments were given an ID number, identifying information was removed, and the shuffled quizzes were scored anonymously with no information concerning when (pre/post-test) or where (control/intervention classroom) a quiz was taken.



Answer the following questions on a scale of 1-6:

S1 How much do you think you learned about spin-spin splitting as a result of **reading the textbook***? *(1=not very much, 6=very much)*

S2 I feel I can predict what the splitting pattern for an indicated proton will be by looking at the overall structure. *(1=strongly disagree, 6=strongly agree)*

S3 I feel I can predict how many adjacent protons there are when given a drawing of a signal from a spectrum. *(1=strongly disagree, 6=strongly agree)*

S4 I understand why a signal is split into particular splitting patterns. *(1=strongly disagree, 6=strongly agree)*

Answer the following questions:

Q1 Briefly explain what a coupling constant (or *J* value) is?

Q2 Why is the peak height ratio of each of the three peaks of a triplet 1:2:1?

Q3 Under what circumstances would a signal be a ‘doublet of doublets’?

Answer the following questions about the following signal:

Q4 What is the name of this signal?

Q5 How many adjacent protons does this signal represent?

*This phrase was replaced in the post-test with either “**the coin-flipping analogy/web app**” or “**traditional lecture**”

Figure 2. List of survey questions (S) and quiz questions (Q).

RESULTS

The Likert survey questions and the content questions were found to be reliable[28] at the pretest stage (4 Likert survey items (survey questions S1−S4), $\alpha = 0.85$; 5 content items (quiz questions Q1−Q5), $\alpha = 0.70$).

Not surprisingly, the students rated their confidence about spin−spin splitting considerably lower after only reading the textbook versus after both the intervention and typical lectures (Figure 3). The relative lack of confidence at the pretest can be explained partially by the subset of students who admitted they did not read the textbook as assigned. Two-factor ANOVA shows that students in the control classroom felt more confident after lecture than students in the intervention classroom after the analogy/web app ($F(1,169) = 15.863$, $p = 0.000$) This can also be seen by comparing the percentage of most confident (6 out of 6) responses for all survey questions in total (20% intervention vs 33% control).

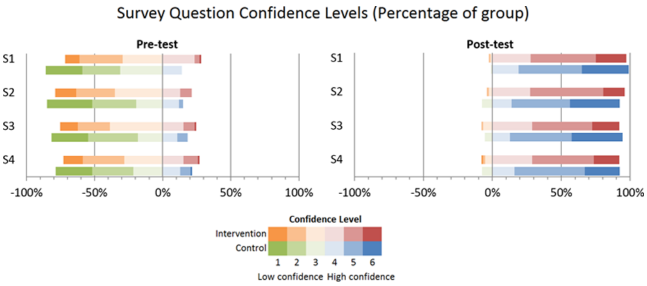


Figure 3. Confidence levels pre- vs post-test. Shading represents percentage of group at that confidence interval. Bars are centered around neutral confidence to illustrate degree of confidence.

Out of 10 possible points, the average quiz score for the pretest was 2.32 for the intervention group and 2.51 for the control group. The average quiz score for the post-test was 7.59 for the intervention group and 7.75 for the control group (Figure 4). The post-test difference between intervention and control is well within the standard deviation (1.9 for the intervention classroom, 1.7 for the control classroom), showing that the overall impact of the intervention is essentially the same as traditional lecture. Two-factor ANOVA shows no statistical significance between the intervention and control over all factors ($F(1,157) = 625.9$, n.s.), showing that the intervention works at least as well as typical lecture in overall analysis of spin−spin splitting.

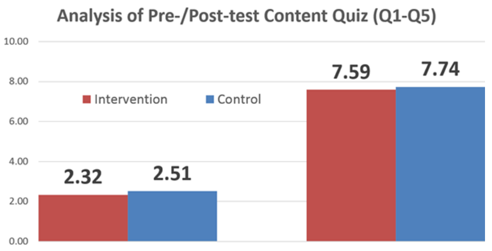


Figure 4. Content quiz average (Q1−Q5), pretest vs post-test.

However, when specifically investigating content question Q2, “Why is the peak height ratio of a triplet 1:2:1?”, which directly assesses the ultimate goal of this intervention, the intervention classroom performs significantly better than the control classroom ($F(1,157) = 8.893$, $p = 0.003$).

DISCUSSION

While the results did not show a statistically significant difference in aggregate, many interesting patterns and relationships can be found in the data.

The relationship between how confident students felt about the material versus how well they actually knew the material can be displayed best as a heat map (Figure 5), where each cell represents the percentage of students in a group who had a particular Likert survey sum paired with a particular quiz score. Darker shading indicates a larger percentage at that score pair. Likert scale response sums were collected into three bins: low

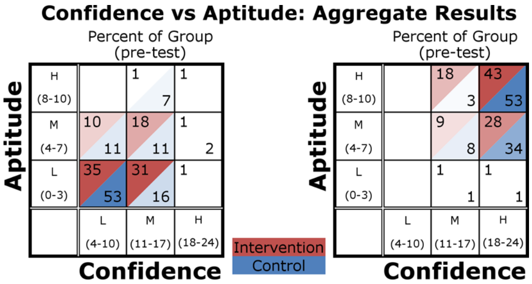


Figure 5. Measuring confidence/aptitude gains pre- vs post-test. Numbers represent percentage of group.

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J. Chem. Educ. XXXX, XXX, XXX−XXX

confidence (4−10), medium confidence (11−17), and high confidence (18−24). Quiz score sums were collected similarly: low aptitude (0−3), medium aptitude (4−7), and high aptitude (8−10). As expected, after reading the textbook, students in both groups did not feel particularly confident, nor did they score particularly well on the content quiz. After either the intervention or lecture, students felt more confident and scored much better on the content quiz.

Of particular interest is a heat map illustrating a specific relationship: how confident students felt on the survey question S4, "I understand why a signal is split into particular splitting patterns" and their score on the content quiz question Q2, "Why is the peak height ratio of a triplet 1:2:1?" As expected, both confidence and aptitude increase in both groups over the pretest; however, 34% of students in the control classroom reported high confidence, yet scored relatively poorly on the corresponding quiz question (Figure 6).

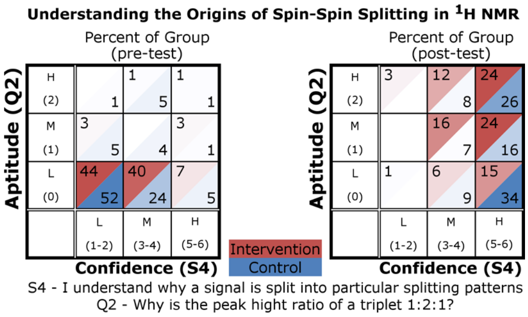

Figure 6. Measuring effectiveness of analogy toward understanding origins of spin−spin splitting. Numbers represent percentage of group.

Statistically, when comparing the responses of survey question S4, students in the control classroom felt significantly more confident (mean =4.94 out of 6) than the intervention classroom (mean =4.67 out of 6) that they understood why a signal is split into a particular pattern ($F(1,153) = 4.731$, $p = 0.031$). Yet, when comparing the responses of content quiz question Q2, students in the intervention classroom performed significantly better (1.16 out of 2) than the control classroom (0.91 out of 2) at actually explaining why a particular signal has the peak height ratio it does ($F(1,157) = 8.893$, $p = 0.003$). Considering the goal of the analogy and web app is to allow students to understand the origins of spin−spin splitting, the analogy holds a significant advantage over traditional lecture.

For students in the intervention classroom, retention was tested on the spectroscopy unit exam and later on the semester final exam. On the unit exam, students were asked to explain, "Why is the peak height ratio of a quartet 1:3:3:1?" The average score was 71%, with 43% of the class (35/82) receiving full marks. Twenty-three percent of the class (19/82) specifically referenced the coin-flipping analogy. On the final exam, students were asked why the [M+] region of a mass spectrum of a tetrabromide shows five peaks in a 1:4:6:4:1 ratio. The average score was 67%, with 38% (29/76) earning full marks, and 13% (10/76) specifically referencing the coin-flipping analogy. This result is remarkable for two reasons: the final exam was three months after the intervention, with no formal refresher on the coin-flipping analogy, and the question tests a similar concept but in a different domain, showing both retention and transference of knowledge.

CONCLUSION

The coin-flipping analogy and corresponding free web app[26] provide a unique way for students to understand the concept of spin−spin splitting in ^{1}H NMR spectroscopy. Broadly, the analogy educated students about spin−spin splitting at least as well as traditional lecture (post-test content quiz average 7.59/10 for intervention vs 7.74/10 for control).

Specifically, students who used the analogy/web app were better able to explain why spin−spin splitting occurs and the origins of the peak height ratio for various signals (Q2:1.16/2 average for intervention vs 0.91/2 average for control). Students showed retention of knowledge about the origins of peak height ratios of signals both on the unit exam and the final exam. On the final exam, students demonstrated transference of this knowledge by answering a question about the origins of a complex [M+] peak of a tetrabromide.

This study provides some evidence that students may gain a deeper understanding of the origins of spin−spin splitting and the reasons why signals have the particular peak-height ratios they do. Presenting this analogy and giving access to the corresponding and easily accessible web app will give students a greater understanding of spin−spin splitting.

ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available on the ACS Publications website at DOI: 10.1021/acs.jchemed.6b00133.

Pre- and post-test (PDF, DOCX)
Suggested narrative (PDF, DOCX)
Excel document to tally in-class simulations (XLSX)

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Notes

The authors declare no competing financial interest.

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