MUNIZ, MARC NICHOLAS. Teaching Tools for Pedagogy at the Nanoscale: Towards the Understanding of Concepts Through Experience and Experimentation. (Under the direction of Maria T. Oliver-Hoyo.)

The field of nanochemistry is at the forefront of the physical sciences, and is increasingly finding diverse applications. As such, there is a need to allow this frontier to be explored thoroughly in undergraduate chemistry curricula. The development of new instructional materials is necessary, as the existing literature in undergraduate nanochemistry education does not provide instructors with adequate resources to help students make connections between core scientific concepts and those pertinent to the nanoscale. As such, we aim to treat nanoscale phenomena not as a niche subject but as an educationally rich portion of chemistry at the interface of discrete and bulk structures. To accomplish this, we have developed and tested instructional materials that are designed to fit directly into the chemistry curriculum and provide instructors with the flexibility to incorporate them in their courses. These teaching tools/modules have been designed using a theoretical framework for analogy and similarity coupled with a bridging framework in order to reinforce students’ physical and chemical concepts and facilitate their recognition of such in the context of nanochemistry. Our approach is to construct concepts related to nanochemistry by tethering them directly, through the use of analogy and similarity, to material commonly covered within the courses, rather than present them in an unrelated fashion or completely outside the students’ current frame of reference. Assessment of these tools has been carried out through a qualitative analysis incorporating a discourse analytical framework applied to individual student interviews and small group discussions. A coding scheme was devised and utilized for consistent characterization of students’ responses and discussions. Results are discussed
critically and pedagogical implications for each activity and the project as a whole are provided.
Teaching Tools for Pedagogy at the Nanoscale: Towards the Understanding of Concepts Through Experience and Experimentation

by
Marc Nicholas Muniz

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APPROVED BY:

_______________________________  ______________________________
Maria T. Oliver-Hoyo  Edmond F. Bowden
Committee Chair

_______________________________  ______________________________
Christopher B. Gorman  Melissa Gail Jones
DEDICATION

I dedicate this work to my beautiful wife, Tamera, my mother, Nancy, and my father, Peter.

Thank you for your unconditional love and support through these years! No words can adequately describe what it has meant to me.
BIOGRAPHY

Marc Nicholas Muniz was born in New Brunswick, NJ on November 2, 1986 to Nancy and Peter Muniz and raised in both Somerset, NJ and Piscataway, NJ. He graduated from Piscataway High School, where he was actively involved in the musical arts and was a member of the award-winning Superchief Marching Band and the Notables honor choir. His interests in the physical sciences and education grew as high school progressed, and he ultimately decided to enroll at Montclair State University with the goal of becoming a high school chemistry teacher. He majored in chemistry, and minored in mathematics and graduated with a B.S. in Chemistry, magna cum laude, in May, 2009. During his time at Montclair State, Marc met his wife, Tamera, who was living in North Carolina. Upon the combined persuasion of his professors and his family, he decided to pursue graduate studies in chemistry. Having conducted undergraduate research at North Carolina State University with Dr. David A. Shultz during the summer of 2008 with the AGEP program, he decided to pursue graduate studies at North Carolina State University. Marc chose to work with Dr. Maria T. Oliver-Hoyo in the area of Chemistry Education Research, where he could develop and apply deep content knowledge in chemistry directly toward progressing education in the field. Marc and Tamera got married on April 24th, 2010 and settled down in Morrisville, NC (the “heart” of the research triangle) while Marc worked on his PhD, which will be defended on March 25, 2014. They have two cats, Roxie and Missie, and a black labrador, Sydnie, who bring them much joy. Marc’s favorite past-times are reading both nonfiction and fiction literature, watching documentary films, and playing German-style board games with friends.
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TABLE OF CONTENTS

LIST OF TABLES ......................................................................................................................... ix
LIST OF FIGURES ......................................................................................................................... xii

CHAPTER 1 Literature Review ......................................................................................................... 1
  1.1 Introduction ........................................................................................................................... 1
  1.2 Instructional Materials in Nanochemistry ............................................................................... 2
    1.2(a) Experiments and Activities on Metallic, Semiconductor, Insulator, and Superconducing Nanomaterials and Their Characteristics ........................................... 2
    1.2(b) Self Assembled Monolayers and Surface Phenomena ............................................... 9
    1.2(c) Experiments and Activities on Carbon-Based Nanostructures .................................. 14
    1.2(d) Experiments and Activities on Surface Enhanced Raman Spectroscopy (SERS) and Imaging Applications ............................................................. 18
    1.2(e) Experiments and Activities Subsection Conclusions .............................................. 21
  1.3 Overview of Nano Courses and Curriculum Integration ..................................................... 21
    1.3(a) Discrete Course-Based Approaches ........................................................................... 22
    1.3(b) Broad Curricular-Based Approaches ...................................................................... 26
    1.3(c) Curriculum Integration Subsection Conclusions .................................................... 29
  1.4 Literature Implications for This Work ................................................................................. 30
  REFERENCES .............................................................................................................................. 35

CHAPTER 2 Theoretical Framework and Research Questions ......................................................... 44
  2.1 Framework for Analogy ....................................................................................................... 44
  2.2 Further Rationale for the Use of Analogy in a Scientific Context ...................................... 49
  2.3 Bridging Concepts .............................................................................................................. 52
  2.4 Research Questions ........................................................................................................... 55
  REFERENCES .............................................................................................................................. 57

CHAPTER 3 Development of Instructional Materials ....................................................................... 59
  3.1 An Acoustic Analogy .......................................................................................................... 59
    3.1(a) Introduction ................................................................................................................. 59
    3.1(b) Background ............................................................................................................... 60
<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.1(c) Activity</td>
<td>63</td>
</tr>
<tr>
<td>3.1(d) Sample Student Results</td>
<td>68</td>
</tr>
<tr>
<td>3.1(e) Summary and Conclusions</td>
<td>73</td>
</tr>
<tr>
<td>3.2 Investigating Quantum Mechanical Tunneling at the Nanoscale via Analogy</td>
<td>74</td>
</tr>
<tr>
<td>3.2(a) Introduction</td>
<td>74</td>
</tr>
<tr>
<td>3.2(b) The Activity</td>
<td>75</td>
</tr>
<tr>
<td>3.2(c) Application of the Theoretical Framework</td>
<td>84</td>
</tr>
<tr>
<td>3.2(d) Summary and Conclusions</td>
<td>86</td>
</tr>
<tr>
<td>3.3 An Analogical Activity Emphasizing the Importance of Surface Area in Dye-Sensitized Solar Cells (DSSCs)</td>
<td>86</td>
</tr>
<tr>
<td>3.3(a) Introduction</td>
<td>86</td>
</tr>
<tr>
<td>3.3(b) The Activity</td>
<td>88</td>
</tr>
<tr>
<td>3.3(c) Application of the Theoretical Framework</td>
<td>93</td>
</tr>
<tr>
<td>3.3(d) Summary and Conclusions</td>
<td>94</td>
</tr>
<tr>
<td>REFERENCES</td>
<td>96</td>
</tr>
<tr>
<td>CHAPTER 4 Methodology and Assessment</td>
<td>101</td>
</tr>
<tr>
<td>4.1 Formulation of Coding Scheme</td>
<td>101</td>
</tr>
<tr>
<td>4.2 Data Collection and Code Application</td>
<td>105</td>
</tr>
<tr>
<td>4.3 Results and Analysis</td>
<td>111</td>
</tr>
<tr>
<td>4.3(a) Acoustic Analogy Analysis</td>
<td>115</td>
</tr>
<tr>
<td>4.3(b) Quantum Tunneling Analysis</td>
<td>142</td>
</tr>
<tr>
<td>4.3(c) DSSC Analysis</td>
<td>172</td>
</tr>
<tr>
<td>REFERENCES</td>
<td>189</td>
</tr>
<tr>
<td>CHAPTER 5 Conclusions, Implications for Implementation, and Future Work</td>
<td>191</td>
</tr>
<tr>
<td>5.1 Conclusions</td>
<td>191</td>
</tr>
<tr>
<td>5.2 Implications for Implementation</td>
<td>198</td>
</tr>
<tr>
<td>5.3 Future Work</td>
<td>203</td>
</tr>
<tr>
<td>5.4 Closing Remarks</td>
<td>206</td>
</tr>
<tr>
<td>REFERENCES</td>
<td>208</td>
</tr>
</tbody>
</table>
APPENDICES .................................................................................................................................................209

Appendix A Instructional Material Student Handouts ..................................................................................210
Appendix B More Examples of Students’ Responses to Pre-Activity Interview Questions
..................................................................................................................................................................241
Appendix C List of Post-Activity Interview Questions ...............................................................................259
Appendix D Additional Group Discourse and Post-Activity Interview Excerpts and
Analysis ..........................................................................................................................................................265
LIST OF TABLES

Table 1: Table adapted from Samet showing traditional and nano-chemistry related concepts that applied to each laboratory experiment in the course .................................................................23

Table 2: Tabulated expressions of different types of possible comparisons between base and target. .................................................................................................................................45

Table 3: Summary of conceptual change, from Gentner’s work, pertaining to the motion of celestial bodies as informed by the analogy drawn by Johannes Kepler ..................................49

Table 4: Summary of mapping of object relations and object attributes between tuning forks and metallic nanoparticles ........................................................................................................61

Table 5: Student prong length and pitch data from Part 1 .................................................................68

Table 6: Application of the theoretical framework to concepts within the activity .........................85

Table 7: Summary of relevant object attributes and relations within the DSSC activity .................94

Table 8: Code application: Examples of physical observation statements and categoricals. This is the most widely applied code ................................................................................106

Table 9: Code application: Examples of misconceptions ................................................................107

Table 10: Code application: Examples of comparison and contrastive statements. This is the most important code for understanding students’ analogical transfers between and within knowledge domains .................................................................108

Table 11: Code application: Examples of reformulations ................................................................108

Table 12: Code application: Examples of background statements .....................................................109

Table 13: Code application: Examples of investigator intervention ..................................................109

Table 14: Code co-occurrence table for Acoustic Analogy activity ...............................................110

Table 15: Code co-occurrence table for Quantum Tunneling activity ............................................112

Table 16: Code co-occurrence table for DSSC activity .................................................................113

Table 17: Example responses from pre-activity interview question “What is oscillatory behavior (OB)?” with assigned score and rationale .................................................................116

Table 18: Example responses from pre-activity interview question, “What is an intrinsic property of a material (IPM)?” with assigned score and rationale ...........................................118

Table 19: Example responses from pre-activity interview question “What is the basic operating mechanism of a UV-Visible spectrometer (BOM-UVS)?” with assigned score and rationale .........................................................................................................................119
Table 20: Fisher’s exact test to compare the number of misconceptions and valid comparisons or contrastive statements to the background knowledge level of the students in each group (cohort). N= total number of students in that particular cohort while n= number of students in a given cohort with a given background knowledge rating.

Table 21: Contingency table for the quantum tunneling activity constructed with statements from groups with high and low investigator intervention to compare spontaneous external transfer and physical observation statements that did not coincide with any type of comparative statement.

Table 22: Example responses from pre-activity interview question “What does a wavefunction describe in a physical system when it is in a quantum chemistry context?” for quantum mechanical tunneling activity with assigned score and rationale.

Table 23: Example responses from pre-activity interview question “What is the difference between an eigenfunction and an eigenvalue (EF/EV)?” with assigned score and rationale.

Table 24: Example responses from pre-activity interview question “In statistical mechanics, what does a partition function tell you about the energy levels, or states, of a quantum mechanical system?” with assigned score and rationale.

Table 25: Fisher’s exact test to compare the number of misconceptions and valid comparisons or contrastive statements to the background knowledge level of the students in each group (cohort) for the quantum tunneling activity. N= number of students who took a pre-activity interview in that particular cohort.

Table 26: Contingency table for quantum tunneling activity constructed with statements from groups with high and low investigator intervention to compare spontaneous external transfer and physical observation statements that did not coincide with any type of comparative statement.

Table 27: Example responses from pre-activity interview question 1 for DSSC activity with assigned score and rationale.

Table 28: Example responses from pre-activity interview question “What is an extinction coefficient (EC) in the context of spectroscopy?” with assigned score and rationale.

Table 29: Example responses from pre-activity interview question 3 “What is the definition of efficiency as far as power is concerned?” with assigned score and rationale.

Table 30: Fisher’s exact test to compare the number of misconceptions and valid comparisons or contrastive statements to the background knowledge level of the students in each group (cohort) for the DSSC activity. N= number of students who took a pre-activity
interview in that particular cohort while n= number of students in a given cohort with a given background knowledge rating

Table 31: Contingency table for DSSC activity constructed with statements from groups with high and low investigator intervention to compare valid comparison or contrastive statements and physical observation statements that did not coincide with any type of comparative statement.

Table 32: Summary of students’ conceptual challenges for each instructional material
LIST OF FIGURES

Figure 1: Schematic adapted from Gentner and Markman showing the comparisons with respect to number of relations and attributes shared. Note that the definitions are not, by any means, discrete.................................................................46

Figure 2: Flowchart connecting knowledge transfer (as facilitated by Gentner and Markman’s framework for analogy and similarity) and the bridge framework in the NanoLeap program54

Figure 3: Linear plots of wavelength of sound vs. the square of prong length for both alloys. Note the vast difference in wavelength between materials at a given prong length..............69

Figure 4: Short, medium, and long Au nanorods used in this activity. All were synthesized in the Nikoobakht and El-Sayed manner .................................................................69

Figure 5: UV-Visible spectrum of short (minimally red-shifted longitudinal mode) Au nanorods. Note the close proximity of the transverse band (first arrow? from left to right) and longitudinal band.................................................................70

Figure 6: UV-Visible spectra of medium and long length nanorods. Note the more pronounced red shift in the longitudinal band as the average rod length increases.............70

Figure 7: UV-Visible absorption spectra of spherical Au and Ag nanoparticles with similar average size (20 nm and 17 nm) according to literature values. An adapted Turkevich and Maillin & Murphy syntheses were used respectively. Note the difference in plasmon resonance wavelength, 520 and 390 nm respectively, despite the size similarities..............70

Figure 8: Screenshot of Audacity displaying recorded results from an aluminum alloy tuning fork. The microphone records in stereo, therefore two channels are present in the data.......71

Figure 9: Waveform plot of a 256 Hz tuning fork........................................................................71

Figure 10: Overlaid waveforms of 256 and 512 Hz tuning forks. Note the clear difference in frequency despite the difference in phase (phase difference is incidental due to the random positioning of the start of data recording).................................................................72

Figure 11: Plot of the results of a Fourier transform performed in Excel on a 256 Hz tuning fork. Note the presence of a prominent peak between 200 and 300 Hz. The actual value obtained from the FFT is around 258.4 Hz (very close to the expected value). As the number of data points utilized increases, the intervals between adjacent frequencies in the transformed function’s domain will decrease, allowing for a more accurate determination of the frequency........................................................................72

Figure 12: Overlay of Fourier transform results from 256 and 512 Hz aluminum alloy tuning forks ..........................................................................................................................73
Figure 13: Image of the ramp used in this activity with a ball that may be dropped from different heights .................................................................78

Figure 14: Student’s qualitative sketch of the lowest energy level wavefunction for a CdSe/ZnS core/shell quantum dot. Note the student’s incorporation of the term tunneling into the portions where the wavefunction decays into the classically forbidden region .......83

Figure 15: Students preparing to press pieces of clay into the craft beads. .................................89

Figure 16: ITO slide coated with TiO$_2$ face-down in crushed raspberries. Note the purple colored stain on the TiO$_2$ surface due to the surface complexation (chemisorption) with the cyanidin dye ..................................................................................................................90

Figure 17: Completed cells. Note the lack of visible difference between the cell based on pure anatase TiO$_2$ and the one based on an anatase-rutile mixture..........................................................91

Figure 18: Solar cell hooked up to a simple voltammeter. The cell is placed on an overhead projector, which has been lined with a paper towel.................................................................92

Figure 19: Top and bottom are both sketches constructed by students to represent the infinite-potential one-dimensional particle-in-a-box approximation to the CdSe quantum dots. .....153

Figure 20: Students’ sketches of double well potential and energy levels pertaining to NH$_3$. ........................................................................................................................................158

Figure 21: Students’ sketches of tunneling in CdSe/ZnS core/shell structures with separate wavefunction and energy diagrams .................................................................163
CHAPTER 1

Literature Review

1.1 Introduction

Publications dedicated to nanoscale research, in general, have increased considerably over the past couple of decades; this review focuses only on those publications pertaining to education. The review of the literature for the present work has been grouped into two prominent categories: individual activities and experiments primarily targeting the undergraduate level, and efforts to incorporate nano science into the general curricula. The former portion centers around the nature of the activities and experiments present in the discipline-based educational research literature. The explicit connection of core principles or concepts to a novel knowledge domain is a challenge to pedagogical approaches concerning education in emerging fields. Therefore, the review will also explore the extent to which material presented in these instructional materials at the nanoscale is explicitly connected to core chemical and physical principles. The latter part of the review gives an overview of a variety of methods utilized to incorporate nanoscale topics into curricula, and will display a range of unique approaches which can be loosely categorized as either broad curriculum based or discrete course based. The plurality of efforts to bring a novel family of concepts (in this case those at the nanoscale) into a broader curriculum will inform the discussion for the types of tools instructors might make use of towards these efforts. Within both portions of the review, the literature will be discussed in terms of how effectively the reviewed instructional materials and curriculum integration approaches are
evidenced-based via assessment of students’ learning in the context of core physical and chemical concepts. This chapter ends with the implications for the present work.

1.2 Instructional Materials in Nanochemistry

Educationally focused experiments and demonstrations in nanochemistry at the undergraduate level range from the synthesis and characterization of metallic and semiconductor nanoparticles and nanomaterials of different sizes and morphologies\textsuperscript{1-26}, to concepts on self-assembly\textsuperscript{16,27-36}, carbon-based nanomaterials\textsuperscript{37-52}, and applications to spectroscopy and imaging such as Surface Enhanced Raman (SER) and Scanning Tunneling Microscopy (STM).\textsuperscript{53-63} The instructional materials within this portion of the review are observed through a pedagogical lens and analyzed by the strength of the instructional tool and the degree to which students’ learning is assessed.

1.2(a) Experiments and Activities on Metallic, Semiconductor, Insulator and Superconducting Nanomaterials and Their Characteristics

Any of the experiments involving the quintessential Au or Ag metallic nanoparticles brings redox chemistry into focus, as the reduced metal that comprises the colloid is originally provided in the form of a metal salt.\textsuperscript{1,2,6-9,12,14-16,19,24} All of these publications involve the synthesis of such particles yet, few of such experiments actually contain a portion meant to allow students to explicitly discover such redox activity pertaining to the formation of the particles.\textsuperscript{1,7,24} For example, Mulfinger’s\textsuperscript{7} laboratory experiment directs students to synthesize and explore silver nano aggregates of various degrees. This is an important part of understanding how the colloidal solutions form from aqueous metal cations, and is a particular example of where a key chemical concept needs to be further brought into the realm of nanochemistry. The authors state that the experiment can reinforce redox chemistry
among other general chemistry topics such as limiting reagents; assessment was limited to students’ personal attitudinal feedback on the activity. Soukupova\textsuperscript{24} details a “voyage” from the macro world to the nanoscale in which students first create a silver mirror via the reduction of Ag\textsuperscript{+}, and explore the redox chemistry implied therein. This is followed by an intermediate experiment in which a large-particle colloidal suspension, black in color, is created and the Tyndall effect, a light scattering effect whose presence is only detected within colloidal suspensions, is illustrated via the use of a laser pointer. Finally, orange silver nanoparticles are synthesized, and the full range of nanoscale effects is observed by students, including the continued presence of the Tyndall effect. Soukupova’s three part synthetic experiment represents one of the few examples that starts at the macroscopic domain and guides students toward discovering effects at the nanoscale. This effort is anomalous relative to the rest of the literature within this category, as often such connections are not explicitly mentioned or incorporated in the learning goals of the experiment.

Campbell et al.\textsuperscript{12} have reported a unique approach to incorporating Au and Ag nanoparticles into a laboratory activity by having students construct stained glass art with the nanomaterials. The incorporation of such nanostructures into art is a different take on the typical laboratory experiment and serves to highlight the wide variation of colors, very much different from the bulk, the structures exhibit. The underlying cause of this size-dependent color variation is known as surface plasmon resonance, a concept that is virtually unavoidable when discussing useful properties of metallic nanoparticles. While authors such as Campbell and coworkers\textsuperscript{12} have given an artistic spin on the size-dependent appearance of metallic (specifically Au and Ag) nanoparticles, the development of
the underlying process of surface plasmon resonance is limited to simply informing the
students that it arises from a collective oscillation of surface electrons. Additionally, many
published resources only dedicate a brief portion of the instructional material to the effect,
and do not weave it in significantly to the pedagogical goals of the experiment.\textsuperscript{1,6,7,9,13,15,19,24}
To exemplify this, Frank’s synthesis of silver nanoprisms of different sizes would benefit
from including an experimental portion dedicated to describing localized surface plasmon
resonance (LSPR) in a context readily accessible to students. This is an important portion of
the laboratory, as the optical properties of metallic nanoparticles result from this
phenomenon. Instructors are instead invited to simply view Campbell and Xia’s plasmon
article.\textsuperscript{64} Though Frank’s laboratory experiment is described as being appropriate for general
chemistry, the Campbell and Xia paper is intended for the physical chemistry or instrumental
analysis level of instruction. Further, Sharma and coworkers\textsuperscript{15} have developed an experiment
in which tea leaves are utilized to reduce and provide the capping agent for Au nanoparticles.
Although the experiment focuses exclusively on the synthesis and electronic absorption
characterization of the particles, the latter of which is exclusively dependent on the LSPR
effect, there is only one paragraph present in the results section in which the effect is
mentioned twice. Instructors and students alike may have benefited from a built in tool by
which this important concept could have been incorporated in laboratory discussions and
reflections. An example of an explicit approach to study surface plasmon resonance is an
acoustic analogy to surface plasmon resonance in which students first experiment with tuning
forks and, later, with Au and Ag nanostructures with the goal of connecting the oscillatory
behavior of the tuning forks to the oscillatory behavior of the surface electrons in the
nanomaterials, which constitutes the LSPR effect.\textsuperscript{2} This serves to directly expose students to oscillatory behavior in a frame of reference they are familiar with and then center the discussion around the LSPR effect in the context of their prior knowledge. There exist a number of experiments and activities centered on exploring semiconductor (i.e. quantum dots) and superconducting nanomaterials. A particularly common theme within some of these publications is the use and extension of the particle-in-a-box model to inform the results of electronic absorption spectra arising from colloidal suspensions of the nanomaterials. Rice and Giffin\textsuperscript{5} report an experiment in which students use polymer embedded CdSe-ZnS semiconductor nanoparticles (quantum dots) to explore how the 3-dimensional particle-in-a-box model applies to the phenomenon of quantum confinement observed in the nanomaterials. Additionally, Winkler et al.\textsuperscript{18} describe a synthesis and subsequent UV-Visible characterization of CdS quantum dots, designed to be performed by students after the particle-in-a-box conjugated dye experiment. It is surprising to note that the student handout in the supplemental instruction however, does not invoke the particle-in-a-box model at all. Nordell\textsuperscript{65} describes an experiment where students synthesize, under safer conditions and lower temperatures than typical protocols, and characterize CdSe quantum dots via electronic absorption spectroscopy (UV-Visible). Instructors are directed to Kippeny et al.\textsuperscript{66} for resources to provide background information to students. Kippeny et al. describe semiconductor nanoparticles as a “powerful visual aid for introducing the particle in a box.” The applied derivations therein, however, are not given a traditional chemical or physical basis upon which to work from besides the description of an extension of the hydrogen-atom problem to an exciton (electron-hole pair). Expressions are derived in the new paradigm
without providing instructors with tools as to how a connection between this core concept and its manifestation at the nanoscale may be made. In particular, the introductory particle-in-a-box equation is introduced in prominent undergraduate texts\textsuperscript{67,68} in the instance of zero potential energy, and certainly not without great difficulty in students’ understanding. Singh and Zhu\textsuperscript{69} have found that even upper division undergraduate and graduate-level physics students express great difficulty in the basic representations of one-dimensional particle-in-a-box wavefunctions. A true connection to a core physical chemistry concept would arguably be beneficial for instructors and students alike, particularly if an aim is to shift students’ frames of reference in the laboratory away from simple “cookbook” experiments and towards deep thought and reflection upon underlying physical and chemical phenomena.

Electronic absorption considerations do not constitute the only central theme upon which activities and experiments involving semiconductor nanoparticles are built. For example, Feng et al.\textsuperscript{20} report an experiment in which dendrimer-capped Cu nanoparticles are used as catalysts for the first-order reduction of \textit{p}-nitrophenol. Students are first required to synthesize the nanoparticles which are then used to catalyze the reduction of \textit{p}-nitrophenol in the presence of BH\textsubscript{4} \textsuperscript{-}; the reaction is monitored via electronic absorption spectroscopy. This experiment does allow students to observe transition metal complexation, redox chemistry, catalysis and chemical kinetics in a novel context, though there are no tools for instructors to explicitly facilitate for students making these connections. Smestad and Grätzel\textsuperscript{25} published an experiment involving the simple assembly of dye-sensitized solar cells (DSSCs), involving nanoparticulate TiO\textsubscript{2} as the semiconductor matrix, anthocyanin-containing fruit juice as the source of the sensitizing dye, and doped tin oxide conductive glass. Though the
experiment makes use of nanocrystalline TiO$_2$, there is little emphasis within the experiment on the important role the size of the semiconductor plays in allowing the cell to be reasonably efficient. Similarly, in a related publication, Smestad$^{26}$ suggested the use of a 75-term glossary to aid in students’ understanding. It is unclear how this approach will facilitate effective pedagogy and allow for students to discover the importance of the high surface area to volume ratio afforded by the nanoscale structures—without which, the DSSC would not function efficiently.

Campbell et al.$^{17}$ describe a demonstration in which common household items (i.e. scissors, binder clips) made of metals and metal oxides are heated with a torch to the point where thin films of metal chalcogenides, some of which are semiconductors (TiO$_2$) others of which are technically insulators (TiN$_{0.6}$ or TiN$_{1.2}$), are produced on the surface. These surface materials, through destructive and constructive interference of reflected light, produce iridescent colors that are readily visible and analogous to structures found in nature (i.e. butterflies, beetles etc.). The demonstration’s principal intended audience consists of students at the second-semester general chemistry level. The nanoscale effect of thin-film iridescence in such semiconductors and insulators is clearly illustrated within the description of the demonstration, though it is unclear how instructors would implement the demonstration in such a way that students are actively invoking the core knowledge from their coursework and applying it to the nanoscale. Further, Bolstad and Diaz$^{21}$ report an experiment in which nanocrystalline Y$_2$O$_3$:Eu$^{3+}$ is synthesized and characterized by powder X-ray diffraction and fluorescence spectroscopy. The experiment serves, in part, to illustrate Scherrer broadening, which occurs for nanoscale crystallites in X-ray diffraction and
represents a method of determining the size of such materials. This is one of the few experiments in the discipline-based education literature in which materials approaching the bulk substance (microcrystalline sizes beyond 100 nm) are contrasted with those at the nanoscale. The experiment also allows students to examine the effect of the particle size on the luminescence of the material, in which a blue shift in the emission spectrum is observed upon comparison of microcrystalline and nanocrystalline structures of this lanthanide-doped insulator material. The authors claim that the experiment “provides a unique means of teaching...nanotechnology concepts”, though evidence from student feedback or assessment is not considered in the work.

An example of an experiment involving superconducting nanoparticles is that described by She and Liu. They report a synthesis of an YBa$_2$Cu$_3$O$_{7-x}$ superconductor for the first year undergraduate chemistry laboratory. The experiment is designed to characterize the product with the evaluation of the Meissner effect. Instructors are encouraged to peruse the literature to find suitable material to enhance the discussion as opposed to having a built in mechanism for providing students with important background knowledge. The experiment misses the opportunity to describe or explore how the system relates to nanochemistry. It is also not necessarily guaranteed that the Meissner effect is well integrated into a majority of undergraduate chemistry curricula. In this particular case, the core scientific knowledge (Meissner effect) is not necessarily in place for students to be able to explore it macroscopically, let alone at the nanoscale.

An example of a qualitative application-based laboratory experiment involving semiconductor nanoparticles is described by VanDorn et al. The authors provide an
An inquiry-based laboratory for upper secondary and first year undergraduate students in which iron(II/III) oxide (magnetite) nanoparticles are used as a medium to adsorb arsenic from water. The colloids of the magnetite are prepared in small (10 mL) vials and a colorimetric investigation of the various concentrations of arsenic is carried out. Bulk iron, in the form of iron filings, is also provided to students as a control condition to illustrate that maximum As(III) and As(V) removal will occur via structures with a high surface-area to volume ratio (an effect that is exhibited at the nanoscale). This particular experiment, in addition to being based on a pedagogical framework for inquiry, backs up its assertion of students’ understanding with pre- and post-tests containing questions pertinent both to core and nanoscale content knowledge and provides a rudimentary statistical analysis of the results (direct comparison of means prior to, but no reported significance tests). The authors also employed a student assessment of learning gains (SALG)-type survey in order to gauge students’ attitudinal response to the activity and found, on a Likert scale of 1 to 7 with 1 being strongly negative and 7 being strongly positive in the context of the items, that the mean student response on each individual question was above 5.4 with a standard deviation no higher than 1.16. This particular activity represents one of few efforts for nanochemistry instructional materials at the undergraduate level to employ both a theoretical framework for pedagogy (inquiry, in this case) and an assessment methodology.

1.2(b) Self Assembled Monolayers and Surface Phenomena

Another important family of concepts pertinent to nanochemistry, and nanoscience as a whole, centers around self-assembly, and the associated surface phenomena. There have been a number of educationally focused publications focused on this subject matter. A series
of colloidal Au experiments reported by Keating et al.\textsuperscript{9} allow students to investigate protein-
Au nanoparticle conjugates, colloidal Au monolayer self-assembly, and colloidal Au surface
self-assembly. The former experiment capitalizes on the concept of colloid conjugated and
unconjugated protein equilibrium, the latter two are in the context of kinetic and
thermodynamic parameters respectively. As the experiment is targeted towards upper
division undergraduate students, some of these concepts are immediately presented in a
rigorous manner. For example, the expression used for nanoparticle adsorption rate on a
two-dimensional surface is present. Also, the Langmuir equation for adsorption isotherms
appears in the portion in which the thermodynamics of colloidal surface assembly are
investigated. These expressions are given in the experimental paper under the assumption of
prior exposure within the physical chemistry course. The experiment would benefit from
having built-in educational measures to ensure students are connecting such formulae with
previously explored concepts or relationships to stimulate knowledge transfer.

There have been some experiments involving self-assembly that have focused principally on
electrochemistry. Gooding and coworkers\textsuperscript{29} have developed a laboratory experiment for
upper division undergraduate students that is focused on the use of cyclic voltammetry to
probe the local (surface) pKa of self-assembled monolayers of mercaptoproponic acid (MPA)
on a gold electrode. This is, in turn, compared to the traditional titration of a solution of the
MPA with NaOH. The authors assert that “students are able to link theory and experiment to
draw conclusions about a system”, yet provide no validated assessment, neither quantitative
nor qualitative, to support this claim. Ito et al.\textsuperscript{35} describe an experiment involving gold
electrodes coated with self-assembled monolayers (cysteamine and thiocytic acid) and,
ultimately, their application in cyclic voltammetric determination of L-ascorbic acid concentration in solution. The authors provide a comparison between the modified surface and a traditional electrode, and describe within the results section that the bare electrode shows significant differences in peak breadth and position (potential). It is not clear, however, how the pedagogy is to be developed in order to link the required fundamental understanding of electrostatics to the unique properties exhibited by the SAM coated electrodes. Schmidt and coworkers\textsuperscript{34} report a laboratory experiment focused on the assembly of a pH responsive electrochromic thin film. This polymer-based laboratory allows students to construct layer by layer (LbL) polyaniline films on a glass substrate without the need for expensive or involved processes such as vapor deposition techniques. The first portion focuses on the color-intensity increase with each additional layer of conductive polymer, and the second focuses on the use of the film on an ITO slide as a working electrode. An ensuing cyclic voltammetric (CV) experiment allows the oxidation states in the polymer to evolve, thus changing the colors observed. The experiment does not provide an assessment as to whether or not students understood the underlying concepts, for instance, of the thermodynamics behind self-assembly or the link between oxidation state and color observed during the CV experiment.

A biologically-focused example is given in a web-based activity by Radak et al.\textsuperscript{36} in which students are to explore transport of ions through membrane channels, modeled as self-assembled cyclic peptide rings, through a module based on Poisson-Nernst-Planck (PNP) theory. The PNP theory is rooted in classical continuum theory and, according to the authors, “the necessary physical concepts called upon should be familiar to students who
have taken a first-year electricity and magnetism course.” Though the activity is discussed as a way to introduce nanotechnology concepts, it is not clear beyond students’ ability to modify size parameters of the simulated channel how the specificity of self-assembly and the implications of the nanoscale are to be developed pedagogically.

Lithography and the modeling of the basics of self-assembly are also represented in materials present in the discipline-based educational literature. McKenzie et al.\textsuperscript{33} report an experiment in which students at the second-year organic chemistry level synthesize alkanethiolate SAMs on a vinyl supported Au substrate. Students vary the terminal group on the alkanethiolate and observe how the polarity of the group affects the contact angle of water and therefore the wettability of the SAM; they also explore the basics of how a plastic pattern coupled with ozone exposure can be used as a “mask”, as also seen industrially in how transistors are often fabricated. Beyond students’ attitudinal feedback on the laboratory, no assessment of learning gains was reported. Meenakshi and coworkers\textsuperscript{32} describe experiments geared towards nanopatterning via replica molding, micro-molding in capillaries, and microcontact printing. This is one of the few examples of so-called “top down” approaches being represented in the educational literature. The techniques are top down in that, for example, micro-contact printing constitutes the transfer of alkanethiols from a stamp that approaches from the top of the substrate rather than the etching away of alkanethiol SAMs already present on a substrate. Haynes et al.\textsuperscript{31} provide a classroom activity which draws connections between macroscale close-packing of spheres (marbles or nylon spheres) in templates and lithography. Talcum powder is shaken over the spheres within a given template, and contact paper below the spheres allows for the pattern between the spheres to be shown clearly when
the objects are removed. It is assumed that “students should recognize that close-packing occurs most naturally (when spheres are placed down in the templates).” Another example of using a macroscopic analogy to self-assembly is given by Burgan and Baker. In their activity, macaroni pieces from instant macaroni packages are heated in a microwave, and the resulting “self-assembly” of the structures into approximate hexagonal close-packed structures. Students are expected to draw connections between this macroscopic paradigm and the spontaneous assembly of lipid bilayers without an educational framework in place to guide instructors towards eliciting students’ connections between relevant components at the macroscale and those at the nanoscale.

Chan and Salaita describe a laboratory activity for first year undergraduate students referred to as the “molecular boat.” A primary purpose of the work is to emphasize the relationship between nanoscale layering of organosilanes on glass coverslips and the ensuing flotation of the coverslips due to an increase in the hydrophobicity of the surface and subsequent increase in contact angle. The authors, under a subsection titled “student experience”, claim that the results of a survey given to eight students who had participated in the laboratory activity indicate that they “gained new knowledge about self-assembled monolayers and their effects.” No evidence is provided to substantiate claims pertaining to students’ learning of concepts during the experiment. Statements such as “This was a most educational demo. I gained a much better understanding of hydrophobic/hydrophilic molecules” cannot be used alone to make claims about students’ knowledge gains.
1.2(c) Experiments and Activities on Carbon-Based Nanostructures

Carbon-based nanostructures play an important role in nanoscience in general, particularly concerning, but not limited to, their promising applications for novel electronic devices, advanced fibers, and sensing devices. Many of such applications are outlined in Basu-Dutt et al.’s description of the chemistry of carbon nanotubes (meant to spark the development of educational activities). Instructional materials based on the fabrication and use of carbon nanotubes, nanofibers, and related materials such as popular forms of carbon-based nanostructures, have been reported by several researchers. Campbell et al. report a demonstration involving the flash ignition of carbon nanotubes. This is essentially coupled with a demonstration of “flash paper”, in which single walled tubes are exposed to an intense flash of light from a camera leading to ignition of the material. It is not clear how students would relate the importance of the nanoscale dimensions in facilitating high levels of absorption in the single-walled tubes, resulting in the flash ignition.

Sun et al. report a laboratory experiment involving the synthesis of conductive polystyrene-carbon nanofiber composite films. The experiment draws on percolation theory as it relates to the threshold of conductive filler present in a composite material. Students take conductivity measurements and determine the percolation threshold based on the amount of carbon nanofiber present. Within the educational objectives of the lab, it is asserted that “...based on the experimental results, the students can easily understand the percolation theory for conductivity.” However, no evidence of an assessment of students’ conceptions was reported. De Dios and coworkers have developed an experiment focused on the synthesis of hybrid materials involving metals incorporated into the broader carbon nanotube
structure. The electrostatic functionalization of carbon nanotubes with Pt nanoparticles produces a composite material that is inevitably stronger than the original tubes themselves. This strength, however, is not widely explored by the experiment, as its focus is on characterization of the materials via microscopy and electronic absorption spectroscopy. An example of applications-based instructional material involving carbon nanotubes is that reported by Ge et al.\textsuperscript{41} In their demonstration, which may also be modified and used as an experiment, a fuel cell is constructed utilizing glucose, enzymes, and filter paper coated with carbon nanotubes. The nanotubes on the filter paper serve to facilitate electron flow at both the cathodic and anodic ends of the fuel cell. While a brief description of the carbon nanotubes is provided in the student handout, there is little focus on the importance of the nanoscale leading to the conductive properties that allow the nanotube to facilitate the cell’s operation. Hobbs and coworkers\textsuperscript{39} describe a biosensor involving carbon nanotubes to determine glucose in a variety of beverages. The carbon nanotube serves as modification to a glassy carbon electrode and acts as an electrocatalyst—a feature directly related to the nanoscale structure of the tubes. Such unique structural considerations did not appear to be incorporated pedagogically into the experiment.

There have also been reports of computational instructional materials related to carbon nanostructures. Simpson et al.\textsuperscript{37} describe a computational laboratory experiment in which students utilize various open source and commercial software programs to investigate the electronic structure, the radial “breathing” vibrational mode, and strain due to the natural curvature of the tubes. This experiment represented one of the few attempts to explicitly show students the size dependent properties at the nanoscale, including how the HOMO-
LUMO gap evolved as a function of number of carbons in the single-walled nanotube. Dunn reports a visualization module for the normal modes present in fullerene (C$_{60}$) via the use of demonstration software. Within the module, users can click on each of the modes (irreps) as determined by group theoretical calculations. These are carried out, visually, in a three-dimensional representation of the fullerene molecule displayed below the adjustable parameters. Fullerenes represent another prominent portion of carbon-based nanostructures, and, like their nanotube counterparts, exhibit unique features such as size-dependent energy gaps (confinement) only present at the nanoscale. Dunn’s work, along with that of Simpson et al., represents one of the few attempts to center attention on fundamental physical or chemical considerations in the context of nanochemistry.

A number of experiments for undergraduates pertaining to fullerenes exist. Among these is a purification procedure (via ultrasonic extraction in toluene or Soxhlet apparatus) followed by crude column chromatography in a disposable glass pipet, and qualitative spectroscopic analysis reported by Maracek and Kuduk. Upon separating the C$_{60}$ out from other fullerenes present in the extract, students may take IR spectra, by way of KBr disk, and electronic absorption spectra. There is no description, however, of how to tie the resulting data to the electronic properties of the fullerene. West and coworkers report a purification experiment via column chromatography prepared in a similar way as described in Maracek and Kuduk. It is reported that a “light purple color” indicates the presence of pure C$_{60}$, though a discussion of the electronic and spectroscopic considerations beyond a confirmatory electronic absorption spectrum of C$_{60}$ and a C$_{60}$/C$_{70}$ mixture is not provided. The generation of C$_{60}$ by way of an evacuated bell jar connected to a high voltage apparatus is described by
Iacoe et al.\textsuperscript{45} This article only gives a method for producing the crude C\textsubscript{60} mixture. Spencer et al.\textsuperscript{47} describe a synthetic laboratory for the second year organic chemistry level focused on the modification of fullerene with N-methylpyrrolidine. The experiment involves widespread confirmatory characterization, including electronic absorption spectroscopy, \textsuperscript{13}C NMR spectroscopy, and MALDI-MS. The learning goals are not centered on unique properties of the nanoscale fullerene structure.

Three consecutive experiments focused on functionalizing, investigating the kinetics of, and probing the electrochemical behavior of fullerene-based compounds are also reported in the literature.\textsuperscript{44,48,51} The first, by Cortes-Figueroa\textsuperscript{44}, is geared towards the upper division undergraduate inorganic laboratory and details the sunlight photosynthesis of (\eta\textsubscript{2}-C\textsubscript{60})Mo(CO)\textsubscript{5} and (\eta\textsubscript{2}-C\textsubscript{60})W(CO)\textsubscript{5} complexes. The use of \textsuperscript{13}C NMR and IR spectroscopy is mostly for confirmatory purposes, though it is expected that students compare \textit{A}\textsubscript{1} CO stretches between the complexes and other pentacarbonyl complexes to understand the pi-acidity of the fullerene as a ligand. The second, by Cortes-Figueroa and Moore-Russo\textsuperscript{51}, involves the displacement of the fullerene ligand in the (\eta\textsubscript{2}-C\textsubscript{60})W(CO)\textsubscript{5} complex by PPh\textsubscript{3}. Students are to use electronic absorption spectroscopy (UV-Vis) to explore the kinetic behavior of the exchange and derive the activation parameters. The third, by Igartua-Nieves et al.\textsuperscript{48} focuses on the electrochemical characteristics of (\eta\textsubscript{2}-C\textsubscript{60})W(CO)\textsubscript{5}. Voltammograms obtained by students are to be interpreted and related to the low lying LUMO states present in the fullerene based on the reversibility of each of the peaks. Though the series of experiments may be carried out sequentially, there is no explicit pedagogy to facilitate students’ discussion about the size-dependent electronic effects that could be clearly related
via a comparison between complexes involving the C$_{60}$ structure and higher-order C$_n$ based complexes.

### 1.2(d) Experiments and Activities on Surface Enhanced Raman Spectroscopy (SERS) and Imaging Applications

Weaver and Norrod$^{53}$ report a laboratory experiment for the physical chemistry laboratory in which students engage in surface-enhanced Raman spectroscopy. The enhancement occurs as a function of a synergetic effect between the localized surface plasmon resonance of metallic nanoparticles and adsorbed analyte molecules. This experiment describes the need for background information in basic Raman spectroscopy; however, it does not compare regular and enhanced Raman spectra of pyridine. Bright et al.$^{56}$ provide an experiment where students use Ag and Au nanoparticles to examine the surface enhanced Raman spectrum of 4-aminobutyric acid. Descriptions of how one might connect the traditional Raman spectrum to the enhanced version (conceptually or mathematically) would considerably strengthen this experiment. Pavel et al.’s$^{54}$ laboratory for the surface enhanced Raman spectroscopy of rhodamine 6-G is the only example of a nano-based SERS experiment where students calculate the enhancement factors from the metallic nanoparticles. A crude description of localized surface plasmon resonance (LSPR), the abstract phenomenon responsible for enhancement, is given.

A specialized form of imaging, whose use to view nanoscale has become ubiquitous, is that of scanning tunneling microscopy (STM). Zaccardi and coworkers$^{58}$ have developed an experiment for first year undergraduate chemistry students in which electrochemical etching is utilized to construct Au tips for use with an STM instrument. The students utilize their
prepared tips to obtain surface images of pieces of tape containing highly oriented pyrolitic graphite (HOPG). Much of the instructional material provided within the publication focuses on procedural details as opposed to how an instructor might incorporate relevant general chemistry concepts into the overall picture. Pullman and Peterson\textsuperscript{62} also report an experiment for the physical chemistry level involving the probing of intermolecular interactions of n-decanol monolayers on a graphite surface with STM. Students are to derive van der Waals parameters from the results of the microscopy, and compare the findings to their hand-sketched images of the monolayer. The quantum mechanical tunneling model is invoked in the discussion of the intermolecular interactions, a concept naturally important to the technique of STM itself.

Hajkova\textsuperscript{59} and coworkers report a couple of short demonstrations aimed at addressing the underlying concepts of scanning probe microscopy for upper level high school and first year undergraduate students. In their first demonstration, a plastic gnome toy is inverted and placed along the crevices of an egg carton. They state, in the context of this demonstration, that “it is easy for the audience to imagine the force acting between the tip and the sample even though they are not in mechanical contact (as even children have experience with attraction or repulsion of permanent magnets at distance).” This assertion appears to be an assumption aligned with the experts who designed the demonstration as opposed to the students themselves. The same pattern holds true with the second demonstration that calls for the use of agar to fill the space between the bumps in the egg carton; the carton is then placed in an aquarium tank, which sits on top of an overhead projector, and ink is added to the water. An inverted glass (meant to emulate a probe tip) is then moved, by hand, just
below the surface of the water. The deeper the inverted glass is submerged, the greater the level of transmission of light from the projector, as with the tunneling current between a real tip and the surface on which it is analyzing. Lorenz et al.⁶³ provide a classroom activity involving the use of refrigerator magnets as an analogue to scanning probe microscopy in general, including AFM, STM, and magnetic force (MFM) techniques. Students are to cut strips of refrigerator magnets and arrange them by their poles (i.e. north next to south next to north, or a number of such combinations etc.). A separate strip is used as a “cantilever” and is dragged across the strips that are placed in a pattern representing the layout of atoms or molecules. It is uncertain the extent to which students are able to connect the core concepts of the magnetic interactions to those related to the assemblies of atoms and molecules at the nanoscale. Campbell et al.⁶¹ describe some demonstrations for the general public, but also applicable to introductory undergraduate education, in which LEGO bricks are used to build apparatuses that mimic imaging instruments such as scanning probe microscopy (SPM), (a subset of which is magnetic force microscopy). These materials have been compiled on a website, and are designed to be integrated, to an extent, with computer software capable of recording data from the responses of the macroscopic models. Like the materials presented by Hajkova et al.⁵⁹, and Lorenz and coworkers⁶³, there is no reported assessment or built-in pedagogical framework through which instructors may explicitly guide students to connect the models of molecules and instruments built with the LEGOS and the actual properties at the nanoscale.
1.2(e) Experiments and Activities Subsection Conclusions

In general, great care needs to be taken in the development and implementation of individual educational resources for teaching concepts at the nanoscale, particularly if a goal is to make such resources easily compatible with all types of curricula at various institutions of higher education. The majority of existing resources do not explicitly provide a pedagogical basis for their design or implementation, and the use of validated tools or methodologies by which to assess the materials is limited as well. There also exist a number of broad claims that are made within reported activities and experiments pertaining to students’ knowledge gains that are unsubstantiated from an educational research frame of reference.

1.3 Overview of Nano Courses and Curriculum Integration

Approaches to integrating nano concepts in undergraduate curricula vary in nature, but can be broadly grouped into two categories: discrete course-based\textsuperscript{73-78}, in which individual courses designed to specifically address nanoscale concepts are introduced, and broad curriculum-based\textsuperscript{79-84} in which concepts related to the nanoscale are woven through the existing curricular structure.

The following portion of the review will categorize reviewed published approaches into either category, though it is important to note that these categorizations leave room for overlap. For example, a broad curricular approach may also describe a specific course utilized for nano concepts, even though the course does not constitute the majority of the curricular development.
1.3(a) Discrete Course-Based Approaches

There have been a number of publications highlighting undergraduate courses in nano science and nanotechnology.\textsuperscript{73-82,85} This section will focus specifically on approaches in which individual courses were the focus of the efforts to introduce nano concepts into the curriculum.

One such course has been created by Samet\textsuperscript{73} that specifically draws upon knowledge learned in other chemistry courses to expose upper level chemistry students to nanochemistry. This course builds upon four experiments from the discipline specific educational literature\textsuperscript{65,86-88} and allows students to explore the topics with reasonable autonomy. Table 1 is adapted from the literature to show the concepts addressed from both traditional chemistry and nanochemistry.
Table 1: Table adapted from Samet\textsuperscript{1} showing traditional and nano-chemistry related concepts that applied to each laboratory experiment in the course

<table>
<thead>
<tr>
<th>Lab Activity</th>
<th>Traditional chemistry topics</th>
<th>Nanochemistry topics</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nanowires</td>
<td>Electrochemistry; redox reactions</td>
<td>Nanowires; nanoelectronics; nanofabrication; STM, AFM, SEM</td>
</tr>
<tr>
<td></td>
<td>Energy and light; spectroscopy; atoms, atomic structure; quantum mechanics, particle-in-a-box model</td>
<td>Nanoparticles; nanocrystals; quantum dots; nanotechnology in medicine</td>
</tr>
<tr>
<td>Quantum Dots</td>
<td></td>
<td></td>
</tr>
<tr>
<td>YBa\textsubscript{2}Cu\textsubscript{3}O\textsubscript{x} superconductor</td>
<td>Stoichiometry; elements, compounds, mixtures</td>
<td>Nanocomposites; nanostructures; nanoelectronics</td>
</tr>
<tr>
<td>Fullerene C\textsubscript{60}</td>
<td>Allotropes, hybridization; cycloaddition reactions; organic reaction mechanisms; separations, chromatography; electronic spectroscopy; nuclear magnetic resonance</td>
<td>Nanomedicine; nanoproducts; history of nanotechnology; nanocatalysts</td>
</tr>
</tbody>
</table>

This course represents one of the few efforts in the literature that addresses core chemical topics meant to be explored in the novel domain of nanochemistry. Lyshevski et al.\textsuperscript{85} describe a wide-angled, multidisciplinary effort at RIT to develop a comprehensive nanotechnology curriculum, which draws from various disciplines including engineering, biology, chemistry, physics, and ethical considerations. Although the approach is highly integrative and relies upon core scientific information, it is designed as a progression of individual courses. The NanoSET course is the introductory module, in which students are qualitatively introduced to nano concepts from multiple perspectives. After a particularly interesting quote from this work: “Due to lack of classroom time, it is impossible
to comprehensively cover broad topics in an introductory course”, the authors suggest that the modular nature of their program is sufficient to capitalize on “cornerstone” topics across multiple scientific boundaries. Questions may be raised, however, as to how truly efficient separate courses are, considering the goal is to expose students from different backgrounds to nanotechnology.

Asmatulu and Misak\textsuperscript{74} describe an individual laboratory course, referred to as the “Introduction to Nanotechnology Laboratory” for upper-division students in the engineering curriculum at Wichita State University. Coverage of nanoscale topics ranged widely from applications such as bionanocomposites and nanolithography to instrumentation extensively used for characterization (such as atomic force microscopy). Moyses et al.\textsuperscript{75} report a nanotechnology survey course as well that takes place over the course of four weeks for introductory level undergraduate students in the department of chemistry at Central Michigan University. This course does include concept maps as a framework for the course, and students were instructed to generate these maps themselves. The concept maps were principally focused on broad individual questions and categories posed to students such as “what is nanotechnology?” and “applications of nanotechnology.” Instructors assessed the course quantitatively by a point system rooted in the relevance of the connections expressed by the students in their maps. Though, in general, the efforts to enable students to effectively communicate concepts related to the nano scale were effective, an interesting statement precipitated from the evaluation of one of the students’ maps related to the applications of nanotechnology: “Nanocharacterization techniques such as AFM and STM are listed as primary branches, in addition to quantum dots and band theory. Though these topics were
discussed during the lecture in their broadest sense, it is clear that this student with no prior frame of reference had trouble finding the relevancy for these advanced concepts.” This suggests that failure to contextualize nanoscience in the realm of what students’ core physical and chemical concepts are may lead to misunderstandings and, as the authors find, erroneous links.

Bentley and Imatani have described a nanomaterials chemistry course developed specifically for middle to upper-division undergraduate students. Topics included self-assembly and analysis of carbon-based nanomaterials such as nanotubes, along with an exploration of social issues pertaining to nanoscience (i.e. nano literacy in the general public). A unique feature of the course was its integration of collaborative efforts amongst students. For example, a networking breakfast was incorporated in which students were expected to present and discuss a number of proposals—principally centered on the role of gold nanoparticles in treating cancer. This course-based attempt at integration of nano topics into the chemistry curriculum with real life relevance missed the opportunity to assess students’ attitudinal and content knowledge gains as a function of their participation in this unique type of course.

The first year undergraduate course described by Tretter, Jones, and Falvo provides a rare window into a well-assessed effort to incorporate nanoscale topics into early undergraduate education. A combination of written assessments and student interviews were utilized to analyze the efficacy of the course at enabling students to think at the nanoscale. In it, students were found to have the ability to tune their conceptions of size and scale to be relatively congruent with those expressed by scientists in the field. This is a particularly
important finding, given that understanding of magnitude and scale is essential to developing normative concepts in the physical sciences altogether.

Englander and Kim\textsuperscript{78} have published material related to the NUE NanoCORE effort within the engineering programs at Florida A&M and Florida State University. This broad approach consists of courses within the curriculum that aim to incorporate concepts and aspects of research and design related to nanoscience and nanoengineering. Englander and Kim’s work is one of the few examples that extensively assessed the impact of such courses on students’ attitudes.

1.3(b) Broad Curricular-Based Approaches

Some publications involve concepts in nanochemistry being applied to the broad chemistry curriculum.\textsuperscript{79-84,89} Augustine et al.\textsuperscript{79} describe such an “evolutionary approach” at James Madison University. Laboratory experiments, demonstrations, and activities were chosen or adapted from the literature to address particular concepts at each level of the chemistry curriculum, ranging from general chemistry to physical chemistry. In accordance with this approach, they also designed a couple of courses targeted at non-chemistry majors: “Physics, Chemistry and the Human Experience” and “Science of the Small: An Introduction to the Nanoworld.” These courses are at the introductory and upper-division levels respectively. The former is designed to teach fundamental chemical and physical principles using nanoscience while the latter applies rigorous quantum theory and physical chemistry concepts to the field. These courses aim to allow students from diverse educational backgrounds to gain familiarity with such concepts in the laboratory.
Shanov et al.\textsuperscript{80} describe a “vertical integration” approach at the University of Cincinnati, in which students from the middle school through graduate level were exposed to nanoscience related topics through a series of presentations, camps, courses, and graduate research. In various portions of the program, students from each level were expected to, essentially, instruct those students at a level below them. For example, undergraduate students would teach nanotechnology concepts to high school students in summer programs at the University. This type of effort offers an opportunity to conduct longitudinal studies. At the undergraduate level, in particular, students take two courses: “Introduction to Nanoscale Science and Technology” and “Experimental Nanoscale Science and Technology.” These lecture and laboratory sections respectively were designed to give students a foundation in nano-related concepts. This approach is quite different from that reported by Augustine et al.\textsuperscript{79} in that the subject is treated separately from a given curriculum, though some concepts may inevitably overlap. The authors claim in their concluding remarks that their initial assessments have indicated that the approach is “efficient for teaching,” yet the meaning or consequences of this approach were not discussed.

Saleh\textsuperscript{81} reports a slightly more diffuse approach to integration of nano topics for first year undergraduates. The nano concepts were designed to be interwoven into basic courses within the first two semesters of the undergraduate’s education at the institution. Assessment of this particular course was carried out via statistical analyses on a combination of quizzes, pre- and post-test items, and attitudinal surveys. Positive results were reported across the board. Like many other publications referenced in this chapter, the assessment did not include students’ ability to link existing or concurrently developing knowledge to the nano world.
Kumar et al.\textsuperscript{82}, in an effort to integrate nano concepts into the existing curriculum, report the use of a “three pronged” approach to nano education, particularly aimed at applied research, within the program at North Carolina A&T State University. In addition to three principal courses: Nanotechnology I, II, and III, efforts were made to integrate nano concepts into the context of existing courses within the curriculum. This is one of few extensive attempts to do so at the undergraduate level, and various modules are introduced to move towards the accomplishment of the integration. Some content in the modules is described as the “core concepts of nanomaterials and unique phenomena at the nanoscale.” Examples of these concepts are: “nanoscale dimension and associated novel properties,” “artificial atoms” and “nanomanufacturing.” An independent study component was also woven into the framework of this approach.

Though the project to be described in this dissertation is focused on nanoscale concepts at the undergraduate level, there exist some notable broad curricular based approaches at the secondary level whose contents are pertinent to this work. Greenberg\textsuperscript{83} presents an integrative effort facilitated by the National Nanotechnology Initiative for the secondary and undergraduate levels of education. At the secondary level, the NanoLeap\textsuperscript{83,89} program has designed its curriculum to bridge core and nano concepts via the use of a transitional concept. For example, a standard concept is given to be “motion and forces” in the general context, while the transitional concept is “attractive intermolecular forces” in the context of a gecko’s feet sticking to a surface, and then “electrical forces” are explored at the nano level. It is important to note that significant gains were reported in secondary students’ core scientific and nanoscale knowledge upon pre- and post-test based evaluation of the approach.
Criswell\textsuperscript{84} describes an effort at the secondary level to provide activity sets that cover core concepts and link them to those in nanochemistry. Their activity set revolves around connecting basic acid/base chemistry with the concept of encapsulation, which is important in the nanochemistry context for processes such as drug delivery. The approach is one that intends to introduce the nanoworld into the curriculum via such activity sets instead of in an individual course manner. This is well described for the secondary school level, as Jones et al.\textsuperscript{90,91} have published texts outlining sets of activities that focus on scale and may be used for grades 6-12. An extension to the undergraduate level would be a valuable contribution to the area of nanochemistry instruction.

\textbf{1.3(c) Curriculum Integration Subsection Conclusions}

Overall, the approaches to incorporating nano concepts in undergraduate curricula found in the literature may be loosely categorized as follows:

\begin{enumerate}
  \item I) Discrete course-based: An approach that allows nano concepts to be taught separately. Example: Samet’s\textsuperscript{73} upper-division capstone course.
  \item II) Broad curriculum-based: An approach in which nano concepts are spread throughout the mainstream curriculum instead of within separate courses alone. Example: The approach at JMU described by Augustine et al.\textsuperscript{79}
\end{enumerate}

Upon considering existing approaches, a continuum between these two extremes is represented. Overall, there are methods described in the literature that lean towards being discrete course-based rather than threaded throughout the curriculum itself at the undergraduate level. Furthermore, as noted in the recent review by Jones and coworkers\textsuperscript{92}, there is not widespread evaluation of the efficacy of nano-based courses in the science and engineering curricula for undergraduate students. Moreover, Chopra and Reddy\textsuperscript{93} state that, pertaining to nanotechnology and nanoscience education in the broader curriculum, “The
basic question that needs to be answered is how to educate undergraduate students in nanotechnology by using conventional fundamental concepts for a specific major.” Based on the evidence within the literature, and the diversity of approaches represented therein, a modular design of instructional materials, in which instructors operating in any type of undergraduate curriculum may have access to versatile teaching tools, would create viable access to nanochemistry and nanoscience in general.

1.4 Literature Implications for This Work

Having reviewed the pertinent literature, both in terms of individual instructional materials, and curricular approaches, there are several key features that are evident. The first is that the activities and experiments that exist, in general, do not serve to explicitly connect students’ core chemical and physical concepts to those at the nanoscale. In addition, these materials are not grounded in theoretical frameworks to accomplish the pedagogy of making core concepts relevant in the nanoscale domain. To further the idea that core concepts ought to be directly connected to those at the nanoscale, it is worth noting that research has shown that students learn best when they are able to apply the concepts they are taught in class in as many different ways as possible.94,95 According to Brown et al.95, “people who use tools actively rather than just acquire them…build an increasingly rich implicit understanding of the world in which they use the tools and of the tools themselves.” Furthermore, Brophy and Alleman96 state that “Difficult new processes should be introduced in the context of applying easy or familiar content” within their principles for effective educational activity development. Nanochemistry can provide an additional layer of depth, in which the students may utilize and experience concepts they have previously learned in a novel context.
Studies have also shown that college-level course material retention can drop significantly within even a one-week period during the same course. For chemistry in particular, Blizard et al. found that the mean relative loss percent in recall for second-year medical students over 16 weeks was -15.1. In order to maximize the effect of both the key chemical concepts learned and the understanding of nanochemistry concepts, it would be beneficial to first reinforce the concepts and then apply them to the new frame of reference. Brophy and Alleman have outlined a general practical framework for the development of educational activities. There are a number of principles that have been proposed to ensure that an activity is effective, one of which partially states that “Implicit assumptions about students’ ability to access and bring to bear relevant prior knowledge or skills must be justified. Mere exposure to needed knowledge or skills is not sufficient…” This is an important observation, as many of the nano-related experiments and activities described in the literature for the post-secondary level do not provide a pedagogical framework to accomplish this.

Additionally, in laboratory experiments, irrespective of subject matter, there is often a separation between core content in theory and what takes place in experiments themselves. This is particularly true with respect to students’ perceptions. For example, in concluding their case study of the disparity between the aims of laboratory experiments and actual outcomes, Hart et al. state that “(T)eachers need to make the pedagogical purpose of laboratory work explicit for students. In doing so, it might better help them to make the links between the tasks in such a way as to build a more holistic view of their science learning experiences.”
Though the study carried out by Hart and coworkers focused on an individual educator’s implementation of laboratory experiments at the secondary level, the implications may be easily extended to the undergraduate level. For instance, Russell and Weaver\textsuperscript{107} state “student engagement in laboratories is governed in part by the perceived importance of different aspects of the laboratory, in general, itself and how those aspects fit into the larger course structure.” Their study, carried out at the undergraduate level, echoes the call made by Hart and coworkers for explicit connections between the conceptual material presented in the laboratory and a move towards higher levels of congruency between instructors’ and students’ goals and aims for the laboratory. Through the analysis of interviews with undergraduate students, Russell and Weaver found that the goals of students were, principally, to complete the laboratory in a timely fashion and not necessarily to incorporate a deeper implication of theoretical concepts learned in the lecture. Students experience the laboratory activities as being decoupled from the core scientific concepts they are purportedly acquiring throughout the curriculum.

The findings from these studies suggest that it is a worthwhile endeavor to design instructional materials based on a framework to explicitly connect core chemical and physical concepts to those at the nanoscale. This constitutes a principal aim of the present work.

Another important point of consideration is that many educational resources for nanochemistry and nano science in general lack rigorous assessment. Such assessment is necessary to provide instructors with the ability to understand their efficacy on students’ learning and the detailed implications for their adoption of the material for their courses. It is
also through rigorous assessment that an instructor adopting a particular instructional tool may preemptively address potential misconceptions by students that could occur during the implementation of the tool. Availability of assessment results may also provide the means by which practitioners can modulate the instructional material such that it is best suited for their particular institution, department, student body, or even level of instruction.

Instructors who intend to adopt such instructional materials will be from a variety of institutions. As is evident in this chapter, the methods to integrating nano concepts into the curricula are widespread. Approaches in the broader curriculum to incorporating nano concepts in the sciences and engineering, chemistry ostensibly being a significant central component to these, vary widely and naturally depend on the focus of the institution and departments themselves. As clearly stated in a recent review by Jones et al., pertaining to existing nanotechnology courses “...most have limited evaluation or educational research that could allow the reader to learn about their impact.” Additionally, one of four educational challenges described in the review was “the need for curricula and teaching materials.” Whether the approach to curriculum integration is broadly sprinkling the topics throughout the existing courses (broad curricular-based) or creating an individual or array of discrete nano-focused courses (discrete course-based), there exists a need for validated, modular teaching tools in the form of experiments and educational activities. In addition to being evident in the review alluded to above, the need for such materials is readily arguable from the observation of the number of different types of approaches in the literature, as outlined in this review. Well-designed resources that can be readily adopted into any form of chemistry
curriculum at the undergraduate level are arguably more effective than those whose impact can be realized only in a limited number of institutions or curricular approaches.

Overall, having discussed the current state of undergraduate educational resources and curricular approaches pertaining to nano education, there exists a need for carefully designed teaching tools to be available to and readily adaptable (modular) for instructors in all undergraduate educational settings. To constitute effective activity design within this paradigm, a theoretical perspective for a pedagogy needs to be employed to tether core chemical and physical concepts to the nanoscale concepts to be explored by students, and a thorough assessment of such activities rooted in accepted theory carried out. Both of these are scarce in the current body of literature in the field.

The research project to be described in this dissertation aims to takes steps towards addressing the lack of rigorously assessed activities and experiments readily adoptable into existing chemistry curricula. It also centers the development of the educational activities on a theoretical framework that lends itself readily to the pedagogy of connecting core chemical and physical concepts to those at the nanoscale. Moreover, the activities have been assessed with perspectives that have been extensively used within educational research as a whole. A detailed description of this work, the results, and implications for instructors and future work are presented in the forthcoming chapters.
REFERENCES


CHAPTER 2

Theoretical Framework and Research Questions

2.1 Framework for Analogy

The principal purpose of this research is to develop activities and experiments for students to draw connections between chemical principles explored in traditional curriculum and nanotechnology; therefore, a suitable theoretical framework is necessary to guide their development. The chosen framework for the development of these instructional materials is Structure Mapping in Analogy and Similarity, developed by Gentner and Markman. In this framework, relationships between domains of knowledge are “mapped” in order to relate one system of information to another. The original source of knowledge is referred to as the “base,” while the new object to which this knowledge is to be mapped is referred to as the “target.” When applying the framework to this research, we shall in the general sense refer to the traditional (core) chemical and physical principles as the base and the nanotechnology aspects as the target.

While comparing sources of information, there are two principal domains within this framework: object attributes and object relations. Object attributes are said to take one argument and are related to the intrinsic characteristics of a given item or concept. For instance, we know that one object attribute of the heme porphyrin is the fact that its appearance to the naked eye is red. Thus, in this simple example, the object attribute is color and the argument is the color red. This would be represented in the formalism of the framework as follows: Heme(red). An object relation takes two arguments and provides information about the behavior or relationship of the components of a knowledge domain. If
we take our heme example, an object relation would be absorbs(heme, light). Suppose we are interested in seeing if the object attribute and object relation map from heme to another porphyrin, chlorophyll. Chlorophyll is green and, as such, the object attribute of “color” does not map from heme to chlorophyll. It is clear, however, that the colors we observe are both a result from the porphyrin’s absorption of electromagnetic radiation. As such, the object relation of “absorbs light” maps: absorbs(heme, light) → absorbs(chlorophyll, light).

When working with this framework, it is important to note what separates literal similarity from analogy, anomaly, and “mere appearance.” The following is a tabular representation of relevant information adapted from Gentner and Markman\(^1,2\):

<table>
<thead>
<tr>
<th>Type of Comparison</th>
<th>Attributes that Map</th>
<th>Relations that Map</th>
</tr>
</thead>
<tbody>
<tr>
<td>Literal Similarity</td>
<td>Many</td>
<td>Many</td>
</tr>
<tr>
<td><strong>Analogy</strong></td>
<td>Few</td>
<td><strong>Many</strong></td>
</tr>
<tr>
<td>Mere Appearance</td>
<td>Many</td>
<td>Few</td>
</tr>
<tr>
<td>Anomaly</td>
<td>Few</td>
<td>Few</td>
</tr>
</tbody>
</table>

As expressed in Table 2, literal similarity is a comparison in which numerous object attributes and object relations match (or map) while an analogy offers few object attributes that map, but many object relations that do map. For mere appearance and anomaly few object relations map. Our intent is to give students as many opportunities as possible to draw connections, via mapping relations, between core and nano concepts. Analogies and literal similarities exploit relations that map, while the other two categories do not. Figure 1 is a visual representation adapted from Gentner and Markman\(^2\) to show such differences.
Figure 1: Schematic adapted from Gentner and Markman\textsuperscript{2} showing the comparisons with respect to number of relations and attributes shared. Note that the definitions are not, by any means, discrete.

As the aim is to exploit relations to provide connections, the focus is mainly on using analogy and literal similarity to promote, in students, the ability to draw connections between traditional chemistry and nanochemistry concepts. Whether analogy or literal similarity is used, the base will always be an educationally enhanced core chemical and/or physical concept. Each activity or experiment shall begin with exploration of these core concepts in order to fully center students around this frame of reference before beginning to extend or make connections to the nanoworld.

The need for clear connections between base and target domains has been highlighted extensively by the work of Gick, Holyoak, and Catrambone.\textsuperscript{3-5} The rationale for this approach is centered on the fact that individuals tend to use previously solved problems to approach new ones.\textsuperscript{3-8} The exposure of subjects to a classical analogical scenario, originally
presented by Duncker, would lead to erroneous results in the connection between the knowledge domains unless explicit instructions are given to utilize the initial story as a foundation for making connections. These results have been confirmed and expanded upon in the study of Needham and Begg, in which better results on positive and spontaneous analogical transfer have been achieved by encouraging subjects to take a problem-solving approach as opposed to a memory oriented one. The problem solving approach, as described in their work, is an encouragement of individuals to critically analyze target stories. The memory condition was one in which individuals were told that they would need to memorize the original materials in order to construct meaningful solutions pertaining to the target. The former outperformed the latter, even in the presence of significant elapsed time between exposure to the base and target stories.

This is powerful, yet can easily break down if there appear to be structural differences between problems, which can lead to something known as “negative transfer.” This occurs when information is improperly mapped from base to target. A plausible example in the context of chemistry in which negative transfer may occur at the general chemistry level can be illustrated by the following. Students in the general chemistry course often learn solution stoichiometry after having learned the process of dilution as described by the simple expression \( C_1V_1 = C_2V_2 \). Instead of recognizing, however, that one cannot simply plug information into the dilution formula while attempting to evaluate solution stoichiometry (a stoichiometric conversion must be carried out from one substance to another), students can still obtain the “correct” numerical answer in cases where the stoichiometric ratio is 1:1. This constitutes negative transfer, as students are improperly mapping attributes of the core
domain (dilution) to the target domain (solution stoichiometry). The relationship is anomalous irrespective of the fact that the numerical result is proper under a certain condition (the 1:1 stoichiometric ratio).

Needham and Begg\(^8\) summarize the needs of an individual if they are to have an adequate chance of properly transferring information from a base to a target domain; the following is a paraphrasing of their stated needs:

1. **Encoding:** The way in which an individual contextualizes the information in the novel (target) knowledge domain.
2. **Retrieval:** Information from the original (base) domain should be readily accessible to the individual.
3. **Selection of the analogue:** Attributes and relations need to be invoked from the base domain instead of information from other, possibly unrelated, knowledge domains.
4. **Adaptation of the solution:** A solution to the problem within the target knowledge domain should be parsed in terms of the base domain.

A quote from the same work\(^7\) speaks pointedly at the notion that specificity must be built into the base and target of an analogical activity in order for it to be effective: “Although there are many reasons for transfer to fail, *subjects who are given hints generally achieve good solution rates on targets*, implying that the *needed information is available in memory and is accessible when cued appropriately*. Therefore, *failures of spontaneous transfer occur either because the target problem fails to retrieve the relevant information from memory, or because the information is retrieved but its relevance for the task at hand is not appreciated.*”

In light of this evidence in the literature and general concerns, our activities are designed with the intention of promoting positive analogical transfer by *explicitly* linking the core concepts to those in nanoscience. They are also designed with the intention of encouraging
active problem solving through strategically placed questions and emphasis on students’ referrals to the core portion of the activity in order to formulate discussions in the latter (target) part.

2.2 Further Rationale for the Use of Analogy in a Scientific Context

Dedre Gentner\textsuperscript{1,2,10}, a principal author of the theoretical framework used in the work herein, outlines in an extensive fashion a highly relevant example of the power of analogy in the scientific world.\textsuperscript{2,10} The case study she details is that of Johannes Kepler’s development of laws of planetary motion, which represented considerable progress towards the understanding of the physical universe. This was an example of an extraordinary use of analogy to progress the field of astronomy.

Table 3: Summary of conceptual change, from Gentner’s\textsuperscript{10} work, pertaining to the motion of celestial bodies as informed by the analogy drawn by Johannes Kepler.

<table>
<thead>
<tr>
<th>BEFORE</th>
<th>AFTER</th>
</tr>
</thead>
<tbody>
<tr>
<td>Planetary system is governed by mathematical laws</td>
<td>Planetary system is governed by physical causality</td>
</tr>
<tr>
<td>Planets’ orbits are crystalline spheres containing planets or eternal circles traveled by planetary intelligences</td>
<td>Planets’ orbits are paths continually negotiated between the Sun and the planets</td>
</tr>
<tr>
<td>Celestial phenomena are separate from earthly physics</td>
<td>Terrestrial knowledge extends to astronomical phenomena</td>
</tr>
<tr>
<td>Planetary paths are perfect circles of uniform speed</td>
<td>Planetary paths are ellipses, faster when closer to the Sun and slower when further from the Sun</td>
</tr>
<tr>
<td>\textit{Anima Motrix} as “spirit” in Sun that moves planets</td>
<td>\textit{Vis motrix} as “force” from Sun that moves planets</td>
</tr>
</tbody>
</table>
As seen in Table 3, the main object relations in both the base and target knowledge domain are contrasted with one another. To exemplify this, consider the second row of the table. The object relation of planets orbiting is initially described as occurring via a form of planetary intelligence. This is in direct conflict with the same relation in the target domain, as it is described in a heliocentric fashion that is not dependent on autonomous planetary motion. Therefore, the object relation does not map between the knowledge domains.

Gentner reviews the original conceptions about planetary motion with which the world was currently working. In addition to the presence of a highly geocentric framework (the Earth itself was, in fact, presumed to be the center of the universe as a whole, and the presence of crystalline structures surrounding the Earth denoted as “heavenly bodies” was also taken as fact), the nature of the composition of planetary bodies was thought to be that of a fifth classical element—“quintessence.” Etymologically this is interesting as it served as the precursor for the word “quintessential.” This material, classically a variety of “crystalline aether”, in modern chemical terms would be referred to as completely inert. In addition to the vast structural and positional differences in the conception of the universe adopted by many of Kepler’s contemporaries, motion of such objects was proposed to be the result of a “mover” (the anima motrix) which itself, in turn, could not be moved. Moreover, all objects in space were viewed, themselves, to have souls which lent autonomy to some of the objects’ motion.

It is noted by Gentner that Kepler questioned the reason why the planets furthest from the sun appeared to move slower. This led him to postulate that the notion of autonomous motion via spirits, as discussed in the previous paragraph, might be dispelled by a central
“spirit” whose origin is the sun. Through this questioning, he drew an analogy to the apparent lag of the outer planets: the effect of a central “spirit” or power on the planets and other objects in space decreases with distance as does the intensity of light. This “motive power” originating from the sun was referred to as the “vis motrix,” replacing the old “anima motrix.”

Though Johannes Kepler’s story serves as a powerful example of analogical thought in the sciences, it speaks largely to the implications for analogy as being compatible with significant conceptual change. Though we have probed for students’ analogical transfers within the context of the instructional materials, as opposed to directly from a conceptual change perspective, it is pedagogically interesting to consider the powerful potential for conceptual change that the use of analogies can provide. In the work presented in this dissertation, the assessment methodology incorporates a discourse analytical perspective as applied to activities whose design is centered on analogy to afford a detailed analysis of students’ language. Duit has noted explicitly that, when treated appropriately, analogies can complement conceptual change—and powerfully so in the context of education in the sciences. This message resonates with the evidence provided by Gentner in her analysis of Johannes Kepler’s work, as discussed above. It is this notion that, in part, has motivated the choice of assessment methodology of this work to analyze students’ language as they navigate both the base and target knowledge domains and has provided further support to construct the activities around a framework for analogy and similarity.
2.3 Bridging Concepts

At times, a concept at the nanoscale may be better revealed to students with the use of a transitional or bridging concept. Bridging concepts have been utilized previously in the educational literature, and have been well described by the work of Clement and coworkers.\textsuperscript{15-17} The invocation of a concept or topic whose structure places it intermediate to that of the base and the target has been discussed by Clement\textsuperscript{17} in the context of physics education. It is here where he details the ‘hand on a spring/book on a flimsy table/book on a solid table’ analogy, where the ‘book on a flimsy table’ intermediate has conceptual overlap with both the hand on a spring (base, or in the language of Clement, “anchor”), and the solid table target.\textsuperscript{15-17} The main aim of that particular analogy by Clement and coworkers was to address misconceptions presented by students in the context of Newtonian mechanics, particularly students’ difficulties conceptualizing the presence of a “normal force.” The importance of such structures within analogies, in addition to being evident given the work of Gick, Holyoak, and others\textsuperscript{3-8}, has been echoed by Duit\textsuperscript{14}. Duit\textsuperscript{14} refers to the bridging analogies, as discussed by Clement, as “the most influential approach of employing analogies in conceptual change settings.” Additionally, it is noted by Chiu and Lin\textsuperscript{18} that when scaffolding activities via the use of multiple analogies coupled to one another, fourth grade students showed marked improvement both quantitatively and from an epistemological point of view in their conceptions of electricity and the basics of circuitry. The use of multiple analogies to scaffold understanding of physics concepts has also been discussed at length in the work of Emig\textsuperscript{19} where analogical activities were used to teach concepts related to simple machines.
An intention of the work in this dissertation is to provide a bridging component where needed, particularly in places where the transition from the core concept to that at the nanoscale is not readily facilitated by direct means. Therefore, for our purposes, the bridging component takes on a weighted significance when making difficult transitions between the knowledge domains. For clarity, it would be fair, as implied by Brown\textsuperscript{20}, to characterize a bridging concept as a subset of multiple analogies. The former implies a concept whose conceptual underpinnings find overlap with the base and the target domains, whereas it is plausible to argue that multiple analogies as a whole could signify limited overlap between any two analogies, but whose overlap with a dominant concept (a target) could be considered significant. One particular activity in the present work, which shall be discussed in upcoming chapters, makes use of multiple bridging analogies as students make the journey from the classical world to the phenomenon of quantum mechanical tunneling.

Such bridging concepts are described in the NanoLeap project, which was designed to teach nanoscale concepts to secondary students, grades 7-12.\textsuperscript{21,22} Their educational framework is a bridging model, in which core concepts are linked to nanoscience via a transitional concept. An example of a transitional concept used in the NanoLeap project is as follows:

Core: “The electric force is a universal force that exists between any two charged objects. Opposite charges attract while like charges repel” – National Science Education Standards p. 180.\textsuperscript{21,22}

Transitional: “The attractive intermolecular forces between and within molecules cause the gecko to adhere to a vertical surface.” -NanoLeap Physical Science Module Objective, Lesson 8.\textsuperscript{21,22}

Nano: “All interactions can be described by multiple types of forces, but the relative impact of these forces changes with scale. On the nanoscale, a range of electrical forces with varying strength tends to dominate the interactions between objects.” -Big Ideas of Nanoscience, p. 28.\textsuperscript{22}
From the description given within the NanoLeap project, and as detailed above in the work of others in contexts outside nanochemistry, the general idea is to utilize a transitional concept to link two rather disparate domains. The use of the transitional, or bridging, concept in certain areas for our teaching tools will be crucial, as it will serve to help with core and nano concepts that may not have as many object relations as needed. Figure 2 shows a basic flowchart of the role the frameworks play in facilitating transfer of knowledge between the domains in each activity:

![Flowchart connecting knowledge transfer](image)

Figure 2: Flowchart connecting knowledge transfer (as facilitated by Gentner and Markman’s framework for analogy and similarity) and the bridge framework in the NanoLeap program.

The development of instructional materials strongly considers learning objectives that relate what is observed in the two frames of reference by directly relating object attributes and
object relations while using transitional concepts when necessary. The rigorous breakdown of systems into components of attributes and relations is expected to avoid creating misconceptions. The frameworks outlined above are used to form the basis for constructing the learning objectives, and therefore the embedded pedagogy in the activities described and analyzed in the forthcoming chapters.

2.4 Research Questions

The review of the literature discussed in Chapter 1 and the choice of a theoretical perspective for the work have led to the formulation of two principal research questions concerning the development and assessment of the instructional materials:

1. Do the newly developed instructional materials promote in students the ability to effectively map core concepts into the realm of nanochemistry? What evidence can be provided to this effect?

2. Does analogical transfer enable students to develop a more scientifically normative viewpoint on both core and nano knowledge domains?

These research questions are evaluated utilizing mixed-method assessment methodologies, adapted from the relevant literature to suit our needs. Student interviews conducted both prior to and after the commencement of activities, along with small-group discussions recorded throughout the progress of the activities, allowed for the evaluation of contextualized discourse on a per-student basis. The codes developed for the interviews and group discussions are based on a discourse analytical view, which will be discussed in detail in Chapter 4.

The development of activities and experiments to fit directly within the undergraduate chemistry curriculum aims to encourage critical thinking on the part of the student by having them apply reinforced core principles to the novel realm of the nanoscale. Rather than
simply assuming prior knowledge, students’ previous knowledge will be explored and enhanced to prepare for its transfer to the nano-related topics. The modular design has allowed for the integration of activity portions meant to address significant concerns in content matter as appropriate for different levels. Furthermore, these activities use both key scientific and everyday objects and problems in order to raise student interest in the subject. Learning objectives in such teaching tools are centered on linking the two frames of reference, core and nano, and are backed by a strong theoretical framework for analogy and similarity.$^{1,2}$
REFERENCES


CHAPTER 3

Development of Instructional Materials

This chapter serves to provide a detailed overview of the design and development of the instructional materials in this work. Gentner’s theoretical framework for analogy provided the foundation for these materials.\(^{1,2}\) This framework serves to explicitly connect and reflect upon the specific attributes and, more importantly, relations relevant to the core physical and chemical (base) and nanoscale (target) knowledge domains. The principal learning objectives in each instructional material are informed by the application of the framework. Student handouts for each of the instructional materials can be found in Appendix A.

3.1 An Acoustic Analogy

3.1(a) Introduction

The concept of Localized Surface Plasmon Resonance (LSPR) in nanochemistry has been previously explored in the chemical education literature.\(^{3-6}\) This phenomenon occurs in metallic nanomaterials when the oscillating conduction-band electrons of the particles resonate with a particular frequency of electromagnetic radiation. At what frequency, and therefore wavelength, the resonance occurs depends on the identity of the metal and the size of the particle.\(^{3,7}\) Although these concepts are described in the literature, there are no examples of established analogies for students that are tangible at the macro scale. Further, there is little presence in the discipline specific educational literature in general of rigorously assessed instructional materials whose purpose is to connect core chemical and physical concepts to those at the nanoscale. This teaching tool, along with the others in this work, utilizes analogy as a framework to guide its pedagogical underpinnings. The assessed
instructional materials in this work are unique in that they explicitly utilize analogy to inform learning objectives centered on connecting core concepts to those at the nanoscale. The power of sound and music in the human mind is unmistakable. From Helmholtz to Nernst, to Planck and Einstein, the connection between sound and some of the most profound discoveries in the scientific world is astounding. For example, Planck described electrons as standing waves on the string of a musical instrument, leading to the concept that electrons may only occupy quantized energy levels. Additionally, the ability of the human mind to easily interpret patterns through sound may provide a valuable tool in order to assist in understanding chemical concepts. By coupling this with a method of visualizing differences in frequency via the use of a basic computer program, the patterns are expected to be further solidified. Hence, by comparing acoustic resonance to LSPR using tuning forks of different sizes and compositions, students are prompted to uncover the links between size, composition, and LSPR frequency. This activity as written is most appropriate for upper level undergraduates and was tested with students who are currently at the physical chemistry level, but may be simplified for general chemistry by choosing to address only the most basic concepts.

3.1(b) Background

Application of Theoretical Framework and Overview of Analogy

Gentner’s structure mapping theoretical framework for analogy has been chosen in order to provide a suitable foundation upon which to build this analogical activity. Table 4 outlines the structure mapping of the relevant object attributes and relations for this activity:
Table 4: Summary of mapping of object relations and object attributes between tuning forks and metallic nanoparticles.

<table>
<thead>
<tr>
<th>Object Attributes:</th>
<th>Tuning Fork Base</th>
<th>Mapping</th>
<th>Metallic Nanoparticles Target</th>
</tr>
</thead>
<tbody>
<tr>
<td>Size</td>
<td>Tuning forks are macroscopic</td>
<td>Does not</td>
<td>Nanomaterials are on the nanoscale</td>
</tr>
<tr>
<td>Composition</td>
<td>Tuning forks are composed of metallic alloys</td>
<td>Does not</td>
<td>The nanomaterials under study are composed of pure metals</td>
</tr>
<tr>
<td>Oscillatory Behavior</td>
<td>Prongs of the tuning forks exhibit oscillatory behavior</td>
<td>Maps</td>
<td>Collectively, the conduction band electrons in the nanostructures oscillate (plasmon)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Object Relations:</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Induction</td>
<td>Striking of a tuning fork on a hard surface induces the oscillation of the fork prongs</td>
</tr>
<tr>
<td>Detection</td>
<td>Oscillation of tuning fork prongs can be detected by hearing or via a microphone</td>
</tr>
<tr>
<td>Resonance Frequency</td>
<td>Tuning fork’s composition and size determines its resonance frequency</td>
</tr>
</tbody>
</table>

This activity capitalizes on the mapping of object relations as the framework suggests. The interaction of the tuning fork prongs with a firm surface is directly compared to the way surface plasmon resonance is induced by the electric field of visible light. Likewise the observation of the size and composition effects on acoustic resonance in the tuning forks are related to the size and composition effects on metallic nanomaterials. These parameters are tunable and, therefore, ideal for experimentation.\textsuperscript{3,13-17} With background information and an activity design founded on a framework for analogy, students explore how oscillatory behavior in tuning forks at the macro scale can be analogous to oscillatory behavior of conduction band electrons in metallic nanoparticles.
Learning Objectives

The principal learning objectives for students in this activity are centered about their discovery that the acoustic oscillation of a tuning fork is analogous to the oscillation of conduction band electrons in metallic nanomaterials. Each learning objective will be measured via targeted questions built into the activity itself, as in the case of questions in the post-activity interview (noted in parenthesis below), or based on evidence present in student group discourse. Details concerning the post-activity interviews and student group discourse are presented in Chapter 4. The individual objectives that comprise the total analogy are as follows:

1. Students will observe that as the resonant frequency of tuning fork oscillation is detected by hearing, the LSPR frequency is detected via UV-Vis spectroscopy.
2. Students will use the Waves and Sound Physics software\(^\text{18}\) to visualize the waveforms of increasing and decreasing frequency along with the frequency changes associated with changing the identity of a metal in a rod-like structure. If appropriate, they directly record the waveforms of the tuning forks they strike and perform Fourier transforms on some of these waveforms in order to visualize the changes in frequency depending on fork prong length and material identity.
3. Students will infer, from their auditory and data-collecting experiences that both the tuning forks and the conduction band electrons of the metallic nanomaterials exhibit oscillatory behavior induced and driven by an external force. (This inference is, in part, probed for in the fifth question of the post-activity interview).
4. Students will correlate an increase in the length of a tuning fork with a decrease in frequency of the pitch observed, therefore indicating a lower frequency. They will likewise deduce that an increase in the length of metallic nanorods will have the same effect on where the LSPR band is observed. The former will be accomplished via listening and Fourier transforms. Transfer to the latter will be accomplished via inspection of the electronic absorption spectra of the nanomaterials. (This correlation and deduction is, in part, probed for in the second and sixth questions of the post-activity interview).
5. Students will conclude that the identity of the metal of both the tuning forks and nanomaterials will lead to a difference in resonant frequencies due to a change in intrinsic parameters, and that this is independent of size. They will draw these conclusions based on the evidence from listening to and Fourier transforming waveforms from tuning forks of the same size but different composition, and from
observing spectra of similarly sized nanomaterials of different composition. (Students’ abilities to reach these conclusions will, in part, be probed for in the third, seventh, and eighth questions of the post-activity interview).

Through experimentation with the tuning forks and nanoparticle solutions, the students are expected to draw the connections between macroscopic acoustic behavior and the behavior of conduction band electrons in metallic nanomaterials.

Pre-Activity Instruction

Students will need to be familiarized with some basic information pertaining to the tuning forks and metallic nanoparticle solutions prior to commencement of the activity. The students need to be proficient with unit conversion, as they will be asked to use constants from the CRC Handbook of Chemistry and Physics during the activity. The majority of this information is detailed in the supplemental instruction and is presented to the students through the student handout. The basic concepts explored in this activity include the relationship between wavelength, frequency, and speed of waves.

3.1(c) Activity

Activity progression

The progression of the activity is centered about the learning objectives, with the ultimate goal being for students to map relevant knowledge from the tuning forks (base) to the metallic nanomaterials (target). The activity itself is split into six parts:

Part 1 serves to establish the first portions of learning objectives 1, 3, and 4:

Students measure the prong length of tuning forks of different sizes, and order these in a tabulated format. They then strike each one, listen to the relative pitches, and place the rankings of these pitches next to the corresponding prong lengths. This aids to establish the
size-frequency relationship with respect to the tuning forks. They are then probed with questions about the following concepts:

- Relationship between tuning fork prong lengths and frequency/wavelength of sound.
- Oscillatory behavior of the tuning fork prongs.
- Requirement of an external force to produce sound.

Part 2 addresses the first portion of learning objective 5:

Students are given four tuning forks used in Part 1, and four of a different alloy composition. The forks of the same material will vary in prong length, but each will have an analogue of a different composition to which its prong length is equivalent. Students repeat Part 1 and answer questions related to the following concept:

- Composition affects wave properties as the observed pitch between two tuning forks of the same prong length, yet different material compositions, is different.

The purpose of Part 3 is to reinforce learning objective 5:

Students utilize the CRC Handbook of Chemistry and Physics, or its associated webpage, to find physical constants (density, Young’s modulus, and radius of gyration) of both sets of tuning forks from Part 2 and construct plots of wavelength vs. the square of prong length. They use mathematical equations that relate frequency of sound produced, prong length, and intrinsic parameters such as Young’s (Elastic) modulus, density, and radius of gyration. Probing questions address the following:

- From a mathematical perspective, explain the reasons for the change in frequency between the two tuning forks of different composition.

Part 4 addresses learning objective 2:

Students load the Waves and Sound Physics software and utilize the “Beat Frequency Simulator” to view the waveforms of five different frequencies. They subsequently use the
“Transverse and Longitudinal Waves” module to vary the density and Young’s modulus, and record their findings with respect to how the frequency of the waves is affected. It is important that students focus solely on how the waves propagate through the metallic rod, as there exists a graph relating velocity of sound to the changing constants. While it is true that the velocity of sound will vary within the rod itself, the medium in which they are experiencing the sound (air) will remain constant. Students are then probed with questions to address the following points:

- Variation of the intrinsic parameters changes the way the waves propagate through the metallic rod.
- Propagation of waves through the metal affects the frequency of sound observed.

For upper division students, Part 4 may be replaced with direct recording of some of the tuning fork waveforms and subsequent Fourier transforms in order to obtain frequencies. This is accomplished by having students strike the tuning forks in front of a microphone attached via USB to the computer. The waveform is recorded in an open source audio editing program, Audacity, and easily exported to Excel or other spreadsheet program. Excel has, built into it, a method for accomplishing these fast Fourier transforms (often abbreviated as FFT), and students will utilize this function to transform the data that they record from the tuning forks directly into a microphone. Students should transform at least two of the aluminum tuning forks and two of the brass tuning forks. In addition to the above learning objectives, the following are added for the use of the Fourier transform portion:

- Module Learning Objective 1: Students will observe and describe the relationship between the waveform characteristics (period) and the position of the peak in the transform (frequency), and the role of the transform in changing the function’s domain. This will be accomplished by students’ evaluation of the waveform and
Fourier transform plots from tuning forks of the same material but different prong lengths.

- Module Learning Objective 2: Students will observe and compare, via the waveform plots and the Fourier transform, the frequency differences between tuning forks of the same size but differing composition. Students’ separation and analyses of these plots will be essential to this part of the activity.

Students are then probed with questions related to the following concepts:

- The relationship between the waveforms observed in the plots and the length of the tuning fork prong.
- How, mathematically, the waveforms relate to the frequencies observed in the transform plots.
- How the waveforms and frequencies observed from tuning forks of different materials (brass and aluminum alloy) are different from one another and why.

In Part 5, the latter portions of learning objectives 1, 2, and 3 are addressed:

Students are provided with 3 nanorod solutions synthesized in the Nikoobakht and El-Sayed\textsuperscript{15} manner. These solutions should contain nanorods of short (approximately 1.5), medium (approximately 2.5), and long (approximately 4) aspect ratios (ratio between the longitudinal and transverse axes), but need not be of an exact value so long as the spectra are readily distinguishable. Students take the UV-visible spectra and record the $\lambda_{\text{max}}$ of the two peaks between 500 and 1000 nm for each solution. Students are then asked a series of questions to address the following concepts:

- The anisotropic nature of the nanorod means its plasmon resonance band will split into two: one corresponding to a transverse mode, and one to a longitudinal mode. The longitudinal mode is always at a longer wavelength due to the fact that this is the greater dimension in which the conduction band electrons may oscillate.
- The longer the maximum wavelength of the longitudinal mode, the longer the average length of the nanorods in a given solution. This is comparable to the fact that one observes a longer wavelength of sound for a longer tuning fork.
- Electromagnetic radiation (light) is impinging upon the metallic nanoparticle, inducing the collective oscillation of the conduction band electrons. This is analogous to the striking of the tuning fork on a hard surface to induce mechanical oscillation leading to sound production.
Part 6 addresses the latter portion of learning objective 4:

Students obtain two solutions of spherical gold and silver nanoparticles respectively. The gold nanoparticles should be synthesized via the modified Turkevich method\textsuperscript{21,22}, and silver particles should be synthesized via the method illustrated in Mallin & Murphy\textsuperscript{23} such that the average particle size of the gold particles is not significantly different from that of the silver.\textsuperscript{13} Students are provided with the knowledge that the average particle size is similar in both cases. They should be probed to predict whether or not the two solutions will absorb at the same wavelength and explain their rationale prior to taking the UV-Visible spectra.

Students are instructed to observe the spectra between 350 and 750 nm. They observe from the spectra a difference of over 100 nm between the two LSPR peaks. This reinforces the size-frequency relationship with respect to the nanomaterials. They are then asked questions to address the following relationships:

- The two peaks are at significantly different wavelengths even though the nanoparticles are of statistically similar average sizes. This is relatable to the fact that tuning forks of the same size but different composition produced very different tones, and thus very different frequencies and wavelengths of sound.
- The surface plasmon resonance peak of the silver nanoparticles is at a shorter wavelength than that of the gold, thus the energy of the LSPR fundamental mode for silver is at a higher energy. Composition is key to observable parameters and this is comparable to the aluminum alloy tuning forks exhibiting a higher pitch of sound relative to their same-size brass analogues.

To wrap up the activity, students are challenged to answer two questions that relate more advanced mathematical formulae to the metallic nanomaterials. These questions are appropriate for students on the physical chemistry level and may be omitted if the activity is to be used for general chemistry. The questions are centered on the following points:
• The displacement of the collectively oscillating electrons on the surface of a nanomaterial may be modeled as the product of the dielectric tensor and the electric field vector, as these metallic nanoparticles are crystalline structures. Since spherical particles are isotropic (nondirectional), the terms in the dielectric tensor will be equivalent. The anisotropy (directionality) of the nanorods along the z axis may be represented by simply designating that portion of the dielectric tensor as being nonequivalent to the x and y terms. This is a mathematical explanation as to why there is one band in the spherical nanoparticle spectra but two bands in the nanorod spectra.

• The complex dielectric function is most responsible for any differences observed in surface plasmon resonance frequency. For spherical particles, its formula shows a dependence on the intrinsic properties of the metal and the radius of the particles. This means that the frequency is directly related both to the dimensions of the material and the composition of the material itself, just like what is observed with the tuning forks.

3.1(d) Sample Student Results

This activity has been performed by undergraduates enrolled in a physical chemistry level laboratory course. Students used commercially available aluminum alloy tuning forks as the full set of eight and four yellow brass analogues that were machined in-house. The following is a sampling of some results from the activity (Table 5, Figures 3-7):

Table 5: Student prong length and pitch data from Part 1.

<table>
<thead>
<tr>
<th>Prong #</th>
<th>Length (cm)</th>
<th>Length (m)</th>
<th>Rank (pitches)</th>
<th>Brass Analogue?</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>12.5</td>
<td>0.125</td>
<td>Lowest</td>
<td>Yes</td>
</tr>
<tr>
<td>2</td>
<td>11.6</td>
<td>0.116</td>
<td></td>
<td>-</td>
</tr>
<tr>
<td>3</td>
<td>11.0</td>
<td>0.110</td>
<td></td>
<td>Yes</td>
</tr>
<tr>
<td>4</td>
<td>10.7</td>
<td>0.107</td>
<td></td>
<td>-</td>
</tr>
<tr>
<td>5</td>
<td>10.2</td>
<td>0.102</td>
<td></td>
<td>-</td>
</tr>
<tr>
<td>6</td>
<td>9.5</td>
<td>0.095</td>
<td></td>
<td>Yes</td>
</tr>
<tr>
<td>7</td>
<td>9.0</td>
<td>0.09</td>
<td></td>
<td>-</td>
</tr>
<tr>
<td>8</td>
<td>8.7</td>
<td>0.087</td>
<td>Highest</td>
<td>Yes</td>
</tr>
</tbody>
</table>
Figure 3: Linear plots of wavelength of sound vs. the square of prong length for both alloys. Note the vast difference in wavelength between materials at a given prong length.

Figure 4: Short, medium, and long Au nanorods used in this activity. All were synthesized in the Nikoobakht and El-Sayed manner.\textsuperscript{15}
Figure 5: UV-Visible spectrum of short (minimally red-shifted longitudinal mode) Au nanorods. Note the close proximity of the transverse band and longitudinal band.

Figure 6: UV-Visible spectra of medium and long length nanorods. Note the more pronounced red shift in the longitudinal band as the average rod length increases.

Figure 7: UV-Visible absorption spectra of spherical Au and Ag nanoparticles with similar average size (20 nm and 17 nm) according to literature values.\(^{13,23}\) An adapted Turkevich\(^{21,22}\) and Mailllin & Murphy\(^{23}\) syntheses were used respectively. Note the difference in plasmon resonance wavelength, 520 and 390 nm respectively, despite the size similarities.
Pictured below, in Figure 8, is a screenshot from the recording of tuning fork sound data in Audacity from the Zoom H2 microphone:

Figure 8: Screenshot of Audacity displaying recorded results from an aluminum alloy tuning fork. The microphone records in stereo, therefore two channels are present in the data.

Figure 9: Waveform plot of a 256 Hz tuning fork.
Additionally, the plots can be overlaid to show the clear difference in frequency between different forks. Figure 10 depicts an example of such an overlaid plot.

![256/512 Hz Tuning Forks Overlaid](image)

Figure 10: Overlaid waveforms of 256 and 512 Hz tuning forks. Note the clear difference in frequency despite the difference in phase (phase difference is incidental due to the random positioning of the start of data recording).

![256 Hz Tuning Fork FFT](image)

Figure 11: Plot of the results of a Fourier transform performed in Excel on a 256 Hz tuning fork. Note the presence of a prominent peak between 200 and 300 Hz. The actual value obtained from the FFT is around 258.4 Hz (very close to the expected value). As the number of data points utilized increases, the intervals between adjacent frequencies in the transformed function’s domain will decrease, allowing for a more accurate determination of the frequency.
Figure 12: Overlay of Fourier transform results from 256 and 512 Hz aluminum alloy tuning forks.

3.1(e) Summary and Conclusions

We have reported an acoustic analogy to allow students to explore the phenomenon of localized surface plasmon resonance in nanoparticles using tuning forks. Students examine the dependence of size and composition on the frequency and wavelength of oscillation with the forks, and extend the same concepts to the frequency of LSPR in nanorods and nanoparticles. Gentner’s analogical framework was used to design learning objectives around the mapping of such concepts from the tuning forks (base) to the metallic nanomaterials (target).

Since the tuning forks are tangible objects, they present an excellent medium in which students may establish a connection to nanochemistry. Furthermore, the fact that the human mind is capable of analyzing patterns easily through sound provides added value to this
activity. This allows students to explore a complex phenomenon in a multisensory fashion and apply enriched prior knowledge to a novel concept in nanochemistry. This activity is published in the Journal of Nano Education.

3.2 Investigating Quantum Mechanical Tunneling at the Nanoscale via Analogy

3.2(a) Introduction

The concept of quantum mechanical tunneling is relevant in several important areas in chemistry, from hydrogen bonding to alpha decay in nuclei, isotope effects and biological systems. As such, it is arguably an important extension of wave-particle duality for undergraduate physical chemistry courses. Several articles have appeared in the educational literature addressing this topic. However, few have explicitly linked the concept of tunneling to nanochemistry and none report on instructional tools where students may explore the phenomenon in multiple chemistry contexts. There is also a lack of educational activities that transition from the classical world to the quantum world in the context of tunneling. Although work has been done in physics education to develop modules for a broad array of topics from energy bands to tunneling, to assess students’ learning of tunneling in modern physics courses, and to confront students’ understanding of energy conservation in tunneling, there remain fundamental misconceptions about the pillars of quantum mechanics. A prime display of such misconceptions among students may be found within Singh and Zhu’s work in which students with robust mathematical backgrounds (senior-level undergraduate physics students) make such conceptual errors as drawing discontinuity in wavefunctions and ignoring the implications of potential energy being on the “y” axis in 2-dimensional diagrams. In order to understand the tunneling model and apply it
to chemical systems, these fundamental conceptual issues cannot be ignored. It also cannot be ignored that students will come to the table with experience living in the classical world—a world from which quantum chemistry is remote.

An activity is described in which students are exposed to quantum mechanical tunneling in the context of nanochemistry. To start with, students focused on a classical physics experiment, as this is the world within which they experience. Students then transition to a common manifestation of quantum mechanical tunneling in a familiar chemical system, and finally explore the phenomenon at the nanoscale.

3.2(b) The Activity

The activity consists of three parts: a classical physics experiment, analysis of tunneling in a familiar chemical system, and evaluation of the tunneling model at the nanoscale.

Initially, a macro-scale ball-and-ramp apparatus is employed as way to center the student’s focus on energy in the classical domain. Students confirm that their abilities to drop the ball from any point on the ramp constitutes a continuum of available energies (distinctly classical feature), and that the only way to transcend the barrier is to drop the ball from a height greater than the height of the barrier itself. Therefore, they are asked to confirm that the potential energy can never be smaller than the kinetic energy required to have access to the other side of the physical apparatus.

In the second part of the activity, a prime example of quantum mechanical tunneling is studied with the inversion of NH₃. This inversion may be modeled with a double-well potential, whose minima represent the C₃ᵥ symmetry of the molecule with the barrier representing the D₃h intermediate. The energy required to go over this potential barrier in the
classical sense would surpass the logical population of vibrational states at ambient temperatures. Yet, the splitting of bands shows that this inversion is indeed taking place at room temperature. We used NH\textsubscript{3} inversion as a transitional concept into the nano domain and to present to students compelling evidence that the laws of classical mechanics do not apply to this system. A rigorous treatment of this topic is outlined in an experiment by Halpern and may be used as complementary information. In the activity we developed, calculation of the relevant vibrational partition function is used to show students that the population of states is such that the tunneling model serves as a plausible explanatory device for why the inversion occurs.

While the first two portions of this activity aim at encouraging students to think critically about tunneling and the energetic rationale for it in the nuclear sense, the third portion employs the use of bare and core/shell quantum dots to explore the use of the tunneling model at the nanoscale and its implications therein. There is an emphasis on expanding the particle-in-a-box model for the electrons in a bare quantum dot to apply a basic tunneling model to the core/shell type and show that electron tunneling from the core material into the shell material is plausible. Students are then asked to discuss what some implications of such a phenomenon in these nanostructures might be.

Learning Objectives

The learning objectives of the activity are focused around students’ explicit experiences with the base, bridge, and target knowledge domains. The following is a summary of the learning objectives of this activity and which portions of the activity the objectives are intended to be accomplished within.
1. Students will directly explore the classical physics apparatus of a steel ball dropped from various heights to explore conditions for transcendence to occur.
2. Students will obtain vibrational spectroscopic data and plot the vibrational partition functions for each to infer that classical transcendence is not probable.
3. Students will plot empirical potentials to directly observe that the AsH$_3$ potential barrier is significantly higher than that of the NH$_3$.
4. Students will construct a qualitative molecular orbital diagram of H$_2$ and analogous representations on the potential energy diagram of the NH$_3$ mode to justify conditions for transcendence to occur. (Students’ justification will be probed for, in part, through the third question of the post-activity interview).
5. Students will plot empirical potentials to directly observe that the AsH$_3$ potential barrier is significantly higher than that of the NH$_3$.
6. Students will construct (sketch) semi-quantitative energy level diagrams of CdSe quantum dots of two different diameters, observe the effects of quantum confinement and determine relative energy levels for confined systems. Further, they will draw a separate diagram for the wavefunctions such that they can differentiate between the eigenvalues and the eigenfunctions.
7. Students will observe core/shell dots’ optical characteristics and will build up, in a qualitative sense, an energy diagram in a square based potential well with a finite barrier on each side (representing the ZnS layer).
8. Students will contrast the treatment of CdSe/ZnS dots with the CdSe in that the latter is treated with an infinite potential and therefore assumes no tunneling of the wavefunction. (This inference is probed for, in part, via post-activity interview question 7).

Part 1:

Physics Apparatus- The Classical Potential Barrier

Part 1 of the activity addresses learning objective 1.

Students investigate a potential energy in the classical sense where the conservation of mechanical energy and conversion between kinetic energy (KE) and potential energy (PE) are explored within a common undergraduate physics approach. Students use a simple ramp to drop a steel ball from various heights and tabulate their observations including the initial
height, calculated PE of the ball, and the PE of the barrier. The total energy expression for this system is:\(^4^2\):

Equation 1: Total energy expression for the simple classical mechanical system of a ball rolling down an incline.

The gravitational potential energy (PE\(_g\)) will be the total energy when the ball is initially at rest from its point of departure, and students are to ignore the relatively small contribution from the rotational kinetic energy. Students conclude that the ball will not transcend the barrier without having been dropped from \textit{at least} the height of the barrier (in reality, a bit higher due to friction). Figure 13 shows the apparatus students use during the first part of the activity.

Figure 13: Image of the ramp used in this activity with a ball that may be dropped from different heights.
Students are probed to think about the following:

- Based on your observations, what are the requirements for the ball to go over the barrier? Support your response with experimental evidence.
- In this experiment, how many events were you monitoring at a given time? (Define an event as the release of the ball from height $x_h$, where $x$ is any of the factors in your table, until it comes to rest.)
- You are designing a classic wooden roller coaster before the use of hydraulic launch is widespread. Can the height of the initial drop be lower than that of subsequent drops without extra chains to pull the cars up further again? What is the limit here? Thoroughly justify your response (adapted from Serway and Jewett). \(^{33}\)

**Part 2:**

*Tunneling with a Familiar Substance: Ammonia Inversion*

Part 2 addresses learning objectives 2-5.

This part of the activity focuses students’ attentions on the infrared spectra of ammonia ($\text{NH}_3$) and arsine ($\text{AsH}_3$). Depending on the resources available to the instructor, the spectrum may be taken by the students or may be provided to them. In accordance with Halpbern et al.’s \(^{31}\) thorough treatment of the subject for undergraduates, students view the $v_2$ vibrational mode of $\text{NH}_3$ and observe the splitting. They are then provided with the potential scheme with the reaction coordinate centered at 0 at the $D_{3h}$ transition state \(^{25,31}\) and the average energy parameters, including the barrier height, and the first couple of vibrational levels (the fundamental transition).

A key concept that must be discovered by the students at this point is that there is not enough energy in the system to allow significant amounts of $\text{AsH}_3$ or $\text{NH}_3$ molecules to go over their respective potential barriers. This may be shown using statistical thermodynamics. Students calculate the vibrational partition function for both $\text{AsH}_3$ and $\text{NH}_3$ to express the sum over
states populated above the zero point energy at a given temperature using the following equation:

\[
\frac{1}{\Omega(T)}
\]

Equation 2: The series convergence form of the vibrational partition function.\(^{44}\) The zero point energy has been taken as the “0th” level, as is common in the convention of expressing partition functions.

Students calculate and discuss the implications of the following:

- The partition function for the single mode of AsH\(_3\) over the 200 to 800 K range.
- The partition function for the relevant vibrational mode, \(v_2\), of NH\(_3\) to inversion tunneling over the 200 to 800 K range.

This may be further extended to the concept of symmetry in quantum mechanics in general. The dipole moment operator, which gives rise to vibrational transitions in the IR region of the electromagnetic spectrum, is itself antisymmetric.\(^{45}\) This leads to the observation of two prominent bands (~930 and 965 cm\(^{-1}\)) in the NH\(_3\) spectrum and is confirmatory of the splitting and therefore the tunneling effect. Students should also observe the spectrum of the structurally analogous AsH\(_3\), whose inversion tunneling period approaches two years\(^{46,26}\) and is not spectroscopically observed in the form of splitting and exhibits only a single band.

Students mix the states qualitatively leading to positive and negative linear combinations for each state. They first do this in the context of simple H\(_2\) molecular orbitals—by which the same energetic configuration occurs (a positive linear combination is lower in energy than a negative combination). They also construct and fully label their own double-well potential plot and represent energy values on this diagram. Through this, students are probed to think about the following:
- Relevant peaks in the spectra and how they relate to the tunneling splitting in the context of the barrier height.
- How the linear combinations of states factors in, and which states correspond to the positive and negative linear combinations (indicate on potential diagram)?
- What leads to the observation of such mixing in the case of NH$_3$? How and why the inversion does not take place via classical activation at room temperature, via interpretation of the partition function, and how quantum mechanical behavior plays a role in this.
- Justification as to why chiral phosphines are more isolated than chiral amines.
- How many events are taking place and being observed spectroscopically; the relation of this to the measurement and the nature of the problem.
- In what limit would there be no tunneling observed by any means whatsoever (the infinite barrier limit)?

**Part 3:**

*Tunneling in Quantum Dots: Effects on Quantum Confinement*

Part 3 addresses learning objectives 6 and 7.

A major factor related to the surge in research related to metallic and semiconductor nanoparticles is the fact that they exhibit interesting and potentially useful optical features. The reasoning behind these unique effects is generally explained via *quantum confinement*. As its name suggests, the confinement of the electronic wavefunctions as the physical dimensions of the material approach the nanoscale leads to a difference in energy levels that becomes significant at this scale. In the case of quantum dots, the simple particle in a box model may be utilized to show energy level differences. In this model, the energies become closer together as the size of the spherical “container” increases. The energy values drift further apart when the “container” is compressed; thus, the actual act of confinement leads to a greater amount of energy required in the form of electromagnetic radiation to induce an electronic transition—an absorption event.
Equation 3: General energy eigenvalue expression in the simple 1-D particle-in-a-box model. This may be used as a simplified approximation of the spherical treatment.27, 28

\[ E_n = \frac{n^2 \pi^2 \hbar^2}{2mL^2} \]

In the first portion of Part 3, students deal with quantum dots of constant composition (CdSe only). Therefore, they work the particle-in-a-box Schrödinger equation and derive the expression for the energy eigenvalue (as seen above). They then utilize the expression to explain variation in the spectra of multiple sizes of quantum dots. This is important for establishing the relevance of the model. Additionally, students are asked to construct a qualitative visual representation of the problem, labeling each component and relating it back to the expressions.

The treatment itself illustrated in Brus’ work is, arguably, beyond the mathematical sophistication of most undergraduate chemistry students. Therefore, a number of approximations were made to simplify the system to a single-dimension.47 The goal is to provide enough mathematical rigor to describe the system while conserving the ultimate aim of this work: connect concepts from more familiar paradigms to one at the nanoscale.

The boundary conditions are, physically, extremely important as they fulfill the requirement that a wavefunction must be differentiable and continuous across all regions for which it is defined. In essence, the nano aspect of this activity is split up into two parts: treatment of the core alone, and treatment of the tunneling of the electronic wavefunction into the ZnS barrier in the core/shell structures.

It is important for students to remember that there are on the order of $10^{22}$ particles in a typical spectroscopic sample. Thus, the seemingly small difference in the energy term
becomes significant. This manifests itself spectroscopically with a slight red shift, as seen in Figure 1 of Dabbousi et al.’s work. The figure from Dabbousi et al. is provided to students for their analyses in this part of the activity.

Another significant point to be made in this portion of the activity is for students to construct separate representative diagrams for the wavefunction extending into the classically forbidden region and the eigenvalues. This is important as a number of physical chemistry texts and educational resources group the wavefunction representation along with the energy levels. This sort of representation could cause confusion with students, especially with respect to what the y-axis in the diagram represents. These entities, although coupled via the eigenfunction-eigenvalue relationship, are distinct: the wavefunction describes the behavior of the particle (electron), while the energy eigenvalue describes the allowed energy levels of the quantized system. The students constructed qualitative sketches of these plots from provided expressions. Figure 14 shows a student’s sketch for the CdSe/ZnS core/shell system.

Figure 14: Student’s qualitative sketch of the lowest energy level wavefunction for a CdSe/ZnS core/shell quantum dot. Note the student’s incorporation of the term tunneling into the portions where the wavefunction decays into the classically forbidden region.
In bare quantum dots, the electron is confined by the entire nanoparticle itself and the energy of absorption/emission remains simply linked to the size of the particle. In core/shell particles, there is a probability that the electron will tunnel into the shell, and the wavefunction will be less confined than in the original core structure. Therefore, the energy levels will be closer together than a bare quantum dot of the same size. This effect may be observed by solving the Schrödinger equation for a system with a potential well (the CdSe) surrounded on either side by a potential barrier of finite magnitude (the ZnS).\textsuperscript{26,47} This one-dimensional approximation is pertinent to the system insofar that it describes the layering of the core and shell, and the behavior of the electronic wavefunction and resulting eigenvalues.

Concluding this part of the activity, students are probed to consider the following:

- The limit of an infinite barrier is needed with the bare core to model the absence of tunneling.
- The particle under study and how it compares to those studied in previous parts.
- How the construction of the wavefunction relates to the physical system—making the mathematical formalism relevant.
- How the wavefunction and corresponding eigenvalues evolve with respect to bare and core/shell nanoparticles. What the effects of confinement are in all cases. Discussion of the effects in the context of Parts 1 and 2.
- The splitting in the spectrum from Part 2, and the slight red shift of the spectrum in Part 3 provide spectroscopic evidence for the tunneling model’s use.

3.2(c) Application of Theoretical Framework

The key element for an effective analogy is the emphasis on object relations mapping from base to target even when relatively few object attributes would map.\textsuperscript{51} In this activity, Part 1 is the classical macroscopic scenario (core) that serves as a base for Part 2, the NH\textsubscript{3} system. The NH\textsubscript{3} system serves as a bridging concept\textsuperscript{52,53} that serves as a base for Part 3, the nanoscale system. Table 6 summarizes the degree of mapping across the three systems.
Table 6: Application of the theoretical framework to concepts within the activity.

<table>
<thead>
<tr>
<th>Object Attributes:</th>
<th>Classical World Base</th>
<th>Maps</th>
<th>Ammonia Inversion Bridge</th>
<th>Maps</th>
<th>Nanoscale World Target</th>
</tr>
</thead>
<tbody>
<tr>
<td>Particle</td>
<td>Steel ball</td>
<td>Does not</td>
<td>Tunneling of a proton (particle in motion) across NH$_3$ plane</td>
<td>Partial</td>
<td>Electrons in motion. Elementary particles but different composition</td>
</tr>
<tr>
<td>Potential Energy</td>
<td>Gravitational potential as related to lowest point</td>
<td>Does not</td>
<td>Motion is quantized and the wavefunctions are able to <em>tunnel through</em> the potential barrier</td>
<td>Does</td>
<td>Quantized energy levels involving the tunneling of the electrons through the barrier at the CdSe/ZnS interface</td>
</tr>
<tr>
<td>Barrier</td>
<td>Physical hill</td>
<td>Does not</td>
<td>D$_{3h}$ intermediate barrier (a function nuclear potential on either side).</td>
<td>Does not</td>
<td>Rectangular potential barrier separating the electron in CdSe from the ZnS layer</td>
</tr>
<tr>
<td>Object Relations:</td>
<td>PE of the ball at the outset must always be $=$ to or $&gt;$ than the potential of the barrier in order for it to cross.</td>
<td>Partial</td>
<td>Only at high T’s there exists the possibility for the NH$_3$ system to classically transcend the barrier, as more vibrational states are populated. At ambient T it does not occur.</td>
<td>Maps</td>
<td>Hydrogen atom in the bridge and the electron in the target can <em>tunnel</em> through a potential barrier as their wavelike qualities allow for penetration into the classically forbidden region.</td>
</tr>
<tr>
<td>Measurable observations</td>
<td>Energy calculated with the classical energy expression.</td>
<td>Partial</td>
<td>Calculated partition function shows not enough energy to classically transcend. IR splitting gives barrier height of the planar inversion intermediate.</td>
<td>Maps</td>
<td>Extension of the electronic wavefunction of the CdSe into the ZnS layer is seen via a slight redshift in the electronic absorption spectrum.</td>
</tr>
<tr>
<td>Multiplicity of events</td>
<td>Single events (steel ball at different heights)</td>
<td>Does not</td>
<td>Tunneling observed spectroscopically as the result of many molecules and <em>many events.</em></td>
<td>Maps</td>
<td>Many events involving the CdSe and CdSe/ZnS quantum dots are being measured spectroscopically</td>
</tr>
<tr>
<td>Limiting case: potential energy</td>
<td>PE of the hill is higher than KE of the ball. Transcendence will not occur.</td>
<td>Does not</td>
<td>PE must approach infinity for no transcendence to occur.</td>
<td>Maps</td>
<td>PE must approach infinity for no transcendence to occur.</td>
</tr>
</tbody>
</table>
As should be noted from Table 6, the focus is on maximizing the number of object relations that map. Further, the role of the bridge is to overlap with the attributes of the base and the target, making two disparate domains more readily linked.

3.2(d) Summary and Conclusions

Students’ explorations of the effect of quantum mechanical tunneling in this activity occurs through a progression between three domains:

- A classical ball-and-ramp apparatus to start in the world students are familiar with.
- The spectroscopic manifestation of tunneling in familiar molecules (NH$_3$/AsH$_3$).
- The tunneling effect as observed at the nanoscale in core/shell quantum dots.

The use of an analogical theoretical framework provided the foundation for an activity whose components are centered about relevant attributes. Rather than isolating phenomena, our approach allows, simultaneously, for the discovery and critical analysis across knowledge domains, ultimately leading to exploration of concepts at the nanoscale. This activity, and its analysis, have been submitted to the Journal of Chemical Education.

3.3 An Analogical Activity Emphasizing the Importance of Surface Area in Dye-Sensitized Solar Cells (DSSCs)

3.3(a) Introduction

The use of nanocrystalline TiO$_2$ in dye-sensitized solar cells (DSSC) is ubiquitous in the literature, and has found its way into the mainstream market of solar devices.$^{54,55}$ This exciting topic has been introduced previously to students of chemistry through experimental activities and demonstrations.$^{56-58}$ However, little has been done to center the students’ thinking around the role that the high surface area plays in ensuring functionality of the cell. The importance of the nanostructure in the feasibility of such cells is crucial, as it is only within this size domain that the appropriate mesoporous structure can be obtained to allow
for maximum adsorption of dye molecules.\textsuperscript{59} It has been found by Park and coworkers that the efficiency of cells constructed with anatase-phase nanocrystalline TiO\textsubscript{2} is higher than that of cells constructed from rutile-phase TiO\textsubscript{2}.\textsuperscript{60} This is due to the fact that the anatase phase allows for spherical-shaped nanoparticles, affording a higher surface area compared to the more rod-shaped rutile particles.

Herein, we describe a macro-scale analogue in which two slabs of modeling clay (one representing the rutile-phase TiO\textsubscript{2}, the other cut into smaller pieces representing the anatase-phase TiO\textsubscript{2} particles) are placed into beds of craft beads representing the dye molecules. As the beads attach to their surfaces, students relate what they learn about the available surface area of the clay and number of beads stuck to the surface to the absorption cross-section of the dye molecules and the surface area it occupies. Ultimately, the students build their own solar cells: one out of a suspension containing pure anatase nanocrystalline TiO\textsubscript{2}, the other with a mixture of rutile and anatase phase nanocrystalline TiO\textsubscript{2}. They take measurements of the efficiency of these cells and are probed to relate the findings back to the clay/bead portion of the activity.

\textit{Learning Objectives}

The learning objectives of the activity draw directly upon the explicit connections between the relevant knowledge domains. In this case, the structure mapping occurs between the macroscopic clay and bead model as the base and the TiO\textsubscript{2} mesoporous structures as the target. The learning objectives are as follows:

1. Students utilize different sized pieces of clay to investigate surface area based on the number of beads each piece is able to pick up. They are expected to conclude that clay cut into smaller pieces will have a higher available surface area than a similarly
sized piece of clay that is not cut up. (Students’ observations are confirmed, in part, by their responses to post-activity interview question 1).

2. Students compare and contrast the effect of a bead’s diameter to the mass of clay it immediately occupies to conclude that the higher overall surface area of a substrate (clay) leads to a larger impact per unit mass of the object occupying it (bead). (This conclusion is probed for, in part, by post-activity interview questions 2 and 3).

3. Students construct two different rudimentary dye-sensitized solar cells (DSSCs to directly observe the effect of chemisorption of the dye. They are expected to conclude that the dye has adhered to the surface of the TiO$_2$ just as the beads had adhered to the clay. (This conclusion is probed for, in part, by post-activity interview question 5 c).

4. Students use voltage and current measurements of each cell to directly compare the two cells by way of relative efficiencies. They observe electron microscopy images from the literature of each type of TiO$_2$ surface and select the one that best represents the surface of each cell. Students are asked to relate the effect of the dye’s absorption cross section on the TiO$_2$ polymorphs to the bead diameter’s impact on the clay. (Students’ relations between the base and target knowledge domains in this context is probed for, in part, via post-activity questions 4 and 5 a and b).

**3.3(b) The Activity**

There are two parts within the activity: the analogous clay/bead portion and the actual cell construction with measurements part. In the first part, students deal directly with a macroscopic system that allows them to directly visualize the differences in surface area between larger portions of a substrate (the modeling clay) and the substrate that has been divided into smaller pieces. In the second part, students construct solar cells and utilize a projector lamp to measure the relative efficiencies of cells created with the different polymorphs of TiO$_2$. It is expected that students critically reflect on the results and relate the sections, explicitly, to one another.

**Part 1:**

*Clay and Bead Surface Area*

Part 1 addresses learning objectives 1 and 2.
Students are given a bin of plastic craft beads and a block of modeling clay. First students utilize digital calipers to measure the average diameter of the beads (they take five measurements). They are then instructed to cut the block of modeling clay in half and weigh one of the halves. The half that has been weighed is then cut further into thirds and each portion is weighed. After they press each side of each piece of clay into their beads, students record the total number of beads picked up and calculate the ratio of the bead diameter to the mass of clay it immediately occupies.

Figure 15: Students preparing to press pieces of clay into the craft beads.

After obtaining these values, students are probed about the following:

- Rationale for why the average of several beads was utilized to calculate the diameter and what a couple of sources of error in the measurement might be.
- Scientific reasoning behind the scenario that produced the largest ratio of bead diameter to mass of clay it immediately occupied and the one scenario that picked up the most beads.
- Discussion about the implications for the ability of an “adsorbed” substance to have an impact on the surface area of the substrate it occupies.
Part 2:

Construction of the Solar Cells and Efficiency Comparisons

Part 2 reinforces learning objectives 1 and 2 and forms the basis for the latter portions of learning objectives 3 and 4.

Students synthesize the two solar cells (one based on pure anatase and one based on the anatase-rutile mix) via methods reported by Smestad and Grätzel in the literature.⁵⁶,⁵⁷ Among the essential supplies, they are provided with slides of conductive glass (ITO), crushed raspberries in a petri dish which provide the cyanidin dye that chemisorbs to the surface of the TiO₂ thus enabling electron transfer into the broader semiconductor array, two suspensions of TiO₂ (one is the pure anatase and the other the anatase-rutile mixture; these are simply labeled as A and B, such that the students are unaware of the polymorphs prior to taking measurements), an I⁻/I₂ electrolyte in ethylene glycol, a rod of graphite or pencil to catalyze the redox cycle (I⁻/I³⁻), and binder clips to hold the cells together.

Figure 16 shows a TiO₂-coated ITO slide face down in crushed raspberries.

Figure 16: ITO slide coated with TiO₂ face-down in crushed raspberries. Note the purple colored stain on the TiO₂ surface due to the surface complexation (chemisorption) with the cyanidin dye.
Students are then to utilize a projector, as a source of high intensity light, to take current and voltage measurements of the cells. This can be accomplished with the use of a simple voltammeter. Of particular interest is the relative efficiency of the two cells. In order to compute this value, Green’s expression for the fill factor (essentially the optimization of current and voltage for maximum power output) must be calculated.\textsuperscript{61} The expression is provided to students as:

\[ FF = \frac{V_{OC,norm} - \ln V_{OC,norm} + 0.72}{V_{OC,norm} + 1} \]

Equation 4: Fill factor expression, where $V_{OC,norm}$ refers to the open circuit voltage (voltage simply measured with the voltammeter under irradiation) normalized to the thermal voltage.

The thermal voltage can be calculated with the following expression:

\[ V_{therm} = \frac{k_b T}{q} \]

Equation 5: Thermal voltage expression. $T$ is the operating temperature of the cell, and $q$ is the charge of the charge carrier (in this case, electrons).
Students obtain the operating temperature of the cell, in K, through the use of a digital IR thermometer (readily available at most hardware stores). Figure 18 displays a typical setup for the measurement of these values.

![Figure 18: Solar cell hooked up to a simple voltammeter. The cell is placed on an overhead projector, which has been lined with a paper towel.](image)

Another value required to obtain the relative efficiencies of the cells is the short circuit current. This is simply the current measured by the voltammeter under irradiation. Upon collection of these values, the efficiency of a given cell is given by the following expression from Grätzel:

\[
\eta = \frac{I_{\text{SC}} V_{\text{OC,norm}} FF}{I_s}
\]

Equation 6: Efficiency calculation for a solar cell, where \( I_{\text{SC}} \) is the short circuit current, \( V_{\text{OC,norm}} \) is the thermal normalized open circuit voltage, FF is the fill factor, and \( I_s \) is the incident intensity flux of the light source.
Given that the value of interest is the relative efficiency between the cells, one does not need the $I_s$ value (assuming the projector source is the same for both measurements). Therefore, the simple division of the two terms cancels the $I_s$ and give the following:

$$\eta_{A,B} = \frac{I_{SC_A} V_{OC_A} FF_A}{I_{SC_B} V_{OC_B} FF_B}$$

Equation 7: Relative efficiency equation for a comparison between cells A and B. A and B are arbitrary labels assigned to the cells constructed with pure anatase and rutile-anatase mixture TiO$_2$.

Students are also provided with an unlabeled TEM image of rutile and anatase TiO$_2$ from the results of Park and coworkers such that they are able to make a judgment as to which image is representative of the surface in each cell.$^{60}$

Upon obtaining these values, students are probed to address the following questions:

- Which cell is more efficient than the other and to what degree?
- Thinking back to the clay and bead portion of the activity, which cell likely allowed more dye molecules to chemisorb to the TiO$_2$ surface?
- How is the value of the absorption cross section of a dye molecule in relation to the TiO$_2$ surface is related to the mass of clay immediately occupied by a bead of a given diameter?
- Which of the cell surfaces corresponds to which of the TEM images from Park and coworkers? How can this be supported with evidence and the data collected?
- How, in general, is the nanoscale important in these dye-sensitized solar cells?

### 3.3(c) Application of Theoretical Framework

Gentner’s theoretical framework for analogy has been applied in this activity to inform the connections to be drawn between the clay and bead system and the dye-sensitized solar cells. Table 7 summarizes the connections between the relevant object attributes and object relations, the latter of which are to be capitalized upon in the activity.
Table 7: Summary of relevant object attributes and relations within the DSSC activity.

<table>
<thead>
<tr>
<th>Object Attributes:</th>
<th>Clay/Bead System Base</th>
<th>Maps</th>
<th>Nanoscale Solar Cell Target</th>
</tr>
</thead>
<tbody>
<tr>
<td>Composition</td>
<td>Organic clay and plastic beads</td>
<td>Does not</td>
<td>Semiconductor TiO$_2$ and individual dye molecules</td>
</tr>
<tr>
<td>Scale</td>
<td>Macro scale objects readily manipulated with the hands</td>
<td>Does not</td>
<td>Structures of TiO$_2$ at the nanoscale, dye molecules on the scale of Å’s.</td>
</tr>
<tr>
<td>Attachment</td>
<td>Many more beads per unit area can attach to clay that has been separated into smaller pieces</td>
<td>Maps</td>
<td>Many more dye molecules can chemisorb to the smaller pure anatase TiO$_2$ particles</td>
</tr>
<tr>
<td>Surface area relationship</td>
<td>Ratio of a single bead diameter, relative to the surface area of a unit it occupies, is larger for smaller units</td>
<td>Maps</td>
<td>The absorption cross section of a dye molecule has a greater impact on the smaller units of TiO$_2$ (pure anatase)</td>
</tr>
</tbody>
</table>

As has been the case in the previous two activities, note the maximization of the mapping between relevant object relations. This forms the basis for the pedagogy within the activity itself. As such, the mapping of object attributes is less important, as these do not constitute the relationship between more than a single component of the knowledge domain.

3.3(d) Summary and Conclusions

Students explore the effect of available surface area in the context of a simple clay and bead portion and, ultimately, explore the effect of high surface area in dye-sensitized solar cells (DSSCs) by comparing relative efficiencies of cells constructed with two polymorphs of TiO$_2$ semiconductor: high surface area pure anatase and a lower surface area anatase-rutile mixture.

Gentner’s analogical framework has, as in the other activities, been invoked to inform the pedagogy of the activity. Each component of the activity, through the questions posed to students, is designed to allow students to critically reflect on the relevant relations between
the base and target knowledge domains. The activity aims to impress upon students the
importance of the nansocale in DSSCs, as this scale is critical to allow for the cell to function
at an appreciable level of efficiency.
REFERENCES


20. Anonymous Audacity. 2013, 2.0.3.


CHAPTER 4

Methodology and Assessment

4.1 Formulation of Coding Scheme

The assessment of the instructional materials developed in this work is centered on providing evidence to answer the principal research questions for each of the instructional modules.

These principal research questions are:

- Do the newly developed instructional materials promote in students the ability to effectively map core concepts into the realm of nanochemistry? What evidence can be provided to this effect?
- Does analogical transfer enable students to develop a more scientifically normative viewpoint on both core and nano knowledge domains?

Given the detailed nature of the activities developed in this body of work, in-depth analysis is more readily obtained via qualitative means. The principal interest is that of students’ interactions with the material in the activities. Therefore, a qualitative approach combining individual student interviews prior to interaction with the activities, recorded discussions within small groups engaging with the activities, and individual student interviews upon completion of the activities will be employed.

In order to rigorously approach a set of qualitative data in a scientifically meaningful way, the approach taken by Duit and coworkers is adapted to suit our needs.¹ ² Their work has illustrated the use of a combination of conceptual change theory and discourse analysis to construct arguments pertaining to students’ gains upon exposure to physics activities. We have largely approached the analysis from the discourse analytical perspective outlined in their work. Although their subjects were 10th grade students studying chaos theory, the framework of analysis is readily importable to the paradigm of this research.
The role of discourse analysis is the primary perspective in this work. From the discourse perspective, the language utilized by individuals provides a window into their conceptions in the context of their social surroundings, both past and present.\textsuperscript{1-3} The researcher-facilitated small-group settings in which the activities have been completed is one example of the social surroundings in which students find themselves, and therefore molds the nature of their responses. Furthermore, the one-on-one interviews with the researcher, both before and after the activity, bring forth yet another social situation in which the student is isolated from her or his peers and is to respond directly to the questions in the presence of an unequal power structure.\textsuperscript{2-4} Moreover, students’ content knowledge backgrounds in the context of experience will be brought forth by the interviews and within the language expressed in the group settings of the activities.\textsuperscript{1} It is this critical social perspective that allows for arguments to be formed on the nature of students’ language in the situations at hand. Most importantly, it allows for the contextualization of arguments made to support or refute the existence of analogical transfer between core and nano knowledge domains upon students’ completion of the activities.

In order to maximize the impact with which the discourse analytical perspective is utilized, the philosophical underpinnings of the language must be deeply studied. In keeping with the framework put forth by Duit\textsuperscript{1,2} and coworkers, the philosophical basis is found in the work of analytic philosopher W. V. Quine.\textsuperscript{5} Duit\textsuperscript{2} has distilled a number of key terms that allow for the categorization of statements within the form of analysis to be adopted for this work. The terms are:
1. **Observation sentences:** Those statements which, individually, constitute a bridge between linguistics and the world of science. An example given in Quine’s \(^5\) *Pursuit of Truth* is as follows: “The pebble is blue.”

2. **Observation categoricals:** Collections of observation statements whose effect is to form a generality. Examples\(^5\) given in *Pursuit of Truth* are: “When a willow grows at the water’s edge, it leans over the water.”

3. **Theoretical sentences:** Statements whose merit is checked by the rigors of established scientific theory. The line of demarcation between an observation and theoretical sentence is largely argued as contextual. Quine\(^5\), for instance, states that “…those once innocent observation sentences are theory laden indeed. An observation sentence containing no word more technical than ‘water’ will join forces with theoretical sentences containing terms as technical as ‘H\(_2\)O’.”

4. **Intersubjectivity:** The degree to which there is congruence between the meaning of statements between “all linguistically competent” observers.\(^5\)

The language categories described by Quine\(^5\) and utilized by Duit\(^1,2\) and coworkers provides a firm epistemological basis for the critical discussion of the efficacy of instructional materials. Its practicality makes it readily incorporated into this work, and allows for careful analysis required for a robust qualitative study.

By adopting, in part, Duit’s\(^1,2\) method of analysis for analogically based activities, arguments can be constructed in this work based on the results of qualitative data from interviews and students’ discussions. Its use as a basis for designing a code to be applied to the data is described below:

1. **Physical observation statements and categoricals:** The most general of the coding components; in congruence with the definitions of W. V. Quine. Principal purpose is to hone in on students’ expressions of what they experience and how these experiences are, in turn, expressed verbally.
2. **Misconceptions:** Erroneous or scientifically invalid statements about any particular component of the activity.
3. **Comparison and contrastive statements:** Statements that compare one component of the activity to another; can be either intra- or inter-domain, or even external in the case of establishing spontaneous analogical transfer. External transfer is a separate sub-code.
4. **Reformulations**: Corrections to misconceptions; such corrections may be group-induced, investigator-induced or carried out by an individual who has expressed their own misconception.

5. **Background statements**: Any statement that invokes a group member’s prior exposure or knowledge of the topic(s) at hand.

6. **Investigator intervention**: Statements made by the investigator to cultivate students’ group discussion or assist in conceptual development. Simple procedural advice is not included in this category.

This coding scheme informs the large qualitative component of the work, and allows for the characterization and contextualization of students’ language in each of the analysis environments.

This theoretical perspective is crucial to understanding how the activities either promote or do not promote analogical transfer from the base to target knowledge domains. This, in turn, assists with the answering of both principal research questions. The discourse analytical perspective serves as a primary component in the analysis. It allows for careful contextualization of the students’ background knowledge, the learning environment, and the interviewer-interviewee relationship during data collection. The coding scheme accounts for discourse analytical perspectives in employing an epistemology to both characterize students’ language related to transfer and the knowledge domains. Misconceptions, comparison and contrastive statements and reformulations serve to inform the study as students move from base domain to target domain. Background statements and investigator intervention assist in clarifying what knowledge students bring to the activity along with the degree to which the investigator is involved with facilitating discussion, allowing for a discourse analytical perspective to be utilized. This serves to increase the detail and efficacy of the qualitative study.
4.2 Data Collection and Code Application

Students in the trials of all three activities were separated into small groups (approximately three to five students each). Data collection consisted of three phases: individual student pre-activity interviews, recordings of group discourse, and individual student post-activity interviews. Prior to data collection, all students were provided with and required to sign informed consent forms. Transcriptions were prepared from each of the recordings and pseudonyms assigned to students based on the small group they were in (i.e. S1G3 for student 1 in group 3). All transcriptions were uploaded into the qualitative and mixed-methods analysis software, Dedoose\(^6\), which allowed for excerpting and applying codes and descriptors to the data.

The pre-activity interview served mostly to gauge individual students’ background knowledge as pertinent to the instructional material. The background knowledge quality was ranked based on both the scientific validity (was it normative?) and the level of detail of the response (was it well developed and not simply a textbook response?). Detailed description of score assignments will be provided in the results section.

Upon aggregating the scores of responses to each question, an overall assessment of each student’s background knowledge quality was given and subsequently stored for contextualizing group discourse and post-activity interview responses, in accordance with the discourse analytical perspective.

Within the group discourse, the full range of codes was used in relevant exchanges between students themselves or between students and the investigator. The data from group
discussions served to monitor and analyze students’ interaction with the instructional modules, and any progression of concepts or analogical transfer.

The post-activity interview was designed to probe for evidence of individual student knowledge gains and of understanding of the connections between the base and target knowledge domains. The questions were designed to focus on the individual components of the instructional materials and enable students to reflect on the relationships between these components. These questions can be found in Appendix C.

It is important to note that codes were pre-defined in that the scheme was constructed prior to data collection. Examples of code application to student discourse, along with explanations, on a pre-activity basis, are given in tables below: Table 8 provides examples of physical observation statements and categoricals, Table 9 of misconceptions, Table 10 of comparison and contrastive statements, Table 11 of reformulations, Table 12 of background statements, and Table 13 of investigator intervention.

Table 8: Code application: Examples of physical observation statements and categoricals. This is the most widely applied code.

<table>
<thead>
<tr>
<th>Acoustic Analogy</th>
</tr>
</thead>
<tbody>
<tr>
<td>S5G2: The, um, smaller one had a quicker frequency of vibration than the bigger one, yeah.</td>
</tr>
</tbody>
</table>

Student S5G2 makes a physical observation statement related to the differences in frequencies between a tuning fork of shorter length to a fork of longer length. This excerpt was also coded as a comparison and contrastive statement, as it directly compared two tuning forks of different sizes to one another.

<table>
<thead>
<tr>
<th>Quantum Tunneling</th>
</tr>
</thead>
<tbody>
<tr>
<td>S1G1: Oooh, this is a linear combination of vibrational wavefunctions that’s the reason, not just of the wavefunction right?</td>
</tr>
</tbody>
</table>


Table 8 Continued:

<table>
<thead>
<tr>
<th>DSSC Activity</th>
</tr>
</thead>
</table>
| S1G1: *Because if you get the appropriate nanoscale structure, you’ll have the best packing and therefore the most absorption, and you’ll have the most...*  
S3G1 (interjects): *Efficiency!* |

Students S1G1 and S3G1 are referring to the appropriate nanoscale structure exhibiting best packing and most absorption leading to higher efficiency. This level of generality constitutes a physical observation categorical, coinciding with the definition of Quine.

Table 9: Code application: Examples of misconceptions.

<table>
<thead>
<tr>
<th>Acoustic Analogy</th>
</tr>
</thead>
<tbody>
<tr>
<td>S7G3: <em>Didn’t the frequency just change the amplitude or something? It was, like, the highest amplitude had something to do with the frequency.</em></td>
</tr>
</tbody>
</table>

This statement came from the Fourier transform module portion. The student mistakenly believes that the amplitude of the waveform is directly related to the frequency obtained in the Fourier transform results. This, therefore, constitutes a misconception.

<table>
<thead>
<tr>
<th>Quantum Tunneling</th>
</tr>
</thead>
<tbody>
<tr>
<td>S1G2: <em>But like the, between two and three, like the gap would be smaller than between one and two.</em></td>
</tr>
</tbody>
</table>

Student S1G2, in referring to the relative energy levels in the particle-in-a-box model, incorrectly characterizes the spacing between higher energy levels as being smaller than between lower energy levels. In fact, the trend is the opposite.

<table>
<thead>
<tr>
<th>DSSC Activity</th>
</tr>
</thead>
<tbody>
<tr>
<td>S3G4: <em>Isn’t the current from all the electrolyte solution? So, if there are more holes, the electrolyte solution would be able to go, electricity will be able to go through it faster. Or more easily? If it’s more compact, it would be harder to get through.</em></td>
</tr>
</tbody>
</table>

S3G4’s misconception centers on the role of the electrolyte solution. The student believes that what appear to be more tightly packed nanostructures in the provided TEM images would lead to more difficulty for the electrolyte to pass through, thus generating current. In reality, the relevant information is that the anatase nanostructures allow for more dye chemisorption, therefore leading to a more efficient cell.
Table 10: Code application: Examples of comparison and contrastive statements. This is the most important code for understanding students’ analogical transfer between and within knowledge domains.

<table>
<thead>
<tr>
<th>Acoustic Analogy</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>S4G2</strong>: <em>Ok. (Strikes forks again). This one’s (aluminum alloy) definitely higher pitched than that one (brass). This one’s definitely higher pitched than that one. (Repeats statements two more times).</em></td>
</tr>
<tr>
<td>Here, the student is directly comparing the difference in pitches between the aluminum alloy tuning fork and its brass analogue. This comparison statement takes place within the same domain, yet contributes to forming the basis for later comparisons between domains (i.e. connecting intrinsic properties of tuning forks to intrinsic properties affecting electronic absorption spectra in nanomaterials).</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Quantum Tunneling</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>S1G3</strong>: <em>Yeah, so since the barrier for NH$_3$ is close enough to, um, well the ground state and the excited state so it will tunnel and vibrate the other way. But for Arsenic, it’s too high, so it doesn’t tunnel.</em></td>
</tr>
<tr>
<td>Student S1G3 compares the relative barrier heights in the double well potential for NH$_3$ and AsH$_3$ respectively. This is an intra-domain comparison, but sets the stage for possible transfer to the target domain later as the student articulates that the AsH$_3$ has too high a barrier for inversion tunneling. Thus, the student expresses understanding of the fact that a higher barrier height decreases the probability of tunneling.</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>DSSC Activity</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>S2G1</strong>: <em>Well, because it’s the, think of the clay, er, the beads as the molecule, er, the dye and then think of our slide as the clay, so...</em></td>
</tr>
<tr>
<td>S2G1 makes a connection from the base domain to the target domain, in that the student believes the beads to be representative of the dye molecules and the clay to be representative of the ITO glass slide. Although the second portion of this comparison statement is misconceived, this qualifies as an example of an inter-domain comparison.</td>
</tr>
</tbody>
</table>

Table 11: Code application: Examples of reformulations

<table>
<thead>
<tr>
<th>Acoustic Analogy</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>S4G3</strong>: <em>(Laughs). Is the pitch different or the same between the two?</em></td>
</tr>
<tr>
<td><strong>S2G3</strong>: <em>The pitch is the same.</em></td>
</tr>
<tr>
<td><strong>S1G3</strong>: <em>The pitch is? As opposed to the note?</em></td>
</tr>
<tr>
<td><strong>S3G3</strong>: <em>Yeah, lower. Yeah.</em></td>
</tr>
<tr>
<td><strong>S1G3</strong>: <em>I think the gold ones are lower.</em></td>
</tr>
<tr>
<td><strong>S5G3</strong>: <em>The gold ones are lower. The yellow ones.</em></td>
</tr>
</tbody>
</table>
The above exchange within group 3 is representative of a misconception formulated by S2G3 (in the second line), and subsequent reformulation (last four lines). Note that S1G3 poses a challenge to the notion that the pitch is the same between the brass and aluminum forks, followed by S3G3’s agreement with the reformulation. This leads to further acceptance that the brass tuning forks are indeed lower in pitch than the aluminum alloy forks.

**Quantum Tunneling**

| S1G1: It looks like the higher the barrier height, the more tunneling is going to happen. |
| S2G1: No, the higher the barrier, the less tunneling. |
| S1G1: If the barrier’s higher, it’s going to tunnel. |
| S2G1: No, if the barrier’s much, much, much higher then it’s going to try to tunnel and then just decay off to nothing. (pause) So this would be the case with the arsenic hydride; this is the case of the ammonia. Um, in this case, our energy of, you know, our excited state energy is comparable to the barrier height, so we’re getting within the range of possible, um, tunneling. Because if I was going to redraw this for arsenic, um, hydride, it would look the same, but this barrier would be about that wide. Just to throw something out there. So you would try to tunnel and it would just decay like that and it would never reach to the other side. |

Here, in response to the misconception put forth by S1G1, S2G1 offers a reformulation. S1G1 asserts that the higher the barrier, the more likely a tunneling event is to occur. S2G1 objects to this and offers a scientifically normative alternative to the misconception.

**DSSC Activity**

| S1G3: Which cell is more efficient? Just because one produces more voltage, that doesn’t mean it’s more efficient does it? |
| S2G3: I think so. |
| S1G3: Oh yeah, because you use the same amount of material and it’s producing more. |

In this exchange, S1G3’s misconception is that a cell with a higher voltage is not more efficient. S2G3 chimes in and begins the reformulation by asserting otherwise, and S1G3 essentially completes the reformulation by recognizing that, in using the same amount of material, one with a higher voltage would be more efficient overall.

**Acoustic Analogy**

| S4G4: (Laughs) it’s so dissonant, the overtones. |
| Investigator: Do you play an instrument? What do you play? |
| S4G4: I play guitar. I’ve been playing in C all day, like. (Laughs). |
Table 12 Continued:

<table>
<thead>
<tr>
<th>Quantum Tunneling</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>S4G4</strong> utilizes language, particularly the term “dissonant”, that is consistent with individuals with a music background. The investigator poses a question concerning whether or not the student plays an instrument, and the student confirms this. The student’s statements are directly related to their background as the musical background forms the types of language utilized to describe the sound from the tuning forks.</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th><strong>Quantum Tunneling</strong></th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>S1G1</strong>: Not really, I don’t understand the concept itself…tunneling. It’s a new one for me.</td>
</tr>
<tr>
<td><strong>S2G1</strong>: You really should’ve talked about it in your quantum.</td>
</tr>
<tr>
<td><strong>S1G1</strong>: No, we haven’t</td>
</tr>
<tr>
<td><strong>S4G1</strong>: Yeah, we didn’t</td>
</tr>
<tr>
<td><strong>S2G1</strong>: Really?</td>
</tr>
<tr>
<td><strong>S1G1</strong>: We never talked about tunneling</td>
</tr>
<tr>
<td><strong>S2G1</strong>: Oh, that was physics. That was my physics class.</td>
</tr>
</tbody>
</table>

Here, students make background statements directly relevant to their coursework pertinent to the knowledge domain concerning quantum mechanical tunneling. S1G1 and S4G1 did not discuss (or do not remember discussing) tunneling in their quantum mechanics course. However, student S2G1 indicates that they have indeed been exposed to the topic in a physics course. This background information is crucial in considering students’ language use and how they confront this abstract concept.

Note that the code for background statements was not applied at any time during the analysis of the DSSC activity. Therefore, no excerpt is provided in Table 12 for that activity.

Table 13: Code application: Examples of investigator intervention

<table>
<thead>
<tr>
<th><strong>Acoustic Analogy</strong></th>
</tr>
</thead>
<tbody>
<tr>
<td>Investigator: So, if I might interject for a second, you guys realize that there are, in each of these there’s two peaks. There’s two main peaks. One here, that appears at about the same wavelength for all of them, and then for these, what about those?</td>
</tr>
</tbody>
</table>

The above excerpt represents non-procedural investigator intervention as the investigator has deemed it necessary to intervene in order to keep students on track within the activity, particularly at a juncture where there is a tendency to for them to get stuck. This takes place within the peak assignment portion of the acoustic analogy activity (transverse and longitudinal plasmon modes).
Table 13 Continued:

<table>
<thead>
<tr>
<th>Quantum Tunneling</th>
</tr>
</thead>
</table>
| **S4G3:** *Just, is it a dimensionless number? I don’t really know what that means. Like, what the q value is.*  
**S2G3:** *(laughter) Well, we ended up with no units.*  
**Investigator:** *I’ll drop you a little tidbit here. Um, what would happen if you put your temperature to zero?* |

The intervention during students’ calculation of the partition function was meant to get students on track by analyzing the meaning of the partition function. Since the value will go to 1 (all entities in the ground state) at absolute zero, the investigator felt it was necessary to give this hint in order to facilitate the discussion and help illustrate the physical meaning associated with the function.

<table>
<thead>
<tr>
<th>DSSC Activity</th>
</tr>
</thead>
</table>
| **S2G3:** *What value are you talking about?*  
**Investigator:** *The value, I’m referring to the absorption cross section. So how would that, how would that relate to the occupied mass and surface area of the TiO2 nanostructure?*  
**S2G3:** *It would increase when the surface area increased. And it would decrease with the occupied mass?*  
**Investigator:** *So the absorption cross section of the dye is intrinsic to the dye, right? It is its own thing; that’s the amount that the dye exposes itself.* |

Students in group 3 were becoming frustrated with the question pertaining to the absorption cross section. The investigator intervened and note that the attempt to clarify the role of the absorption cross section, in the final line of the above excerpt, guide S2G3 away from the misconception that the absorption cross section decreased with higher occupied mass (TiO$_2$ surface occupied by the dye molecules).

### 4.3 Results and Analysis

Upon thorough coding of the transcripts and relevant excerpts, the results were compiled and patterns in the data elucidated in order to provide evidence of effective mapping of core concepts into the realm of nanochemistry and/or the development of a more scientifically normative viewpoint on both core and nano knowledge domains. A portion of seeking out patterns came from utilizing the code co-occurrence analysis tool in Dedoose. This tool enables viewing cases in which codes were applied simultaneously within all the data. The
following tables are the code co-occurrence results for each of the three instructional materials. Abbreviations utilized for the codes are:

- Background statements - Bck. S.
- Comparison and contrastive statements - Comp./Cont.
  - External spontaneous transfer (a subset of Comp./Cont.) - E.S.T.
- Investigator intervention - I. I.
- Misconceptions - Miscon.
- Physical observation statements and categoricals - Phys. Obs.
- Reformulations - Reform.

Table 14: Code co-occurrence table for Acoustic Analogy activity.

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Bck. S.</td>
<td>5</td>
<td></td>
<td>5</td>
<td>10</td>
<td>5</td>
<td></td>
<td>20</td>
</tr>
<tr>
<td>Comp./Cont.</td>
<td>5</td>
<td>1</td>
<td>7</td>
<td>44</td>
<td>3</td>
<td></td>
<td>60</td>
</tr>
<tr>
<td>E. S. T.</td>
<td>1</td>
<td></td>
<td>1</td>
<td></td>
<td>2</td>
<td></td>
<td>2</td>
</tr>
<tr>
<td>I. I.</td>
<td></td>
<td></td>
<td>3</td>
<td></td>
<td>3</td>
<td></td>
<td>3</td>
</tr>
<tr>
<td>Miscon.</td>
<td>5</td>
<td>7</td>
<td>12</td>
<td>1</td>
<td>25</td>
<td></td>
<td>25</td>
</tr>
<tr>
<td>Phys. Obs.</td>
<td>10</td>
<td>44</td>
<td>3</td>
<td>12</td>
<td>11</td>
<td></td>
<td>81</td>
</tr>
<tr>
<td>Reform.</td>
<td>3</td>
<td></td>
<td>11</td>
<td></td>
<td>15</td>
<td></td>
<td>15</td>
</tr>
<tr>
<td>Totals</td>
<td>20</td>
<td>60</td>
<td>2</td>
<td>3</td>
<td>25</td>
<td></td>
<td>15</td>
</tr>
</tbody>
</table>

Table 15: Code co-occurrence table for Quantum Tunneling activity.

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Bck. S.</td>
<td>2</td>
<td>1</td>
<td>2</td>
<td>7</td>
<td>2</td>
<td>2</td>
<td>12</td>
<td>12</td>
</tr>
<tr>
<td>Comp./Cont.</td>
<td>2</td>
<td>6</td>
<td>1</td>
<td>2</td>
<td>30</td>
<td>2</td>
<td>44</td>
<td>44</td>
</tr>
<tr>
<td>E. S. T.</td>
<td></td>
<td>1</td>
<td>1</td>
<td>11</td>
<td>51</td>
<td>4</td>
<td>68</td>
<td>68</td>
</tr>
<tr>
<td>I. I.</td>
<td>1</td>
<td>2</td>
<td>11</td>
<td>30</td>
<td>29</td>
<td>35</td>
<td>45</td>
<td>45</td>
</tr>
<tr>
<td>Miscon.</td>
<td>2</td>
<td>2</td>
<td>11</td>
<td>30</td>
<td>29</td>
<td>35</td>
<td>45</td>
<td>45</td>
</tr>
<tr>
<td>Phys. Obs.</td>
<td>7</td>
<td>30</td>
<td>2</td>
<td>51</td>
<td>30</td>
<td>29</td>
<td>149</td>
<td>149</td>
</tr>
<tr>
<td>Reform.</td>
<td>2</td>
<td>4</td>
<td>2</td>
<td>29</td>
<td>29</td>
<td>35</td>
<td>35</td>
<td>35</td>
</tr>
<tr>
<td>Totals</td>
<td>12</td>
<td>44</td>
<td>8</td>
<td>68</td>
<td>45</td>
<td>149</td>
<td>35</td>
<td>35</td>
</tr>
</tbody>
</table>
Upon viewing Tables 14-16, it is readily noticeable that physical observation statements and categoricals tend to co-occur with comparison and contrastive statements. This is not surprising given that students must, in order to make a meaningful comparison or contrastive statement, root their comparison with observation statements directly about the objects in the relevant knowledge domains. It is also readily deduced that if a comparison and contrastive statement is scientifically normative, then that particular statement cannot overlap with the application of the misconception code. Further, it is noticeable that misconceptions never co-occur with external spontaneous transfer.

It was, therefore, decided certain code comparisons might lend themselves to a quantitative component to serve in a subordinate yet complementary fashion to the larger qualitative picture of the analysis. This quantitative treatment was invoked under two premises:

- To weigh the number of misconceptions versus valid comparison and contrastive statements against the background knowledge quality of the students who made the statements.
- To examine the effect of high or low levels of investigator intervention on the number of physical observation statements and categoricals and the instances of spontaneous external analogical transfer.
The intent in the first case was to determine within the individual instructional material trials whether or not students’ background knowledge in these group environments determined if they exhibit significantly higher (or lower) tendency to state misconceptions as opposed to valid comparison or contrastive statements or vice-versa. In the second case, the interest was whether or not high levels of non-procedural intervention from the investigator was associated with higher (or lower) levels of physical observation statements/categoricals or spontaneous external analogical transfer.

In order to carry out the quantitative treatment, small sample statistics were employed. The Fisher’s exact test was utilized and, for contingency tables with higher frequencies in one or more of the cells, the Yates’ corrected chi-square test was carried out. Both of these tests were performed utilizing interactive calculation tools by Preacher and Briggs. This small quantitative component along with the broader qualitative nature of the methodology allows for the rigorous analysis of students’ language during their interactions with the instructional materials in both the context of their prior knowledge and the learning environment itself.

Another important component is the degree to which a given instructional material is procedural. Talanquer and coworkers’ research on students engaged in small group activities characterized one portion of students’ language as procedural, which was found to be seven percent of their overall discourse within particular activities. Depending on the relative weight of procedural and conceptual demands of a given activity, it is plausible that this could have a significant impact on the distribution and nature of students’ group discourse. Within this chapter, activities will be ranked based on the degree to which procedure is involved in the protocol, but it should be emphasized that further research would
be required to assess this rigorously. This forms the basis of some arguments for future work, which is elaborated on in Chapter 5.

What follows are the analysis results for each activity provided along with the context-pertinent excerpts from pre-activity interviews, group discourse, and post-activity interviews.

4.3(a) Acoustic Analogy Analysis

The acoustic analogy activity involves a blend of procedural (i.e. data collection) and theoretical portions (students calculate frequencies for tuning forks based on theory, and are asked to explore some theoretical considerations of the LSPR phenomenon). This activity is intermediate to the highly procedural nature of the DSSC activity and the highly theoretical nature of the quantum tunneling activity.

Background Knowledge Assessment via Pre-Activity Interviews

Students’ background knowledge in the context of the relevant content material of the activity was determined by assigning scores of 0 (weak), 1 (medium), or 2 (strong) to their responses to the pre-activity interview questions. For three background knowledge questions, the maximum possible score would be 6 (2 points on each question). An aggregate score of 0-2 would be considered weak background knowledge, a 3-4 would be medium, and a 5-6 would be high. The following content-specific questions were asked during the pre-activity interview for the acoustic analogy activity:

1. What is oscillatory behavior?
2. What is an intrinsic property of a material?
3. What is the basic operating mechanism of a UV-Visible spectrometer?

A fourth content specific question: “What is a Fourier transform and how is it utilized in science?” only elicited “black-box” type responses. Therefore, it was decided that this
question would not be factored into the pre-activity assessment of the students. This issue will be elaborated on further in the analysis.

Scores were assigned based on two factors:

- The degree to which the answer was scientifically normative
- The level of depth of the description (i.e. the student’s answer ought to be phrased in their own words, not simply a “textbook” style statement).

The following tables consist of student responses that are characterized as weak, medium and strong with respect to the background knowledge. Each question is addressed in a separate table, and includes a rationale as to why a particular score was assigned.

Table 17: Example responses from pre-activity interview question “What is oscillatory behavior (OB)?” with assigned score and rationale.

<table>
<thead>
<tr>
<th>ID #</th>
<th>Interview Transcript Excerpt</th>
<th>Score and Rationale</th>
</tr>
</thead>
</table>
| S2G3 | Investigator: *What is OB?*  
S2G3: *Um, like rotations. Like rotations of molecules.*  
Investigator: *Um, can you, oh ok, so I guess that would be your example of a physical system that exhibits oscillatory behavior.* | Student S2G3’s response refers directly to the rotation of molecules. Though the rotation of molecules is quantized, implying that its behavior can be characterized by a wavefunction (which, by its very nature is periodic), the student does not provide any elaboration in their response to this effect. The response was not developed well enough to indicate whether or not the student understood oscillatory behavior at a fundamental level. This response **was scored a 0 out of a possible 2.** |
Table 17 Continued:

| S2G2   | Investigator: *What is OB?*  
|        | S2G2: *Oscillatory behavior? Like something behaving like sine and cosine functions maybe?*  
|        | Investigator: *Can you name some examples of physical systems that exhibit oscillatory behavior?*  
|        | S2G2: *Uh. Wavefunctions? Like. I guess wavefunctions...*  
|        | S2G2 correctly invokes sine and cosine functions as possible models for physical systems that exhibit oscillatory behavior. Further, when probed to give an example, the student refers to a wavefunction (ostensibly in the quantum mechanical sense) as a physical system that exhibits oscillatory behavior (though, rigorously, the wavefunction merely describe a system exhibiting such behavior). Missing was the crucial development that oscillatory behavior implies motion between two extremes. **Therefore, a score of 1 out of a possible 2 was assigned to this response.** |

| S3G1   | Investigator: *What is OB?*  
|        | S3G1: *Uh. Like, I want to use oscillation in the definition, but, like vibration between two points. Would that be good?*  
|        | Investigator: *Can you name some examples of ...?*  
|        | S3G1: *Um, consider a linear molecule, like H₂, oscillatory vibrations. Or, consider like the harmonic oscillators energies.*  
|        | In this response, student S3G1 gives a clear reference to an entity moving back and forth between two points (two extremes). This is a scientifically normative response. Furthermore, the quantum mechanical examples given by the student centered on the harmonic oscillator approximation—the quintessential oscillatory model in both classical and quantum mechanics. **As a result, this response was given a score of 2 out of a possible 2.** |

Students’ responses, in order to be considered scientifically normative, needed to include the defining characteristic of any oscillation: movement between two extremes. Many students could provide at least an example of sinusoidal functions being representative of oscillatory behavior, as was the case of student S2G2. In order to assign a physical meaning to any oscillatory function, however, it is necessary to discuss the behavior in terms of two extremes, as student S3G1 did in their response. Subsequent tables will not have examples
of students’ responses assigned a score of 0. Additional examples of such responses can be found in Appendix B.

Table 18: Example responses from pre-activity interview question, “What is an intrinsic property of a material (IPM)?” with assigned score and rationale.

<table>
<thead>
<tr>
<th>ID #</th>
<th>Interview Transcript Excerpt</th>
<th>Score and Rationale</th>
</tr>
</thead>
<tbody>
<tr>
<td>S1G2</td>
<td>Investigator: <em>What is an IPM?</em> S1G2: <em>Of a material?</em> Investigator: <em>Yeah.</em> S1G2: <em>Intrinsic?</em> Investigator: <em>Intrinsic.</em> S1G2: <em>Uh, like boiling point, melting point, this stuff. Right?</em></td>
<td>Student S1G2 correctly identifies boiling point and melting point as being intrinsic properties of a material. However, the notion that the property itself does not depend on the amount of substance present is not found in the response. <strong>Therefore, a score of 1 out of a possible 2 was assigned to this response.</strong></td>
</tr>
<tr>
<td>S6G3</td>
<td>Investigator: <em>What is an IPM?</em> S6G3: <em>Uh, it’s a property that a material has by itself without any external factors.</em> Investigator: <em>... an example?</em> S6G3: <em>Um. Uh. Intrinsic property. I don’t know, like a textile dye, some of them are intrinsically, um, carcinogenic because of the azo bonds.</em></td>
<td>Here, the student is aware that an intrinsic property is something that a material possesses itself. The example given is scientifically normative: a chemical substance can be carcinogenic due to particular bonds present in that compound. Since the bonds define the compound, this is intrinsic to the material itself. <strong>This response was given a score of 2 out of a possible 2.</strong></td>
</tr>
</tbody>
</table>

In question two, students were asked to consider intrinsic properties which are inherent to the material itself. Some students, such as S1G2, would provide an example of an intrinsic property but would not indicate a general understanding of the term. Others did not know whatsoever what the term meant, or could not recall from earlier chemistry courses. A few, such as S6G3, properly identified the intrinsic property as inherent to the material, and gave examples that were scientifically normative.
Table 19: Example responses from pre-activity interview question “What is the basic operating mechanism of a UV-Visible spectrometer (BOM-UVS)?” with assigned score and rationale.

<table>
<thead>
<tr>
<th>ID #</th>
<th>Interview Transcript Excerpt</th>
<th>Score and Rationale</th>
</tr>
</thead>
</table>
| S4G3 | Investigator: *What is the BOM-UVS?*  
S4G3: UV-vis. *The basic operating mechanism?*  
Investigator: *Yeah, like what are the most basic requirements for a spectrum to be taken?*  
S4G3: *Ok, so I know for the UV-vis, you need to put it in a quartz cube, you put it in the middle and you shine like a laser through it, and it takes the wavelengths.*  
Investigator: *Uh, describe the role of light, electromagnetic radiation, in the spectrometer.*  
S4G3: *Like the light beam that’s being shot through?*  
Investigator: *Yeah.*  
S4G3: *I think it’s to determine which wavelengths are being absorbed.* | This response contained a misconception related to the nature of the incident light provided in the spectrometer (it is not a laser, but typically a deuterium lamp for the UV and a tungsten lamp for the visible). In addition, the student does not directly characterize the role of light as being the energy introduced into the system in order to induce absorption. **A score of 1 out of 2 was assigned to the response.** |
| S5G1 | Investigator: *What is the BOM-UVS?*  
S5G1: UV-visible. *Uh, operating mechanism?*  
Investigator: *Yeah, like, uh, what are the most basic components required for a spectrum to be taken?*  
S5G1: *Uh, you need a lamp. You need a detector. You need a monochromater. You need your sample.*  
Investigator: *Ok, so describe the role of light, electromagnetic radiation, in the spectrometer.*  
S5G1: *Um, you’re using light to excite particles. So are you talking about absorption, I’m guessing, or?*  
Investigator: *Yeah, UV-visible absorptions spectroscopy.*  
S5G1: *Oh, yeah, using light and then whatever material absorbs, you measure what is absorbed.* | Student S5G1 is able to identify the basic components required, including the lamp and the detector. Further, when asked about the role of electromagnetic radiation in the spectroscopy, the student understands that the light is meant to provide a source of energy to excite the particles in the sample. This is a scientifically normative development. The response, therefore, was given a score of 2 out of a possible 2. |
It is important to note that there was a tendency for students to initially claim that they “did not know” any of the basic components required for a UV-Visible spectrometer to operate. However, upon further probing, most students were actually aware of some of these basic components.

In order to investigate the effect of student background knowledge on the tendency to make misconceptions during the group discourse versus making valid comparison and contrastive statements, 2X2 contingency tables were constructed and the Fisher exact test utilized. This is intended to be a small, quantitative complement in support of the broader qualitative nature of the study. As detailed in the data collection and code application section of this chapter, this ancillary part of the analysis was motivated by examination of the code co-occurrence tables. Below are the results from the 2X2 contingency table from each of the four student cohorts (groups) of the acoustic analogy activity:

Table 20: Fisher’s exact test to compare the number of misconceptions and valid comparisons or contrastive statements to the background knowledge level of the students in each group (cohort). N= total number of students in that particular cohort while n= number of students in a given background knowledge rating.

<table>
<thead>
<tr>
<th>COHORT 1 (N=6)</th>
<th>Misconceptions</th>
<th>Valid Comparison/Contrastive Statements</th>
<th>Tail 1</th>
<th>Tail 2</th>
<th>2-Tail</th>
<th>Stat. Sig.?</th>
</tr>
</thead>
<tbody>
<tr>
<td>Strong Background (n=4)</td>
<td>3</td>
<td>11</td>
<td>0.45</td>
<td>0.95</td>
<td>0.45</td>
<td>No</td>
</tr>
<tr>
<td>Medium/Weak Background (n=2)</td>
<td>1</td>
<td>1</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>COHORT 2 (N=7)</td>
<td>Misconceptions</td>
<td>Valid Comparison/Contrastive Statements</td>
<td>Tail 1</td>
<td>Tail 2</td>
<td>2-Tail</td>
<td>Stat. Sig.?</td>
</tr>
<tr>
<td>Strong Background (n=2)</td>
<td>3</td>
<td>5</td>
<td>0.647</td>
<td>813</td>
<td>0.721</td>
<td>No</td>
</tr>
<tr>
<td>Medium/Weak Background (n=5)</td>
<td>4</td>
<td>6</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Table 20 Continued:

<table>
<thead>
<tr>
<th>COHORT 3 (N=7)</th>
<th>Misconceptions</th>
<th>Valid Comparison/Contrastive Statements</th>
<th>Tail 1</th>
<th>Tail 2</th>
<th>2-Tail</th>
<th>Stat Sig.?</th>
</tr>
</thead>
<tbody>
<tr>
<td>Strong Background (n=1)</td>
<td>0</td>
<td>3</td>
<td>0.295</td>
<td>0.517</td>
<td>No</td>
<td></td>
</tr>
<tr>
<td>Medium/Weak Background (n=6)</td>
<td>6</td>
<td>10</td>
<td>1</td>
<td>0.028</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>COHORT 4 (N=4)</th>
<th>Misconceptions</th>
<th>Valid Comparison/Contrastive Statements</th>
<th>Tail 1</th>
<th>Tail 2</th>
<th>2-Tail</th>
<th>Stat Sig.?</th>
</tr>
</thead>
<tbody>
<tr>
<td>Strong Background (n=1)</td>
<td>0</td>
<td>2</td>
<td>0.375</td>
<td>0.5</td>
<td>No</td>
<td></td>
</tr>
<tr>
<td>Medium/Weak Background (n=3)</td>
<td>6</td>
<td>8</td>
<td>1</td>
<td>0.5</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Note that, in each of the cases, the result is not statistically significant (p values are all relatively large). This indicates that, within the specific groups (cohorts) of students participating in this activity trial, there is no discernable tendency (from a quantitative perspective) for students of medium/weak background knowledge in a given paradigm to make significantly more (or fewer) misconceptions relative to valid comparison/contrastive statements. Given this portion of the study’s ancillary relationship to the broader analysis, it is important to note that subsequent analysis of students’ discourses does indeed show that background knowledge matters.

The final part of the quantitative interlude involves weighing the number of physical observation statements and categoricals made by students against the number of valid comparison and contrastive statements made, while taking into consideration the level of investigator intervention. Due to the fact that all groups were aggregated for this table, the
Pearson chi-square test with the Yates approximation was employed to handle the larger individual values in the contingency table.\textsuperscript{7,9,11} The following table summarizes the results:

Table 21: Contingency table for the quantum tunneling activity constructed with statements from groups with high and low investigator intervention to compare spontaneous external transfer and physical observation statements that did not coincide with any type of comparative statement.

<table>
<thead>
<tr>
<th>Acoustic Analogy-All Groups</th>
<th>Physical Observation Statements (non comp.)</th>
<th>Valid Comparison/Contrastive Statements</th>
<th>Yates Chi-Square</th>
<th>Yates p-value</th>
<th>Stat. Sig.?</th>
</tr>
</thead>
<tbody>
<tr>
<td>High Investigator Intervention</td>
<td>81</td>
<td>23</td>
<td>1.251</td>
<td>0.26362</td>
<td>No</td>
</tr>
<tr>
<td>Low Investigator Intervention</td>
<td>52</td>
<td>23</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

As is observable from Table 21, the degree of investigator intervention is not significantly associated with a propensity for students to make non-comparative physical observation statements as opposed to valid comparison or contrastive statements. It is interesting to note, however, that the number of physical observation statements is higher in the cases with higher investigator intervention.

Students’ Conceptual Challenges

Key conceptual challenges revealed by the analysis of the data consisted, broadly, of the following: a) difficulty in modifying the dielectric tensor expression to properly reflect the anisotropy of a nanorod as opposed to a sphere (this manifested itself in the interpretation of the absorption spectra as well) and b) tendency to assume that difference in density was a factor in the differences in plasmon absorption in the Ag and Au nanoparticles. With regards to the first of these two main challenges, consider the following excerpt from group 3:
AA Group Excerpt 1

S4G3: Modify the equation to describe a nanorod, because that equation is for a spherical nanoparticle.
S2G3: Ok.
S4G3: And so we’re trying to modify it for a nanorod. How do we do this?
S2G3: (Laughs). Good question.
S1G3: I don’t see anything spherical about this.

Of particular note is the comment made by student S1G3, who claims that there is “nothing spherical” about the expression. There was no pre-activity interview question to probe for knowledge pertaining to concepts related to spherical symmetry, anisotropy and their manifestation in matrix expressions. Therefore, it is plausible to assume that this is a background knowledge issue that was unaccounted for by the current study. Immediately following this exchange, investigator intervention was required:

AA Group Excerpt 2

Investigator: So what do you notice about the dielectric matrix?
S2G3: It is a three by three.
Investigator: Yeah, what do you notice about the terms in there? Are any of them different?
S2G3: No, they’re the same.
S2G3: Because a sphere has the same x, y, and z coordinates. So the rod’s going to have different x, y, and z coordinates.
S4G3: So, instead we would have-.
S5G3 (Interjects): The z would be different, right?

Note that the investigator poses a general question about the nature of the dielectric matrix, to which a very general response is given by S2G3—who simply states that the matrix dimensions are three by three. When the investigator follows up this question with one directly confronting whether the terms are different, the nature of the discourse immediately changes. Student S2G3, in their comparison and contrastive statement, becomes aware of the fact that the coordinates of the sphere will remain equivalent, in a Cartesian sense, but that
they will need to modify the coordinates. The follow up from S5G3 specifies, correctly, that
the z-axis would need to be modified.

In addition to students’ difficulties assigning the proper longitudinal bands in the absorption
spectra and interpreting the effect on the dielectric tensor, students had problems with
anomalously mapping the differences in density of the material to the differences between
the plasmon absorption in the spherical nanoparticles. Consider this excerpt from group 1:

<table>
<thead>
<tr>
<th>AA Group Excerpt 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>S2G1: Why, why is the silver before the gold?</td>
</tr>
<tr>
<td>S5G1: It’s a different metal.</td>
</tr>
<tr>
<td>S6G1: We don’t know if it’s going to be before or after, we just know it’s going to be different.</td>
</tr>
<tr>
<td>S2G1: Oh, ok.</td>
</tr>
<tr>
<td>S3G1: We can make a guess as to the density of the material.</td>
</tr>
</tbody>
</table>

Student S2G1 poses a question asking why the spherical Ag nanoparticles would exhibit a
plasmon band at a lower wavelength than the Au. S5G1 is aware that this is due to the fact
that the metals are of different identities. Further, student S6G1 properly recognizes that,
given the information they have immediately available to them, the only prediction they
would be able to make is that the plasmon bands would be at different wavelengths. Student
S3G1, however, makes a misconception statement that the density is directly related to the
differences in the positions of the plasmon bands within the spectra. While Au and Ag
certainly have different densities, it is the difference in the dielectric functions for each of the
metals that leads to the difference in plasmon absorption energy.

It is important to briefly touch on the fact that the Fourier transform module required such
extensive investigator intervention and time to carry out that the efficacy in its current form
is questionable. Beyond some students’ abilities to characterize the transform as a means to
change domains from time to frequency, the remainder seemed extremely challenging to students and even led to some misconceptions. For example:

### AA Group Excerpt 4

| S2G3: Well, I think that the relationship is definitely that the longer the length of the prong. (Laughs). The longer the length of the prong, then, um, yeah. (Laughs). |
| S5G3: Then what? |
| S1G3: The amplitude of the waveform? |
| S6G3: Yeah? |
| S1G3: Is bigger, is. |
| S4G3: So, the longer the length of the prong-. |
| S2G3 (Interjects): The longer the wavelength |
| S4G3: The higher the amplitude. |
| S2G3: And the longer the wavelength. |

Student S2G3 is immediately stuck on relating the differences in the waveforms between tuning forks of different lengths. S1G3 then suggests that the amplitude of the waveform should be taken into consideration. Between S4G3 and S2G3, the misconception is made that longer prong lengths will lead to higher amplitudes in the waveforms. What is not present in the argument is the fact that it is readily discernable that the wavelengths are different between the two tuning forks.

Another interesting source of challenges came, surprisingly, from students with musical backgrounds. Students with musical backgrounds were identified on the basis of background statements made within the group discourse. Consider the following exchanges:

### AA Group Excerpt 5

| S6G1: Alright, that’s C-512. We’re going down the major scale. We’re going down the c-major scale. It’s exactly what we’re doing. They’re named after the notes. There’s two C’s, they’re different frequencies. I play guitar. |
| S4G1: Wait, why are there two C’s? |
| S6G1: Because you start on the higher C-octave. |
| S4G1: Oh, that’s the high C to the low C. (...) |
| S2G3: They’re an octave apart. They’re an octave apart. |
S6G3: *Wait, are we comparing the silver to the-.*
S2G3 (Interjects): *You’re comparing them to each other.*
S6G3: *Oh, well, where’s the one that matches?*
S2G3: *Same pitch, an octave apart.*
(...)
S3G4: *Ok, so, is the observed pitch different? Yes.*
S4G4: *Well, the. Wait, is it saying the pitch is lower or, like, the-.*
S2G4 (Interjects): *It’s asking if it’s different from the other, from these. From the silver ones.*
S4G4: *It’s the same note, but it’s just an octave lower.*

S6G1 makes their background in music known, and identifies the scale properly in accordance with the frequencies of the commercially produced tuning forks. Further, in group 3, student S2G3 made it known that their background was as a cello player. However, the same student created a misconception pertaining to the differences in pitches between forks.

Student S2G3 asserts that the aluminum alloy and brass tuning forks are an octave apart, and that, due to them supposedly being an octave apart, the two forks are the same pitch. However, none of the aluminum alloy tuning forks are exactly an octave apart from their brass analogues. Further, even if the forks were to be an octave apart (as is the case between the largest and smallest forks *within* the set of aluminum alloy tuning forks), they are not the same pitch. Pitch is directly associated with human perception of frequency, and frequencies between tuning forks are always different unless they are the same size and same composition.

The characterization of the pitches as an octave apart extends to student S4G4, who has a musical background in guitar.
Though the presence of a musical background is certainly, from a constructivist perspective, an overall asset in enriching the students’ experiences, it must be cautioned that this asset can also create room for the type of misconceptions illustrated from groups 3 and 4.

Evidence of analogical transfer

In focusing on students’ abilities to make normative connections both intra- and inter-domain, and moving towards analogical transfer, it is found that there is significant evidence to this effect present in the discourse. First, the establishment of the base knowledge domain was, generally, strong. Students in all groups were able to establish the relationship between prong length and frequency and wavelength of sound produced quite readily. Evidence for this is summarized in the following collection of excerpts below:

<table>
<thead>
<tr>
<th>AA Group Excerpt 6</th>
</tr>
</thead>
<tbody>
<tr>
<td>S6G1: Longer prong length corresponds to lower frequency.</td>
</tr>
<tr>
<td>S3G1: Yeah. What can be said about the relationship between prong lengths and wavelengths of sound?</td>
</tr>
<tr>
<td>S6G1: Longer prong length is shorter wavelength. No.</td>
</tr>
<tr>
<td>S2G1: Larger.</td>
</tr>
<tr>
<td>S6G1: Yeah.</td>
</tr>
<tr>
<td>S1G1: What was it, faster frequency?</td>
</tr>
<tr>
<td>S2G1: Larger wavelength, or. Longer prong length equals longer wavelength.</td>
</tr>
<tr>
<td>S1G1: Wait, is that right?</td>
</tr>
<tr>
<td>S3G1: Yeah. Larger wavelength, smaller frequency.</td>
</tr>
<tr>
<td>S1G1: Right, but.</td>
</tr>
<tr>
<td>S6G1: So, the frequency of the two C’s are different.</td>
</tr>
<tr>
<td>S1G1: So the longer the prong length, the smaller the.</td>
</tr>
<tr>
<td>S3G1: Frequency.</td>
</tr>
<tr>
<td>(...)</td>
</tr>
<tr>
<td>S5G2: That one’s quicker (referring to the shorter fork).</td>
</tr>
<tr>
<td>S3G2: That one’s faster? That’s the higher pitch.</td>
</tr>
<tr>
<td>S5G2: Mhm. Well, I mean, it probably has a higher frequency than that one.</td>
</tr>
<tr>
<td>...</td>
</tr>
<tr>
<td>S3G2: (Reads question 1). The shorter it is, the higher the frequency. Right?</td>
</tr>
<tr>
<td>S5G2: Yup.</td>
</tr>
<tr>
<td>S4G2: Indeed.</td>
</tr>
</tbody>
</table>
S3G2: (Reading latter portion of question 1). ‘What can be said about the relationship between prong lengths and wavelength of sound?’ It would be an inverse relationship.
S5G2: Mhm.
(...)
S4G3: Ok, so, the relationship and frequency of sound is that, as length increase-
S1G3 (Interjects): Shorter the length, the higher the frequency.
S4G3: Yeah, shorter the length, higher frequency.
...
S5G3: So, higher frequency is low wavelength.
S6G3: Short length.
(...)
S3G4: The increase in pitch means more frequency.
S2G4: And what can be said about the relationship between prong length and wavelength?
...
S4G4: We already said the relationship; as the prong length gets shorter, the pitch goes up.
S1G4: That would make sense, yes.
S3G4: So what did you say?
S2G4: The prong length, yeah. Isn’t that what we said? It has a higher pitch if it’s shorter, yeah. We just said it.
S4G4: It’s just like guitar, if you slide your finger up the strings, the string gets shorter and it gets higher pitched.

Take notice of the spontaneous transfer given by student S4G4, whose earlier background statement is indicative of their musical background. S4G4 links the changing lengths of the tuning forks to the placement of one’s finger on a guitar: shortening the guitar string leads to a higher pitch. This is a prime example of how analogical transfer, even intra-domain, can be facilitated and enriched directly by students’ prior knowledge and experiences.

Also within the base domain, students were particularly successful at understanding the idea that banging the tuning forks provided energy to the system to induce the oscillations. This is exemplified in the following excerpt from group 2:
Students come to the conclusion that the fork must be struck in order to lead to the production of sound. Note also how student S5G2 encourages the group to move towards answering the question in a scientifically normative fashion. This can be interpreted, in part, by the setting in which learning is taking place: the investigator is present, and the group is composed of upper-division students in chemistry. In general, groups were also effective in properly characterizing the differences between the tuning forks of the same size but differing composition (i.e. aluminum alloy tuning forks vs. brass). This can be seen in the following collection of excerpts:

**AA Group Excerpt 7**

<table>
<thead>
<tr>
<th>Speaker</th>
<th>Dialogue</th>
</tr>
</thead>
<tbody>
<tr>
<td>S3G2:</td>
<td>(Reads question 3). Hit it against the thing? Can I just write that? (Laughs).</td>
</tr>
<tr>
<td>S4G2:</td>
<td>Hit it against the thing (Laughs).</td>
</tr>
<tr>
<td>S5G2:</td>
<td>Is that scientific? (Laughs).</td>
</tr>
<tr>
<td>S6G2:</td>
<td>(Mutters; inaudible).</td>
</tr>
<tr>
<td>S3G2:</td>
<td>I like what you were going to say, what was that?</td>
</tr>
</tbody>
</table>

**AA Group Excerpt 8**

<table>
<thead>
<tr>
<th>Speaker</th>
<th>Dialogue</th>
</tr>
</thead>
<tbody>
<tr>
<td>S2G1:</td>
<td>‘If the prong lengths are the same, how can any variation in pitch and therefore the resonance frequency be accounted for?’</td>
</tr>
<tr>
<td>S3G1:</td>
<td>Intrinsic properties of the material?</td>
</tr>
<tr>
<td>S4G1:</td>
<td>Because it’s a different metal, and different metals resonate at various.</td>
</tr>
<tr>
<td>S6G1:</td>
<td>Because of the stiffness of the metals for different properties.</td>
</tr>
<tr>
<td>S2G1:</td>
<td>Maybe, like, density of the metal? (…)</td>
</tr>
<tr>
<td>S6G2:</td>
<td>I think we’re supposed to be comparing the ones of different composition.</td>
</tr>
<tr>
<td>S3G2:</td>
<td>Yeah, eventually you’re going to be comparing.</td>
</tr>
<tr>
<td>S6G2:</td>
<td>Yeah.</td>
</tr>
<tr>
<td>S4G2:</td>
<td>Alright, so this one’s lowest, highest, this one’s second lowest.</td>
</tr>
<tr>
<td>S3G2:</td>
<td>No, between each other.</td>
</tr>
<tr>
<td>S4G2:</td>
<td>Oh. Now do it between each other?</td>
</tr>
<tr>
<td>S3G2:</td>
<td>Yeah.</td>
</tr>
<tr>
<td>S4G2:</td>
<td>Ok. (Strikes forks again). This one’s (aluminum alloy) definitely higher pitched than that one (brass). This one’s definitely higher pitched than that one. (Repeats statements two more times). (…)</td>
</tr>
</tbody>
</table>
S1G4: That one’s (referring to the brass fork) lower. That one’s a lot lower. For these we only have four?

...  
S2G4: Ok. (Reads question 1). I think they’re lower than the other. 
S1G4: That, that’s what I thought, when I. (Silence). Yeah, they’re a lot lower.

In terms of transfer to the target domain via mapping the object attributes and relations of the base, students had a high level of success in understanding the induction of oscillatory behavior in each domain. For example:

**AA Group Excerpt 9**

S6G1: Ok, what is exciting these plasmon modes? The input of light?
S1G1: Yeah.
S6G1: Just like us banging the tuning fork, we’re shining light on it.

Note, in this short excerpt, the fact that student S6G1 maps the activity of striking the tuning forks to the light impinging on the metallic nanostructure. This type of comparison and contrastive statement is associated with mapping across knowledge domains, and moves towards the establishment of analogical transfer. There exists an excerpt that provides direct evidence for transfer between the length of the tuning fork prongs and the length of the gold nanorods. Students in group 1 had the following discussion:

**AA Group Excerpt 10**

S2G1: What’s the question?
S3G1: It’s saying as the rods get longer, will the frequency or wavelength of light get longer or shorter? Based on our-
S6G1 (Interjects): Based on increasing average rod length.
S3G1: So if you remember the longer tuning forks had the lower tone which was higher in energy? Or was it lower in energy?
S2G1: Higher. No.
S6G1: The lower the tone is lower in energy.
S3G1: So the longer it is, it requires less energy. So that’s an analogy to this, that means the shorter one should be, right, lower. So blue would be the shortest.
Student S3G1, in response to the question within the activity, immediately links the length of the tuning forks to the length of the rods. They do not, however, immediately remember the relationship between the prong length and energy. At this point, student S6G1 intervenes with their physical observation statement that asserts that lower tone corresponds to lower energy. This is then explicitly mapped to the target domain by student S3G1 at the end of the excerpt.

Other groups, eventually, had success characterizing the relationship between nanorod length and longitudinal peak position, though a direct, explicit mapping between base and target domains through the use of comparison and contrastive statements is not present.

In characterizing the role of intrinsic properties in both the tuning forks and nanomaterials, students were generally successful outside of the anomalous transfer described in the students’ conceptual challenges section of the analysis. Consider the following excerpt from group 1:

<table>
<thead>
<tr>
<th>AA Group Excerpt 11</th>
</tr>
</thead>
<tbody>
<tr>
<td>Investigator: This is the silver and this is the gold.</td>
</tr>
<tr>
<td>S6G1: Ok, so light blue (referring to the color on the spectrum plot) is silver, and.</td>
</tr>
<tr>
<td>Investigator: They’re the same exact size as that.</td>
</tr>
<tr>
<td>S2G1: Right.</td>
</tr>
<tr>
<td>S6G1: (Reading question initially). So this is like the brass compared to the aluminum.</td>
</tr>
<tr>
<td>S3G1: I guess we were supposed to discuss that before.</td>
</tr>
<tr>
<td>S6G1: Um, so, yeah it’s an analogy to the. Yeah. Ok.</td>
</tr>
</tbody>
</table>

Student S6G1 refers, in a comparison and contrastive statement, to the current domain (the target: metallic nanomaterials) in the context of the base domain, stating that the gold and silver are like the brass and aluminum. The notion that the intrinsic differences between the metals motivated the mapping from base to target within the comparison and contrastive
statement can be seen in the next excerpt when students are answering the second challenge question:

<table>
<thead>
<tr>
<th>AA Group Excerpt 12</th>
</tr>
</thead>
</table>
| S6G1: *(Reads question)*. Part 6, was that gold and silver?  
Investigator: Yeah.  
S6G1: Ok, so r doesn’t change. I guess, I mean e bulk and that constant both change.  
S4G1: What is e bulk?  
S6G1: So basically. Uh, dielectric constant in the bulk. So basically those variables which represent an intrinsic property of the metal, uh, are what are affecting the observed plasmon frequencies of the metal? Is that right?  
Investigator: What do you guys think, or?  
S1G1: I agree.  
S2G1 (simultaneously with S1G1): I agree.  
S5G1: You’re saying, these two change.  
S4G1: Yeah, as long as the radius is the same, then pretty much everything else changes.  
S2G1: Wait what are we changing? What?  
S4G1: Um, the radius doesn’t change appreciably.  
S2G1: Oh, ok. Yeah, yeah, ok.  
S6G1: We’re looking at how intrinsic properties affect the plasmon frequencies. |

Here, it is clear that the students understand that, for a constant radius, the only factors that allow for differentiation between the Au and Ag nanomaterials are the intrinsic properties. This is made clear in the physical observation statement by S6G1 concerning the variables that represent intrinsic properties, and further echoed by students S1G1, S2G1 and S4G1. Therefore, it is reasonable to postulate that the mapping in the brief statements that took place in this excerpt was motivated by an understanding that the intrinsic properties changed between materials in both the base and target knowledge domains. Overall, it can be seen that some explicit and normative connections are, at times, made from base to target domains within the group discourse. Through the questions posed to students within the activity, their discussions are centered on comparing the domains. Note, however, that even in the presence of questions that guide comparisons between domains with the
purpose of inducing analogical transfer, sometimes transfer does not occur or occurs in an undesired fashion. This is true across all analyzed activities, as will be presented in the remainder of this chapter.

Post-Activity Interviews

The post-activity interviews from the acoustic analogy activity reflected the successes and challenges found within the group discourse. Students tended to be much stronger in transferring the fact that intrinsic properties differing between the tuning forks of different materials maps to the differences between spherical Au and Ag nanoparticles than they were in transferring the relationship between tuning fork length and the length of the Au nanorods. In fact, success in the latter tended to require significant investigator probing to uncover.

To begin with, it is important to mention that students were very effective in the base knowledge domain, as they directly experienced the properties of and relationships among the tuning forks. This is exemplified in the following excerpt from student S3G3’s post-activity interview:

<table>
<thead>
<tr>
<th>AA Post-Activity Interview Excerpt 1</th>
</tr>
</thead>
<tbody>
<tr>
<td>Investigator: <em>Describe the process the tuning forks underwent in order for sound to be detectable.</em></td>
</tr>
<tr>
<td>S3G3: <em>In order for sound to be detectable, you had to, um, hit it at a horizontal angle onto the surface with the two rods parallel.</em></td>
</tr>
<tr>
<td>Investigator: <em>Uh, what was required for a sound to be detectable from the fork itself? Like what did you, what did you. What needed to happen within the tuning fork?</em></td>
</tr>
<tr>
<td>S3G3: <em>Um, the rods had to oscillate and, uh, sound waves resonate off of each, uh, bar.</em></td>
</tr>
</tbody>
</table>

Student S3G3 goes into depth as to how the fork needed to be held relative to the table in order for sound to be produced and, further, describes the fact that the prongs themselves
needed to oscillate and resonate. This indicates a scientifically normative understanding of the base domain in the context of this activity.

Students were also able to articulate the frequency, pitch, and wavelength trends within tuning forks of constant composition. Consider the following response to the second post-activity interview question by student S6G3:

**AA Post-Activity Interview Excerpt 2**

<table>
<thead>
<tr>
<th>Investigator:</th>
<th>Uh, describe the relationship between the length of the tuning fork prongs, and the frequency and wavelength of sound observed.</th>
</tr>
</thead>
<tbody>
<tr>
<td>S6G3:</td>
<td>Um, well the shorter the length of the prongs, the shorter the wavelength and the higher the frequency.</td>
</tr>
<tr>
<td>Investigator:</td>
<td>What occurred to the pitch of sound as you progressed from tuning forks of shorter length to those of longer prong length?</td>
</tr>
<tr>
<td>S6G3:</td>
<td>Um the shorter ones were higher pitched, and the longer ones were lower pitched.</td>
</tr>
</tbody>
</table>

As with student S6G3’s response, students were generally able to utilize brief comparison and contrastive statements to qualify the differences between tuning forks of the same composition but differing prong lengths. Students were also able to extend comparisons into the next post-activity interview question, which centered on the brass and aluminum tuning forks. A prime example of this can be observed in student S6G1’s response to the third question:

**AA Post-Activity Interview Excerpt 3**

<table>
<thead>
<tr>
<th>Investigator:</th>
<th>What similarities or differences did you notice between the aluminum alloy tuning forks and brass tuning forks?</th>
</tr>
</thead>
<tbody>
<tr>
<td>S6G1:</td>
<td>Well the, the uh, the trend, you know, was established between length and frequency was the same between the two.</td>
</tr>
<tr>
<td>Investigator:</td>
<td>Any differences?</td>
</tr>
<tr>
<td>S6G1:</td>
<td>Any differences was that the length of the aluminum, and the uh, if it was equivalent to the length of the brass, that did not mean that they produced equivalent frequencies.</td>
</tr>
<tr>
<td>Investigator:</td>
<td>Ok, so uh, what properties of the alloys accounted for any differences in the sound produced by each type of fork?</td>
</tr>
<tr>
<td>S6G1:</td>
<td>Um, density, I would say. And stiffness.</td>
</tr>
</tbody>
</table>
Student S6G1 is cognizant of the fact that the length and frequency trend holds in each of the materials. However, S6G1 notes, upon being prompted to provide differences, that the frequencies were different between tuning forks of the same size but different composition. They then go on to properly characterize the rationale for the difference as the density and the stiffness, which is related to the elastic (Young’s) modulus. Not all answers to this question were as well developed as that of student S6G1, but the differences between brass and aluminum tuning forks of the same size were, in general, normatively discussed by students.

As expected, given students’ difficulties with the Fourier transform module, the responses given by students to the pertinent post-activity interview question were not particularly well developed. One of the better examples of such responses would be that of student S4G1:

<table>
<thead>
<tr>
<th>AA Post-Activity Interview Excerpt 4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Investigator: What did the use of the Fourier transform accomplish during the course of this activity?</td>
</tr>
<tr>
<td>S4G1: It converted the time measurements into frequency measurements that can be, uh, used to understand it better.</td>
</tr>
<tr>
<td>Investigator: Ok, uh, how might this technique be helpful in areas outside of just analyzing sound?</td>
</tr>
<tr>
<td>S4G1: Uh, the Fourier, the Fourier transform?</td>
</tr>
<tr>
<td>Investigator: Fourier.</td>
</tr>
<tr>
<td>S4G1: Fourier, whatever (laughs). I guess it can be used to, um, convert how much a sample, an NMR sample, um, goes up and down in the, in the NMR machine and it can convert that into the frequency that it went at so that it can be more or less understood.</td>
</tr>
</tbody>
</table>

S4G1 makes the somewhat normative statement that the technique converts time measurements into frequency measurements, but the language of domain change is not incorporated into the response. Nor, in the latter portion of the question, is the “black-box” understanding removed: the procedure behind the conversion of the time domain to the
frequency domain is not elaborated on in the context of NMR spectroscopy. It remains simply a surface-level response due to students’ having ostensibly been exposed to the notion of Fourier transform NMR spectroscopy. More work needs to be carried out in reconfiguring the module to guide students to go beyond a surface-level understanding of the Fourier transform.

In congruence with findings in the group discourse, students were highly effective in mapping the concept that the tuning forks needed to be struck on the table to induce the oscillations, just as the electromagnetic radiation from the UV-Visible spectrometer had to fall upon the metallic nanomaterial solutions in order to induce LSPR. Consider student S3G2’s response to the fifth post-activity interview question:

<table>
<thead>
<tr>
<th>AA Post-Activity Interview Excerpt 5</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Investigator:</strong> <em>What physical process occurred with the gold nanorods and the gold and silver spherical nanoparticles in order for there to be collective oscillatory behavior of the surface electrons?</em></td>
</tr>
<tr>
<td><strong>S3G2:</strong> Physical process? Well, we had to, like, put light into the system. Um. So, like the light beam actually, uh, from the UV-Vis, actually had to go through the sample before anything could happen.</td>
</tr>
<tr>
<td><strong>Investigator:</strong> And how is that related to what was observed with the tuning forks?</td>
</tr>
<tr>
<td><strong>S3G2:</strong> It’s similar to us, again, introducing, like, en-, energy into the system, so before we hit it against the table, um, to create the vibrations but instead we use a light source to do it with the samples.</td>
</tr>
</tbody>
</table>

Notice the direct connection, within the comparison and contrastive statement provided by S3G2, to the base knowledge domain. The student essentially states that light had to be introduced into the system containing the nanomaterials in order for the desired observation to be obtained and, when prompted to contextualize in terms of the tuning forks, states that energy needed to be introduced into the system by banging it on the table. The student directly mapped the nature of the light exciting the plasmon modes in the nanomaterials to
the act of striking the fork on the table thus inducing vibrations in the material. This trend, in general, held for the majority of students during the post-activity interview, indicating that this aspect of the analogical transfer was broadly successful.

Group discourse revealed that students had some difficulty articulating the link between the length of the tuning fork prongs and the length of the Au nanorods. In general, significant amount of investigator probing was required to elicit a normative student response. Take, for example, student S4G1’s response to the sixth post-activity interview question:

<table>
<thead>
<tr>
<th>AA Post-Activity Interview Excerpt 6</th>
</tr>
</thead>
<tbody>
<tr>
<td>Investigator: Uh, what determines the frequency or the wavelength that is observed in the UV-vis spectrum of the gold nanorods? Remember the different gold nanorods?</td>
</tr>
<tr>
<td>S4G1: Mhm.</td>
</tr>
<tr>
<td>Investigator: Um, and how is this related to your observations with the tuning forks?</td>
</tr>
<tr>
<td>S4G1: Let’s see. (Silence).</td>
</tr>
<tr>
<td>Investigator: Like, what did the gold nanorods have to do with the tuning forks themselves?</td>
</tr>
<tr>
<td>S4G1: Umm. I guess the different concentrations could be compared to the, um, different lengths of the tuning rods because, while it’s the same, they have the same intrinsic properties, they have different extrinsic properties that would, um, affect the, the signal.</td>
</tr>
</tbody>
</table>

Notice that, even upon further prompting, the exchange between investigator and student S4G1 results in a case of undesired transfer: the student believes that it is the concentrations that are different between the different solutions rather than the lengths of the nanorods.

Note that the scientific language within the base domain is normative: they have the same intrinsic properties, but they have different extrinsic properties (i.e. the length is being modified). However, the student attempts to map this to different concentrations instead of different lengths due to the misconception in the target domain.

An example of a student who was eventually able to reach a reasonable conclusion in answering the sixth post-activity interview question is S5G3:
**AA Post-Activity Interview Excerpt 7**

Investigator: *What determines the frequency or wavelength that’s observed in the UV-visible spectrum of the gold nanorods?*

S5G3: *Um. Does it have to do with, like, the um, displacement I guess?*

Investigator: *Ok, so, um, how was that different in each of the solutions of gold nanorods?*

S5G3: *Um. Well it depends. So. They were. I don’t know. They were, they occurred at different, um, wavelengths.*

Investigator: *Yeah, so, each one, each one had two bands, right?*

S5G3: *Uh huh.*

Investigator: *And, you remember, one of them stayed about the same.*

S5G3: *That was the xy.*

Investigator: *Ok, and then what happened to the other one?*

S5G3: *It, um, so the z displacement was, occurred at different wavelengths for the different samples.*

Investigator: *Ok, so what would affect that?*

S5G3: *Um. Density I guess?*

Investigator: *Ok, um, how is that related to your observation with the tuning forks?*

S5G3: *Um, the density affected how. Um, well, no, ok, so length, I guess, is really what affected it. So, the longer ones occurred at long-, er, I guess higher wavelengths.*

Investigator: *Why do you say that?*

S5G3: *Um because that’s what happened with the tuning forks.*

There are two crucial aspects of this excerpt to take note of. The first is the extent of investigator probing that is required to elicit a definitive response. Further, the student is able to reformulate their own misconception that the density of the material was leading to the differences in LSPR bands as opposed to the length (the growth of the z-direction). Upon being asked about the relationship between the nanomaterials and the tuning forks, the student is immediately able to recognize that the density does not affect the LSPR wavelength. Therefore, they were able to map the base domain to the target domain in a scientifically normative fashion after correcting their misconception statement in the target knowledge domain.

Students were more readily able to map from the base to target domain the idea that different materials, despite being the same size, exhibited different resonance frequencies. The degree
to which they understood that the intrinsic property of density did not play a large role in determining the LSPR modes (rather, it was the difference in dielectric functions) was less apparent. This was elaborated on earlier in the analysis of the group discourse, but its results extend to the post-activity interviews. For instance:

<table>
<thead>
<tr>
<th>AA Post-Activity Interview Excerpt 8</th>
</tr>
</thead>
<tbody>
<tr>
<td>Investigator: <em>Why were the absorption wavelengths significantly different in the gold and silver nanoparticles, despite their being of average, similar average diameters?</em></td>
</tr>
<tr>
<td>S7G3: <em>Because since they were different, uh, materials they had different densities and elasticities like the tuning forks.</em></td>
</tr>
</tbody>
</table>

Student S7G3 appears to understand that the fact that Au and Ag are different materials leads to different oscillatory behavior. They mistakenly assumed, however, that the difference in density and elasticity, as seen in the tuning forks, directly maps to the paradigm of metallic nanomaterials. The student does not make the more abstract connection that the dielectric functions of the Au and Ag nanomaterials have an effect on the observed LSPR frequencies, despite comparable average size. In their overall assessment of the connections present in the activity, students tended to focus appropriately on the length (or size) and intrinsic properties (usually, and errantly, density). The following collection of excerpts represents a sampling of students’ responses from each group to the eighth question of the post-activity interview:

<table>
<thead>
<tr>
<th>AA Post-Activity Interview Excerpt 9</th>
</tr>
</thead>
<tbody>
<tr>
<td>Investigator: <em>Describe in the context of everything experienced in the activity and what we’ve just discussed what the, what the overall connections are between both segments of the activity.</em></td>
</tr>
<tr>
<td>S6G1: <em>Well, the connections are we started with something that we’re more familiar with, which is the tuning fork, and the uh, uh, how size is directly related to, uh, frequency, right? And so that was mirrored in the uh gold nanoparticles, or the nanorods, right, so that was analogous to that experiment which showed that differing lengths of rods corresponded to different frequencies of light, and then, uh, the other one in the tuning fork experiment when we compared, um, tuning forks of the same size but different, uh, molecular makeup, uh, showed that they did not, in fact, emit the same sound, um, the same sound frequency.</em></td>
</tr>
</tbody>
</table>
analogous to us comparing gold nanoparticle spheres with silver nanoparticle spheres and, uh, showing that despite their almost equivalence in, statistical equivalence in size, they, uh, did not absorb light at the same wavelength or frequency.

(...)
Investigator: Describe in the context of what you’ve experienced with the activity and what we’ve discussed, what the connections are, the overall connections are between both segments of the activity.
S3G2: It shows you how, like, the same concepts can be utilized with various, I guess, experiments because, I mean, obviously the first part we were just looking at the different pitches or listening to the different pitches and, you know, we were using tuning forks versus when we go we look at a metal like, different metals, like silver and gold and compare their frequencies and how those same concepts of changing certain factors, such as their, you know, modulus of elasticity, or how obviously their densities are different, how those little factors are going to change the overall system as far as their, not only their frequency, like, to determine their pitches but also just the wavelength and the energy of the system in general.

(...)
Investigator: Describe in the context of all you’ve experienced with the activity and what we’ve discussed, uh, what the connections are, like the overall connections are between each segment of the activity.
S7G3: Uh, the tuning forks and the spherical particles both you have things that are the same size and length that behave differently because of the metal they’re composed of, like the difference in density and different constants.

(...)
Investigator: Describe in the context of all you’ve experienced with the activity and what we’ve discussed what the overall connections are between both segments of the activity.
S2G4: Basically, like, if it’s a different material or made up of something different and more dense then it’s going to have different, um, properties and wavelengths I guess.

Within this cross section of responses, one can observe well-developed and normative responses alongside those which were less strongly focused or articulated. Note that student S6G1’s response is highly congruent with the learning objectives of the activity. They are able to directly connect, through valid comparison and contrastive statements, the relevant object relations between base and target knowledge domains, as they describe in their response. On the other end of the spectrum, the response provided by student S2G4 is much more general and does not explicitly connect the knowledge domains. Further, the response
omits the consideration of differences in size (which is crucial to the understanding of the nanoscale domain), and focuses solely on intrinsic property differences.

**Summary of Results**

The analysis of the acoustic analogy activity yields results that both uncover some misconceptions and instances of undesired transfer as well as some positive analogical transfer and appropriate mapping of relations from base to target knowledge domains. Despite these difficulties, however, there is evidence for some students making valid connections based on the role of intrinsic properties across domains as well as the understanding of prong length/frequency/wavelength relationships in the tuning forks and how these relate to the LSPR in the Au nanorods. This evidence is found both within the group discourse and the post-activity interviews.

Throughout the course of this module, however, it can be seen that students’ prior knowledge does not necessarily map properly to the target knowledge domain. This is evident, for example, in some students’ errant transfers of density as the main intrinsic property responsible for differences in sound frequency in the tuning forks to the differences in LSPR modes in Au and Ag spherical nanoparticles. There are instances through group discourse and within the post-activity interviews of such misconceptions being mitigated through reformulation.

There exist some misconceptions and errant mapping brought forth by students’ backgrounds with density as a prominent intrinsic property and electronic absorption spectroscopy as a means to determine concentrations via the Beer-Lambert law. Reformulations provide
evidence of change either facilitated by the remainder of a given student group, by the individual student, or through facilitation by the investigator.

**4.3(b) Quantum Tunneling Analysis**

In the analysis of the quantum tunneling activity, students’ discourses are the most rich and, therefore, readily analyzed of the instructional materials in this work. This may be due to the fact that it is also the least procedural module.

*Background Knowledge Assessment via Pre-Activity Interviews*

In order to assess background knowledge, the same scores (0 for weak, 1 for medium, or 2 for strong) were assigned based on the same factors: scientifically normative statements and depth of knowledge. The three interview questions were based on content knowledge:

1. What does a wavefunction describe in a physical system when it is in a quantum chemistry context?
2. What is the difference between an eigenfunction and an eigenvalue?
3. In statistical mechanics, what does a partition function tell you about the energy levels, or states, of a quantum mechanical system?

The following tables consist of examples of students with medium and strong backgrounds. Each content-specific question in the pre-activity interview is addressed in a separate table.
Table 22: Example responses from pre-activity interview question “What does a wavefunction describe in a physical system when it is in a quantum chemistry context?” for quantum mechanical tunneling activity with assigned score and rationale.

<table>
<thead>
<tr>
<th>ID #</th>
<th>Interview Transcript Excerpt</th>
<th>Score and Rationale</th>
</tr>
</thead>
</table>
| S3G2  | Investigator: *Um, ...question 1?*  
S3G2: *I guess a manifestation of sort of where the wave slash particle can be.*  
Investigator: *Ok.* | The response to this question is not assertive nor completely developed, but is normative in the sense that the student invokes duality (wave/particle) and, in referring to where the entity might be. Further, the student displays some understanding of the probabilistic nature of the wavefunction. **This was scored as a 1.** |
| S2G1  | Investigator: *...Question 1?*  
S2G1: *Repeat that?*  
Investigator: *What does a wavefunction describe in a physical system when it is in a quantum chemistry context?*  
S2G1: *Ok. Ok, the wavefunction describes the phase of an electron, um, throughout space as a function of time and space.*  
Investigator: *Ok.*  
S2G1: *Um, square it you get the probability of, uh, the electron being there.*  
Investigator: *Ok.*  
S2G1: *And you use it with all sorts of operators to get physical derived quantities.* | S2G2 demonstrates a clear understanding of the probabilistic interpretation of the wavefunction. Further, they indicate that it is the square of the wavefunction that allows for the probabilistic interpretation to be possible. Despite being yet another case in which a student only refers to the electron as a possible system of study, the content of the response is at a high level. Therefore, **this response was given a score of 2.** |

The first pre-interview question was meant to gauge students’ understanding of the wavefunction’s role in describing the quantum mechanical system, in addition to the role of its square as a probability density. A basic understanding of wavefunctions is essential to the
pedagogy of the quantum mechanical tunneling activity, as students actively utilize them in diagrams and descriptions. Note from the rationale that the student who gave a response with limited detail (S3G2) did not receive the highest possible score of 2.

Table 23: Example responses from pre-activity interview question “What is the difference between an eigenfunction and an eigenvalue (EF/EV)" with assigned score and rationale.

<table>
<thead>
<tr>
<th>ID #</th>
<th>Interview Transcript Excerpt</th>
<th>Score and Rationale</th>
</tr>
</thead>
<tbody>
<tr>
<td>S2G2</td>
<td>Investigator: Alright, number two, what does a wavefunction describe in a physical system when it is in a quantum chemistry context? S2G2: Wavefunction, as in the ones that are in cm inverse? No, those are wavenumbers, I’m sorry. Investigator: Wavefunction, like in a quantum chemistry context. S2G2: Like Schrödinger’s equation? Doesn’t it...? Is it like the state of the matter? Mostly? Investigator: So how is the wavefunction associated with a given energy value then? S2G2: Well, there’s an eigenvalue in front of each wavefunction, so I guess there’s like a... I don’t know to be honest.</td>
<td>The student refers to the wavefunction as the “state of the matter,” which is normative considering the wavefunction is also known as the state function. The student also knows that the eigenvalue is positioned in front of the wavefunction, however they fail to make the connection to the physical interpretation of the eigenvalue (that it corresponds to an observable. The score assigned was a 1 out of 2.</td>
</tr>
<tr>
<td>S2G1</td>
<td>S2G1: Eigenfunction is something when you operate on and you get it out, eigenvalue is, um, what is a scalar multiple. Investigator: How are eigenvalues and eigenfunctions used in quantum chemistry? S2G1: Um, eigenfunctions are most often the wavefunctions. Eigenvalues, you have an operator that can, uh, corresponds to a certain observable when you operate the operator on the eigenfunction, you get out the eigenvalue which corresponds to the value of the observable.</td>
<td>In this response, the student clearly demonstrates knowledge of the role of eigenfunctions as wavefunctions in quantum mechanical systems. Further, S2G1 states that the eigenvalues, upon the act of operating on the eigenfunction with an operator, represent quantifiable observables. This response warranted a 2.</td>
</tr>
</tbody>
</table>
The second pre-activity interview question was geared towards assessing students’ understanding of what the role of eigenfunctions and eigenvalues are in a quantum mechanical context. Appropriate familiarity with this relationship is critical to understanding how mathematical descriptions of the physical system (wavefunctions) are used with the Schrödinger equation or, with operators other than the Hamiltonian, in order to quantify observables (eigenvalues). Students who demonstrated a normative, well-developed understanding of the relationship of eigenvalues and eigenfunctions (e.g. S2G1) were given a full score of 2 out of 2.

Table 24: Example responses from pre-activity interview question “In statistical mechanics, what does a partition function tell you about the energy levels, or states, of a quantum mechanical system?” with assigned score and rationale.

<table>
<thead>
<tr>
<th>ID #</th>
<th>Interview Transcript Excerpt</th>
<th>Score and Rationale</th>
</tr>
</thead>
</table>
| S2G1 | Investigator: *Uh, last question, ...question 3?*  
S2G1: *Partition function describes how the energy function, uhh excuse me, how the energy levels are split throughout, um, energy, um, usually a function of temperature and, d, degeneracy.*  
Investigator: *Ok.* | Student S2G1 states that the partition function is a function of temperature and degeneracy. The student also takes into account the fact that the way in which energy levels are split does factor in, though it is not clear whether or not they understood the implications of how many accessible states there were. Further, the degeneracy is a coefficient in the expression rather than a variable. **This response received a 1.** |
Pre-activity interview question 3 was designed to characterize students’ knowledge regarding the partition function. Since a significant part of the activity revolves around utilizing the vibrational partition function to show that most molecules are in the ground vibrational state at ambient temperatures, a suitable physical interpretation of the partition function is necessary. No student achieved a full score of 2 on this question and only one student received a score of 1.

To examine how students’ background knowledge related to the number of misconceptions as opposed to valid comparison or contrastive statements, a 2X2 contingency table was set up within each cohort and Fisher’s exact test calculated. The results are as follows:
Table 25: Fisher’s exact test to compare the number of misconceptions and valid comparisons or contrastive statements to the background knowledge level of the students in each group (cohort) for the quantum tunneling activity. N= number of students who took a pre-activity interview in that particular cohort while n= number of students in a given cohort with a given background knowledge rating.

<table>
<thead>
<tr>
<th>COHORT 1 (N=5)</th>
<th>Misconceptions</th>
<th>Valid Comparison/Contrastive Statements</th>
<th>Tail 1</th>
<th>Tail 2</th>
<th>2-Tail</th>
<th>Stat. Sig.?</th>
</tr>
</thead>
<tbody>
<tr>
<td>Strong Background (n=2)</td>
<td>7</td>
<td>6</td>
<td>0.71173 7</td>
<td>0.584695</td>
<td>1</td>
<td>No</td>
</tr>
<tr>
<td>Medium/ Weak Background (n=3)</td>
<td>8</td>
<td>6</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>COHORT 2 (N=3)</td>
<td>Misconceptions</td>
<td>Valid Comparison/Contrastive Statements</td>
<td>Tail 1</td>
<td>Tail 2</td>
<td>2-Tail</td>
<td>Stat. Sig.?</td>
</tr>
<tr>
<td>Medium Background (n=2)</td>
<td>10</td>
<td>9</td>
<td>0.07065 2</td>
<td>1</td>
<td>0.118083</td>
<td>No</td>
</tr>
<tr>
<td>Weak Background (n=1)</td>
<td>5</td>
<td>0</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>COHORT 3 (N=3)</td>
<td>Misconceptions</td>
<td>Valid Comparison/Contrastive Statements</td>
<td>Tail 1</td>
<td>Tail 2</td>
<td>2-Tail</td>
<td>Stat. Sig.?</td>
</tr>
<tr>
<td>Strong Background (n=1)</td>
<td>4</td>
<td>2</td>
<td>0.05072 02</td>
<td>0.815432</td>
<td>1</td>
<td>No</td>
</tr>
<tr>
<td>Medium/ Weak Background (n=2)</td>
<td>17</td>
<td>13</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Note in Table 25 that this analysis involves the number of statements that fall into a particular category, not the number of students—which will vary from cohort to cohort. For example, in cohort 1, there were seven misconception statements made by students with a strong background. The ultimate goal was to determine to what extent students’ background knowledge levels related to their propensity toward making valid comparison/contrastive
statements or stating misconceptions. In Group 2, there were no strong background students in the group and, therefore, the separation needed to be between those with weak and medium backgrounds. Still, the p-value (p=0.118) is not statistically significant at confidence levels that are reasonable to such small data studies. The results of the exact test indicate that there is no discernible relationship between the students’ backgrounds and their tendency to make a valid comparison or contrastive statement as opposed to a misconception or vice versa. This suggests that nuances in the students’ discussions, as they struggle with the abstract concept of tunneling, will be most revealing when considering the overall implications of the activity.

The three groups that performed the activity managed to discuss and adopt the language required for describing tunneling effects both within the paradigm of a familiar molecular structure (NH$_3$/AsH$_3$) and in a novel nano domain. For instance:

<table>
<thead>
<tr>
<th>QMT Group Excerpt 1</th>
</tr>
</thead>
<tbody>
<tr>
<td>S4G3: Alright, so both sides of the barrier are interacting, that means that you would be able to make it over the potential without having that much energy.</td>
</tr>
<tr>
<td>S1G3: Yeah, so you’d have to, um...</td>
</tr>
<tr>
<td>S4G3: <em>(Interjects)</em> Which doesn’t make sense in the classical sense. <em>Since, like, with the ball it sort of stops.</em></td>
</tr>
<tr>
<td>(...)</td>
</tr>
<tr>
<td>S1G2: Yeah, <em>I mean on the outside of the box, I mean but that’s representative of the tunneling effect, which you know back in, when we’re doing like the ball, the steel ball thing...</em></td>
</tr>
<tr>
<td>S2G2: <em>Yeah, the classical mechanics doesn’t do it at all.</em></td>
</tr>
<tr>
<td>S1G2: <em>That didn’t occur.</em></td>
</tr>
</tbody>
</table>

These discussions were meaningful, despite students’ representational challenges (see supporting information) pertaining energy diagrams and wavefunction representations in multiple parts of the activity.
The language utilized is both peer-facilitated and at times investigator-facilitated. One point of interest is that not all groups received the same amount of non-procedural investigator facilitation. It was noted, through the code application and code co-occurrence tables obtained, that the number of spontaneous external transfer events seemed to be lower in groups with higher instances of investigator intervention. To test this quantitatively, another contingency table was set up to compare spontaneous transfer statements to non-comparative physical observation statements from students in groups with low and high investigator intervention alike. This time, a Pearson chi-square approximation with Yates correction\textsuperscript{9,11} was utilized in order to account for data, as some of the numbers were large yet over 20\% of the contingency table consisted of values below 5. Note that, under the Pearson chi-square approximation with the Yates correction, the p-value indicates statistical significance (p<0.005).

Table 26: Contingency table for quantum tunneling activity constructed with statements from groups with high and low investigator intervention to compare spontaneous external transfer and physical observation statements that did not coincide with any type of comparative statement.

<table>
<thead>
<tr>
<th>QMT-All Groups</th>
<th>Physical Observation Statements (non comp.)</th>
<th>Spontaneous External Transfer</th>
<th>Yates Chi-Square</th>
<th>Yates p-value</th>
<th>Stat. Sig.?</th>
</tr>
</thead>
<tbody>
<tr>
<td>High Investigator Intervention</td>
<td>232</td>
<td>1</td>
<td>10.418</td>
<td>0.00124793</td>
<td>Yes</td>
</tr>
<tr>
<td>Low Investigator Intervention</td>
<td>75</td>
<td>6</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Students’ Representational Challenges

Students experienced some difficulties right at the beginning of the activity, while considering how to draw out the potential energy surface of the ball and ramp apparatus. They had a tendency to confuse what the axis of translation was and also how the sketch itself would appear. Consider, for example, the following exchange between two students in group 1:

**QMT Group Excerpt 2**

| S1G1 | Translational so as the x coordinate moves...what’s our x? I guess x would be height. |
| S2G1 | No, x is from our start drop distance along the track. |
| S1G1 | (interjects): Ooh, so you have to do it like that? |
| S2G1 | And so potential energy would start fairly high and then go down and then go back up. |

Here, S2G1 intervenes to offer a reformulation to S1G1’s misconception that the x-coordinate (or the translational coordinate) is height. Further, S2G1 recognizes that the potential energy is directly related to the position of the ball within the track, and that it starts high initially, goes to a minimum at the bottom of the trough, and rises again as the barrier is approached. Consider, as well, the following excerpt from students in group 3:

**QMT Group Excerpt 3**

| S2G3 | So, um, in terms of energy, that would be in distance? Or would the energy be the translational coordinate of the x axis? How would you read the potential? |
| S1G3 | Uh, the potential energy? As you increase the height... Right, so this would be like n equals .25, .5, .75, 1. |
| S2G3 (Interjects): | Right, and then your potential energy would go up. One would think it would be linear, but we don’t necessarily know that for a fact. Two five...zero point five... |
| S1G3 | Uh. Is it...should it be linear? |
| S4G3 | Wouldn’t we sketch, basically, like the device thing? Because the x axis would be your, how far the ball travels and the potential energy as like the ball rolls down be whatever position or point it is on that curve? |

Here, S4G3 provides a reformulation to the physical observation statement and misconception brought forth by S2G3. Once again, the axis distinction is not immediately
clear to students, and it takes a degree of peer-assisted reformulation within the group to address the problem.

Such representational difficulties extended into the second (NH$_3$ bridge) portion of the activity, when students were asked to consider the vibrational partition function of the ammonia symmetric bending mode. Here, it is primarily a problem concerned with properly assigning units, or lack thereof, to the function. The following exchange in group three took place pertaining to this issue:

**QMT Group Excerpt 4**

<table>
<thead>
<tr>
<th>S2G3:</th>
<th>What is our, what is our y axis?</th>
</tr>
</thead>
<tbody>
<tr>
<td>S4G3:</td>
<td>Uh...</td>
</tr>
<tr>
<td>S2G3:</td>
<td>Arbitrary units?</td>
</tr>
<tr>
<td>S4G3:</td>
<td>Whatever it was that was in the original thing. Which was here. Absorbance?</td>
</tr>
<tr>
<td>S2G3:</td>
<td>Absorbance.</td>
</tr>
<tr>
<td>(...)</td>
<td></td>
</tr>
<tr>
<td>S4G3:</td>
<td>Wait, sorry, I’m not sure if the y-axis would be absorbance. That, that’s what it was in the first plot, in the second plot it would be something else. It would just be...</td>
</tr>
<tr>
<td>S2G3 (interjects):</td>
<td>q? So we plotted q versus this equation, so.</td>
</tr>
<tr>
<td>S4G3:</td>
<td>Yeah. So as a function of time, er not time, temperature.</td>
</tr>
<tr>
<td>S2G3:</td>
<td>q versus, um, versus temperature. So at 350, our q value is at 1.019... Is that wavenumber? Is that what that is?</td>
</tr>
<tr>
<td>S4G3:</td>
<td>Just, is it a dimensionless number? I don’t really know what that means. Like, what the q value is.</td>
</tr>
</tbody>
</table>

Here, there is considerable confusion related to whether or not the partition function had units. S4G3, in their pre- and post-activity interviews, expressed some difficulty with the concept of the partition function.

Eventually, investigator intervention was required, such that students may eventually determine that the main concept from this subsection of the activity is that the majority of the molecules occupy the ground vibrational state at ambient or spectroscopic temperatures. Therefore, classical transcendence would largely be ruled out.
Perhaps the most pronounced representational challenge is found in the third portion of the activity, where students are required to express, in a qualitative sense, one-dimensional particle-in-a-box approximation to the quantum dots. Though the activity explicitly instructs students to separate the wavefunction and the potential sketch with the energy levels in congruence with suggestions found in the physics education literature\textsuperscript{12-14}, representations that do precisely the opposite are found in prominent physical chemistry texts\textsuperscript{15,16} and even in a recent discipline specific research publication.\textsuperscript{17} Therefore, it does not come as a surprise that students who have been exposed to energy and wavefunctions in such a manner tend to hold on to such representations, at least initially. Consider the following excerpt from group 1, as the students attempted to represent the particle-in-a-box model with infinite potential at the sides:

<table>
<thead>
<tr>
<th>QMT Group Excerpt 5</th>
</tr>
</thead>
<tbody>
<tr>
<td>S1G1: Does it [the wavefunction] have to touch the ends?</td>
</tr>
<tr>
<td>S4G1: Yeah.</td>
</tr>
<tr>
<td>S1G1: Can’t it touch the sides of the box here?</td>
</tr>
<tr>
<td>S4G1: No, because the potential is zero, so there’s zero probability that it can be there.</td>
</tr>
<tr>
<td>S2G1 (simultaneously): No.</td>
</tr>
<tr>
<td>S1G1: I just remember seeing a graph...</td>
</tr>
<tr>
<td>S2G1: Because you probably saw it like this. [Draws potential with wavefunctions superimposed on the energy levels].</td>
</tr>
<tr>
<td>S1G1: Yes.</td>
</tr>
<tr>
<td>S2G1: This is multiple, overlayed at each other.</td>
</tr>
<tr>
<td>S1G1: Ahh.</td>
</tr>
<tr>
<td>S2G1: This, right here, zero.</td>
</tr>
<tr>
<td>S4G1: Yeah, it’s still zero, yeah.</td>
</tr>
<tr>
<td>S1G1: Well, how does this one work then because it’s going up?</td>
</tr>
<tr>
<td>S4G1: It’s like, it’s like if you put a new line through it, yeah.</td>
</tr>
<tr>
<td>S1G1: Ok, I see what you’re doing.</td>
</tr>
</tbody>
</table>
Note that S2G1, whose background is designated as strong, needed to offer a reformulation that included the drawing of the type of overlaid plot, which was the origin of S1G1’s misconception in the first place. Examples of such overlaid plots can be seen in Figure 19:

![Figure 19](image)

Figure 19: Top and bottom are both sketches constructed by students to represent the infinite-potential one-dimensional particle-in-a-box approximation to the CdSe quantum dots.

Note that in each of the sketches in Figure 19, the overlay gives the suggestion that the eigenfunctions themselves have a higher $\psi(x)$ value with increasing quantum number, $n$. In
this sense, the first of the images is somewhat more realistic, as it establishes a new “zero point” for each of the n=1 and n=2 functions. Further, the first of these images correctly assigns the wavefunction, \( \psi \), as the y-axis value whereas the second simply states that the wavefunction is not present beyond the confines of the box.

Another issue with the representation of the potential came, briefly, with the confusion of the quantum number, \( n \), with the coordinate. This particular instance, in group two, involved investigator intervention:

**QMT Group Excerpt 6**

<table>
<thead>
<tr>
<th>S1G2:</th>
<th>So we want to construct a, construct two diagrams, one representing energy versus coordinate, the coordinate equals ( n ), right?</th>
</tr>
</thead>
<tbody>
<tr>
<td>S2G2:</td>
<td>That should be... a parabolic, right? Because it’s ( n )-squared, it’s not ( n ). So when ( n )’s two, it’s just...</td>
</tr>
<tr>
<td>Investigator:</td>
<td>( n ) is just the quantum number, right?</td>
</tr>
<tr>
<td>S1G2:</td>
<td>Just the quantum number... So when you say coordinate, energy versus the coordinate, with the first energy level clearly marked...</td>
</tr>
<tr>
<td>Investigator:</td>
<td>So what is the physical coordinate here? Like what is...just think about what you’re modeling, right?</td>
</tr>
</tbody>
</table>

Further, the distances between energy levels became an issue with which students needed to struggle:

**QMT Group Excerpt 7**

| S2G2: | So like as you go higher, the distance keeps getting bigger and bigger. |
| S1G2: | But like the, between two and three, like the gap would be smaller than between one and two. |
| S2G2: | It would be bigger. Because, between two and three, technically it goes from four to nine. |

Here, it can be seen that S2G2 intervenes with a reformulation to ensure that the energy level spacings on the qualitative diagram are not drawn in a converging manner. It is plausible that S1G2 may have been confusing the relationship between energy levels in an anharmonic potential with those in the particle-in-a-box model.
Investigator interventions were required in a number of instances, though the majority of such instances were related to students representing the diagrams properly. Even still, students ultimately turned in diagrams whose axes were either partially labeled or not labeled at all (images from students’ responses are included in the supplemental information). Considering the evidence from students’ discourses and the sketched responses provided, it is of importance that an instructor adopting this module remains vigilant in ensuring that students focus attention on scientifically valid representations of these physical systems.

Evidence of Analogical Transfer

In moving towards addressing the research questions, it is important to consider the extent to which students were able to successfully connect the relevant information from the core concepts to those pertaining to tunneling at the nanoscale. Numerous occasions were found where students uttered comparison and contrastive statements comparing relevant features of the classical world to the model of quantum mechanical tunneling. The students’ backgrounds played a large role in the ease with which these comparisons were made.

Consider, for instance, the following exchange in group 1 dealing with the barrier height and amount of tunneling observed in the NH₃/AsH₃ system:

<table>
<thead>
<tr>
<th>QMT Group Excerpt 8</th>
</tr>
</thead>
<tbody>
<tr>
<td>S1G1: Barrier height in this case would be the top of that. Splitting... So in this case, NH₃ has a split of two, right? I don’t understand the splitting concept.</td>
</tr>
<tr>
<td>S4G1: Or tunneling, yeah I’ve never been over tunneling before.</td>
</tr>
<tr>
<td>S2G1: Saying that there’s a chance to possibly tunnel through the barrier at the very, very top. To go from almost planar to just tunnel through to almost planar on the other side.</td>
</tr>
<tr>
<td>S4G1: Oh, so instead of going over the barrier, going like...</td>
</tr>
<tr>
<td>S2G1: Yeah it’s...it’s really weird. It’s really cool actually.</td>
</tr>
<tr>
<td>S4G1: Yeah, I think I get what you’re saying.</td>
</tr>
</tbody>
</table>
It is clear from the above exchange that S2G1’s background in the subtopic is stronger than the other students, particularly when considering the background statement given by S4G1 about never having been over tunneling in a prior course. Later in the same dialogue:

**QMT Group Excerpt 9**

| S1G1: It looks like the higher the barrier height, the more tunneling is going to happen. |
| S2G1: No, the higher the barrier height, the less tunneling. |
| S1G1: If the barrier’s higher, it’s going to tunnel. |
| S2G1: No, if the barrier’s much, much, much higher then it’s going to try to tunnel and then just decay off to nothing. (Pause). So this would be the case with the arsenic hydride; this is the case of the ammonia. Um, in this case, our energy of, you know, your excited state energy is comparable to the barrier height, so we’re getting within the range of possible, um, tunneling. Because if I was going to redraw this for arsenic, um, hydride, it would look the same, but this barrier would be about that wide. Just to throw something out there. So you would try to tunnel and it would just decay like that and it would never reach the other side. |
| S1G1: This is a new concept... |
| S2G1: It wouldn’t tunnel. |
| S5G1: Yeah. |
| S1G1: So the higher the barrier, the less tunneling. |

In this exchange, the comparison between a molecule whose barrier to inversion is comparatively higher (AsH$_3$) relative to NH$_3$ ensues, and the misconception stated by S1G1 at the beginning is reformulated by S2G1’s reformulation and comparison and contrastive statement. Another exchange relevant to this part of the activity takes place in group 3:

**QMT Group Excerpt 10**

| S4G3: Alright, so both sides of the barrier are interacting, that means that you would be able to make it over the potential without having that much energy. |
| S1G3: Yeah, so you’d have to, um... |
| S4G3: (Interjects) Which doesn’t make sense in the classical sense. Since, like, with the ball it sort of stops. |
| S1G3: Yeah, so, yeah that excitement isn’t enough, it’s not greater than the barrier right? So the only way it can interact is tunneling out of the... |
| S4G3: So I guess since the, uh, the wavefunctions are probability distribution, so I guess there’s some very small probability that it would be, like, flipped. So that’s how it would occur at room temperature. |
| S1G3: Yeah. |
Here, it is clear that there is a comparison to the classical world in student S4G3’s statements directly referring to the base knowledge domain: “...with the ball it sort of stops.” The language of quantum mechanical tunneling is utilized by student S1G3, with the recognition that interaction can only be occurring across the barrier without having to go over it classically. Also note the entrance of the discussion pertaining to the probabilistic nature of the wavefunction. Though not part of an explicit comparison statement, S4G3’s designation of the wavefunction as a “probability distribution” draws a clear line of demarcation between the classical and quantum worlds. It is worth noting that S1G3, who had a high level of background knowledge as ascertained by the pre-activity interview, tended to refer to the wavefunction (more correctly) as a probability density whereas student S4G3, with a medium-level of background knowledge, mostly refers to it as a probability distribution. The exchanges that occurred around this portion of the bridge concept led to well-drawn approximate schematics of the energy of the system, as can be observed in the following figures:
Figure 20: Students’ sketches of double-well potential and energy levels pertaining to NH₃.

Note that, in the first image of Figure 20, the inversions are properly drawn as one looks down the principal axis of the NH₃ molecule. The splitting in the first excited state is clearly labeled in both representations. The linear combination of functions leading to the splitting is depicted, albeit not normalized, in the second image while it is left out in the first. The transitions are more clearly marked in the first diagram.
Another set of interesting exchanges centered on the definition of events and how those manifested themselves at each scale. For instance:

**QMT Group Excerpt 11**

| S4G1: | So I guess this is obviously like, much greater number of events than... |
| S1G1: | Yeah; higher probability. |
| S2G1: | Everything is stat mech... |
| S1G1: | See in the other one, the ball being released is just one event. In this one...the events...What would be considered an event in this one? |
| S4G1: | I guess it would just be like the excitation? Maybe? |
| S2G1: | On the order of Avogadro’s number. |
| S4G1: | Yeah. |

Here, the physical observation statement by S4G1 opens the discussion of how many events are observed in a spectroscopic sample as opposed to how many are observed in the classical example. S1G1 enters with the direct comparison, recognizing that the observation of whether or not the ball transcends the barrier is an event itself, and, finally S2G1 implies that the spectroscopic sample would involve a large number of molecules such that the events being monitored are on the order of Avogadro’s number. A discussion as to whether or not there are separate events that take place ensues:

**QMT Group Excerpt 12**

| S4G1: | That’s like the ball, the ball was one event because it could only do one thing, but like a molecule can do two things [referring to each orientation of the inversion], you know, so it’s... |
| S5G1: | Yeah, so I’m looking at like one molecule. |
| S1G1: | Well you can think of the molecule as a ball, the two peaks, the two peaks are basically being released at two different points. So that’s. If that’s the case, then it’s only technically one event. Because the ball, in our case, we monitored one event. It was being dropped at different locations. If that’s, and we think about the peaks as the ball, as in this case, as the places where the ball can inverse, then it’s just the same thing. One event. One event. |
| S5G1: | In your case there would be twice as many events as there are molecules, ‘cause each molecule can do two different things. Right? |
| S1G1: | No, no, no. You can’t think about it like that. Because... |
| S2G1: | No, picture each molecule as an independent system. Um, the reasoning of two events total would be like saying there are two types of people on Earth therefore there are only two people. |
Ultimately, no consensus was found and both considerations were given in the students’ written answers in group 1. However, it is worth noting the external spontaneous analogical transfer exhibited by student S2G1, as they compared the molecules’ abilities to be inverted to there being two types of people on Earth. It appears the comment was largely directed at the idea of an ensemble insofar as there are many events being monitored in the case of the molecular systems, given that there are many molecules, as opposed to a single molecular entity.

Group 3 experienced somewhat similar exchanges pertaining to the number of events observed:

<table>
<thead>
<tr>
<th>QMT Group Excerpt 13</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>S2G3:</strong> Hmm. Events. I guess what we’re seeing is actually there’s two events right? Because you have the one peak on the other side there. But with the ball we only had one event...</td>
</tr>
<tr>
<td><strong>S4G3:</strong> (Interjects) Right.</td>
</tr>
<tr>
<td><strong>S2G3:</strong> ...and then we saw one each time.</td>
</tr>
<tr>
<td><strong>S4G3:</strong> Like, a lot.</td>
</tr>
<tr>
<td><strong>S2G3:</strong> Right. But this is two events happening at the same time.</td>
</tr>
<tr>
<td><strong>S4G3:</strong> Well, you’re observing, like, a bunch of different molecules, so each one can only have, like, one state sort of. So you’re observing a bunch of them, some of them end up in one state, some of them in another.</td>
</tr>
<tr>
<td><strong>S2G3:</strong> (Interjects) Ahh.</td>
</tr>
<tr>
<td><strong>S4G3:</strong> So it would be like a bunch of balls at once. (...)</td>
</tr>
<tr>
<td><strong>S4G3:</strong> What I was thinking is that the spectrographic, the spectroscopic measurement would be like if we had that device [ball and ramp] but had like a bunch of them like in front of each other and just dropped a bunch of balls, like one on each one.</td>
</tr>
<tr>
<td><strong>S2G3:</strong> (Interjects) So you think it happens like ‘duh duh duh duh duh’[noise attempting to emulate balls falling on ramp]. Like all at the same time?</td>
</tr>
<tr>
<td><strong>S4G3:</strong> Yeah, so like, you’d see like one right here and then another one behind it right there, so like...</td>
</tr>
<tr>
<td><strong>S2G3:</strong> I see what you’re saying. Right.</td>
</tr>
</tbody>
</table>
It can be seen from this exchange that S4G3 has molded the discussion towards analyzing in terms of the number of entities present, hence the comparison statement implying that the spectroscopic measurement was akin to measuring many balls being dropped on the ramp.

Group 2, however, gave a different argument:

<table>
<thead>
<tr>
<th>QMT Group Excerpt 14</th>
</tr>
</thead>
<tbody>
<tr>
<td>S1G2: <em>So, like I said, we decided that we observed four events with the steel ball.</em></td>
</tr>
<tr>
<td>S2G2: <em>I guess technically we observed two things, the two energies are just intrinsic.</em></td>
</tr>
<tr>
<td>S1G2: <em>Yeah.</em></td>
</tr>
<tr>
<td>S2G2: <em>So here the events...</em></td>
</tr>
<tr>
<td>S1G2: <em>(Interjects) I think it’s when we drop the ball from a specific height...</em></td>
</tr>
<tr>
<td>S2G2: <em>Right.</em></td>
</tr>
<tr>
<td>S1G2: <em>That’s an event.</em></td>
</tr>
<tr>
<td>S2G2: <em>Did it pass or not.</em></td>
</tr>
<tr>
<td>S1G2: <em>That was the second event. Whether or not the ball made it over the second barrier.</em></td>
</tr>
<tr>
<td>S2G2: <em>What was the third one?</em></td>
</tr>
<tr>
<td>S1G2: <em>Well...</em></td>
</tr>
<tr>
<td>S2G2: <em>Look in the answers [that the students had already written down] see what was the third one.</em></td>
</tr>
<tr>
<td>S1G2: <em>That was whether or not the ball made it over the barrier.</em></td>
</tr>
<tr>
<td>S2G2: <em>Oh, ok. I mean, that’s still an event, right?</em></td>
</tr>
<tr>
<td>S1G2: <em>Well, yeah, that’s what I’m saying. That was an event and then dropping the ball was an event. And we said the height of the barrier was an event, but that doesn’t make any...; that’s not an actual event. I think there’s two events.</em></td>
</tr>
<tr>
<td><em>(...)</em></td>
</tr>
<tr>
<td>S2G2: <em>That would be the three events that happened.</em></td>
</tr>
<tr>
<td>S1G2: <em>Hold on one sec.</em></td>
</tr>
<tr>
<td>S3G2: <em>So the absorption.</em></td>
</tr>
<tr>
<td>S2G2: <em>Then being flat, and then the inversion. Like, flattening, and then um, inverting.</em></td>
</tr>
<tr>
<td>S1G2: <em>And then going from the macroscopic scale to the microscopic scale, the potential energy barrier does not necessarily have to be eclipsed for a, uh, there to be a transition.</em></td>
</tr>
</tbody>
</table>

In these exchanges, it is clear that group 2 focused largely on the individual events. They did not take into account the fact that they are measuring many more events as the scale is changed, though S1G2 did make a comparison statement, relevant to connections between the base and bridge knowledge domains, that at the microscopic scale the energy barrier does
not need to be transcended. Despite the differences in the approach taken by group 2, the following is an excerpt from the latter portion of the activity involving the quantum dots:

**QMT Group Excerpt 15**

S1G2: Without, you know, being able to observe or examine something with a spectroscopic technique, you might be only able to see, you know, two events. You know? Uh.
S2G2: Ok. Or like events that are big enough for us to see with our eyes.
S1G2: Yeah, that are macroscopic as opposed to, you know, this microscopic technique allows you to see there’s other things going on.
S2G2: Even things that are really small can, can...
S1G2: Yeah, see...it’s kind of like a microscope. You see something on the outside, use a microscope and you can see...

Note, particularly, the spontaneous analogical transfer by student S1G2 in comparing microscopy to spectroscopic techniques, and the recognition that there exists a disparity considering how materials at different scales are measured.

Extension to the nano scale (target portion of the activity) yielded some interesting results among students’ discourses. Within group 1, S1G1, whose pre-activity interview indicated a medium-level background knowledge, struggled with the concept of tunneling throughout the activity. This led to attempts from the other group members to explain tunneling in the context of their prior knowledge, leading to statements of external spontaneous transfer:

**QMT Group Excerpt 16**

S1G1: I don’t understand tunneling at all actually.
S4G1: I think... I think maybe, [name of S1G1], you could think about it as just like, you know how things, um, like things can relax from a singlet state to a triplet state. I think that’s kind of what it’s like, only there’s like a theoretical barrier between them and you’re just jumping through a barrier.
S1G1: The way I see it it’s just a shortcut.
S4G1: Yeah, I mean I think that’s what it is.
Group 3 also discovers that the quantum confinement, or reduction of confinement in the case of the core-shell structure, at the nanoscale is directly associated with the tunneling effect:

**QMT Group Excerpt 17**

| S1G3: | Yeah, um, like so it wouldn’t be in a classical [wouldn’t be in the classically forbidden region] because its potential is too high for the energy. Like, uh, the energy level of the particle is lower than the potential energy, so classically it wouldn’t be able to get out there, but, get outside the box. But, since it can tunnel then it can, and we can show that it is because the wavelength is shifting when you put the shell around it. So it’s acting like it has a larger box. |
| S2G3: | Hmm. |
| Investigator: | Any other comments? |
| S2G3: | Seems reasonable. |
| S4G3: | Yeah, so like the steel ball would never end up somewhere where it doesn’t have enough potential energy. |

These discussions ultimately led to an excellent diagram, from group 3, which appears as follows:

![Diagram of tunneling in CdSe/ZnS core/shell structures](image)

Figure 21: Students’ sketches of tunneling in CdSe/ZnS core/shell structures with separate wavefunction and energy diagrams.
The wavefunction diagram and the energy level diagram are completely separated, with the y-axes clearly marked at the right of Figure 21. Though the potential well was not drawn with a bottom, and the exponential decay of the wavefunction extended into negative values of $\psi(x)$ (which is impossible for the n=1 level), the most important conceptual issue is addressed: separation of eigenfunction and eigenvalue.

As seen in the excerpt prior to the image, there is a clear awareness that the classical system, as the base, differs in its behavior from the target, and that the electron under consideration within the CdSe core becomes slightly less confined when the ZnS shell is placed around it. Also, in S1G3’s portion of the excerpt, the spectroscopic evidence involving the red shift due to decreased confinement is invoked.

**Post-Activity Interviews**

In general, post-activity interview results indicated that students were able to critically reflect on the connections made between the base, bridge, and target knowledge domains. An example of such reflection can be found in the following excerpt of student S2G2’s interview:

<table>
<thead>
<tr>
<th>QMT Post-Activity Interview Excerpt 1</th>
</tr>
</thead>
<tbody>
<tr>
<td>Investigator: <strong>Ok, um, describe the particle in each of the cases, the classical, the ammonia, and the quantum dots.</strong></td>
</tr>
<tr>
<td>S2G2: <strong>So the classical particle was the ball that we rolled down the ramp and then, yeah, the quantum particles they have, like how would you want me to describe them?</strong></td>
</tr>
<tr>
<td>Investigator: <strong>Well, what they were to you.</strong></td>
</tr>
<tr>
<td>S2G2: <strong>Ok so like the second part was ammonia and then arsine I believe, and then the third part, and then of course we did a little bit of a comparison between arsine and phosphine in the second part, then the third part, um, we just pretty much took, um, CdSe and then we put it in a shell of ZnS and then tried to look at the energy through tunneling.</strong></td>
</tr>
<tr>
<td>Investigator: <strong>And what was the particle within the CdSe that you were studying directly?</strong></td>
</tr>
<tr>
<td>S2G2: <strong>The electrons?</strong></td>
</tr>
</tbody>
</table>
The first question in the post-activity interview aimed to probe for students’ conceptions about the nature of the particles under study in each knowledge domain. It can be seen through this exchange that the student identifies the particle as the ball in the base case, the ammonia and arsine in the second case, and the electrons within the CdSe and ZnS of the core and core/shell nanostructures in the third case.

In the second question, students were asked about the role of potential energy in each of the three cases. Consider the following excerpt from student S1G3’s post-activity interview:

### QMT Post-Activity Interview Excerpt 2

<table>
<thead>
<tr>
<th>Investigator: Um, how did potential energy play a role in each of the cases?</th>
</tr>
</thead>
<tbody>
<tr>
<td>S1G3: Um, well so the first one was classical, so the um, the, with the, well, the potential energy of the ball was based on the height and whether it was going to get over the barrier to the other, um, local minimum in potential energy, it had to have more potential energy than the barrier, um. The, uh, second part, the, there was a potential barrier at, um, as the hydrogens, um, as the shape of the molecule moved from trig bipyramidal, or trig pyramidal, to uh planar, and then pyramidal the other way. At that planar section, that was the potential barrier. Um, and potential energy in the third part was the, uh, environment outside of the quantum dot, the um, yeah so, the quantum dot by itself in the organic solvent was, um, considered an infinite potential energy, um, where the, uh, zinc sulfide shell would lower the potential, um, yeah.</td>
</tr>
</tbody>
</table>

Note that the student, in the base, bridge, and target domains alike, explicitly refers to the potential energy in the context of what the particle in each case needs to overcome (the barrier) in their physical observation statements. This is critical to students’ development of scientifically reasonable answers to the third post-activity interview question, which focuses explicitly on the barrier. Consider this excerpt from student S3G2’s response to the third question:

### QMT Post-Activity Interview Excerpt 3

<table>
<thead>
<tr>
<th>Investigator: Uh, describe the role the barrier played in each case.</th>
</tr>
</thead>
<tbody>
<tr>
<td>S3G2: So the barrier was just the amount of energy that our object needed to, uh, I guess excite given its level.</td>
</tr>
</tbody>
</table>
Investigator: *Uhh, are there other differences in the ways in which particles were able to cross or not cross the barrier and how so?*

S3G2: *Yeah, so in the steel ball example it just needed a certain amount of energy put into the system to cross the barrier, and then in the ammonia example I guess if it did have that amount of energy put into it, it would’ve crossed the barrier but it, we saw that it crossed the barrier anyway, and so that was due to quantum tunneling. And then in the third example, we saw that even though the electrons may not have the energy to sort of break out the particle in a box rule they still could because of the quantum tunneling.*

Student S3G2 incorporates the language of quantum mechanical tunneling, in a scientifically normative sense, based on their physical observation statements and experiences with the activity. They are able to identify that, in the two non-classical cases (the bridge and the target knowledge domains), the laws governing classical mechanics no longer rigorously apply.

The fourth and fifth questions ask students to reflect on the ways in which events were quantified and the number of events that are observed in each of the knowledge domains.

S1G1 gave the following response:

**QMT Post-Activity Interview Excerpt 4**

<table>
<thead>
<tr>
<th>Investigator: <em>In each case, how many events were observed or measured or quantified?</em></th>
</tr>
</thead>
<tbody>
<tr>
<td>S1G1: <em>For classical only one event. For both the NH$_3$ and the cadmium, those events, based on my perspective, would be a lot because you’re looking at all the vibrational modes, you’re looking at excitation, and a lot of different electrons, and these excitations don’t happen once, they happen many times so you can’t, I can’t really, well the best way would be to say Avogadro’s number.</em></td>
</tr>
</tbody>
</table>

| Investigator: *Ok.* |
| S1G1: *Would be the number of events, but you know, you can’t, I can’t say for sure the exact number in the classical sense.* |

It is important for the students to be cognizant of the fact that, in a spectroscopic setting, they are measuring many individual events over a large quantity of molecular species as opposed to the classical setting in which each individual event can be easily seen and monitored via simple inspection. S1G1 is immediately aware of the fact that for the classical case, one
event is monitored at a time. For the others, they correctly identify the types of transitions taking place in the species (vibrations in NH$_3$ and electronic transitions in the quantum dots) along with the fact that there are on the order of Avogadro’s number of such events taking place in a spectroscopic sample. These physical observation statements combined to form a normative argument in response to the question that was posed.

The sixth question aimed to center students’ attention on what the limits were in each case for the particle to transcend the barrier. Consider student S3G2’s response to this question in the following excerpt:

<table>
<thead>
<tr>
<th>QMT Post-Activity Interview Excerpt 5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Investigator: Um, what are the limits in each case for the particle transcending the barrier?</td>
</tr>
<tr>
<td>S3G2: Would that just be the potential energy barrier?</td>
</tr>
<tr>
<td>Investigator: Yeah, so like, yeah and how are like the limits different in a classical system as opposed to a quantum mechanical system?</td>
</tr>
<tr>
<td>S3G2: I think classical is more rigid because it’s just a certain amount and if you don’t have that certain amount, there’s really no way to get around it.</td>
</tr>
<tr>
<td>Investigator: Um, so high, how high must, uh, the barrier truly be in order for a quantum mechanical system to not have any probability to transcend the classically forbidden region?</td>
</tr>
<tr>
<td>S3G2: It would have to be infinitely high.</td>
</tr>
<tr>
<td>Investigator: Ok.</td>
</tr>
<tr>
<td>S3G2: For there to be absolutely no chance for tunneling.</td>
</tr>
</tbody>
</table>

Note that student S3G2 identifies the classical case as being more “rigid.” This implies that there is, indeed, some flexibility to the rules of classical mechanics once one crosses paradigms into the world of quantum mechanics. Upon further probing by the investigator’s follow-up question, the student acknowledges that a barrier must be infinitely high in order for there to be no probability of tunneling to the classically forbidden region. Note that the student utilizes the tunneling terminology in a normative scientific way without the investigator having used the word during the course of the question.
The seventh post-activity interview question for this activity served to probe students to describe the general connections that were to be made within the course of the activity. A dominant theme that emerges in the answers to this general question is that the activity draws a clear line of demarcation between the classical and quantum mechanical worlds. The following excerpt is exemplary of such responses to this question:

<table>
<thead>
<tr>
<th>QMT Post-Activity Interview Excerpt 6</th>
</tr>
</thead>
</table>
| Investigator: Um, describe in the context of all you’ve experienced with the activity and what we’ve discussed what the connections are between each segment of the activity.  
S2G2: So I guess the first part kind of tells you ‘hey this is the world that we live in, this is what ninety nine percent of things that we see and experience, this is the way they look’ but then we go down the smaller microscopic site and then we see that you can actually treat these with quantum mechanics and then have many more variables to observe and then how they actually change the perspective of potential energy from what you see in real life to small molecules and particles.  
Investigator: Ok.  
S2G2: So we just like went down by a level each time. |

Note, in particular, the language utilized in student S2G2’s response. They focus on the differences in scale exemplified in the activity as what the student refers to as “…the world that we live in” progresses into a “smaller microscopic site.” There is awareness of the fact that the movement from base, to bridge, to target constitutes going a “level down” in each instance. The ability to link, in a reasonable fashion, these facets of each knowledge domain is crucial to allowing for the possibility of transfer of concepts between base and target to occur.

Some misconceptions were made apparent in the post-activity interviews. Consider, for example, the following excerpt of student S5G1’s post-activity interview:
SSG1 mistakenly applies the condition of the bridge knowledge domain, one in which the focus is on molecular inversion, to the target domain, which focuses on quantum confinement of electrons in quantum dots.

One particular student (S1G2), whose background knowledge was determined to be weak, expressed a relatively large number of misconceptions. The following two partial excerpts point out a couple that are notable:

In the former excerpt, the misconception is centered about the idea that the potential energy directly governs whether or not one observes a spectrum. In each of the quantum mechanical cases, one observes a spectrum irrespective of the degree of tunneling. It is the nature of the spectrum that changes depending on the degree of tunneling allowed. In the latter, an anomalous, and seemingly classically-rooted response is given when the investigator attempted to probe for the language of quantum mechanical tunneling. It is important to note
that this student (with a weak background knowledge), made a background statement in the post-activity interview that helped clarify this:

**QMT Post-Activity Interview Excerpt 9**

S2G3: Ok. Well I, I'm not, it's been a long time since I've had p-chem and some of these things in, in, some of these theories I never came across. We never even talked about particle in a box, I just learned that just recently, and that theory of potential...

Having very little prior exposure to quantum mechanical topics, it is certainly plausible that the responses from student S2G3 could be considered “outliers,” even in the context of a qualitative study. It is critical, however, to analyze these results as they offer insights into some potential misconceptions and barriers to formation of novel conceptions that may arise in students with higher degrees of background knowledge.

A final note on student S2G3’s post-activity interview helps illustrate the fact that quantum mechanical tunneling, and arguably most quantum phenomena, are at odds from a conceptual standpoint with the daily experience of a human being in the macroscopic world. Consider the following excerpt, which takes place during the fifth question of the post-activity interview:

**QMT Post-Activity Interview Excerpt 10**

Investigator: Ok, um, what does this have to do with the scale and the nature of the systems? Does, does anything factor into the experimental observations?

S2G3: (Silence). I think that, you know, on a macro level like with the ball and roller, we were able to observe that fairly clearly.

Investigator: Mhm.

S2G3: Once you start getting into, um, more the spectrophotometric or spectro-, spectrometry, then you’re able to observe a, uh, you’re able to observe the spectra and may, and you, you try to describe what that spectra (sic) represents. When you go on to the third and the fourth, uh, what y-, you’re doing there is you’re going into more of a modeling, more of a much (sic) theoretical. Although, you can make analogies of the first scenario and the second scenario, and the third and the fourth, I don’t necessarily know whether those apply anymore. Because,
S2G3 refers to the macro-scale system (the base domain) as being clearly observable, while referring to the spectroscopic results as much more theoretical. Further, S2G3 goes on to refer to the application of the quantum mechanical models as speculation and as “esoteric theories.” This is strongly indicative of the intense confrontation a student must have with the physical underpinnings of the classical world if they are ever to think at a deep level about the quantum mechanics that describes the microscopic world.

Summary of Results

It is found through the analysis of the data that some students have difficulty expressing their ideas at a quantum mechanical level upon transitioning from the classical world. These difficulties manifest themselves in students’ diagrams and group discourse alike. However, overall, the data points towards reasonable progress in students’ abilities to make normative connections from the base, to bridge, and finally to the nano domain. This evidence has been expanded on, and is present in both students’ group discourse and individually in post-activity interviews.

In the tunneling activity, it is evident that the majority of students—even those with some exposure to the topic—do not come with prior direct knowledge associated with the quantum mechanical phenomenon of tunneling, as they live in the classical world. To understand the phenomenon requires an abandonment of the laws governing classical motion—the paradigm of physics with which students and all human beings have a direct physical exposure to and basic understanding of. Students are first required to experience the classical world with
which they are familiar (ball and ramp apparatus) and then are presented with evidence that
directly contradicts the laws of the classical world in the bridge portion of the activity in the
context of familiar molecular structures. This new knowledge (tunneling) is then intended to
be transferred, via analogy, to the nanoscale quantum dot structures.

4.3(c) DSSC Activity Analysis

For the DSSC activity, it is notable that the amount of relevant student discourse for analysis
is the weakest among all three analyzed instructional modules. This may be related to the
degree to which students’ discourses are composed of procedural language. This is the most
procedure-intensive of the activities: students must physically work with the clay and beads
in the base portion of the activity while, in the target portion, they must construct the dye-
sensitized solar cells. In light of this, the layout of the analysis is presented in a slightly
different format than the previous analyses: group discourse and post-activity interview data
are intertwined as opposed to explicitly separated.

Background Knowledge Assessment via Pre-Activity Interviews

The same scoring scheme was assigned for the pre-activity interviews as was in the previous
two instructional materials, with 0, 1, and 2 corresponding to weak, medium and strong
background knowledge qualities respectively. In this activity, the scoring was based on the
following three content-related interview questions:

1. What kinds of transitions can take place in a molecule when light in the visible region
   of the electromagnetic spectrum impinges on it?
2. What is an extinction coefficient in the context of spectroscopy?
3. What is the definition of efficiency as far as power is concerned? Express this
   mathematically.
The following tables present examples of the code application in the pre-activity interview for each of the background-related questions.

Table 27: Example responses from pre-activity interview question 1 for DSSC activity with assigned score and rationale.

<table>
<thead>
<tr>
<th>ID #</th>
<th>Interview Transcript Excerpt</th>
<th>Score and Rationale</th>
</tr>
</thead>
</table>
| S1G3 | Investigator: *What kind of transitions can take place in a molecule when light in the visible region of the electromagnetic spectrum hits it.*  

S1G3: Uh. You go through a rotational transition, um, and also a, uh, you can change, the electrons can go from a gr-, to an excited state. That’s electronic transitions.  

Investigator: *Mhm. Any others in particular? Any other kind at all?*  

S1G3: Um. *(Silence).* I know not vibrational.  

Investigator: *Ok.*  

S1G3: *Um, yeah, those are the two that I can think of.*  

Student S1G3’s response correctly acknowledges light in the visible region of the electromagnetic spectrum leading to electronic transitions, yet the student believes that rotational transitions would be allowed while vibrations would not be. This does not make sense from an energetic standpoint, as vibrational transitions are intermediate in energy to rotations and electronic transitions. **This response was assigned a 1 out of 2.** |

| S1G1 | Investigator: *What kinds of transitions can take place in a molecule when light in the visible region of the electromagnetic spectrum hits it?*  

S1G1: *Uhh, it could be enough to promote an electron from one level to another.*  

Investigator: *Mhm.*  

S1G1: *Which, I mean that’d be a, electronic transition, whereas the vibrational transitions are smaller and then rotational transitions which are even smaller.*  

Student S1G1 is clearly aware that electronic transitions are possible in the visible part of the electromagnetic spectrum. They also correctly order lower-energy transitions that might also accompany the electronic transitions. **The response earned a score of 2.** |
The first pre-activity interview question for the DSSC activity was meant to investigate students’ understanding of the possible transitions that can occur under irradiation of visible light. Since DSSC’s largely take advantage of the visible region of the solar spectrum, students should be familiar with the concept that electronic transitions are the dominant transitions in this particular region of the electromagnetic spectrum. Students should also be aware that rotational and vibrational transitions are possible, due to the relative magnitudes of such transitions to electronic absorption (they are smaller). Student S1G1’s response is representative of a normative and well developed understanding of the types of transitions that can take place in a molecule under visible light.

Table 28: Example responses from pre-activity interview question “What is an extinction coefficient (EC) in the context of spectroscopy?” with assigned score and rationale.

<table>
<thead>
<tr>
<th>ID #</th>
<th>Interview Transcript Excerpt</th>
<th>Score and Rationale</th>
</tr>
</thead>
</table>
| S1G1 | Investigator: *What is an EC ...?*  
S1G1: *Uhh. It's the ‘e’ in the Beer-Lambert law (laughs).*  
Investigator: *That’s a start.*  
S1G1: *And, is it not, is it related to the slope if you would take the, uh, look at the spectra, it's related to slope, that's uh, about all I got. (Laughs).* | S1G1 appears to be aware of the quantitative use of the EC: it is, indeed, the slope in the Beer-Lambert equation used to fit spectroscopic absorption as a function. Yet there is no link to the fact that the value is intrinsic to a specific species at a specific wavelength. **The response was assigned a 1 out of 2.** |
| S2G4 | Investigator: *Uh, what is an extinction coefficient in the context of spectroscopy?*  
S2G4: *Uh, extinction coefficient. Uh (laughs). I know that it ranges from extremely small up to thousands of, uh, whatever the units are, but it’s an intrinsic property of the molecule. I know that much, um, and I’m not too sure about that.* | Two key features are illustrated in the response to this question: the acknowledgement that the quantity varies largely and that it is unique for a given molecule (or species altogether). **This response was assigned a score of 2 out of 2.** |
The second pre-activity interview question was created in order to assess students’ understandings of the extinction coefficient. The extinction coefficient of a molecule is related to the absorption cross section by a simple conversion factor of $1 \times 10^{-3}$ L/cm$^3$ times Avogadro’s number to obtain the familiar units of L/cm$^3$/mol$^{-1}$. Since the absorption cross section of a molecule is what determines the direct impact of that molecule on the individual nanostructure it occupies, it follows that a qualitative understanding of the role of extinction coefficients in general is appropriate as a prerequisite to the activity. Students who understood that the value spans a wide range and, more importantly, that it is intrinsic to a given substance received points for this particular question.

Table 29: Example responses from pre-activity interview question 3 ”What is the definition of efficiency as far as power is concerned?” with assigned score and rationale.

<table>
<thead>
<tr>
<th>ID #</th>
<th>Interview Transcript Excerpt</th>
<th>Score and Rationale</th>
</tr>
</thead>
<tbody>
<tr>
<td>S2G2</td>
<td>Investigator: ..., finally, what is the definition ...? S2G2: Efficiency as far as power is concerned, I feel like I should know that (laughs). Um. I assume it has something to do with the energy output over the energy input. Investigator: Ok. S2G2: So, something like that.</td>
<td>S2G2’s response is indicative of some understanding that output and input must be expressed relative to one another. Beyond this, however, the answer is vague. For a full score, the response would need to express the overall concept of efficiency; the amount of power or energy produced relative to the amount of power or energy put into a system. This response was assigned a score of 1 out of a possible 2.</td>
</tr>
</tbody>
</table>
Table 29 Continued:

| S2G4 | Investigator: *what is the definition ...?*  
|      | S2G4: *Uh, the amount of. Um. Putting it into words is so hard* (laughs).  
|      | Investigator: *It’s ok.*  
|      | S2G4: *Um. Efficiency, basically, so if you have a 100% efficiency, you, there’s no energy wasted from that through things like heat or sound or whatever, so efficiency is the amount of, um, power for what you want with respect to wasted power.*  
|      | Here, S2G4 is cognizant of the fact that one hundred percent efficiency refers to a condition in which none of the input energy is lost. Further, there exists a clear understanding that a comparison between the amount of power utilized for the desired task (i.e. work from a machine) and that which is lost to non-useful processes. **This response was assigned a score of 2 out of a possible 2.** |

Question 3 serves to probe students’ knowledge about efficiency, both from a qualitative standpoint and mathematically. In the context of the DSSC activity, perhaps the most important feature is the relative efficiencies of the two different cells. It is the difference of available surface area in each of the TiO$_2$ nanostructures (rutile and anatase) that leads to the difference in cell efficiency (which students measure themselves). S2G4 is able to contextualize it both qualitatively (e.g. what efficiency is, how it relates to energy), and, to an extent, quantitatively (e.g. comparing energy that is wasted to that which is used for the intended purpose).

As with the quantum mechanical tunneling activity, a 2X2 contingency table was set up for the results from the DSSC activity, weighing the student’s background information against the instances of valid comparison or contrastive statements. It is important to note that only cohorts (student groups) for which a significant amount of discourse took place were selected for inclusion in the tabulation. The results are summarized in the following table:
Table 30: Fisher’s exact test to compare the number of misconceptions and valid comparisons or contrastive statements to the background knowledge level of the students in each group (cohort) for the DSSC activity. N= number of students who took a pre-activity interview in that particular cohort while n= number of students in a given cohort with a given background knowledge rating.

<table>
<thead>
<tr>
<th>COHORT 1</th>
<th>Misconceptions</th>
<th>Valid Comparison/Contrastive Statements</th>
<th>Tail 1</th>
<th>Tail 2</th>
<th>2-Tail Stat. Sig.?</th>
</tr>
</thead>
<tbody>
<tr>
<td>Strong Background (n=1)</td>
<td>1</td>
<td>3</td>
<td>0.571428</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Medium/Weak Background (n=2)</td>
<td>0</td>
<td>3</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>COHORT 2</th>
<th>Misconceptions</th>
<th>Valid Comparison/Contrastive Statements</th>
<th>Tail 1</th>
<th>Tail 2</th>
<th>2-Tail Stat. Sig.?</th>
</tr>
</thead>
<tbody>
<tr>
<td>Strong Background (n=1)</td>
<td>1</td>
<td>0</td>
<td>0.5</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Medium/Weak Background (n=2)</td>
<td>2</td>
<td>3</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Similar to the findings in the quantum mechanical tunneling activity, the relationship between students’ background knowledge and the number of misconceptions and valid comparison or contrastive statements made is not statistically significant. Once again, the dynamics present in the students’ discourse and interactions with the material in the activity, approached from a qualitative angle, are important in considering the overall implications. It is important to note that, within this particular activity, the procedural demands were relatively high given the students’ focus on constructing and characterizing the solar cells. Therefore, greater emphasis was placed on the post-activity interviews when compiling evidence for the qualitative portion of the analysis.
The remaining quantitative measurement is the Fisher’s exact test arising from the 2X2 contingency table containing the degree of investigator intervention and physical observation statements along with valid comparison/contrastive statements. In this case, it is important to note that we have compared the investigator intervention to the valid comparison contrastive statements as opposed to instances of external spontaneous transfer. This is due to the fact that there were too few instances of such transfer present in the results of this activity to warrant their use in the comparison. The following table summarizes the results:

Table 31: Contingency table for DSSC activity constructed with statements from groups with high and low investigator intervention to compare valid comparison or contrastive statements and physical observation statements that did not coincide with any type of comparative statement.

<table>
<thead>
<tr>
<th>DSSC-Groups 1, 2, and 3</th>
<th>Physical Observation Statements (non comp.)</th>
<th>Valid Comparison/Contrastive Statements</th>
<th>Tail 1</th>
<th>Tail 2</th>
<th>2-Tail</th>
<th>Stat. Sig.?</th>
</tr>
</thead>
<tbody>
<tr>
<td>High Investigator Intervention</td>
<td>3</td>
<td>1</td>
<td>0.291022</td>
<td>0.956656</td>
<td>0.582043</td>
<td>No</td>
</tr>
<tr>
<td>Low Investigator Intervention</td>
<td>7</td>
<td>9</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

In this case, the degree of investigator intervention does not have a statistically significant relationship with the number of comparison or contrastive statements made by students when weighed against the number of physical observation statements whose purposes were not to describe a comparison.
Students’ Conceptual Challenges

Within the course of this module, there were a couple of key areas in which students struggled. The first of these can be broadly characterized as confusion between packing efficiency and the surface area to volume ratio. There was some tendency for students to focus largely on the packing of the TiO$_2$ nanostructures themselves rather than incorporating the relationship between the number of beads, the total surface area of the clay and the amount of dye. A prime example of such within the students’ group discourse is found in the following exchange in group 1:

**DSSC Group Excerpt 1**

| S1G1: | [Reads question]. Oh, that’s the question is determine which one. |
| S2G1: | Determine which one’s which? |
| S1G1: | Which one packs better? |
| S2G1: | This one packs better because they, I mean, if you think about it, like, we had smaller pieces of clay, had better efficiency, it’s a smaller piece. |

Here, students are reflecting on the provided electron microscopy images of rutile and anatase TiO$_2$ surfaces. Note that S1G1 is concerned with which cell packs better as opposed to which picks up more dye molecules due to higher available surface area. Student S2G1’s physical observation statement, along with their comparison and contrastive statement, directly relates the packing efficiency to the overall efficiency of the cell, while disregarding the fact that the number of dye molecules chemisorbed to the semiconductor surface is highly important.

Within the post-activity interviews, the packing argument persists. Consider the following excerpt from student S1G1’s interview:
DSSC Post-Activity Interview Excerpt 1

Investigator: You took measurements of efficiency of the solar cells that you constructed and matched up the cells with specific TEM images of the semiconductor surface, which is the TiO2 annealed to the conductive glass; why did you make the assignments you did? I have the sheet here. And, again, these were arbitrary.
S1G1: Right, right. I think we generally looked at the picture and looked at the, like, which one like packed the tightest and had more surface area to the picture because I guess that’d be how light would hit it, and so we chose the three smaller blocks to be the one that looked more efficient because like I said the three smaller blocks had a greater surface area.

S1G1, in their comparison statement, correctly assigns the more efficient cell as being analogous to the clay that was cut up into smaller pieces leading to more available surface area. Their argument here, however, starts with a statement referring to which structure appeared to pack tighter.

It would appear, in general, that the reference to packing derives largely from the target domain, as there was no portion in the base part of the activity demanding that students attempt to close-pack the clay pieces. Therefore, it is plausible that the focus on packing efficiency stems from students’ prior exposures, likely at the general chemistry level, to close-packed structures when learning the basics of solid state chemistry. Though this postulation is not explicitly expressed (i.e. no student made any direct reference to solid state close-packed structures), this could possibly be an example of external interference in the analogical transfer process.

Another main challenge students faced concerned the understanding of the absorption cross section of the dye relative to the titania nanostructure, and relating this back to the bead diameter relative to the mass of clay it immediately occupied. The lack of evidence for transfer in this portion extended across all students.

Consider the following discussion that took place in group 3:
At this point, all the students in group 3 are having difficulty articulating their conceptions about the significance of the absorption cross section. Even upon investigator intervention, the lack of a definitive conception is present. For instance, student S2G3, in their physical observation statement and misconception, implies that the absorption cross section itself would increase along with a surface area increase. Further, they assert that the value decreases when the occupied mass decreases. The implication is that they are not viewing the absorption cross section as an intrinsic feature of the dye molecule, but are rather, viewing it as something that evolves with the change in surface area or occupied mass of the TiO₂.
nanostructure. The misconceptions associated with the absorption cross section along with
the inability to articulate transfer between the relationship between the bead diameter to the
immediately occupied piece of clay and the absorption cross section to the immediately
occupied TiO$_2$ nanostructure is further reflected in post-activity interviews. Consider a
clearer understanding of the absorption cross section expressed in the following excerpt from
student S2G2’s post-activity interview:

<table>
<thead>
<tr>
<th>DSSC Post-Activity Interview Excerpt 2</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Investigator:</strong> Um, the absorption cross section of a molecule is, essentially, a measurement of its exposure to incoming electromagnetic radiation at which point an absorption event can occur. Uh, it’s directly related, in this sense, to the extinction coefficient at a given wavelength. Um, what is the importance of this value in the context of this activity? S2G2: The cross section? Investigator: Mhm. S2G2: Uh, I guess it. In the activity, I guess the cross section... Investigator: Overall. S2G2: ...yeah, overall it means like a larger cross section means you’re more likely to have an absorption event I suppose. Investigator: Ok. S2G2: If that’s what you’re asking. Investigator: Yeah. Um, to which component of the solar cell, uh, would this parameter apply? Which, which part of the solar cell? S2G2: The square, the titanium oxide square. Investigator: Ok, specifically what within it? S2G2: Um, the dyes.</td>
</tr>
</tbody>
</table>

In this case, the understanding of the absorption cross section is indicated in their physical
observation statement that relates the magnitude of the cross section to the probability of an
absorption event. This is congruent with the fact that S2G2 received a score of 2 out of a
possible 2 on the relevant question concerning the extinction coefficient during the pre-
activity interview. It is worth pointing out that S2G2 first thought of the “titanium oxide
square” when probed as to which component the absorption cross section applied. It took an
intervention from the investigator to elicit from the student that it was the dye specifically whose absorption cross section one would be interested in.

Post-activity interview data provides no evidence of transfer between the bead diameter to occupied clay mass ratio and the relationship between the dye’s absorption cross section and the nanoscale structure it immediately occupies. The same is true for data from students’ group discourse, as detailed above.

Overall, the two principal sources of students’ conceptual challenges were found to be a focus on packing efficiency of the nanostructure as opposed to strictly its available surface area and misconceptions concerning the absorption cross section of the molecule, along with failure to relate the relationship of this value to the size of the nanoscale structure the dye occupies.

Evidence of analogical transfer

Within both the student discourse and, to a greater extent, in the post-activity interviews, there is evidence of successful analogical transfer. First, students had a high degree of success in understanding the surface area relationships within the base, which proved useful for students’ proper assignments of the TEM images to the cells in the target portion of the activity. Consider the following excerpt from student S3G3’s post-activity interview:

<table>
<thead>
<tr>
<th>DSSC Post-Activity Interview Excerpt 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Investigator:  <em>Um, in which part of the clay portion of the activity did you have the greatest surface area available?</em></td>
</tr>
<tr>
<td>S3G3:  <em>Um, where we did the least amount of the clay, or the third of the half of the clay.</em></td>
</tr>
<tr>
<td>Investigator:  <em>Ok.</em></td>
</tr>
<tr>
<td>S3G3:  <em>So sixth I guess. (Laughs).</em></td>
</tr>
<tr>
<td>Investigator:  <em>Yeah, it was sixths, yes.</em></td>
</tr>
</tbody>
</table>
S3G3 is aware that the smaller portions of clay led to a higher overall available surface area. This observation is also echoed in most other post-activity interviews (only two out of the eleven students who completed the post-activity interview had misconceptions while answering this portion). Also present is a general understanding that the higher available surface area led to an increase in the number of total beads picked up relative to the mass of the clay. Examples of students’ responses concerning number of beads picked up per total mass of clay are as follows:

<table>
<thead>
<tr>
<th>DSSC Post-Activity Interview Excerpt 4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Investigator: <em>Um, how did the act of cutting the clay into smaller pieces affect the number of beads relative to the total mass of clay?</em></td>
</tr>
<tr>
<td>S1G2: <em>Uh, it increased the number of beads relative to the total mass of clay.</em></td>
</tr>
<tr>
<td>(...)</td>
</tr>
<tr>
<td>Investigator: <em>Um, how did the act of cutting the clay into smaller pieces affect the number of beads relative to the total mass of clay?</em></td>
</tr>
<tr>
<td>S1G4: <em>It increased it, because now have the interior faces exposed. So, even though you had a smaller mass per each block, you had more beads attached to it.</em></td>
</tr>
<tr>
<td>(...)</td>
</tr>
<tr>
<td>Investigator: <em>Um, how did the act of cutting the clay into smaller pieces affect the number of beads relative to the total mass of clay?</em></td>
</tr>
<tr>
<td>S1G1: <em>I believe it increased it. The more pieces there were, the higher number of beads there were.</em></td>
</tr>
</tbody>
</table>

There is not enough evidence to state that the student *associated* the two phenomena (this would need to be present explicitly in the language), but that the cut up clay is properly chosen based on students’ physical observations for each of the questions is encouraging in terms of setting up the *potential* for positive analogical transfer to the target domain. If the base knowledge is not established, there can be no possibility for positive transfer.

Students were also able to relate the available surface area of each part of the clay portion of the activity to the analogous available surface area in the TiO$_2$ nanostructures. Note that this
is separate from students’ fixations on packing efficiency, which represented an extra layer that was detailed above in the students’ challenges portion of the analysis. A prime example of positive transfer in this context occurred in group 1:

<table>
<thead>
<tr>
<th>DSCC Group Excerpt 3</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>S1G1:</strong> So its relative efficiency is automatically comparing A to B. So, I imagine so it’s a whole, uh, large number it means A is more efficient than B.</td>
</tr>
<tr>
<td><strong>S1G1:</strong> We only did one cell, so I think we can ignore that.</td>
</tr>
<tr>
<td><strong>S2G1:</strong> The answer is A because, um, if it’s that much more efficient, think about how much smaller.</td>
</tr>
<tr>
<td><strong>S1G1:</strong> Yeah but I think it, we’re trying to base it on the earlier bead stuff.</td>
</tr>
<tr>
<td><strong>S2G1:</strong> Right!</td>
</tr>
<tr>
<td><strong>S1G1:</strong> I thought you were, the whole like, in the earlier thing was like you made two cells and one had like smaller surface area than the other and that’s why it would...</td>
</tr>
<tr>
<td><strong>S2G1</strong> (interjects): Wait, but we’re talking about A vs. B...</td>
</tr>
<tr>
<td><strong>S1G1</strong> (interjects): Are we?</td>
</tr>
<tr>
<td><strong>S2G1:</strong> Yes.</td>
</tr>
<tr>
<td><strong>S1G1:</strong> Ok.</td>
</tr>
<tr>
<td><strong>S2G1:</strong> So.</td>
</tr>
<tr>
<td><strong>S3G1:</strong> I don’t see how the beads and clay are related to A versus B.</td>
</tr>
<tr>
<td><strong>S1G1:</strong> Neither do I.</td>
</tr>
<tr>
<td><strong>S2G1:</strong> Well, because it’s the, think of the clay, er, the beads as the molecu-, er the dye and then think of our slide as the clay, so...</td>
</tr>
<tr>
<td><strong>S1G1</strong> (interjects): Right.</td>
</tr>
<tr>
<td><strong>S2G1:</strong> ...comparing A and B.</td>
</tr>
<tr>
<td><strong>S1G1:</strong> But the difference between A and B was the surface area.</td>
</tr>
<tr>
<td><strong>S1G1:</strong> What’s the difference between A and B, like, uh, chemically? [Investigator points at TEM images]</td>
</tr>
<tr>
<td><strong>S1G1:</strong> Oh, ok.</td>
</tr>
</tbody>
</table>

S2G1 immediately recognizes the fact that the individual TiO₂ structures need to be smaller in order to have a higher available surface area, as evident in their physical observation statement. S1G1 is aware of the fact that there needs to be a comparison of the TEM images related to the types of cells built by the all the students, to the earlier bead and clay portion. This, however, is not immediately clear to the group as each member, with the exception of student S2G1, indicates that they are unaware of the relationship to the base knowledge
domain. It is at this moment that S2G1 makes a comparison and contrastive statement relating the beads and clay to the dye molecules and conductive glass slide explicitly. Though the slide is not the substrate itself in the target knowledge domain (it is, rather, the TiO$_2$ structure), the statement nonetheless indicates that the student understood that the bead represents the dye and the clay represents some substrate upon which the dye molecules adhere.

The relation of the beads and clay to the target domain is present in post-activity interviews and these excerpts can be found in Appendix D.

A meaningful exchange can be found within the discourse of group 2:

<table>
<thead>
<tr>
<th>DSSC Group Excerpt 4</th>
</tr>
</thead>
<tbody>
<tr>
<td>S2G2: [Reads question]. Which cell is more efficient than the other... (etc.).</td>
</tr>
<tr>
<td>S2G2: Ok, so A, cell A has allowed more dye molecules to absorb...</td>
</tr>
<tr>
<td>S1G2: Mhm.</td>
</tr>
<tr>
<td>S2G2: ...um.</td>
</tr>
<tr>
<td>S2G2: [Reading portion of question] Construct an argument based on evidence from both portions of the activity. Ok, so we have to, like, say why.</td>
</tr>
<tr>
<td>S2G2: So, essentially the reason cell A is more efficient is because it allows more dye to bond to it. Ok, and so. I. To explain that. Do we need to look at these to explain that? Investigator: These as well, right?</td>
</tr>
<tr>
<td>S1G2: Which one is which?</td>
</tr>
<tr>
<td>Investigator: Ahh. Which one would you think would represent which?</td>
</tr>
<tr>
<td>S1G2: I think this one, because these look like smaller pieces and therefore there’s more surface area.</td>
</tr>
<tr>
<td>S2G2: So. Um. (Long pause). Um, with what, smaller, the titanium surface for A is smaller bits? Or what-not.</td>
</tr>
<tr>
<td>S1G2: The um. Well, what is this? Like.</td>
</tr>
<tr>
<td>S2G2: Which one? This one? Ok, this is. Well, this would be, uh, electron, you know, microscope picture of both surfaces of titanium. Because there are two different titanium oxide...</td>
</tr>
<tr>
<td>S1G2: Right.</td>
</tr>
<tr>
<td>S2G2: ...compounds. This one should be A and that one should be B.</td>
</tr>
<tr>
<td>S1G2: I see what you’re saying. Um, the. The, the cells of the titanium in our sample, in A, are... S2G2 (simultaneously with S1G2): were smaller...</td>
</tr>
<tr>
<td>S1G2: ...than in the other sample, and because they were smaller, there was greater surface</td>
</tr>
</tbody>
</table>
Within this portion of the students’ discussion, S2G2 is immediately aware that what led to an increased efficiency of cell A is the fact that it allowed more dye molecules to “absorb” (the correct term would be adsorb, specifically chemisorb, but aside from this linguistic issue the general concept is present in the student’s language). This viewpoint is furthered by the same student upon viewing the representative TEM images of the two different titania surfaces as they, more appropriately, refer to the dye as “bonding” to the TiO$_2$ surface. S1G2 is cognizant that the smaller nanostructures of the anatase allowed for more dye to adhere to the surfaces, as is noted by their physical observation statement in the latter part of the excerpt. Note also that student S1G2 explicitly connected the smaller size of the individual particulates of TiO$_2$ to higher available surface area. S3G2 concurs, and a group consensus is reached. While this excerpt does not show direct analogical transfer between the clay and bead portion (base) of the activity to the target, it is nonetheless relevant as it shows how students are able to reason out the role of surface area in the efficiency of the solar cell. This was achieved with a limited amount of investigator intervention.

**Summary of Results**

The analysis of these data uncovers that students bring with them language and conceptions related to packing efficiency that interfere with the notion of efficiency of the solar cells being related to the amount of dye chemisorbed to the TiO$_2$ surface. It was evident in the post-activity interviews that the vast majority of students were aware that the higher surface
area condition—clay cut into smaller pieces—led to more beads being picked up. Some were able to apply this knowledge to the target domain, which aimed largely to have students understand that dye-sensitized solar cells constructed of a rutile/anatase mixture (lower available surface area) would be less efficient than those constructed of a pure anatase TiO$_2$ nanostructure. However, much probing was required in order to elicit normative responses with respect to the connection between the bead/clay and dye/TiO$_2$ structure relationship was concerned. There was, however, significant transfer made by the students between the domains once the appropriate questions were posed by the investigator in the post-activity interviews.

Students’ tendencies to immediately relate higher surface area structures to “packing efficiency” demonstrates a need for instructor intervention in guiding students’ attentions towards the role of surface area and the amount of dye molecules that are able to chemisorb to the TiO$_2$ surface. The fixation on packing efficiency likely comes from students’ prior knowledge, likely at the general chemistry level, in which basic solid-state chemistry principles are taught. This is an example of one prior conception that must be refocused in order to maximize the possibility for positive analogical transfer. The prior knowledge is not in direct conceptual conflict with the knowledge domains, but represents an obstacle in facilitating appropriate transfer from base to target domains.
REFERENCES


CHAPTER 5

Conclusions, Implications for Implementation, and Future Work

5.1 Conclusions

The work described herein has addressed a gap in discipline-based education research by a) creating novel, modular instructional materials that explicitly connect core chemical and physical concepts to those at the nanoscale and b) assessing their effectiveness on promoting analogical transfer between different knowledge domains. To aid in the development of the instructional materials, Gentner’s theoretical framework for analogy was invoked as a basis for the design. The instructional materials were constructed with the goal of focusing on comparisons (or mapping) between relevant object relations in the base (core chemical and physical concepts) and target (concepts specifics to the nanoscale) knowledge domains. This framework, therefore, informed the construction of the learning objectives which, in turn, guided the flow and construction of probing questions within the instructional materials.

To assess the efficacy of these instructional materials in promoting analogical transfer between the base and target knowledge domains, cohorts of upper-division chemistry students tested the instructional materials. An assessment methodology, utilized in the science education literature by Duit and coworkers, was adapted to suit our needs. This methodology is predominantly qualitative in nature and is rooted in a discourse analytical perspective which assisted in further contextualizing students’ language. Coding was, in part, based on the analytic epistemology of V.W. Quine, as it was in Duit et al.’s work. Data collected consisted of audio transcripts of individual pre-activity and post-activity interviews as well as relevant group discourse. Upon compiling the data and applying the
codes to both student interviews and discourse transcripts, it was found that a couple of
categories lent themselves well to small scale quantitative analysis: the number of
misconceptions versus valid comparison and contrastive statements weighed against student
background knowledge, and the number of physical observation statements versus valid
comparison and contrastive statements weighed against the degree of investigator
intervention. This analysis produced 2X2 contingency tables and small data statistics, thus
the appropriate tests of significance (Fisher’s exact test and Yates corrected chi-square) were
implemented. These quantitative measures represent a secondary component in the
broader context of the qualitative study. It was found that, quantitatively, there was no
statistically significant relationship between students’ background knowledge and the
propensity to make misconceptions as opposed to valid comparison and contrastive
statements. Further, only the quantum mechanical tunneling activity yielded a statistically
significant p-value when comparing the degree of investigator intervention to the number of
physical observation statements and spontaneous external transfer. The former finding
suggests that the activities are accessible to students with a range of background knowledge,
though this dimension is afforded a more nuanced analysis with a qualitative lens. The latter
indicates that investigator intervention ought to be utilized prudently, as students may
provide higher levels of physical observation statements and categoricals (prompted by the
investigator or instructor), but might be less likely to utilize their own experiences or
language to make comparison and contrastive statements.

The overarching motivation for the analysis was to provide evidence in order to critically
address the two principal research questions proposed in this work.
The first research question was:

- Do the newly developed instructional materials promote in students the ability to effectively map core concepts into the realm of nanochemistry? What evidence can be provided to this effect?

When considering the evidence presented in the previous chapter, it is first worth noting that, in each of the assessed instructional materials, students experienced both conceptual challenges and successes with analogical transfer. For example, in the quantum mechanical tunneling activity, representational challenges were abundant even for students with relatively high levels of background knowledge. However, within these investigator-facilitated small group settings, the opportunities for reformulation were found to be relatively high, and the evidence for this has been presented within all three instructional materials. Though some misconceptions inevitably proliferated beyond the group discourse and even beyond the post-activity interviews, within each of the instructional materials, there were notable instances of highly appropriate and normative analogical transfer between the base and target domains. Some of these were broad. For example, students in the acoustic analogy activity were overwhelmingly successful in understanding the comparison between striking the tuning forks to induce the oscillation of the forks and the role of electromagnetic radiation in exciting the plasmon modes of the metallic nanomaterials. The object relation of induction, therefore, was properly mapped from base to target. This constituted a significant step towards the overall goal of facilitating analogical transfer between core chemical and physical concepts and those in the nanoscale domain.

Others occurred less frequently, but were nonetheless profound and indicative of the type of discourse that can be promoted by these instructional materials. At times, normative external
spontaneous transfer occurred. Take, for example, the case in group 1 of the quantum tunneling activity (see QMT excerpt A1 in Appendix D). A particular student was struggling with the overall concept of quantum mechanical tunneling and another student within the group utilized their classical mechanical knowledge to draw up their own analogy to the decrease in confinement due to tunneling. They compared a bouncing ball in a steel box to one in a plastic bag, and justified how the latter would be like the tunneling of wavefunction in a bound state and the former would be like the case with infinite potential walls. The exhibition of this type of spontaneous transfer was encouraging, in addition to the evidence provided for students’ abilities to communicate their conceptions and move the group discourse towards a scientifically normative conclusion.

Students in the DSSC activity were able to connect, through directly manipulating clay and beads, the general concept of surface area to relative efficiencies in solar cells due to different amounts of chemisorbed dye molecules present on rutile and anatase TiO$_2$ nanostructures. Though this, often times, needed to be elicited in the post-activity interviews, the evidence is still present that students could map the core physical concept of available surface area in the clay (base) to the TiO$_2$ structures in the solar cells allowing dye molecules to chemisorb (target). Further, they were able to directly quantify the cells’ relative efficiencies and reason, through mapping from the base knowledge domain that the surface of the more efficient cell corresponded to the TEM image that appeared to have more available surface area.

Based on the evidence provided in the analysis, it is reasonable to draw the conclusion that for many of the relevant object relations the instructional materials are successful in
facilitating students’ mapping such relations from base to target domains. This is not to claim that there are not challenges, drawbacks, or limitations, as these have been detailed alongside the students’ successes. Rather, it is to claim that there are enough instances across multiple student cohorts and within each of the developed instructional materials that explicitly show that analogical transfer from core chemical and physical concepts to those at the nanoscale occurs and can be facilitated either within the group or by the investigator (or an instructor).

The second principal research question to be addressed is as follows:

- Does analogical transfer enable students to develop a more scientifically normative viewpoint on both core and nano knowledge domains?

Given the nature of our research methodology, this question must be answered carefully by generalizing the development of the language students utilized to describe the phenomena that they were considering in each of the knowledge domains. Students came into the activities with varying levels of core chemical and physical knowledge as ascertained by the pre-activity interview data. Thus, the degree to which their physical observation statements are normative is qualitatively dependent on the richness of this background knowledge.

It can be argued that a significant component of students’ progressions of scientifically normative concepts lie within their abilities to develop, apply, and express knowledge in a novel domain (in this case the nanoscale). In fact, this principle is compatible with the crux of social constructivism, and the associated epistemology expressed such as those elaborated on by Staver.⁹ Four principles distilled by Stayer are as follows:

1. “Knowledge is actively built up from within by individuals and by communities.”
2. “Language-based social interactions are central to the building of knowledge by individuals and communities.”
3. “The character of cognition and a language which is employed to express cognition is functional and adaptive.”

4. “The purpose of cognition and language is to bring coherency to an individual’s world of experience and a community’s knowledge base, respectively.”

For example, in the acoustic analogy activity, the evidence through the students’ group discourse (learning communities developing a knowledge base) and post-activity interviews (individual expressing world of experience) showed that the relationship between tuning fork length and resonance frequency/wavelength were not viewed as simply applying to an object readily examined by the eyes and ears. Rather, students became aware that this basic relationship, readily observed in a core physical paradigm, could be used to describe the LSPR phenomenon in metallic nanoparticles—whose size dependence greatly affected the optical properties in such structures as opposed to the acoustic properties in the base domain. Therefore, the knowledge in the target domain was constructed as a manifestation, and expansion, of object relations in the base domain. This construction, in order to be scientifically normative, relied on a strong application and extension (mapping) of the relations in the base domain. The normative development of students’ viewpoints in each domain was readily observable in their ability, guided or autonomously, to move between domains and move towards analogical transfer.

In the quantum mechanical tunneling activity, students were guided to confront the failure of classical mechanics to describe quantum phenomena in the context of familiar molecule structures (NH₃/AsH₃). They then were to extend the quantum mechanical tunneling concept to the paradigm of quantum dots and the effect of a finite potential barrier on confinement. This sequence, arguably, solidified for many students the notion that the rules of the classical world were not transportable to the quantum world and, ultimately, to the nanoscale. Further,
the quantum tunneling considered in the bridge domain manifests itself somewhat differently in the target domain (one is characterized by inversion tunneling, the other through a slight spectroscopic red shift). By emphasizing the laws of classical mechanics with the base portion of the activity, students were eventually able to articulate the stark differences between classical and quantum phenomenon, as was evident in the analysis of their group discourse and interview data. This enhanced the core knowledge domain, as it allowed for direct confrontation of the limitations of the classical mechanical construct. They, therefore, needed to adapt their language and cognition to suit the quantum mechanical paradigm.

Once this was confronted, the concepts related to quantum mechanical tunneling were built up in the bridge domain and, finally, transferred to the nanoscale in the context of quantum dots. The bridge to target transition enhanced students’ discussions of the nanoscale and allowed for the effect of tunneling on a quantity that is highly capitalized on in nanochemistry (particularly with quantum dots): the confinement energy. There was also evidence that students utilized spontaneous external analogical transfer, as detailed earlier, to mold discourse with the normative use of scientific principles towards describing quantum mechanical tunneling. This helped establish coherency within each group.

As a third example, the DSSC activity group discourse data shows that students recognized that the increased surface area available in the anatase-based TiO$_2$ solar cells would lead to a more efficient cell. This act of transfer serves to enhance the knowledge within the nano domain, as the students observe that availability of surface area for the dye molecules to chemisorb has a direct impact on the efficiency of the solar cell. Likewise, the notion of
available surface area no longer exists solely in the context of clay and beads: it then formed a basis for the understanding of fundamental concepts related to nanochemistry.

This contextualization, and active use of knowledge across domains exemplifies growth of students’ viewpoints. They are able to apply core chemical and physical knowledge to the nanoscale and, further, characterize the unique manifestation of size dependence in nanochemistry. The development of an understanding that size-dependent phenomena are dominant at the nanoscale moves towards the development of a scientifically normative understanding in that knowledge domain.

### 5.2 Implications for Implementation

Upon interpretation of students’ conceptual challenges uncovered during the assessment of these instructional materials, a number of implications for implementation can be set forth. In this sense, it is best to characterize the dominant challenges for each of the instructional materials and then provide recommendations on an activity-by-activity basis. Table 32 summarizes these succinctly:
Table 32: Summary of students’ conceptual challenges for each instructional material.

<table>
<thead>
<tr>
<th>Instructional Material</th>
<th>Students’ Conceptual Challenges</th>
</tr>
</thead>
</table>
| Acoustic Analogy           | -Modification of the dielectric tensor to express anisotropy of nanorods: Difficulty focusing in on the difference between the x,y directions (transverse) and the z direction (longitudinal).  
                            | -Improper transfer of density to the target domain: Problems implicating the dielectric function difference between the Au and Ag nanomaterials as a primary source of the LSPR difference.  
                            | -Fourier transform module: Limitations to students’ mathematical backgrounds and advanced Excel usage.                                                                                                                                                                                             |
| Quantum Tunneling          | -Representations of wavefunctions and energy eigenvalues: Particularly separation of diagrams, establishing proper boundaries, and properly labeling axes.                                                                                                                                                                                                 |
| Dye-Sensitized Solar Cells | -Packing efficiency language often coincides with available surface area: Focusing in on ability of TiO$_2$ to pack as opposed to the role of surface area in allowing more dye to chemisorb.  
                            | -The role of the absorption cross section: Lack of a physical understanding or exposure to the absorption cross section parameter in the context of spectroscopy.                                                                                                                                                                                                 |

Beginning with the acoustic analogy activity, students’ difficulties with the modification of the dielectric tensor may be addressed by instructors with the introduction of a secondary analogy involving a comparison of scaling matrices. The scaling matrix can, first, be employed in an isotropic fashion (i.e. all elements in the scaling matrix are equivalent, as in the case of the dielectric tensor of the spherical nanoparticles). After this, the matrix can take on an anisotropic form in a way analogous to the dielectric tensor of the Au nanorods. Below is an example of a scaling matrix in Cartesian coordinates:
Equation 8: Scaling matrix in Cartesian coordinates.

If $sc_x = sc_y = sc_z$, then the scaling is isotropic; the transformation from $x$ to $x'$, $y$ to $y'$, and $z$ to $z'$ is equivalent. If, however, $sc_x \neq sc_y \neq sc_z$, the scaling is anisotropic. The case of $sc_x = sc_y \neq sc_z$ may be used as a base to illustrate the particular anisotropic associated with the Au nanorods. Actual numbers may be substituted in so that students are able to directly observe the effects of scaling on the coordinates.

In order to address students’ fixations on the density in the target domain, the instructor, as facilitator, must take steps to guide students’ discussions towards thinking broadly about intrinsic properties. A suggestion along these lines might be to guide students to discuss density, in the base—along with the Young’s modulus—as a subset of intrinsic properties. Once students have utilized the language in the base domain in a scientifically normative sense, they might then, in the target domain, pose the question “what are the relevant intrinsic properties with regards to the Au and Ag spherical nanoparticles?” The equation from the second challenge question may be brought up to assist students in formulating an argument that the dielectric function is what differs between the two, as well as the bulk dielectric constant. This may move towards establishing more reliable positive transfer between domains with regard to this object attribute.

The Fourier transform module presented a unique combination of procedural issues to the students (i.e. within the manipulation of Excel) as well as mathematical difficulties (e.g.
understanding the notion of a “transform,” and the use of the discrete Fourier transform expression). As such, it took a large amount of time to complete and may have the effect of detracting from the overall learning objectives of the activity if utilized as it stands. It would perhaps be more prudent instead of having the students to collect the data by banging the tuning forks in front of the microphone for the instructor to utilize this as a demonstrative interlude. This way, varying student abilities with Excel manipulation can be eliminated as a factor, and the module would not overshadow the broader context of the instructional material. Students can still answer the module questions, and the time on task will ostensibly be significantly reduced.

In the quantum mechanical tunneling activity, the overarching source of students’ challenges came from representational issues. This is understandable, given the current nature of eigenfunction/eigenvalue representations in widely adopted physical chemistry texts, as alluded to in Chapter 3. More research is needed into designing and assessing instructional and curricular tools to hone students’ representational literacy in the domain of quantum chemistry. This will be elaborated on further in the future work section. As the activity stands, students within their groups did eventually overcome some of the representational challenges. It is to be expected that instructors will need to intervene at times and refocus students’ attentions on the portions of the instructions that make explicit the need to separate these representations.

Within the dye-sensitized solar cell activity, the students had a tendency to transfer the notion of “packing efficiency” into the target knowledge domain, while seeming to be less focused (at least initially) on the available surface area. This was argued to be due to students’
exposure to the term “packing efficiency” during their experience in general chemistry within the context of solid-state chemistry. While instructors’ encounters with this will vary widely across institutions (the degree to which basic solid state principles are covered in first year chemistry will inevitably vary), it is something that needs to be taken into consideration. Should the problem arise, guiding the students’ discourses towards the utilization of the term “efficiency” only to refer to the operating efficiency of the cell, within this context, might be one way to move towards mitigating this issue. Further, it might be effective for instructors to, when the students observe the TEM images, directly ask the student groups to consider how the images relate to what was observed with the clay and beads. Since students did not have a tendency to make packing efficiency arguments in the context of the base knowledge domain, this might have the effect of centering students’ focus back on available surface area.

Students’ difficulties in transferring the ratio of the bead diameter to the clay to the role of the absorption cross section of a dye relative to the TiO$_2$ structure it immediately occupies is understandable. First, the concept and mathematical development of the extinction coefficient is something that is not readily clear to students, as ascertained from the pre-activity interviews. Many students are only aware that the extinction coefficient is the slope of the absorption vs. concentration plot they make during their study of the Beer-Lambert law. Within the DSSC activity, a physical interpretation of the absorption cross section—which is related to the extinction coefficient by a factor of $1 \times 10^3$ cm$^3$/L over $N_A$—is required. To accomplish this, instructors might allot some time during students’ syntheses of the solar cells to briefly go through a derivation of the molar extinction coefficient and show
its relation to absorption cross section. Further, a brief discussion about the cross section’s implications, particularly its relationship to the probability of an absorption event, should be given. Students also ought to be guided away from the literal interpretation of cross section as a distinct “area,” but rather towards the probabilistic understanding of the parameter.

5.3 Future Work

There are two main lines of future work that will be discussed in this section:

1. Characterization of level of procedural demand as well as task complexity and difficulty of the instructional materials and its effects on students’ group discourse.
2. Addressing representational competence in quantum chemistry.

The inspiration for the first line came from the analysis portion of this work in which it was observed that the degree to which students’ discourses are procedural might affect the way in which students interact in a group setting. If the nature of the language is highly procedural, to what extent would any subsequent drop in development of content-related discussion affect analogical transfer? Young and Talanquer’s work may set the basis for further investigation as in their study, discourse of students participating in scaffolded activities in small groups was analyzed. These activities were facilitated by pre-service science teachers, and video recorded qualitative data was collected and analyzed. The researchers found that, within their small group activities, the nature of students’ talk could be subdivided as follows:

- 5% Personal
- 6% Off-Task
- **7% Procedural**
- 33% Other
- 49% Content-related
  - Fact based (27%)
  - Meaning making (22%)
Of particular note is the 7 percent dedicated to procedural discussion. Given the varied nature of the activities presented in this dissertation, it is hypothesized that this value would be highest for the DSSC activity, and lowest for the quantum mechanical tunneling activity. It would be interesting to carry out further analyses to characterize the extent of procedural language and its encroachment on content-related language expressed by student groups for each of the activities. Further, to quote Young and Talanquer, “…science instructors are more likely to spontaneously focus their attention on procedural rather than conceptual issues when interacting with students during experimental activities than during whole class discussions. If this is the case, the nature of group conversations will be determined not only by task goals and structure but also by students’ and instructors’ implicit beliefs about expected types and levels of intellectual engagement in different task environments.” A more large-scale qualitative study of the nature of students’ language in the presence of instructors who focus mostly on procedural guidance, in comparison to those who focus largely on conceptual guidance, would be of interest in furthering the recommendations to instructors for these instructional materials.

Given students’ initial difficulties with representations of eigenfunctions and eigenvalues within the quantum mechanical tunneling activity, and the associated literature confirming these representational issues across chemistry and physics, further research into students’ representational competence in quantum chemistry is necessary. There are not a large number of studies specifically focused on the representational competence of upper-division chemistry students, particularly within a quantum chemistry context. Significant work on symbolic understanding of chemical thermodynamics has been carried out by Towns and
Becker.¹¹ In their study, the multitude of partial differentials that occur in classical
thermodynamics was confronted with questions that required the use of these expressions.
The results corroborated with work done by Meredith and Marrongelle¹² in which the
findings essentially showed that students experience difficulty in knowledge transfer between
the mathematical knowledge domain and the physics (or in the case of Towns and Becker,
chemistry) knowledge domain. The symbolic portion, however, is only one dimension in
understanding quantum chemistry. Representations of eigenfunctions and eigenvalues, as
seen in this work, play a key role in students’ linking of the rigorous mathematical formalism
of quantum chemistry to meaningful visual representations. To further this line of research,
several key questions must be asked. Are students able to identify eigenfunctions and
eigenvalues as separate entities? Are they able to effectively translate the meaning of
boundary conditions from the symbolic domain in differential equations to the plots and
diagrams they generate? Do their conceptions of boundary conditions and the nature of
wavefunctions, potential energy plots, and energy level diagrams extend (transfer) to cases
beyond simple one-dimensional systems? In short, the area of quantum chemistry we have
investigated, with the quantum mechanical tunneling activity, must be further explored and
expanded upon. The design of analogically based activities must be informed, within this
quantum chemistry paradigm, by a framework for design of instructional materials that are
based heavily upon the use of multiple representations to foster representational competence.
One possible framework upon which to accomplish this would be the DeFT (Design,
Functions, Tasks) framework by Ainsworth.¹³ The design parameters offered by Ainsworth
in her framework are:
1. Number: Choosing an appropriate number of representations to constitute the learning environment.
2. Information: Relates to the conveyance of information within a given representation and the degree of overlap between content in different representations.
3. Form: The media through which the representations are made available. (In subsequent activities, students would, as within our current work, be constructing and interacting with their own representations rather than simply being provided with them).
4. Sequence: Relates the choice of which representations students will be guided to construct first or last within the instructional materials.
5. Translation: The relevant aspect of translation put forth by Ainsworth is “...whether support is provided at the syntactic (surface) level or the semantic (deep) level.” The latter (semantic) will be emphasized in subsequent activity design.

The ability for students to translate seamlessly between their own representations of complex and abstract phenomena is crucial to being able to interpret and produce scholarly work in chemistry and the physical sciences in general. An opportunity exists, through the use of the DeFT guidelines, to address fundamental concerns such as eigenvalues and eigenfunctions within upper-division chemistry courses.

5.4 Closing Remarks

We have successfully utilized a framework for analogy to design modular instructional materials to explicitly connect core chemical and physical concepts to those at the nanoscale. Through the results of our qualitative study we have shown that the instructional materials may successfully promote analogical transfer between base (core) and target (nano) domains. Further, we have argued that the students were able to express scientific concepts in an increasingly normative fashion between the core and nano knowledge domains. By tethering the object relations between the two knowledge domains, students moved towards a better understanding of both core physical chemical concepts and phenomena relevant to nanochemistry.
The quantitative component of the work indicates that students of multiple background knowledge qualities can effectively engage in the instructional materials, and that investigator (or instructor) intervention should be utilized cautiously to ensure that students are building upon their own knowledge as much as possible.

More work remains to be done to characterize the nature of procedural language within these activities, along with work on representational competence in quantum mechanics (given the important role quantum mechanics has in nanochemistry). However, this work has shown the potential of these materials to facilitate analogical transfer in students from core chemical and physical concepts to those at the nanoscale, and promote their use of scientifically normative language across both knowledge domains.
REFERENCES


APPENDICES
Appendix A

Instructional Material Student Handouts

*Acoustic Analogy Student Handout*

Please read *all* directions carefully.

Items needed:

- Computer with spreadsheet application (e.g. Excel)
- Notebook or word processing software to record observations

**Part 1.**

You are provided with a set of 8 tuning forks (composed of an aluminum alloy), a ruler and a cloth. Measure the length of the fork prongs (see figure below) using the provided ruler (in cm). Construct a table to organize all your data and express these measurements in meters.
Image of two tuning forks (brass and aluminum alloy respectively) to illustrate prong length

Once you have finished measuring the prong lengths of all eight forks, place the cloth on the edge of the lab benchtop, so that you will not damage the surface when striking the forks.

Holding the fork at the base, strike it on the cloth protected surface such that the prongs are perpendicular to the edge of the surface. Quickly bring the fork up to your ear, so you may observe the pitch being produced. Repeat this process for all eight forks and, next to the corresponding prong length measurements, rank the observed pitches from low to high.

Take the two forks with the highest and lowest pitches respectively. Strike these forks again, but this time gently place your fingertips on the very top of the fork prongs and carefully record your observations.

In your report, answer the following questions pertaining to Part 1:

1. Knowing that an increase in pitch corresponds to an increase in frequency of sound, what can be said about the relationship between prong lengths and the frequency of sound? What can be said about the relationship between prong lengths and wavelength of sound?
2. Based on what you observed by damping the highest and lowest pitched tuning forks with your fingers, describe the behavior in the prongs that is leading to production of sound.
3. What action did you have to take to produce sound from the tuning forks?

Part 2.

You are now provided with four tuning forks that are composed of yellow brass (a copper, zinc alloy). These tuning forks are the same in length as four of the aluminum alloy tuning forks used in Part 1. Match each of the new tuning forks with the aluminum alloy forks of the same prong length. Repeat the striking procedure from Part 1 and record your pitch observations. Add the new data to your existing table. Answer the following questions:
1. Is the observed pitch different or the same between analogous tuning forks of different composition?
2. If the prong lengths are the same, how can any variation in pitch and, therefore, resonance frequency be accounted for?

**Part 3.**

Using the prong lengths from Part 2 (in meters) calculate the frequencies of oscillation of the tuning forks using the following equation:

\[ f = \frac{\pi}{8L^2} \left( \frac{EK^2}{\rho} \right)^{1/2} \]

Where E is the Young’s modulus of the material (a parameter that describes a material’s elasticity), \( \rho \) is its density, and K is the radius of gyration. L is your experimental prong length. The radius of gyration for all our forks may be taken to be \( \frac{5 \times 10^{-3}}{\sqrt{12}} \), or the cross-sectional length of a prong multiplied by \( \frac{1}{\sqrt{12}} \) (Narayan, V.A. 1996; Rossing, T.D. et al. 1992).

Since the terms under the radical will remain constant for a constant material, we may simplify the equation as follows:

\[ f = \frac{\pi}{8L^2} C \]

C for the aluminum alloy tuning forks is 4.07. Use the CRC handbook to calculate C for the brass (referred to in the handbook as “yellow brass”).
You may now calculate the frequencies for both the aluminum alloy and brass tuning forks. Convert these into wavelengths using the following relationship:

\[ \lambda = \frac{v}{f} \]

Where \( v \) is the speed of sound (taken to be constant at 343 m/s), \( f \) is the frequency, and \( \lambda \) is the wavelength.

On the same graph, make two plots of wavelength vs. the square of prong length, one for the four aluminum alloy tuning forks and the other for their brass analogues. Record your observations. Answer the following question:

1. Why would one observe a different wavelength and frequency of sound when the material changes? Why is this true even when you are comparing two tuning forks of the same dimensions? You may use mathematics to supplement your argument.

Part 4.

Load the Waves and Sound Physics software. At the main page, access the Beat Frequency Simulator. Here, you will find a virtual oscilloscope with a virtual slider that controls two frequencies. For our purposes, both sliders must remain at the same frequency at all times.

Start the simulator with the default frequency. Change the frequency three or four times, being sure to change both simultaneously, and observe the waveforms. Record your observations with regard to frequency and wavelength.

Exit this portion of the program and return to the main page. Open the “Transverse and Longitudinal Waves Simulator.” Click on the simulator of longitudinal waves through a metallic rod. You will notice that the density and Young’s modulus may be modified with
sliders. Without making any modifications to these parameters, focus solely on the representation of waves travelling through the rod. Record your observations. Now, change the parameters at will. Do this several times and record your observations. Does changing the Young’s modulus and density of the material have an effect on the way the mechanical waves propagate through the rod? Provide an explanation.

**Part 5.**

Obtain the three solutions of gold nanorods. On the UV-Visible spectrophotometer, take your blank spectrum of water once you’ve waited for the lamps to warm up. Prepare cuvette samples of each gold nanorod solution. Take the spectrum of each solution and observe the region between 500 and 1000 nm. Record the $\lambda_{\text{max}}$ (in nm) of each of the significant peaks in the spectra. Organize your data in a new table. Answer the following questions:

1. Given the following schematics of a nanorod, and given that the surface electrons are free to oscillate collectively (this is known as a plasmon mode), which band is likely to correspond to the mode travelling longitudinally with the rod ($z$ axis)? Along the transverse plane ($x,y$ plane)?

![Basic nanorod schematic with Cartesian axes. Y and X are equivalent.](image)

2. Based on the maximum wavelengths observed in the band pertaining to the longitudinal mode, and what you discovered with changing the tuning fork length, how would you order these solutions in terms of increasing average rod length?

3. What is exciting these plasmon modes? Compare this to what you needed to do to produce sound from the tuning forks.
Part 6.

Obtain the solutions of gold and silver spherical nanoparticles. Note that the average particle size in the gold and silver sols – or colloidal solutions- is statistically equivalent. Prepare a sample of each solution in a cuvette.

Before taking the spectra, answer the following question and turn it in to the instructor:

1. Based on information discovered with the tuning forks, what can you predict about where the two solutions will absorb relative to one another? Will their plasmon resonances take place at the same wavelength? Different? Explain.

Take the spectra, observing it between 350 and 750 nm, and record the $\lambda_{\text{max}}$ (in nm) for each substance (you will only observe one band each in this case). Record your observations and answer the following questions:

1. Why are the two peaks observed at vastly different wavelengths despite the similarity in particle size? How does this relate to what you observed with the tuning forks?
2. Based on the spectra, which material, gold or silver, has the higher energy fundamental mode for plasmon resonance? How does this relate to what was observed with the tuning forks?

Challenge questions:

1. Refer back to the nanorod schematic. The displacement, $D$, of the collective electrons on the surface of the nanoparticle may be described as the product of the dielectric tensor and the electric field vector in 3 dimensions. The terms in the dielectric tensor have both a real and an imaginary term, as you will observe in the upcoming equation (Bohren, C. F. & Huffman, D. R., 1983):

\[
e_0 \begin{bmatrix}
\varepsilon_i + i\varepsilon_i & 0 & 0 \\
0 & \varepsilon_i + i\varepsilon_i & 0 \\
0 & 0 & \varepsilon_i + i\varepsilon_i
\end{bmatrix}
\begin{bmatrix}
E_x \\
E_y \\
E_z
\end{bmatrix} = D = e_0 \left[(\varepsilon_i + i\varepsilon_i)E_x + (\varepsilon_i + i\varepsilon_i)E_y + (\varepsilon_i + i\varepsilon_i)E_z\right]
\]

The above equation describes the displacement in a spherical nanoparticle. Modify the equation to describe the displacement in a nanorod. What does this information
say about the number of discrete resonance modes observed in the UV-Vis spectra in each case?

2. Given that the portion of the dielectric function most responsible for the change in surface plasmon resonance frequency is the imaginary part, $e''$, what portions of the following equation are responsible for the difference in observed plasmon frequency between the two solutions in Part 6? How does this relate to what was observed in the tuning forks?

$$e^* = e''_{bulk} + \frac{\Omega}{r}$$

Where $e_{bulk}$ refers to the dielectric constant in the bulk metal, $\Omega$ is a constant specific to the metal, and $r$ is the radius of the spherical nanoparticle (Bohren, C. F. & Huffman, D. R., 1983).
Fourier Transform Module Handout

This portion of the activity will focus on the Fourier transform—an important mathematical technique utilized extensively in the physical sciences and in science in general. It allows one to convert a function of time into one of frequency. More generally, it allows for a function of one variable to be transformed into a function whose domain is that independent variable’s inverse.

On the computer, make sure that the provided microphone is functional (its display should be on, and the USB cable attached to the computer). Open the computer program Audacity. This will be the interface through which you will record the waveforms of the tuning fork directly.

Select two of the aluminum alloy tuning forks and two of the brass tuning forks of the same prong length. Have a group member click the red “record” button as soon as you strike the first tuning fork on the cloth. Hold the tuning fork close to the microphone such that at least 10 or 15 seconds of sound is recorded. Stop the recording and zoom into the data if necessary (there is a magnifying glass icon in the main toolbar within Audacity).

Select an area (it need not be more than approximately 2 or 3 seconds worth of data), preferably in the middle of the data, in which the sound does not appear to taper off significantly. Once you have made this selection, navigate to the top of the program and click on the “analyze” menu. There, you will find the option for “sample data export.” Click this and limit the output to 2048 data points, set the measurement scale to linear from the drop down menu, and set the file data format to a .csv file. Make sure you are aware of what
you named the file and where it is saved. Repeat this data collection and storage process for
the other three tuning forks.

Once you are done collecting the data, open the .csv files in Excel. You will notice that the
sample rate is 44.1 kHz, and that the total time duration of the 2048 data points is given in
the information as well. The columns of data are the amplitude of the waveform. In order to
express this as a function of elapsed time, you will need to divide the total time duration by
the number of data points taken (2048). This gives the time interval between each data point
that is collected. Therefore, if your first point is at time t=0, then the next point will be
shifted by the time interval (I), 0+I. Likewise, the point thereafter will be at time t=0+2I etc.

Construct a plot of the amplitude of the waveform vs. time.

After constructing the waveform plot, it is now time to carry out the Fourier transform. The
Fourier transform of a function of time can be written out as follows:

\[ G(f) = \int_{-\infty}^{\infty} g(t)e^{-i\omega t} \, dt \]

Where G(f), a function of frequency, is the Fourier transform of g(t), a function of time. The
complex exponential factor is referred to as the phase factor, where \( \omega \) is the angular
frequency (2\pi f).

Using basic complex number manipulations, this can be expressed in terms of sine and
cosine (Euler’s rule):

\[ e^{ix} = \cos(x) \pm i \sin(x) \]

\[ G(f) = \int_{-\infty}^{\infty} g(t) \cos(\omega t) - i \sin(\omega t) \, dt = \]

\[ \int_{-\infty}^{\infty} g(t) \cos(\omega t) dt - i \int_{-\infty}^{\infty} g(t) \sin(\omega t) dt \]
In reality, we deal with data that are not infinitesimally spaced over time (i.e. we deal with $\Delta t$ instead of $dt$). Therefore, the discrete Fourier transform is the basis for actual calculations performed on data:

$$G(f) = \sum_{k=1}^{N} g(t) \cos\left(\frac{2\pi k}{N}\right) - i \sum_{k=1}^{N} g(t) \sin\left(\frac{2\pi k}{N}\right)$$

Common algorithms employed in software such as Excel utilize a number of data points, $N$, that is a power of 2. For example, the number of data points you are utilizing is 2048 which is $2^{11}$.

Select the amplitude data from your waveform and open Excel’s data analysis tab. Built in here is a fast Fourier transform (FFT) algorithm that will return the discrete Fourier transform of the data. Select to have the results displayed in a separate sheet. Here, you will notice that you are provided with both the real and imaginary components of the transform. As you are interested only in the real portion, simply type =imabs(cells)^2, which returns the square of the real portion of the data in the cells. Make sure this is placed several columns over to the right, as you will need frequency values as an independent variable.

In order to calculate the frequency values, you first need a running count of the data points. Fill all of these in, starting with “0.” You should end at 2047, as 0 was the first point. In the next column, write a formula such that the data point number, from the previous column, is divided by the product of data points (2048) and the point to point time interval. This will yield the frequency, in Hz. Make a plot of the imabs data vs. the frequency. You will notice that the data appears to mirror itself. This is due to the Nyquist sampling theorem that disallows frequencies in the transformed function that are larger than that resulting from $\frac{1}{2}$
the sampling period. Thus, it is only necessary to plot the first half of the data resulting from the Fourier transform, as the remainder of it will simply be a mirror image. Note that the Nyquist frequency is nothing more than one half of the frequency corresponding to the sampling period. Make sure that you have done all this for all four tuning forks, then answer the following questions:

1. What is the relationship between the waveforms observed in your plots and the length of the tuning fork prong?
2. How do these waveforms relate to the frequencies observed in your transform plots? Construct an argument in terms of the principles of the Fourier transform.

What do you notice about the waveforms and frequencies observed from tuning forks of brass as opposed to those of the aluminum alloy? What are your predictions as to the reasoning for any differences? Support your response with experimental evidence.

References:

1. deLevie, R. Advanced Excel for Scientific Data Analysis; Atlantic Academic LLC, Orr’s Island, Harpswell, Maine, 2012; pp 217-223
Quantum Mechanical Tunneling Activity Student Handout

Part 1.

You are provided with a simple ball-and-ramp apparatus. The barrier has a height of \( h_0 \) (measure this, and record it in your notebook). Use a balance to record the mass of the ball. Utilizing your knowledge of classical mechanics (\( \text{PE}_g = \text{mgh} \)), calculate the potential of the ball at the top of the barrier.

You will now drop the ball from various percentages of the height of the barrier (see table below). Record the potential difference between the initial position of the ball and that of the ball at the top of the barrier (record in terms of \( \text{PE}_g \) ball-\( \text{PE}_g \) barrier).

<table>
<thead>
<tr>
<th>Initial Height ( nh_0 ) (m)</th>
<th>( \text{PE}_g ) of ball</th>
<th>( \text{PE}_g ) of barrier</th>
<th>Difference</th>
</tr>
</thead>
<tbody>
<tr>
<td>n=0.25</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>n=0.50</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>n=0.75</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>n=1.00</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>n&gt;1.00</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Sketch, by hand, a qualitative two-dimensional diagram of the physical scenario that you have just explored, complete with the following labels: energy (y-axis), translational coordinate (x-axis).

Having completed the experimentation in this portion, answer the following questions:

1. Based on your observations, what are the requirements for the ball to go over the barrier? Support your response with experimental evidence.
2. In this experiment, how many events were you monitoring at a given time? (Define an event as the release of the ball from height \( xh \), where \( x \) is any of the factors in the first column of your table and \( h \) is the height of the barrier, until it comes to rest)
3. You are designing a classic wooden roller coaster before the use of hydraulic launch is widespread. Can the height of the initial drop be lower than that of subsequent drops without the requirement of an additional pulley system to pull the cars further up? What is the limit here? Thoroughly justify your response in the context of this experiment.

**Part 2.**

Obtain the experimental or NIST data for the FTIR spectrum of NH$_3$ either from your instructor or from the link to the site. Plot the data, using a spreadsheet application, in terms of %-transmittance vs. wavenumber in the range of 915-985 cm$^{-1}$.

Take particular note of the *split* in the spectrum of NH$_3$ (look at the two largest features within the range plotted). In this case, it is the *mixing* of wavefunctions that accounts for such an effect. Also, make a note of the fact that AsH$_3$ exhibits a *single band* for this mode at 906 cm$^{-1}$.

For each of the prominent features (two for NH$_3$, one for AsH$_3$ for a total of 3), calculate the contribution to the vibrational partition function in the temperature range 200-800K (using a spreadsheet plot the partition function (q) vs. temperature in Kelvin (T)):

$$q^v = \frac{1}{1 - e^{-(\hbar \omega)/kT}}$$

**Intermediate question:** What does this partition function tell you in each case about the population of the ground vibrational state relative to higher states at spectroscopic temperatures (think: no more than about 350K in a closed gas cell)? Record your answer for later reference.

Draw three-dimensional structural representations (using wedges and dashes) of NH$_3$ and AsH$_3$ in your notebook. Notice that if one were to invert, like an umbrella in strong wind, a considerable change in the H-N-H and H-As-H angles would need to occur (maxing out at 120° in the planar intermediate). One can consider this planar intermediate to be a *barrier to*
the inversion of the molecule. In order to explore the effect the change in angle has on the potential energy, one can plot the potential as a function of angle as it approaches the 120° intermediate. A suitable function for doing so is: $V(\alpha) = A(\Delta \alpha)^2$, where $V(\alpha)$ is the potential, $A$ is a constant specific to the molecule (see below), and $\Delta \alpha$ is the amount by which the angle changes to. Thus, the maximum potential (i.e. the height of the potential barrier) is given by the potential corresponding to the largest change in angle—that is, the equilibrium bond angle to that at the planar intermediate. Given that $A=38897$ for NH$_3$ and -45607 for AsH$_3$, and the equilibrium bond angles in radians and degrees, complete the following table below:

<table>
<thead>
<tr>
<th>Compound</th>
<th>$V_{\text{max}}$, (cm$^{-1}$), calculate from angle in radians</th>
<th>$\Delta \alpha$, rad (deg)</th>
<th>Alpha final, rad (deg)</th>
<th>Alpha eq., rad (deg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NH$_3$</td>
<td>1.86 (106.8)</td>
<td></td>
<td></td>
<td>1.86 (106.8)</td>
</tr>
<tr>
<td>AsH$_3$</td>
<td>1.598 (91.56)</td>
<td></td>
<td></td>
<td>1.598 (91.56)</td>
</tr>
</tbody>
</table>

**Intermediate question:** For which molecule is the barrier to inversion higher?

An alternative way in which one may construct the potential energy diagram is by considering the displacement of the N or As from the planar intermediate (i.e. considering the position at the intermediate to be 0, and then + or – some amount, in Angstroms, as it assumes an apical position in the pyramidal structure). The following empirical potential by Laane works quite well for NH$_3$: $V(z)=14.22(z^4-0.745z^2)+1.973$. Where $V$ is the potential and $z$ is the apical displacement from the planar intermediate in Angstroms. Construct a fully labeled plot of this, ranging from $z=-1$ to $+1$, using a spreadsheet application.
1. Observe the spectra of NH$_3$ and AsH$_3$ about the relevant peaks of the $v_2$ vibrational mode. Given that the ground state energy is approximately 546 cm$^{-1}$ in NH$_3$, what is/are the energy(s) of the excited state(s)? Assume the ground state splitting is negligible on the order of IR calculations. Label these energy level(s) on your potential curve. What is the relationship between barrier height and the amount of tunneling “splitting” occurring? Explain this in terms of NH$_3$ and AsH$_3$ barriers to inversion.

2. A linear combination of vibrational wavefunctions is required for any splitting observed in the spectrum of NH$_3$. This is analogous to the combinations of electronic wavefunctions taken, say, in simple H$_2$ molecular orbital formation (draw the MO diagram!). Knowing this information, what line represents the positive linear combination, which represents the negative? Represent this with (+/-) designations on a sketch of the empirical potential curve you plotted, and construct symbolic, normalized linear combinations using wavefunctions representative of each side of the potential.

3. In order for the wavefunctions to “mix” as such, both sides of the barrier must be able to interact. Based on what you discovered with the partition function calculations, is such “mixing” possible in a classical sense? How could the inversion possibly be taking place at ambient temperatures? In what sense is the overcoming of the barrier different in this case from that observed with the steel ball?

4. Experimental results show that chiral phosphines, which have a period of inversion tunneling intermediate to NH$_3$ and AsH$_3$, are significantly easier to isolate than chiral amines. Why might this be the case? Justify your response using evidence from this activity.

5. How many events are being observed in the spectroscopic measurement relative to the number of events observed in the steel ball experiment? How does the way in which we observe events change at different scales? Explain.

6. Using what you observed about the relative degrees of tunneling in NH$_3$ and AsH$_3$, in what limit would there be absolutely no tunneling occurring? Explain in terms of the barrier height.

**Part 3.**

Quantum dots are semiconductor nanoscale structures that are finding wide ranging applications from medical imaging to low-energy LED sources. A conduction band electron in such a structure can be modeled using a simple one-dimensional particle-in-a-box approximation:

$$\psi = \left(\frac{2}{l}\right)^{1/2} \sin \left(\frac{n\pi x}{l}\right); \quad E_n = \frac{n^2\hbar^2}{8m_0 l^2}$$
Utilize the one-dimensional particle-in-a-box approximation for a CdSe particle with a diameter of 4.0 nm to obtain a) the general expression for the electron energy, and b) the general expression for the wavefunctions describing an electron. Assume that the quantum dot you are modeling is surrounded by organic solvent with an infinite potential. Construct two separate diagrams: one representing energy vs. the coordinate (with the first energy level clearly marked), and one representing the first wavefunction vs. the coordinate.

Repeat the steps above for a CdSe particle with a diameter of 6.0 nm. After this, please answer the following questions:

1. Upon studying the mathematical formulae utilized to construct your diagrams and obtain your functions and values:
   a. What is the significance of the eigenfunction/eigenvalue relationship in this quantum mechanical context? What does each tell us about the physical system? Use examples from your diagram to support your answers.
   b. What do you notice about the effect of confinement—that is, the limitation of the electronic wavefunction to various nanoscale dimensions—on the energy levels obtained? How would you expect this to manifest itself spectroscopically?

2. Give a physical argument as to why you are separating the two representations: energy (eigenvalue) and wavefunction (eigenfunction). Refer back to Parts 1 and 2, and basic quantum mechanical principles to strengthen your argument.

3. What were the boundary conditions here? What, specifically, gave rise to such conditions?

Now, consider a situation in which the quantum dot is encapsulated by a layer of ZnS—called a “shell.” This ZnS shell presents a barrier to the electron in the CdSe core of about 0.9 eV. First, sketch a rough potential diagram of how this system can be represented (think back to the particle-in-a-box model you recently used, but instead replace the potential of your organic layer with the ZnS potential).

**Intermediate question:** Given this energy profile, how must the boundary conditions be approached? What separates this from the case in which we approximated the barrier of a “bare” CdSe quantum dot to be infinite? Think back to how the magnitude of a barrier affected the extent of tunneling in the case of NH$_3$ and AsH$_3$. Use evidence from Part 2 and Part 3 section 1 to support your answer.
For the electron in the CdSe core region, the wavefunction can be allowed to take the form:

\[ B \sin(kx + \varphi) \]

where \( k \) is the wavevector, and \( \varphi \) is a phase angle.

**Intermediate question:** Observe the form of this equation. Plot a simple sine function (say, \( f(x) = \sin(x) \)). On the same plot, show a function \( g(x) = \sin(x + \varphi) \), where \( \varphi \) is a constant you vary. What is the effect of the constant \( \varphi \) on the plot? How might this factor into the physical interpretation of the system at hand?

The wavefunction in the remaining areas (the ZnS layers) can be described as \( A e^{kx} \) and \( C e^{-kx} \).

As seen in the simple case, in order to make the wavefunctions relevant to the physical system, boundary conditions must be established and the normalization constants found.

In order to find the energy levels of this system, the wavevector of the electron in the second region (the CdSe core region) must be found for each energy level. This can be accomplished by solving the following transcendental equation—that is, an equation that cannot be solved analytically\(^1\):

\[ kL = n\pi - 2\arcsin\left(\frac{k}{b}\right); \quad b = \sqrt{\frac{2m_0V_0}{\hbar}} \]

The most simple approach to finding values of the wavevector, \( k \), is to plot each side of this expression vs. the wavevector, and look for intersections (i.e. the straight line \( f=kL \), and the curves \( n\pi - 2\arcsin\left(\frac{k}{b}\right) \), on the same plot vs. \( k \), and observe at which values of \( k \) the functions intersect). To see the effect this has, make plots for \( n=1, 2, \) and 3 for a core diameter of 4.0 nm (i.e. \( L=4.0 \) nm). Use of a spreadsheet application is strongly recommended.
Once obtaining the values for the wavevectors, you can easily (as before with the bare dots) calculate the energy levels, $E$, for $n=1, 2, \text{ and } 3$ (recall that $k = \sqrt{\frac{2mE}{\hbar^2}}$). You may now also find the phase factor, $\phi$, via the following expression: $\sin(\phi) = \frac{k}{b}$.

**Intermediate question:** Compare the lowest-level energy values obtained from the first portion of Part 3 (for the 4.0 and 6.0 nm bare quantum dots) with that obtained for the 4.0 nm core CdSe with ZnS shell. Comment on any differences in these energy levels, and how this relates to each of the systems physically. What do you expect to observe spectroscopically? Observe the results of Dabbousi et al. and comment on whether or not your predictions hold true and why.

**Intermediate question:** Having observed the spectra of bare CdSe and CdSe/ZnS core/shell quantum dots with similar core sizes, along with bare CdSe of different sizes, what is the difference between having an “infinite” or a finite barrier on the spectrum?

It is now time to normalize the wavefunction in all areas for which it is defined. Given the following expressions for the normalization constants:

$$A = \frac{\hbar k}{\sqrt{2m_0V_0}} B ; \quad C = e^{iL} \frac{\hbar k}{\sqrt{2m_0V_0}} B$$

$$|A|^2 \int_{-\infty}^{0} \psi_1^2(x)dx + |B|^2 \int_{0}^{4 \times 10^6} \psi_2^2(x)dx + |C|^2 \int_{4 \times 10^6}^{\infty} \psi_3^2(x)dx = 1$$

Once you have found the normalization constants, make a fully labeled plot of the wavefunction corresponding to the first energy level vs. coordinate ($x$). Sketch a separate diagram with the just energy levels (as before with the CdSe core only model and the NH3 double potential diagram). Then, answer the following questions:

1. Observe the value of the wavefunction at the boundaries of the core (0 nm and 4.0 nm respectively). How do these particular values of the wavefunction compare to that of the bare nanoparticles? Why is this? Provide an argument based on quantum mechanics.
2. Is the wavefunction present in any area(s) in which it would not be in a classical scenario? Compare this situation to part 1 in which you observed a steel ball travelling down a ramp. What is this process called? How does this relate spectroscopically with respect to what you have learned about confinement?
3. Spectroscopy allows us to probe quantum mechanical effects. Refer back to Parts 1 and 2 to discuss how this is relevant in the context of even slight energy changes (think of the number of events observed in each part and why it is an important fundamental consideration).

4. What, combining applied theory in Parts 2 and 3 with the spectroscopic results, gives us evidence to support the quantum mechanical tunneling model? How do these compare between the portions of the activity?
References:

1. Mitin, V. V. *Quantum Mechanics for Nanostructures*; Cambridge University Press, UK, 2010; pp 81-84.
Dye-Sensitized Solar Cells (DSSC) Activity Student Handout

Part 1. Base portion (Clay/bead activity)

You will be provided with the following materials:

- A slab of modeling clay
- Some plastic jewelry beads
- Electronic calipers (metric)
- A ruler with metric units
- Plastic knife or other tool with which to cut clay
- A plastic bin (or paper towel)
- A balance

Record all numbers in a suitable tabular format.

Section 1.

Place enough beads in the bottom of the plastic bin (or paper towel) such that the bottom is completely covered with beads. Take five beads from the main pile (i.e. not from the plastic bin) and set them aside.

Turn on the electronic calipers, and be sure they are set to metric units. Carefully measure the diameters of each of the five beads you set aside and record the numbers to the precision given on the calipers. Compute the average of these readings, and record this value.

Obtain your block of modeling clay and unwrap it if it has not already been done. Cut the slab into halves. Select one of the halves, weigh it, and set the other aside.

Press each face of the piece of clay into the beads at the bottom of the plastic bin, applying enough pressure so the beads stick firmly into the clay surface.

Observe how many beads have stuck to the clay. Compute the following values:

- Ratio of the (average) diameter of a single bead to the mass of the clay it occupies
- Number of total beads picked up
Section 2.

Obtain the other half of clay and weigh it. Cut this one up into thirds (widthwise with respect to this piece as well). Restock the bottom of your bin with plastic beads, as described in section 1.

Carefully press each side of each clay piece into the beads, once again ensuring that the beads that stick do not simply fall off. Compute the following values:

- Ratio of the (average) diameter of a single bead to the mass of a single portion of the clay
- Number of total beads picked up

Using the data you have compiled from Parts 1 and 2, answer the following questions:

1. Why was an average of five beads used to calculate the diameter if all the beads are the same? What are at least two sources of error in this rudimentary measurement?
2. a. Considering the results from both parts, which portion had the largest ratio of bead diameter to mass of each clay unit?
   b. What does this suggest about the ability of a component of a system (such as a bead in this case) to have an impact on the surface area of the substrate it immediately occupies?
3. Which of the two scenarios picked up the most beads overall? Why? Construct an argument in terms of the available surface area.

Part 2. Experimental portion (Dye-Sensitized Solar Cells):

You will be provided with the following materials:

2cm x 2cm cardboard template

Digital multimeter with voltage, current, and resistance settings, and probes

Two (2) alligator clips

Digital Infrared thermometer

Squirt bottle containing ethanol

Laboratory wipes (i.e. Kimwipes)

Two (2) petri dishes containing cyanidin dye (from crushed frozen raspberries)
Electrolyte solution in a dropper bottle (I/I₃ redox couple, KI and I₂ in ethylene glycol)
Graphite rod or a #2 pencil
Four (4) binder style clips
Four (4) fluorine doped tin oxide (FTO) or indium doped tin oxide (ITO) conductive glass slides
Clear tape
A glass stir-rod
Two (2) dropper bottles of TiO₂ slurry (labeled A and B respectively)
A hot plate
Tongs
Oven Cloth (not a standard cloth, as this will catch fire)
An overhead projector
Two (2) TEM images

Section 1. Cell Construction:

The synthesis of the cells is based on a common procedure reported in the literature. Such cells are reported in the educational literature by Grätzel and Smestad¹, and the procedure for cell construction described below is derived from this work.

First, test to see which side of each piece of glass is conductive. This can be done by utilizing the multimeter (in resistance mode) and placing both probes on the same side of the glass. If it is the conductive side, a small resistance (on the order of 40 ohms or so) should register. If it is on the nonconductive side, it should read zero.
Clean two of the ITO or FTO slides with ethanol and laboratory wipes. Tape, with a couple small pieces of transparent tape, the 4 cm$^2$ cardboard template to the bottom-center of the **nonconductive** sides of the pieces of glass. Set the other two pieces aside for now. Set the glass slides conductive side up on the benchtop (or on a clean paper towel), and use the template, which you can now see directly through the glass, to carefully trace the area with tape such that there is a cleanly taped off 4 cm$^2$ area exposed directly over the template on each of the pieces of glass. This will create an area within which the TiO$_2$ thin film can be constructed.

Turn on the hot plate to the highest setting possible. Allow this to warm up while you perform the coating of the 4 cm$^2$ area with the TiO$_2$ slurries.

Obtain the two dropper bottles of TiO$_2$ slurry. For one cell, which you should refer to as “A”, utilize the bottle marked “A.” Place a couple of drops of the slurry in the middle of the area. You will then utilize the glass stir rod to make quick motions back and forth, without rolling the rod, to spread out the slurry on the surface. Try to minimize any gaps in coverage.

Repeat this process for cell B. It will now be necessary to ensure that you know the difference between the two so you do not lose track of it during the sintering process.

After this, allow for the drying of the cells for a couple of minutes in air. Transfer it to the hot plate and set it TiO$_2$-coated side up for sintering. This will take approximately 20 minutes. Once this period of time has ended, carefully remove the glass slides from the hot plate with tongs or tweezers and transfer them to a clean oven cloth. Here, they should be allowed to cool down for about 5-10 minutes.
After cooling, obtain the petri dishes containing the cyanidin dye. The glass slides should be placed TiO\textsubscript{2} side face-down in the dye and allowed to sit for about 10-15 minutes. Upon removal, it should be air dried for a minute and then rinsed with the ethanol squirt bottle. Dab, do not wipe, the surface of the glass and then carefully with a laboratory wipe.

Obtain the remaining two glass slides and place them conductive side up on your workspace. Using the graphite rod or a #2 pencil thoroughly coat this side of the glass. This will serve as a counter electrode. This glass should be annealed for 5 minutes on the hot-plate to preserve its integrity. Upon cooling, rinse the finished electrode with the ethanol squirt bottle and set them aside.

At this point, you will take the clips and sandwich the two portions together, with the conductive sides of the glass facing one another (i.e. TiO\textsubscript{2} side against graphite side). This must be done at an offset, such that the measurements portion of this activity becomes feasible. Otherwise, the alligator clips from the multimeter will not be useful. The clips should be placed at the sides that are flush with one another.

The electrolyte solution can now be used. A few drops of the solution should be placed along the edges of the glass slides, and a back-and-forth clipping and unclipping motion (one after the other) can be utilized to ensure that the electrolyte is fully “massaged” into the middle region.

Once this is accomplished, the cells are complete and ready for use in measurements.
Section 2: Measurements

Introduction

After having synthesized, or being provided with, the two dye-sensitized solar cells, you will take a series of measurements. It is worthwhile to first discuss some of the theory behind the operation of the cells. First and foremost, the dye molecules chemisorb to the surface of the TiO$_2$ semiconductor and act as light harvesting molecules. This chemisorption is constituted by a complexation of the quinonoidal form of the dye to the titania on the surface. The more dye molecules chemisorb to the surface, the more efficient the cell. The dye molecules absorb electromagnetic radiation in the visible range of the spectrum and “inject” electron density into the broader nano-titania structure. These electrons, then, require a medium through which to travel. The I/I$_3^-$ redox cycle, along with the graphite-coated counter electrode, allows for the electrons to pass through a potential that enables electrochemical work to be performed.

You are going to be measuring current and voltage readings from each of the two cells, whose only difference is the mineral form of the semiconductor nanoparticles, TiO$_2$. The ultimate goal is to measure the relative efficiencies of the two and to deduce, both from experimental evidence here and from evidence in Part 1 of the activity, the reason for one’s superior efficiency. One contains pure anatase phase, the other contains a mixture of rutile and anatase. The structures of the unit cells can be seen below:
Rutile (Top) and anatase (Bottom) unit cells respectively. The grey atoms are Ti(IV), and the red are O$^{2-}$.

Measurements and Data Collection:

Your task for the measurements portion is to obtain current and voltage readings under the illumination of the projector lamp.$^1$

First, you will need to set up the projector lamp. Set up the following circuit with the first solar cell (cell A, for example) and the multimeter (set to mV readings) by placing the positive (red) and negative (black) alligator clips to the glass coated with the graphite and TiO$_2$/dye respectively.
You can now take measurements of the voltage (in mV) and the area-normalized current (in mA/cm², where the values are simply divided by the area of the TiO₂ coated region of the cell). Make sure the reading on the multimeter stabilizes and you do not shift the cell around to a large degree while you are taking the readings or block the light. Have one person in your group use the thermometer to keep track of the cell’s operating temperature by pointing the laser at the cell itself. Record this value, in K, for later. For the best results, any shades in the room should be drawn and any extra light in the room should be turned off. Record your voltage and current in a small table, either within a notebook or on a spreadsheet program. You will need these values for data analysis later.

Repeat this process for the second cell and compile your data.

The most important terms to calculate here are as follows:

- The open circuit voltage needs to be extracted. This is simply the maximum voltage that a cell exposed to radiation can achieve. It is the voltage reading obtained by simply placing the cell under the lamp of the projector and obtaining a voltage reading.
- The fill factor (FF): This represents the area of the largest rectangle created from the product of current and voltage whose upper right-hand vertex lies precisely on the point of the cell’s maximum power (often described in the literature as the “knee” of a current vs. voltage curve). Essentially, it is an optimization of the voltage and current for maximum power output of the cell. While there exists no trivial solution to finding this value, the simple empirical formula given by Green² provides a means of calculating it that is, at times, superior to graphical methods:

\[
FF = \frac{V_{\text{OC,norm}} - \ln V_{\text{OC,norm}} + 0.72}{V_{\text{OC,norm}} + 1}
\]

Where \( V_{\text{OC,norm}} \) is, in this case, normalized to the thermal voltage, which—from statistical mechanics—is²:

\[
V_{\text{therm}} = \frac{k_B T}{q}
\]

Where T is the temperature (in K), q is the charge of an electron, and \( k_B \) is Boltzmann’s constant.
The short circuit current, $I_{SC}$, normalized to the cell area also must be obtained. This value represents the maximum current that a cell exposed to radiation can achieve. It is obtained simply by setting the multimeter to measure current and dividing by the area in cm$^2$.

Ultimately, we wish to compare the relative efficiency of cell A to B (or B to A). The efficiency of such cells is given by the following expression$^3$:

$$\eta = \frac{I_{SC}V_{OC}FF}{I_s}$$

Where $I_s$ is the incident intensity flux, in this case from the projector.

Since we are interested in relative efficiencies, however, the intensity of the incident light from the projector cancels and is irrelevant for our purposes. Therefore, the condensed expression is:

$$\eta_{A,B} = \frac{I_{SC_A}V_{OC_A}FF_A}{I_{SC_B}V_{OC_B}FF_B}$$

Calculate and record this value.

**Section 2. Reflection:**

After you have completed these steps, answer the following questions:

1. Which cell is more efficient than the other and by what factor? Explain your reasoning and show calculations.
2. Recall the earlier portion of this activity where you investigated the relationship between the diameter of beads and the mass and surface area of pieces of clay. Which of the cells do you suspect has been able to allow the most dye molecules to adsorb to its TiO$_2$ semiconductor surfaces overall? Construct an argument based on evidence from both portions of this activity.
3. The absorption cross section of a dye molecule is roughly the portion of the molecule that “exposes” itself to the incident electromagnetic radiation. How would this value relate to the occupied mass and surface area of the TiO$_2$ nanostructure factor into the efficiency of a cell? Explain succinctly and clearly.
4. You were provided with TEM images that show the morphology of cells A and B. Based on what you have discovered in each part of this activity, decide which TEM image is of the phase of TiO$_2$ used in cell A, and which is of cell B. Support your answer with evidence.
5. What is the overall implication of the importance of the incorporation of nanoscale structures, in particular, into this type of solar cell?
References:

Appendix B

More Examples of Students’ Responses to Pre-Activity Interview Questions

Acoustic Analogy Pre-Activity Interview Responses

The following tables consist of student responses that are characterized as weak, medium and strong with respect to the background knowledge. Each question is addressed in a separate table, and includes a rationale as to why a particular score was assigned.

Example responses from pre-activity interview question 1 for acoustic analogy activity with assigned score and rationale.

<table>
<thead>
<tr>
<th>ID #</th>
<th>Interview Transcript Excerpt</th>
<th>Score and Rationale</th>
</tr>
</thead>
</table>
| S2G3 | Investigator: *What is oscillatory behavior?*  
S2G3: *Um, like rotations. Like rotations of molecules.*  
Investigator: *Um, can you, oh ok, so I guess that would be your example of a physical system that exhibits oscillatory behavior.*  
S2G3: *Yeah.* | Student S2G3’s response refers directly to the rotation of molecules. Though the rotation of molecules is quantized, implying that its behavior can be characterized by a wavefunction (which, by its very nature is periodic), the student does not provide any elaboration in their response to this effect. The response was not developed well enough to indicate whether or not the student understood oscillatory behavior at a fundamental level. This response was scored a 0 out of a possible 2. |
| S2G2 | Investigator: *What is oscillatory behavior?*  
S2G2: *Oscillatory behavior? Like something behaving like sine and cosine functions maybe?*  
Investigator: *Can you name some examples of* | S2G2 correctly invokes sine and cosine functions as possible models for physical systems that exhibit |
physical systems that exhibit oscillatory behavior?
S2G2: Uh. Wavefunctions? Like. I guess wavefunctions...

Further, when probed to give an example, the student refers to a wavefunction (ostensibly in the quantum mechanical sense) as a physical system that exhibits oscillatory behavior (though, rigorously, the wavefunction merely describe a system exhibiting such behavior). Missing was the crucial development that oscillatory behavior implies motion between two extremes. Therefore, a score of 1 out of a possible 2 was assigned to this response.

Investigator: What is oscillatory behavior?
S3G1: Uh. Like, I want to use oscillation in the definition, but, like vibration between two points. Would that be good?
Investigator: Can you name some examples of physical systems that, uh, exhibit oscillatory behavior?
S3G1: Um, consider a linear molecule, like $\text{H}_2$, oscillatory vibrations. Or, consider like the harmonic oscillators energies.

In this response, student S3G1 gives a clear reference to an entity moving back and forth between two points (two extremes). This is a scientifically normative response. Furthermore, the quantum mechanical examples given by the student centered around the harmonic oscillator approximation—the quintessential oscillatory model in both classical and quantum mechanics. As a result, this response was given a score of 2 out of a possible 2.
Students’ responses, in order to be considered scientifically normative, needed to include the defining characteristic of any oscillation: movement between two extremes. Many students could provide at least an example of sinusoidal functions being representative of oscillatory behavior, as was the case of student S2G2. In order to assign a physical meaning to any oscillatory function, however, it is necessary to discuss the behavior in terms of two extremes, as student S3G1 did in their response.

Example responses from pre-activity interview question 2 for acoustic analogy activity with assigned score and rationale.

<table>
<thead>
<tr>
<th>ID #</th>
<th>Interview Transcript Excerpt</th>
<th>Score and Rationale</th>
</tr>
</thead>
</table>
| S3G2 | Investigator: *What is an intrinsic property of a material?*  
S3G2: *Uh, intrinsic. Gosh, that’s going back (laughs). Um. Properties. I can’t remember. I feel like intrinsic, something within the system, so properties that can change within the system? I don’t; yeah.* | S3G2’s response to this question is a misconception statement in that it implies that the property itself can change “within the system.” This is not scientifically normative, as an intrinsic property does not change within systems but, rather, between systems. Further, no example of such a property was given. Therefore, the response was scored a 0 out of a possible 2. |
| S1G2 | Investigator: *What is an intrinsic property of a material?*  
S1G2: *Of a material?*  
Investigator: *Yeah.*  
S1G2: *Intrinsic?*  
Investigator: *Intrinsic.*  
S1G2: *Uh, like boiling point, melting point, this stuff. Right?* | Within their response, student S1G2 correctly identifies boiling point and melting point as being intrinsic properties of a material. However, the notion that the property itself does not depend on |
the amount of substance present is not found in the response. Therefore, a score of 1 out of a possible 2 was assigned to this response.

| S6G3 | Investigator: *What is an intrinsic property of a material?*  
S6G3: *Uh, it’s a property that a material has by itself without any external factors.*  
Investigator: *Can you give an example?*  
S6G3: *Um. Uh. Intrinsic property. I don’t know, like a textile dye, some of them are intrinsically, um, carcinogenic because of the azo bonds.* |

Here, the student is aware that an intrinsic property is something that a material possesses itself. Further, the example given is scientifically normative: a chemical substance can be carcinogenic due to particular bonds present in that compound. Since the bonds define the compound, this is intrinsic to the material itself. **This response was given a score of 2 out of a possible 2.**

In question two, students were asked to consider intrinsic properties which are inherent to the material itself. Some students, such as S1G2, would provide an example of an intrinsic property but would not indicate a general understanding of the term. Others did not know whatsoever what the term meant, or could not recall from earlier chemistry courses. A few, such as S6G3, properly identified the intrinsic property as inherent to the material, and gave examples that were scientifically normative.
Example responses from pre-activity interview question 3 for acoustic analogy activity with assigned score and rationale.

<table>
<thead>
<tr>
<th>ID #</th>
<th>Interview Transcript Excerpt</th>
<th>Score and Rationale</th>
</tr>
</thead>
<tbody>
<tr>
<td>S3G3</td>
<td>Investigator: <em>What is the basic operating mechanism of a UV-visible spectrometer?</em> S3G3: <em>Can you repeat that?</em> Investigator: <em>What is the basic operating mechanism of a UV-visible spectrometer?</em> S3G3: <em>I don’t know.</em> Investigator: <em>Like, what are the most basic components required for a spectrum to be taken?</em> S3G3: <em>Um, I don’t know.</em> Investigator: <em>Ok, uh, describe the role of light, or electromagnetic radiation, in a spectroscopy experiment or spectrometer.</em> S3G3: <em>Um. Light goes through the object and you see how much it absorbs or, uh makes it emit.</em></td>
<td>Student S3G3 is unaware of the basic components required for the UV-visible spectrometer to work. Though they provide a normative response to the follow-up portion of the question, the contextualization in terms of the experiment is lost due to the absence of a response to the main question. Therefore, the response was scored a 0 out of a possible 2.</td>
</tr>
<tr>
<td>S4G3</td>
<td>Investigator: <em>What is the basic operating mechanism of a UV-visible spectrometer?</em> S4G3: <em>UV-vis. The basic operating mechanism?</em> Investigator: <em>Yeah, like what are the most basic requirements for a spectrum to be taken?</em> S4G3: <em>Ok, so I know for the UV-vis, you need to put it in a quartz cube, you put it in the middle and you shine like a laser through it, and it takes the wavelengths.</em> Investigator: <em>Uh, describe the role of light, electromagnetic radiation, in the spectrometer.</em> S4G3: <em>Like the light beam that’s being shot through?</em> Investigator: <em>Yeah.</em> S4G3: <em>I think it’s to determine which wavelengths are being absorbed.</em></td>
<td>This response contained a misconception related to the nature of the incident light provided in the spectrometer (it is not a laser, but typically a deuterium lamp for the UV and a tungsten lamp for the visible). In addition to this, the role of light is not directly characterized by the student as being the energy introduced into the system in order to induce an absorption. A score of 1 out of 2 was assigned to the response.</td>
</tr>
<tr>
<td>S5G1</td>
<td>Investigator: <em>What is the basic operating mechanism of a UV-visible spectrometer?</em> S5G1: <em>UV-visible. Uh, operating mechanism?</em> Investigator: <em>Yeah, like, uh, what are the most basic components required for a spectrum to be</em></td>
<td>Student S5G1 is able to identify the basic components required, including the lamp and the detector. Further, when</td>
</tr>
</tbody>
</table>
Investigator: Ok, so describe the role of light, electromagnetic radiation, in the spectrometer.
S5G1: Um, you’re using light to excite particles. So are you talking about absorption, I’m guessing, or?
Investigator: Yeah, UV-visible absorptions spectroscopy.
S5G1: Oh, yeah, using light and then whatever material absorbs, you measure what is absorbed.

asked about the role of electromagnetic radiation in the spectroscopy, the student understands that the light is meant to provide a source of energy to excite the particles in the sample. This is a scientifically normative development. The response, therefore, was given a score of 2 out of a possible 2.

The most important detail, perhaps, about the responses to the third pre-activity interview question is that there was a tendency for students to initially claim that they “did not know” any of the basic components required for a UV-Visible spectrometer to operate. In the case of student S3G3, as seen in the above table, the claim persists and no response is given. However, upon further probing, most students were able to at least be assigned a score of 1 out of a possible 2, and were actually aware of some of these basic components.

*Quantum Mechanical Tunneling Pre-Activity Interview Responses*
Students with a total score of 0-2 were classified as having weak background knowledge, 3-4 would be medium, and 5-6 would be strong. The following tables consist of examples of students with weak, medium, and strong backgrounds respectively. Each content-specific question in the pre-activity interview is addressed in a separate table.
Example responses from pre-activity interview question 1 for quantum mechanical tunneling activity with assigned score and rationale.

<table>
<thead>
<tr>
<th>ID #</th>
<th>Interview Transcript Excerpt</th>
<th>Score and Rationale</th>
</tr>
</thead>
</table>
| S2G3 | Investigator: *What does a wavefunction describe in a physical system when it is in a chemi-, when it is in a quantum chemistry context.*

S2G3: *In a wavefunction means that, um, when you’re, there’s, I think of waves in two different, uh, two different contexts. One context is that we always think of photons moving in waves because they have a wavelength, and they have a wave frequency, so in that particular thing, that’s sort of the definition of a proton, or a photon, when it’s moving in a wave. But, also what happens is in fixed systems like, uh, electrons, they have a wavefunction in that there are harmonics. And, so, I try to visualize a wave in terms of what is a particular electron doing in terms of spin and its interaction within those particular waves, within perhaps like a benzene ring. If there’s a harmonic there, it could be a one, a two, a four, an eight harmonic, but you have to kind of think of them as terms of the waves.*

Though student S2G3’s response was long and mentioned various possible systems to study, the content of the response was lacking in terms of being scientifically normative. The student utilizes words seemingly without contextualizing them in the relevant knowledge domain. Given the response’s lack of clarity and rigorous scientific validity, it was scored a **0 out of a possible 2.** |
| S3G2 | Investigator: *Um, what does a wavefunction describe in a physical system when it is in a quantum chemistry context?*

S3G2: *I guess a manifestation of sort of where the wave slash particle can be.*

Investigator: *Ok.*

The response to this question is not assertive nor completely developed, but is normative in the sense that the student invokes duality (wave/particle) and, in referring to where the entity might be. Further, the student displays some understanding of the probabilistic nature of the wavefunction. **This was scored as a 1 out of a possible 2.** |
S2G1 | Investigator: *What does a wavefunction describe in a physical system when it is in a quantum chemistry context?*
S2G1: *Repeat that?*
Investigator: *What does a wavefunction describe in a physical system when it is in a quantum chemistry context?*
S2G1: *Ok. Ok, the wavefunction describes the phase of an electron, um, throughout space as a function of time and space.*
Investigator: *Ok.*
S2G1: *Um, square it you get the probability of, uh, the electron being there.*
Investigator: *Ok.*
S2G1: *And you use it with all sorts of operators to get physical derived quantities.*

S2G2 demonstrates a clear understanding of the probabilistic interpretation of the wavefunction. Further, they indicate that it is the square of the wavefunction that allows for the probabilistic interpretation to be possible. Despite being yet another case in which a student only refers to the electron as a possible system of study, the content of the response is at a high level. Therefore, this response was given a score of 2 out of a possible 2.

The first pre-interview question was meant to gauge students’ understanding of the wavefunction’s role in describing the quantum mechanical system, in addition to the role of its square as a probability density. A basic understanding of wavefunctions is essential to the pedagogy of the quantum mechanical tunneling activity, as students actively utilize them in diagrams and descriptions. Table 11 shows students’ responses resulting in each of the three possible scores (0, 1, or 2). Note from the rationales that students who either gave a response with limited detail (S3G2) or a response severely lacking scientific normativity (S2G3) did not receive the highest possible score of 2.
Example responses from pre-activity interview question 2 for quantum mechanical tunneling activity with assigned score and rationale.

<table>
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<tr>
<th>ID #</th>
<th>Interview Transcript Excerpt</th>
<th>Score and Rationale</th>
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| S3G2 | Investigator: *What is the difference between an eigenfunction and an eigenvalue?*  
S3G2: *An eigenvalue, I guess, is sort of a, a possible answer to an eigenfunction?*  
Investigator: *So how are each of those used in quantum chemistry?*  
S3G2: *I think they give a good way to sort of work in all the physical, um where they, the selection rules. They sort of let the selection rules be worked into the mathematics.*  
Investigator: *So, um, elaborate on the meaning, like, of the Schrödinger equation in terms of how classical quantities, for example energy or momentum, are expressed and obtained. What are these called in, like, in the language of quantum mechanics?*  
S3G2: *Could you repeat that question?*  
Investigator: *Sorry, uh, elaborate on the meaning of the Schrödinger equation in terms of how classical quantities, for example, energy or momentum are expressed and obtained, uh, what are these called in the language of quantum mechanics?*  
S3G2: *The wavefunctions? So I guess the Schrödinger equation can show the parameters and how the different parameters affect the wavefunctions.*  
Investigator: *Ok.* | Here, the student is unaware of the physical meaning of eigenfunctions and eigenvalues.  
Expressing the eigenvalue as “a possible answer to an eigenfunction” does not provide enough evidence to support that the student understands the fact that it is the value obtained upon operating on the eigenfunction with the operator corresponding to a physical observable.  
Further, the student’s invocation of selection rules is anomalous to the question being asked.  
A score of 0 out of a possible 2 was assigned to this answer. |
| S2G2 | Investigator: *Alright, number two, what does a wavefunction describe in a physical system when it is in a quantum chemistry context?*  
S2G2: *Wavefunction, as in the ones that are in cm inverse? No, those are wavenumbers, I’m sorry.*  
Investigator: *Wavefunction, like in a quantum chemistry context.*  
S2G2: *Like Schrödinger’s equation? Doesn’t it...?* | Here, the student refers to the wavefunction as the “state of the matter,” which is normative considering the wavefunction is also known as the state function. The student also |
Is it like the state of the matter? Mostly?
Investigator: So how is the wavefunction associated with a given energy value then?
S2G2: Well, there’s an eigenvalue in front of each wavefunction, so I guess there’s like a... I don’t know to be honest.

knows that the eigenvalue is positioned in front of the wavefunction, however they fail to make the connection to the physical interpretation of the eigenvalue (that it corresponds to an observable. The score assigned was a 1 out of 2.

S2G1: Eigenfunction is something when you operate on and you get it out, eigenvalue is, um, what is a scalar multiple.
Investigator: How are eigenvalues and eigenfunctions used in quantum chemistry?
S2G1: Um, eigenfunctions are most often the wavefunctions. Eigenvalues, you have an operator that can, uh, corresponds to a certain observable when you operate the operator on the eigenfunction, you get out the eigenvalue which corresponds to the value of the observable.

In this response, the student clearly demonstrates knowledge of the role of eigenfunctions as wavefunctions in quantum mechanical systems. Further, S2G1 states that the eigenvalues, upon the act of operating on the eigenfunction with an operator, represent quantifiable observables. This response warranted a 2 out of a possible 2.

The second pre-activity interview question was geared towards assessing students’ understanding of what the role of eigenfunctions and eigenvalues are in a quantum mechanical context. Appropriate familiarity with this relationship is critical to understanding how mathematical descriptions of the physical system (wavefunctions) are used with the Schrödinger equation or, with operators other than the Hamiltonian, in order to quantify observables (eigenvalues). Students who demonstrated a normative, well-developed
understanding of the relationship of eigenvalues and eigenfunctions (e.g. S2G1) were given a full score of 2 out of 2.

Example responses from pre-activity interview question 3 for quantum mechanical tunneling activity with assigned score and rationale.

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<tr>
<th>ID #</th>
<th>Interview Transcript Excerpt</th>
<th>Score and Rationale</th>
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<tbody>
<tr>
<td>S1G1</td>
<td>Investigator: <em>Last question. In statistical mechanics, what does a partition function tell you about the energy levels or states of a quantum mechanical system?</em> S1G1: <em>Uhhh. I have no idea.</em> Investigator: <em>Ok, so think about like when you did Boltzmann distribution?</em> S1G1: <em>Uh huh.</em> Investigator: <em>What’s the denominator?</em> S1G1: <em>Uh. The Boltzmann distribution, the denominator is the square root of the number of points, right?</em> Investigator: <em>The Boltzmann distribution, right, when you’re talking about um the probability of finding one state in many? What would the denominator of that represent?</em> S1G1: <em>All of the possible states, right?</em> Investigator: <em>Ok.</em></td>
<td>Here, S1G1 appears to confuse the Boltzmann distribution with the formula for reduction of signal-to-noise ratio. Although there is brief mention of “all of the possible states” when the investigator probes further, it is unclear that there is a distinction between this and the student’s anomalous response previous to it. Given the misconception and lack of a clear reformulation, the student’s response to this question was assigned a 0 out of a possible 2.</td>
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</table>

| S2G1 | Investigator: *Uhh, last question, in statistical mechanics, what does the partition function tell you about the energy levels or the states of a quantum mechanical system?* S2G1: *Partition function describes how the energy function, uhh excuse me, how the energy levels are split throughout, um, energy, um, usually a function of temperature and, d, degeneracy.* Investigator: *Ok.* | Here, student S2G1 states that the partition function is a function of temperature and degeneracy. The student also takes into account the fact that the way in which energy levels are split does factor in, though it is not clear whether or not they understood the implications of how many |
In statistical mechanics, what does a partition function tell you about the energy levels or states of a quantum mechanical system?

S4G1: A partition function? Um, well, is that the one that tells you, oh gosh I’m thinking of perturbation, I guess is partition just telling you the different levels?

Investigator: Ok, elaborate on that, so if you think about the Boltzmann distribution what takes place in the denominator of the Boltzmann distribution?

S4G1: In the denominator? Um, I think it’s k T. And the top it’s like e to the energy, or delta E over k T.

Investigator: And what is that all telling you basically?

S4G1: Um, the probability of where, of the, of having that energy?

Student S4G1 had the most normative description of the partition function out of all students in the study. They recognize that it is directly linked to the energy levels. They do, however, mistakenly denote the denominator of the Boltzmann distribution as being the denominator of the exponential term. The response was not strong enough to warrant a full score of 2 out of 2, but was assigned a score of 1 out of 2.

Pre-activity interview question 3 was designed to characterize students’ knowledge regarding the partition function. Since a significant part of the activity revolves around utilizing the vibrational partition function to show that most molecules are in the ground vibrational state at ambient temperatures, a suitable physical interpretation of the partition function is necessary. No student achieved a full score of 2 out of 2 on this question. Student S4G1, with a score of 1 out of 2, came closest to appropriately relating the partition function to the available energy levels of the system.
Dye-Sensitized Solar Cells Pre-Activity Interview Responses

The following tables present examples of the code application in the pre-activity interview for each of the background-related questions.

Example responses from pre-activity interview question 1 for DSSC activity with assigned score and rationale.

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<tr>
<th>ID #</th>
<th>Interview Transcript Excerpt</th>
<th>Score and Rationale</th>
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<tbody>
<tr>
<td>S3G2</td>
<td>Investigator: Yeah. Uh, what kinds of transitions can take place in a molecule when light in the visible region of the electromagnetic spectrum hits it? So, like, visible light. S3G2: Ok, yeah. Transitions. Umm. I mean, are we talking about like the bonding, like vibrations, or? Investigator: Just in general, yeah. Anything you think. S3G2: Uh, I don’t know how to answer the question. (Laughs). Investigator: So like if light hits this, if I have a sample of a molecule or something and light in the visible region like, just, maybe even light from this room... S3G2: Mhm. Investigator: ...hits it, what kind of transitions occur in terms of energy? S3G2: Um. Bond vibrations, the, maybe uh, bending? I’m not sure. Investigator: Ok sure. Any others? Any other kinds of? S3G2: N-, none that, it’s just not coming out, so.</td>
<td>The student’s response to this question would have been appropriate if the region of electromagnetic radiation under study was the infrared. Further the student appears to be completely unsure of their response altogether. Taking this lack of normative scientific reasoning into consideration, a score of 0 out of a possible 2 was given for this response.</td>
</tr>
<tr>
<td>S1G3</td>
<td>Investigator: What kind of transitions can take place in a molecule when light in the visible region of the electromagnetic spectrum hits it. S1G3: Uh. You go through a rotational transition, um, and also a, uh, you can change, the electrons can go from a gr-, to an excited state. That’s</td>
<td>Student S1G3’s response correctly acknowledges light in the visible region of the electromagnetic spectrum leading to electronic transitions, yet</td>
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</table>
electronic transitions.
Investigator:  Mhm.  Any others in particular?  Any other kind at all?
S1G3:  Um.  (Silence).  I know not vibrational.
Investigator:  Ok.
S1G3:  Um, yeah, those are the two that I can think of.

The first pre-activity interview question for the DSSC activity was meant to investigate students’ understanding of the possible transitions that can occur under irradiation of visible light. Since DSSC’s largely take advantage of the visible region of the solar spectrum, students should be familiar with the concept that electronic transitions are the dominant transitions in this particular region of the electromagnetic spectrum. Though the electronic transitions are dominant in this region, students should also be aware that rotational and vibrational transitions are possible, due to the relative magnitudes of such transitions to electronic absorption (they are smaller). Student S1G1’s response is representative of a
normative and well developed understanding of the types of transitions that can take place in a molecule under visible light.

Example responses from pre-activity interview question 2 for DSSC activity with assigned score and rationale.

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<th>ID #</th>
<th>Interview Transcript Excerpt</th>
<th>Score and Rationale</th>
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<tr>
<td>S3G2</td>
<td>Investigator: So, what is an extinction coefficient in the context of spectroscopy? S3G2: I guess how long it takes for the signal to, uh, go away or, um. Investigator: Ok, so like when you do, when you used to do, like, UV-vis, you know like where you put the sample and you make a plot... S3G2: Right. Investigator: ...how does the extinction coefficient factor in there? S3G2: How is it determined? Investigator: Yeah. How does it factor it, like, what is it? Basically, what is it, what does it do? What does it contribute to the understanding of the system? S3G2: I don’t know.</td>
<td>Here, the student appears to be parsing their response in such a way that they’ve taken the literal meaning of “extinction” and placed it into a kinetic context: “I guess how long it takes for the signal to, uh, go away…” They are unable to express the physical meaning of the extinction coefficient in the context of the spectroscopy experiment. Therefore, a score of 0 out of a possible 2 was assigned to the student’s response.</td>
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<tr>
<td>S1G1</td>
<td>Investigator: Uh, what is an extinction coefficient in the context of spectroscopy? S1G1: Uhh. It’s the ‘e’ in the Beer-Lambert law (laughs). Investigator: That’s a start. S1G1: And, is it not, is it related to the slope if you would take the, uh, look at the spectra, it’s related to slope, that’s uh, about all I got. (Laughs).</td>
<td>S1G1 appears to be aware of the quantitative use of the extinction coefficient: it is, indeed, the slope in the Beer-Lambert equation used to fit spectroscopic absorption as a function. The student does not, however, link their response to the fact that the value is intrinsic to a specific species at a specific wavelength. The response was assigned a 1 out of 2.</td>
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S2G4: Investigator: *Uh, what is an extinction coefficient in the context of spectroscopy?*  
S2G4: *Uh, extinction coefficient. *Uh (laughs). I know that it ranges from extremely small up to thousands of, uh, whatever the units are, but it’s an intrinsic property of the molecule. I know that much, um, and I’m not too sure about that.

Two key features are illustrated in the response to this question: the acknowledgement that the quantity varies largely and that it is unique for a given molecule (or species altogether). This response was assigned a score of 2 out of 2.

The second pre-activity interview question was created in order to assess students’ understanding of the extinction coefficient. The extinction coefficient of a molecule is related to the absorption cross section by a simple conversion factor of $1 \times 10^{-3}$ L/cm$^3$ times Avogadro’s number, to obtain the familiar units of L*cm$^{-1}$*mol$^{-1}$. Since the absorption cross section of a molecule is what determines the direct impact of that molecule on the individual nanostructure it occupies, it follows that a qualitative understanding of the role of extinction coefficients in general is appropriate as a prerequisite to the activity. Students who understood that the value spans a wide range and, more importantly, that it is intrinsic to a given substance received points for this particular question.

Example responses from pre-activity interview question 2 for DSSC activity with assigned score and rationale:

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<tr>
<th>ID #</th>
<th>Interview Transcript Excerpt</th>
<th>Score and Rationale</th>
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| S3G3 | Investigator: *What is the definition of efficiency as far as power is concerned?*  
S3G3: *(Silence).* Um, not really sure.  
Investigator: *Like, when you hear the word efficiency, what do you think of?*  
S3G3: *Uh, well I think about green chemistry.* | The student initially thinks of green chemistry when asked the question about efficiency, which would be a valid domain from which to develop a response. |
| Investigator:  *Ok, sure.*  
S3G3:  *Um. (laughs).*  
Investigator:  *Yeah, that’s certainly valid.*  
S3G3:  *Yeah, um.*  
Investigator:  *What does it tell you, like what is it?*  
S3G3:  *I can’t think of another word besides efficient (laughs).*  
Investigator:  *Ok, sure, ok. So how would you put that mathematically, like if I wanted to say how efficient something is?*  
S3G3:  *I learned this in p-chem, I cannot remember…*  
Investigator:  *That’s fine.*  
S3G3:  *…the formula for it, um.*  
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<tr>
<td>However, S3G3 is unable to define the term mathematically or use it in a scientifically meaningful sense. As S3G3 claims themselves: they cannot think of another word to describe efficiency with other than “efficient.” A <strong>score of 0 out of a possible 2 was assigned to the student’s response.</strong></td>
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</table>
| S2G2  
**Investigator:**  *Um, and, finally, wh-, what is the definition of efficiency as far as power’s concerned?*  
**S2G2:**  *Efficiency as far as power is concerned, I feel like I should know that (laughs). Um. I assume it has something to do with the energy output over the energy input.*  
**Investigator:**  *Ok.*  
**S2G2:**  *So, something like that.*  
| S2G2’s response is indicative of some understanding that output and input must be expressed relative to one another. Beyond this, however, the answer is vague and does not go beyond simply taking a ratio of two values. In order for a full score to be assigned, the response would need to be expressed in such a way that the overall concept of efficiency is noticeable; that one is interested in the amount of power or energy produced relative to the amount of power or energy put in to a system. **This response was assigned a score of 1 out of a possible 2.** |
| S2G4  
**Investigator:**  *And what is the definition of efficiency as far as power’s concerned?*  
**S2G4:**  *Uh, the amount of. Um. Putting it into*  
| Here, S2G4 is cognizant of the fact that one hundred percent efficiency refers to
words is so hard (laughs). Investigator: It’s ok. S2G4: Um. Efficiency, basically, so if you have a hundred percent efficiency, you, there-, there’s no energy wasted from that through things like heat or sound or whatever, so efficiency is the amount of, um, power for what you want with respect to wasted power. a condition in which none of the input energy is lost. Further, there exists a clear understanding that a comparison between the amount of power utilized for the desired task (i.e. work from a machine) and that which is lost to non-useful processes. This response was assigned a score of 2 out of a possible 2.

Question 3 serves to probe students’ knowledge about efficiency, both from a qualitative standpoint and mathematically. In the context of the DSSC activity, perhaps the most important feature is the relative efficiencies of the two different cells. It is the difference of available surface area in each of the TiO\textsubscript{2} nanostructures (rutile and anatase) that leads to the difference in cell efficiency (which students measure themselves). Therefore, it is a crucial topic to understand both mathematically and qualitatively. Student S3G3 is neither able to provide a scientifically normative definition of efficiency nor contextualize it. At the other end of the spectrum, S2G4 is able to contextualize it both qualitatively (e.g. what efficiency is, how it relates to energy), and, to an extent, quantitatively (e.g. comparing energy that is wasted to that which is used for the intended purpose).
Appendix C

List of Post-Activity Interview Questions

*Note: Interviews were semi-structured. Follow-up questions were utilized at the investigator’s discretion.

*Acoustic Analogy Post-Activity Interview Questions*

1. Describe the process the tuning forks underwent in order for a sound to be detectible.
   a. What was required for a sound to be detectable from the tuning fork?

2. Describe the relationship between the length of the tuning fork prongs and the frequency and wavelength of sound observed.
   a. What occurred to the pitch of the sound as you progressed from tuning forks of shorter length to those of longer prong length?

3. What similarities or differences did you notice between the aluminum alloy tuning forks and the brass tuning forks?
   a. What properties of the alloys accounted for any differences in the sound produced by each type of fork?

4. What did the use of the Fourier transform accomplish during the course of this activity?
   a. How might this technique be helpful in areas outside of analyzing sound?

5. What physical process occurred with the Au nanorods and the Au and Ag spherical nanoparticles in order for there to be collective oscillatory behavior of the surface electrons (LSPR)? How is this related to what was observed with the tuning forks?
6. What determines the frequency (or wavelength) that is observed in electronic absorption spectra of the Au nanorods? How is this related to your observations with the tuning forks?

7. Why were the absorption wavelengths significantly different in the Au and Ag nanoparticles, despite their being of similar average diameters? How does this relate to the tuning fork portion of the activity?

8. Describe, in the context of all you have experienced with this activity and what we have discussed, what the connections are between both segments of the activity.

Quantum Mechanical Tunneling Post-Activity Interview Questions

1. Describe the particle in each of the cases (the classical, the NH$_3$/AsH$_3$ and the quantum dots).

   a. What is the difference between a “particle” as described in a classical system as opposed to a quantum mechanical system?

      i. (If sidetracked, rephrase slightly) Try to stick to the particle as an entity itself. Is there something different about the description of a “quote-quote” particle itself in a classical system and a quantum mechanical system?

2. How did potential energy play a role in each of the cases? (the classical, the NH$_3$/AsH$_3$, the quantum dots, the core/shell quantum dots).

   a. What was the nature of the potential energy in each? Start with the classical system and work your way up to the others.
i. (If sidetracked) Try to focus only on the potential energy itself. What were the similarities or differences in its nature across the activity?

3. Describe the role the barrier played in each case.
   a. What kind of energy constitutes the barrier in every case?
   b. Are there differences in the ways in which particles were able to cross or not cross the barrier? How so?
      i. (If tunneling is not mentioned) What is the process referred to as in a quantum mechanical context? When is the term appropriate?

4. In each case, how were events observed measured or quantified?
   a. How did you measure the energy related to the ball and ramp apparatus?
   b. How did the experimental results you were given provide evidence for what was happening energetically with the NH$_3$/AsH$_3$ system and the core/shell quantum dots?
      i. (If splitting and red-shift are not mentioned) In the NH$_3$/AsH$_3$ system, you observed that there is a splitting in the former, but not in the latter. What does this have to do with the potential barrier? In the ZnS/CdSe core/shell system, what occurs? How do these compare with the classical case?

5. Events were defined within the activity. How did the number of measurable events change from the classical to the quantum world?
   a. What does this have to do with the scale and nature of the systems? Does this factor into experimental observations? Please elaborate.
i. (If more elaboration is needed) Is it possible to measure every single vibrational or electronic transition of every molecule or nanostructure in an instrument that does not perform single-molecule spectroscopy? How, then, do we infer about a system in which we can only measure some of the objects under study? How is this similar or different from the classical case?

6. What are the limits in each case for the particle transcending the barrier?
   a. How are the limits different in a classical system as opposed to a quantum system?
      i. (Elaboration—if necessary) What is meant by the term “classically forbidden”? Contextualize that in terms of this activity.
      ii. How high must the barrier truly be in order for a quantum mechanical system to not have any probability to transcend the classically forbidden?

7. Describe, in the context of all you have experienced with this activity and what we have discussed, what the connections are between each segment of the activity.
   a. (More specific) How is the ball-and-ramp portion related to the NH$_3$/AsH$_3$, quantum dot and core/shell quantum dot portions?
      i. Specifically, what are the components that are common or uncommon between each? You can reflect upon our discussion here and the questions you answered within the activity itself. Be as thorough and detailed as you can.
Dye-Sensitized Solar Cells Post-Activity Interview Questions

1. In which part of the clay portion of the activity did you have the greatest surface area available?

2. How did the act of cutting the clay into smaller pieces affect the number of beads relative to the total mass of clay?

3. In which case does the diameter of the bead measure largest relative to the mass of clay it immediately occupies?

4. The absorption cross section of a molecule is, essentially, a measurement of its “exposure” to incoming electromagnetic radiation at which point an absorption event can occur. It is directly related, in this sense, to the extinction coefficient at a given wavelength. What is the importance of this value in the context of this activity?
   a. To which component of the solar cell would this parameter apply?

5. You took measurements of efficiency of the solar cells you constructed and matched up the cells with a specific TEM image of the semiconductor surface (the TiO$_2$ annealed to the conductive glass). Why did you make the assignments you did?
   a. How do your choices relate to what you observed with the clay and the number of beads picked up?
      i. Think of the number of beads relative to the total mass of the class, the bead diameter relative to the mass of the individual piece, and how surface area plays a role.
   b. Which components from the clay and bead part of the activity are related to the determination of the solar cell efficiency?
c. What do the relationship between the beads and the clay have in common with the relationship of two important components in the solar cell? What are these components?
Appendix D

Additional Group Discourse and Post-Activity Interview Excerpts and Analysis

Acoustic Analogy Additional Group Discourse Excerpts

<table>
<thead>
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<th>AA Group Excerpt A1</th>
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| S3G4: *Which band is most likely to correspond to the mode travelling longitudinally with the rod. I have no idea what that means.*  
S4G4: *What’s a band?*  
S2G4: *One of these.*  
S3G4: *I think, right?*  
Investigator: *So, how many bands does each gold nanorod solution have?*  
S3G4: *Three? Or. I don’t know what you mean by bands.*  
S4G4: *Is it like a wrist band, or?* *(Laughs).* |

Student S4G4 is unaware of the terminology “band” insofar as it is applied to spectroscopy. This is another background-related issue, though it was not probed for in the pre-activity interview (student S4G4 was determined to have a high level of background knowledge).

Student S3G4 is also unaware as to what a band is in this context, and mistakenly states (or, more likely, guesses) that there are three bands for each nanorod solution. Further investigator intervention was required in order to guide students:

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<th>AA Group Excerpt A2</th>
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| Investigator: *This is one solution, these are the other solutions right?*  
S2G4: *So they each have one band, right?*  
S3G4: *No, they each have. See, I don’t know, I still don’t know what you mean by bands.*  
Investigator: *(Pointing to spectra). This is one band, this is the other band. This is one band this is the other band.*  
S3G4: *Ok, so just where it spikes, I guess?*  
S2G4: *They each have two? Ok. Um.*  
S3G4: *I’d say it’s the highest one, right? I don’t.*  
S2G4: *For the z-axis?*  
S3G4: *Yeah.* |

Upon this intervention, student S3G4 refers to a band in a somewhat more normative sense in that they identify a band as where the spectrum “spikes.” The students still have not formed
definitive conceptions as to where the transverse and longitudinal bands lie. As is clear from the excerpt, much of the discussion at this point is speculation without any reasoning provided based on evidence. This required yet more investigator intervention:

**AA Group Excerpt A3**

Investigator: *Look at the schematic.*
S3G4: *Oh, so these are all equivalent, because these are the x and the y. And this is what’s going to be different. Because the z’s are all different, right? Let’s go back to the question.*
S2G4: *Ok, so it is the highest one.*
S3G4: *No, it’s just the first one. This is x, that’s y. Maybe. Is that?*
Investigator: *This here is not a band. This is a band and then these are bands.*
S3G4: *Ok.*
S2G4: *So the first band is the z-axis?*
S3G4: *No, no, no. The second band is. The second band is going to be the one that’s different. Because. Wait, do they all have the same diameter? Or do they have the same.*
Investigator: *That’s for you guys to figure out.*
S3G4: *Ok, well, they, I’m pretty sure they have the same diameter.*
S2G4: *The second band is the.*
Investigator: *What do you define as diameter?*
S3G4: *What do you mean?*
Investigator: *Like, on the schematic, what would you define as diameter?*
S3G4: *The x and y.*
S1G4: *Like the maximum or the?*
Investigator: *Then yes.*
S1G4: *Ok, and so these are in the same spot?*
S2G4: *So those are x and y?*
S1G4: *And then there are different ones?*
S3G4: *Yeah, because they’re different lengths.*
S1G4: *Ok.*
S3G4: *And that’s the z axis.*

The moment after the investigator asks the group to refer back to the schematic, student S3G4 becomes aware, as indicated by their comparison and contrastive statement, that any bands pertaining to x and y are equivalent between each of the nanorod solutions. Though the two follow up statements are misconceptions, due to the students focusing on the wrong portions of the absorption spectra, brief investigator intervention to point out which are bands
sets students on the correct path. Student S2G4 initially thinks that the first band corresponds to the $z$-axis, but this misconception is quickly reformulated by student S3G4’s awareness that, for a constant diameter, the second (longitudinal) band will be changing between solutions. The investigator asks questions to ensure that the students’ definitions of the diameter show this, which is confirmed by S3G4. Through the investigator’s careful intervention, the students are able to close in on a scientifically normative interpretation of the relationship between the electronic absorption spectra and the schematic of the nanorod.

Once students reached the challenge question pertaining to the dielectric tensor, the following exchange took place:

<table>
<thead>
<tr>
<th><strong>AA Group Excerpt A4</strong></th>
</tr>
</thead>
<tbody>
<tr>
<td>Investigator: <em>So what do you guys notice about the matrix in the equation? About the terms in the matrix?</em></td>
</tr>
<tr>
<td>S3G4: <em>They’re all the same.</em></td>
</tr>
<tr>
<td>Investigator: <em>Ok. And what are they describing?</em></td>
</tr>
<tr>
<td>S3G4: <em>The displacement.</em></td>
</tr>
<tr>
<td>Investigator: <em>A star, a, uh.</em></td>
</tr>
<tr>
<td>S3G4: <em>A sphere.</em></td>
</tr>
<tr>
<td>S2G4 (simultaneously): <em>Sphere.</em></td>
</tr>
<tr>
<td>S3G4: <em>So that’s in three dimensions, so we only need two dimensions?</em></td>
</tr>
<tr>
<td>Investigator: <em>So, the rod’s still in three dimensions.</em></td>
</tr>
<tr>
<td>S3G4: <em>Oh yeah, so I guess that’s a good point. (Laughs).</em></td>
</tr>
<tr>
<td>S2G4: <em>But aren’t y and x the same? Oh wait, they are.</em></td>
</tr>
<tr>
<td>S3G4: <em>Ok, so one of these needs to be changed.</em></td>
</tr>
<tr>
<td>S2G4: <em>We just said that. Y and x, actually, I just said it. But.</em></td>
</tr>
<tr>
<td>S3G4: <em>Yeah, y and x are the same but the z needs to be changed. Modify the equation to describe the displacement in a nanorod.</em></td>
</tr>
<tr>
<td>Investigator: <em>So if you were to rewrite the expression.</em></td>
</tr>
<tr>
<td>S3G4: <em>Rewrite the matrix? Or rewrite the expression?</em></td>
</tr>
</tbody>
</table>

What is particularly notable in this excerpt is, first, that student S3G4 makes the physical observation statement that only two dimensions are needed once the students have realized that the terms in the matrix describe a sphere. This is not true in a rod-like object, since even
the conversion to cylindrical coordinates (as an approximation) would constitute three dimensions, though there would only be two variables \((r, \theta)\) for constant length. The statement is addressed by an investigator intervention, after which S2G4 and S3G4 agree that only one dimension needs to be modified. Also of note is S3G4’s question at the end of the excerpt, concerning rewriting the matrix or the expression. The two entities are, essentially, one in the same—it is merely an expansion of the matrix multiplication that leads to the expression.

Later, the students still struggle a bit with modifying the terms within the dielectric tensor:

**AA Group Excerpt A5**

<table>
<thead>
<tr>
<th>S2G4 (Interjects):</th>
<th>Wait, you have to actually rewrite it?</th>
</tr>
</thead>
<tbody>
<tr>
<td>Investigator:</td>
<td>Yeah. You could just write the product of those two matrices there. I won’t make you write out the, the expanded form.</td>
</tr>
<tr>
<td>S4G4:</td>
<td>What are we doing?</td>
</tr>
<tr>
<td>S2G4:</td>
<td>We have to write the matrices or the product.</td>
</tr>
<tr>
<td>S3G4:</td>
<td>So, I really haven’t done matrices in a while.</td>
</tr>
<tr>
<td>S2G4:</td>
<td>Basically, just, is it two plus this? I don’t.</td>
</tr>
<tr>
<td>Investigator:</td>
<td>The equation would be the exact same form, it’s just a matter of what are you designating differently.</td>
</tr>
<tr>
<td>S3G4:</td>
<td>We’re just going to put this one as like e3?</td>
</tr>
<tr>
<td>Investigator:</td>
<td>You can do that.</td>
</tr>
<tr>
<td>S3G4:</td>
<td>Just do that. And then, uh.</td>
</tr>
<tr>
<td>Investigator:</td>
<td>Why that one though?</td>
</tr>
<tr>
<td></td>
<td>...</td>
</tr>
<tr>
<td>S3G4:</td>
<td>I guess it’s just an imaginary term, and it’s not going to matter anyway.</td>
</tr>
</tbody>
</table>

Students S2G4 and S3G4 struggle with the rewriting of the terms, and this requires more investigator intervention. S3G4 makes a background statement, indicating that they have not done matrix mathematics for some time, which would be a possible explanation for their earlier question about rewriting the matrix as opposed to the expression. After the investigator intervenes and lets students know that the form of the equation is the same, but
only the terms are modified, S3G4 makes an interesting statement about the imaginary term: they assume that it can be disregarded. The understanding of complex numbers in order to interpret dielectric functions is crucial.

**AA Group Excerpt A6**

<table>
<thead>
<tr>
<th>S2G3: <em>(Reads first question aloud).</em></th>
</tr>
</thead>
<tbody>
<tr>
<td>S7G3: <em>Just because they’re different densities, right? Same thing as the tuning forks.</em></td>
</tr>
<tr>
<td>S5G3: <em>What did we decide?</em></td>
</tr>
<tr>
<td>S1G3: <em>The densities.</em></td>
</tr>
<tr>
<td>S6G3: <em>Density. That’s always the answer.</em></td>
</tr>
</tbody>
</table>

Student S7G3 makes a direct comparison and contrastive statement linking the different densities in the tuning forks to the different densities in Au and Ag nanostructures. However, as developed earlier, the mapping in this case is undesired. What is desired is the connection between different densities of tuning fork materials (Al alloy and brass), and different dielectric functions in the Au and Ag nanostructures (both object attributes are intrinsic properties; therefore, the base maps to the target domain). S6G3 makes a comment that density is “…always the answer.” This is particularly troubling, in the way that statements that include “always the answer,” without proper justification, undermine the level of critical engagement that students are intended to partake in while doing the activity.

Students within group 3 try and qualify the differences in densities of Au and Ag:

**AA Group Excerpt A7**

<table>
<thead>
<tr>
<th>S2G3: <em>Oh, I’m reading this backwards. Yeah. It’s the silver. And which one’s more, more dense?</em></th>
</tr>
</thead>
<tbody>
<tr>
<td>S1G3: <em>I was just thinking the-.</em></td>
</tr>
<tr>
<td>S2G3 <em>(Interjects): “I think silver is more dense, because gold floats. Gold floats, gold particles.”</em></td>
</tr>
<tr>
<td>S1G3: <em>I have no idea.</em></td>
</tr>
<tr>
<td>S2G3: <em>I think, is silver not more dense than gold?</em></td>
</tr>
<tr>
<td>S1G3: <em>Is it not on there?</em></td>
</tr>
<tr>
<td>S6G3: <em>I don’t know.</em></td>
</tr>
<tr>
<td>S2G3: <em>I think silver is more dense on gold, because-.</em></td>
</tr>
</tbody>
</table>
S6G3 (Interjects): *I can tell you.*  
S2G3: *Gold particles float on water.*  

Student S2G3 is insistent on guiding the group’s discourse towards considering the densities. 

They make the argument that gold is less dense than silver, given that gold can float on water. In reality, silver is more dense than gold. The operative issue to take into consideration, however, is that the fixation is still on density while it ought to be on the dielectric functions or, at the very least, on intrinsic properties as a whole. 

In the Fourier transform module: 

**AA Group Excerpt A8**

<table>
<thead>
<tr>
<th>Student</th>
<th>Quote</th>
</tr>
</thead>
<tbody>
<tr>
<td>S7G3</td>
<td><em>Didn’t the frequency just change the amplitude or something? It was, like, the highest amplitude had something to do with the frequency.</em></td>
</tr>
<tr>
<td>S5G3</td>
<td><em>Let’s go with that.</em></td>
</tr>
<tr>
<td>S4G3</td>
<td><em>Write it down.</em></td>
</tr>
<tr>
<td>S7G3</td>
<td><em>Frequencies affected the amplitudes of the waveforms or something like that.</em></td>
</tr>
</tbody>
</table>

At this point, the language is utilized by students in a completely anomalous form. 

Frequency, according to S7G3, is simply linked to the amplitude of the waveform without scientifically normative justification. The rest of the group members who were participating in the discussion seem to be content to accept the ambiguous answer and move on to the next portion of the activity. 

Student S3G4, at the end of the following exchange, summarizes the extent to which the Fourier transform module could have, in its current form, on even upper division students: 

**AA Group Excerpt A9**

<table>
<thead>
<tr>
<th>Role</th>
<th>Quote</th>
</tr>
</thead>
<tbody>
<tr>
<td>Investigator</td>
<td><em>Just, just contextualize it in terms of what it is a function of.</em></td>
</tr>
<tr>
<td>S4G4</td>
<td><em>Amplitude or waveform?</em></td>
</tr>
<tr>
<td>Investigator</td>
<td><em>The amplitude is a function of what in the waveform?</em></td>
</tr>
<tr>
<td>S3G4</td>
<td><em>Amplitude of this?</em></td>
</tr>
</tbody>
</table>
S1G4: We’re still talking about time, right?
S3G4: Yeah, the other one’s hertz.
S2G4: So just change it to frequency.
S3G4: Yeah, just change the x axis really. That’s all I’m getting out of this. I mean, I don’t know what else to put for that.

The students’ view seems to be that the result is just to change the x-axis. While, on a surface level, this is true, the reason motivating the change in the axis (the mathematical procedure behind the transform itself) is apparently lost in translation.

An interesting discussion is developed in group 1:

**AA Group Excerpt A10**

S5G1: Well the question is asking why, why does the sound go away when you touch it, right?
S3G1: No, it’s what is leading to the production of sound. I said the vibration of the prongs is vibrating the air molecules and that is propagating and your ear drum’s picking it up. It’s simply to show that stopping the vibration of the prongs stops the production of sound, so therefore sound is vibration.
S6G1: What is the height of the wave, like.
S1G1: Amplitude.
S5G1: Like, how hard you hit it?
S6G1: It’s either the amplitude, or, basically, look, this vibrates a lot more, right? So it’s distance from that equilibrium point is going to be twice as far as this one.

At this point of the discourse, student S3G1 makes a scientifically valid and normative argument as to what is leading to the production of sound. However, student S6G1 diverts the discussion towards focusing on the amplitude of the sound produced. This leads to a misconception that is reformulated by the students as the discourse continues:

**AA Group Excerpt A11**

S6G1: The distance, like the farthest distance from the equilibrium point of the oscillation of this (the shorter tuning fork) is going to be twice as much as this (the longer tuning fork). That’s why they’re the same note. Twice as much, or some factor. Probably, like, a factor of pi actually.
S5G1: The reason is the frequency, like, if you have one wavelength, have that one, and then you just have, like, they fit together and that’s what causes them to be the same note.
S6G1: Like, ok, if this is the equilibrium position, right?
S5G1: I don’t know if it has anything to do with amplitude. Amplitude is how much-
S6G1 (interjects): Amplitude is how loud it would be, and this is time, and this would be, uh.
S1G1: It would be the period of the-
S5G1 (interjects): Yeah, I’m saying, so like if they fit together, if every note is the same, that’s what makes them sound the same. But one would have more nodes than the other.
S6G1: Right, so it either looks like, the other graph, it either looks like this, see what I’m saying, so it’s twice, it still has the same note, yeah, like there, or I was saying, it could look like that (amplitude based), but you’re saying that wouldn’t matter.
S5G1: Yup.
...
S6G1: You’re right, (name of S5G1), about this. Because it’s a longer wavelength if it’s longer, so it’s gonna have the same nodes, it’s just that this has more nodes. That’s why it goes back and forth faster.
S5G1: Mhm.
S6G1: So it doesn’t vibrate as fast.
S5G1: That’s what I was; they were the same amplitude.
S6G1: The amplitude just depends on how hard you hit it.

Initially, student S6G1 continues to argue that the amplitude of oscillation is what leads to the differences in pitch observed. However, S5G1 refutes this notion and instead suggests that the relative positions of the waves (i.e. comparing the wavelengths) between different tuning forks is what’s important. Student S6G1 begins to take part in reformulating their own misconception when they comment on the fact that the amplitude is simply proportional to how hard the fork is struck. Though the number of nodes is simply related to the quantized energy levels of the sound produced (e.g. a given overtone within one fork would have more nodes than a fundamental, not the fundamentals compared between two tuning forks), and this constitutes a misconception in its own right, the focus of the discussion properly shifted towards characterizing the difference in pitch as a difference in frequency and away from anomalously relating it to amplitude.

Consider the following excerpt from group 4:
**AA Group Excerpt A12**

S2G4: *(In reference to question 3)*. What is exciting these?
S3G4: The light.
S2G4: Oh, the light?
S3G4: Yeah, the IR.
S4G4: Hmm. This is pretty cool, I’ve never seen that before.
S3G4: It’s still just putting energy.
S2G4: Putting energy into the system?
S3G4: It’s saying compare this to what you needed to do with the forks, they’re both yeah, putting energy into the system.

Note that S3G4 recognizes that the light is leading to the excitement of the plasmon modes, as seen in the absorption spectra. Further, through their comparison and contrastive statement at the end of the excerpt, they are able to characterize both cases as introducing energy into the system.

*Acoustic Analogy Additional Post-Activity Interview Excerpts*

It is important to mention that students were very effective in the base knowledge domain, as they directly experienced the properties of and relationships among the tuning forks. This is exemplified in the following excerpt from student S2G2’s post-activity interview:

**AA Post-Activity Interview Excerpt A1**

Investigator: *Describe the process the tuning forks underwent in order for sound to be detectable.*
S2G2: Um, they were struck on the table.
Investigator: Um, what was required for a sound to be detectable from the tuning fork? Like, specifically.
S2G2: What was required for a sound to be heard?
Investigator: Yeah.
S2G2: Um, for them to vibrate. The prongs to vibrate.

Note that S2G2 is aware of the fact that the tuning fork prongs had to vibrate, upon being struck, in order for the sound to be heard. This is, ostensibly, a result of students’ direct experiences with the materials.
**AA Post-Activity Interview Excerpt A2**

Investigator: Why were the absorption wavelengths significantly different in gold and silver nanoparticles despite their being of similar average diameters?

S2G1: Um, I guess it would have to be the intrinsic property of, some intrinsic property of each metal. We possibly thought it could’ve been density.

Investigator: H-, how does that relate to the tuning fork portion of the activity?

S2G1: Um. Can you repeat the first question one more time?

Investigator: Uh, why were the absorption wavelengths significantly different in the gold and silver nanoparticles despite them being of similar average diameters?

S2G1: Ok, uh, they were different, I mean they were, the tuning forks were different; one was an all-, like one was an alloy of brass and then one was aluminum, so intrinsic properties within those forks also affected how they, um, the frequency after they were struck on the um table.

Though student S2G1 properly designates the properties causing the differences in LSPR absorption frequencies as intrinsic, they still harbor the misconception that it was the density of the metallic nanomaterials that led to these differences. Their argument in the latter part of the question is more general, yet more contextually appropriate when mapping from base to target. The student uses their comparison and contrastive statement pertaining to the brass and aluminum tuning forks to argue that the intrinsic properties led to different frequencies in the tuning forks.

In their overall assessment of the connections present in the activity, students tended to focus appropriately on the length (or size) and intrinsic properties (usually density).

**Quantum Mechanical Tunneling Additional Group Discourse Excerpts**

**QMT Group Excerpt A1**

S1G1: So did we do those questions, “comment on any difference of the energy levels…”

S2G1: Yes.

S1G1: What did we say?

S2G1: Confinement effect.

S1G1: Well that’s just two words. What the, what the (expletive) does it mean?

S2G1: Well in the event of the infinite box, you know, just CdSe in a (sic) organic matrix, you have effectively an infinite box. In the case that you coat it with the ZnS you give it a squishy outer layer. You give the box, um, not so rigid sides. Instead of a steel box, you make it like a
paper bag.
S5G1: So it loses some energy.
S2G1: Yeah so it can relax a little.
S1G1: Pshhht. I give up on tunneling; I don’t understand tunneling...I just...
S5G1: Don’t think of it as tunneling, just think of it as like, ok, if you have like he was saying a metal box and you throw a bouncy ball in it, like it’s going to hit, like you know.
S1G1: I don’t see how this relates to any of this energy.
S5G1: Yeah, no, like that’s what I’m saying. Like it has much more strict, it has a lot higher energy because it’s bouncing off the walls like it’s very confined. Whereas if you put it in a big plastic bag that’s like blown up and you bounce it it’s going to smash into the walls and you know it’s going to have like, it’s going to lose a lot of energy because it’s not as confined.

Here, it is important to note that S5G1 built upon S2G1’s initial comparison and contrastive statement, utilizing an external base knowledge domain (the steel box and bag), and actually described the confinement effect along with tunneling in the context of the classical world (spontaneous external transfer). S1G1, having become very frustrated and, in a largely peer-occupied environment, utilizing the language expected of their surroundings, expressed the frustration and the group responded with support as dictated by their learning environment (peer group) and prior knowledge (everyday experience with the classical world).

Quantum Mechanical Tunneling Additional Post-Activity Interview Excerpts

<table>
<thead>
<tr>
<th>QMT Post-Activity Interview Excerpt A1</th>
</tr>
</thead>
<tbody>
<tr>
<td>Investigator: Um, describe in the context of what you’ve experienced in the activity and what we’ve discussed, um, what the connections are between each segment of the activity. S3G2: So I guess when comparing the three activities, we would look at a system and we would look at sort of an excitation or the first one you can think of it as an excitation, and we compared the macroscopic classical mechanics versus the microscopic quantum mechanics and we saw that there were differences. Investigator: Ok, um, so, specifically like what are the components that are common or uncommon between each? S3G2: So we saw the quantum examples exhibited tunneling as sort of an extra factor into what was going on and so that just shows that there are more events that dictate I guess the quantum mechanics versus the classical mechanics.</td>
</tr>
</tbody>
</table>
QMT Post-Activity Interview Excerpt A2

Investigator: Describe in the context of what you’ve experienced with the activity and what we’ve discussed, um, what the connections are between each segment of the activity.
S1G1: Um, the classical sense one was just making us understand the potential energy in the classical sense, how everything has to work for cer-, you can like, it’s analogous to reactions and stuff like that. And for NH, the NH₃ one, you get into a little bit more, you, you kinda go in between the classical and the quantum, quantum um theory. For this one, you can understand that if you pass through the energy barrier, you can go to the other inverted position, but there’s also a tunneling effect in which it can go through when you get to that one. Quantum dots, it’s, um, you go through the straight quantum sense and you don’t no-, you no longer have to break the barrier, you can go out, you can actually go outside of it.

QMT Post-Activity Interview Excerpt A3

Investigator: Ok, so, um describe the particle in each of the cases, the classical, the ammonia part, and the quantum dots.
S1G2: Alright, so the classical one we’ll start with, uh, the particle was confined in a (sic) organic solvent with infinite potential, so basically it was, you know, the standard particle in a box. Um, so, it was able to, there was, there was no tunneling effects given the infinite potential, so basically just followed, um, the you know we did it at different energy levels, uh, it followed, you know, standard.

Here S1G2 errantly refers to the particle-in-a-box as being related to the classical case. It is unclear as to whether or not this was simply an accidental statement or a true misconception, but it is still not a scientifically normative statement as it stands.

Dye-Sensitized Solar Cells Additional Group Discourse Excerpts

DSSC Group Excerpt A1

S1G3: (Laughs) It says construct an argument based on what’s here.
S3G3: That’s an argument.
S2G3: It’s a good argument.
S1G3: [Reads response]. Cell B because it packs better. Ok. I can see that. Cell B because it’s more efficient.

Student S1G3’s physical observation statement that the more efficient cell simply “packs better” constitutes another example of students’ focus on their perceptions of packing
efficiency as opposed to higher surface area available for dye chemisorption. As students’ meaningful discourses in this particular activity were limited, likely due (in part) to the high demand of focusing on physically constructing the cells, it is informative to turn to the post-activity interviews.

*Dye-Sensitized Solar Cells Additional Post-Activity Interview Excerpts*

A post-activity interview example of a student utilizing a packing efficiency argument is that of student S2G3:

### DSSC Post-Activity Interview Excerpt A1

**Investigator:** Um, it’s just one versus the other. Um, and, uh, where was I. Yeah, so you matched them up with a specific TEM image, uh, of the semiconductor surface, uh, which represents the TiO$_2$ annealed to the conductive glass. Uh, why did you make the assignments you did?

**S2G3:** I think we chose this assignment. I think. I think it was based basically on the packing of the cells, just looking at this, how each one was packed, how this one was, it seemed, I don’t know if ordered is the right word, there seemed to be less empty space with this as compared to that.

Student S2G3 makes the physical observation statement that the group made their higher efficiency selection, based on the TEM images of anatase and rutile nanostructures, by selecting the one which appeared to have less empty space. This is in congruence with the statements made by S1G1 in their post-activity interview. Another example of such packing efficiency arguments can be found in S3G1’s interview:

### DSSC Post-Activity Interview Excerpt A2

**Investigator:** Which one, the left or the right, do you think would, um, would correspond to the more efficient cell and why?

**S3G1:** I would say the right, because they seem smaller so they have more efficient packing.

**Investigator:** Mhm.

**S3G1:** There’s less wasted space.

**Investigator:** Mhm. Um. How do your choices relate to what you observed with the clay and the number of beads picked up? Like how does that choice...
S3G1: *The, uh, when you made the clay blocks smaller they would pick up a greater, a greater number of beads relative to their mass.*

What is particularly interesting about S3G1’s response is the fact that they did not invoke the packing efficiency when referring to the base knowledge domain, though the student was explicitly asked how the choice of the TEM image related to the clay and bead part of the activity. It would appear, in general, that the reference to packing derives largely from the target domain, as there was no portion in the base part of the activity demanding that students attempt to close-pack the clay pieces. Therefore, it is plausible that the focus on packing efficiency stems from students’ prior exposure, likely at the general chemistry level, to close-packed structures when learning the basics of solid state chemistry. Though this postulation is not explicitly expressed (i.e. no student made any direct reference to solid state close-packed structures), this would possibly be an example of external interference in the analogical transfer process.

The relation of the beads and clay to the target domain is present in post-activity interviews. For example, consider this excerpt from student S2G1’s post-activity interview:

**DSSC Post-Activity Interview Excerpt A3**

Investigator: *Um, you took measurements of efficiency of the solar cells, uh, that you constructed, and matched up the cells with specific TEM image of the semiconductor surface, you know the TiO2 that’s annealed to the conductive glass. Um, why did you make the assignments you did? And I have them here. So, this is to jog your memory.*

S2G1: *Um, because the more efficient one had the smaller, um, I guess molecules, or packing. Like, more efficient packing, so…*

Investigator: *Ok, so which one on there is representative of that, the left or the right or.*

S2G1: *Right. The ‘c.’*

Investigator: *Ok. And, um, and h-, how do your choices relate to what you observe with the clay and the number of beads picked up?*
S2G1: Um, the same way those, um, smaller blocks of clay picked up more beads, so the smaller molecules that packed better would, uh, absorb more.

Of note here is the fact that the connection between the smaller blocks of clay (higher available surface area) picking up more beads is immediately related to the efficiency of packing, which was highlighted earlier as part of the students’ major challenges. However, upon further probing, the student’s answer becomes significantly more refined and the proper transfer more readily apparent:

<table>
<thead>
<tr>
<th>DSSC Post-Activity Interview Excerpt A4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Investigator: Ok. Uh. Ok. Which components from the clay and bead part of the activity are related to determining the solar cell efficiency? I think you kind of said it already, but, um.</td>
</tr>
<tr>
<td>S2G1: I don’t understand what you’re asking.</td>
</tr>
<tr>
<td>Investigator: Oh, what I’m saying is, um, which components from the clay and bead part of the activity, like from the beginning, are related to dye, are related to the determination of the solar cell efficiency?</td>
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<tr>
<td>S2G1: So like the size of the clay?</td>
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<tr>
<td>Investigator: Mhm. And, um, anything else.</td>
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<tr>
<td>S2G1: And the amount of beads would be the amount of, um, dye particles that would absorb. That can attach to the molecule.</td>
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<tr>
<td>Investigator: Ok. And then, finally, um, what do the relationships between the beads and the clay have in common with the relationships of, uh, two of the important components in the cell? And which are these components? Which, again, I think you already said.</td>
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<tr>
<td>S2G1: Yeah, it’s the, um, the clay would be like the molecules and the beads that cover it would be like the, um, er I’m sorry the TiO₂ molecules, and the beads that cover it is the dye and it’s how much, how efficient they can do that.</td>
</tr>
</tbody>
</table>

Here, S2G1 explicitly links, with their comparison statements, the clay to the TiO₂ structures and the beads to the dye molecules. Though they improperly refer to the TiO₂ as a molecular substance, there is an understanding that the number of dye molecules on the surface of the TiO₂ nanostructure is directly related to efficiency, and that the base part of the activity (the clay and beads) is representative to this relationship.