Research article

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Educational reconstruction of size-depended-properties in nanotechnology for teaching in tertiary education

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Abstract: There is an overarching theme in Science Education to integrate in the school and university curriculum interdisciplinary state-of-art innovations. The field of Nanotechnology is such an example, because it combines the aforementioned interdisciplinarity and novelty with a well-documented educational value. Herein, a novel teaching approach concerning size-dependent properties at the nanoscale for chemistry and physics undergraduate students is proposed. The analysis of the scientific content and its following reconstruction for teaching purposes is based on the theoretical framework of the Model of Educational Reconstruction (MER). This analysis yielded two fundamental concepts and a series of activities that can be the main core of teaching Nanotechnology at a university level.

Keywords: model of educational reconstruction; nanotechnology; science education; tertiary education.

Introduction

Nanoscale Science and Engineering (NSE), is a novel interdisciplinary field of modern science. Studies in NSE consist of the manipulation of matter at the nanoscale (typically 1–100 nm) in order to yield novel properties, e.g. optical, mechanical, biological (Bhushan, Luo, Schricker, Sigmund, & Zauscher, 2014). Many of those properties are size-dependent, meaning that the size of the nanostructure directly affects the material's macroscopic properties (e.g. optical properties of quantum dots) (Biju, Itoh, Anas, Sujith, & Ishikawa, 2008). The application of such materials in various fields like medicine, environmental studies, and the food industry are already well studied in the literature (Deka, Mojumbar, Parisse, Onesti, & Casalis, 2017; Rezaei, Boroujeni, & Ensafi, 2016; Wang, Qu, Shao & Jiang, 2011).

A variety of studies underscore the enhancement of student's nano-literacy (Bhushan, 2016; Jones, Gardner, Falvo, & Taylor, 2015; Stevens, Sutherland & Krajcik, 2009) and a wide range of educational projects based on NSE have been already implemented (Jackman, Cho, Jackman, Sweeney, & Cho, 2020). The main arguments about nanotechnology integration in science curricula underline its great educational value in terms of interdisciplinarity (Mandrikas, Michailidi & Stavrou, 2019) and of acquainting students with a novel

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concept of the nature of science using a state-of-the-art scientific field (Schank, Wise, Stanford, & Rosenquist, 2009). Moreover, Nanotechnology comprises a field that may act as a suitable context in order students to develop an understanding about core scientific ideas as “structure–property relationships” and their underlying principle that the physicochemical properties of materials are determined by the structure and composition of submicroscopic components (Talanquer, 2018). Finally, nanotechnology education researchers also highlight the fact that there is an increasing need for future scientists familiarized with NSE, in order to meet the needs of the employment markets (Healy, 2009). However, it is worth noting that most of the aforementioned studies are addressed to K-12 education, even though there is a fundamental value in the inclusion of NSE and size-dependent properties in tertiary education, as a great part of students’ career decisions is made during their university studies.

The inclusion of NSE and size-dependent properties in K-12 and tertiary education is not a novel idea and it has been the target of a wide variety of scientific studies. In K-12 in particular this inclusion is well documented in the literature of the last 10 years (e.g. Blonder & Sakhnini, 2012; Sakhnini & Blonder, 2015; Mandrikas, Michailidi, & Stavrou, 2019). An important milestone in these studies was achieved when Stevens, Sutherland, and Krajcik (2009) summarized the fundamental principles of NSE and highlighted their educational value in “Nine Big Ideas” (Table 1) divided into four categories. Each domain or discipline of NSE is represented in one or more of these Big Ideas (Stevens, Delgado, & Krajcik, 2010). Of them, the concept of size-dependent properties will be the main target of this study as it is described in Big Idea five by Stevens et al. This does not mean that the other Big Ideas are excluded from the study, since, as it is evident from Table 1, there is extensive overlap between them. For example, the first four Big Ideas act as the foundational science content, while the following two describe its application in different phenomena (e.g. self-assembly).

In tertiary education there is also an abundance of published studies aimed at the inclusion of NSE in university curricula, mainly as undergraduate laboratories (e.g. Jenkis, Wax, & Zhao, 2016; Winkelmann, Noviello, & Brooks, 2007). Specifically, many studies have been published on the inclusion of size dependent properties (e.g. magnetic or optical) as laboratory experiments like synthesis and characterization of gold nanoparticles (Larm et al., 2020) or iron oxide nanoparticles (Dalverny, Leyral, Rouessac, Bernaud, & Filhol, 2018).

Between these two approaches of including size-dependent properties in science curricula there is a distinct difference. In K-12 education, the vast majority of the published research is founded in a theoretical framework from the field of Science Education, while the educational reconstruction of the scientific knowledge of size-dependent properties for tertiary education is almost absent with the scientific content presented “as is” to the students. To the best of authors’ knowledge, only a few studies explored the inclusion of NSE in tertiary education (Rodgers, Kong, Dux, & Madhavan, 2014; Wansom et al., 2009) with educationally reconstructed scientific content.

Taking into consideration all aforementioned, despite the well-grounded need for familiarization of university students with the NSE concepts, the existing teaching approaches are not founded on educational reconstruction processes; instead, they tend to directly transfer scientific structures into teaching sequences. Educationally reconstructed NSE content for tertiary education will balance the science content and the cognitive and affective variables of students (Duit, Komorek, & Wilbers, 1997). The current study makes a first step towards this direction, describing in detail the didactic analysis (Klafki, 1995) of size-dependent optical properties of nanoparticles and its reconstruction according to the Model of Educational Reconstruction (Duit, Gropengießer, Kattmann, Komorek, & Parchmann, 2012). Additionally, a number of activities are proposed in order to introduce these concepts in a teaching learning environment. This reconstruction is an ongoing investigation of development and evaluation of teaching–learning sequences for undergraduate students, mainly chemists and physicists.

Table 1: The nine big ideas, according to Stevens, Sutherland, and Krajcik (2009).

Number	Name	Category
1	Size and scale	Foundational science content
2	Structure of matter	Foundational science content
3	Forces and interactions	Foundational science content
4	Quantum effects	Foundational science content
5	Size-dependent properties	Applying the foundational science content
6	Self-assembly	Applying the foundational science content
7	Tools and instrumentation	Moving NSE forward
8	Models and simulation	Moving NSE forward
9	Science, technology and society	NSE and society

Methodology

Model of Educational Reconstruction

The "Model of Educational Reconstruction" (MER – Kattmann, Duit, Gropengießer, & Komorek, 1997) has been developed as a theoretical framework for studies investigating if a particular science concept, principle or process is possible to be taught to a specific audience. This framework is embedded in the European Didactic tradition and its goal is to balance science content and educational concerns in development of teaching learning sequences (Meheut & Psillos, 2004). Since its introduction, MER has been proven a powerful framework in a number of studies by various researches (Johann, Groß, Messig, & Rusk, 2020; Kersting, Henriksen, Boe, & Angell, 2018; Stavrou & Duit, 2014; Stavrou, Michailidi, & Sgouros, 2018).

The MER consists of three interconnected pillars (Duit, Gropengießer, Kattmann, Komorek, & Parchmann, 2012):

- the clarification and analysis of science content
- the exploration of students' perspectives on this content
- the development of teaching–learning environments

According to the MER, the scientific content is reconstructed from domain-specific knowledge into schooling knowledge which will contribute to the student's scientific literacy. That is why the first and primary focus is set on the analysis of subject matter, both from an academic and an educational viewpoint. Particularly, the MER is founded on Klafki's concept of didactic analysis, according to whom, there are specific factors that have to be taken into account when designing an instruction or a teaching and learning sequence:

- the detection and clarification of the elementary features of the general idea that is to be taught (e.g. phenomena, principles, laws, methods).
- the pedagogical significance of that content knowledge for students' academic life.
- the significance and relevance of that knowledge to students' everyday life.
- the appropriate structuring of the detected elementary features into a teaching sequence, taking into account students' perspectives.
- the particular content representations (e.g. experiments, pictures, situations, models) that are appropriate to render the content interesting and understandable for the students.

Based on the above, the first step towards the educational reconstruction of a topic is the process of *elementarization*. The term *elementarization* refers to the clarification of a specific scientific content into a series of elementary concepts that will act as a basis for designing the final teaching and learning environment. These ideas must stem from both the clarification of the scientific content and the student's perspective. Afterwards, these elements are appropriately constructed, in order to be suitable for the targeted audience, and the teaching sequences and environments are designed (Figure 1).

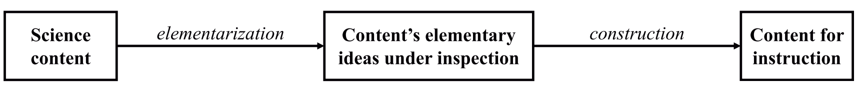

Figure 1: The steps towards the construction of a content structure for instruction (Duit, Gropengießer, Kattmann, Komorek, & Parchmann, 2012).

Applying MER framework in this study

In this study the theoretical framework of MER, with its main assumptions, guided us through the elementarization of the scientific content of size-dependent properties and specifically of the optical properties of nanoparticles into a series of fundamental concepts. Additionally, based on these concepts and on tertiary students' perspectives, a series of activities were developed as part of a teaching learning sequence.

Elementarization

The *elementarization* of size-dependent properties in Nanotechnology in this study led us to the following two fundamental ideas: (i) *"A material's intensive properties are affected by its size in the nanoscale"* and (ii) *"A materials properties are affected by the quantization of its energy levels"* What follows outlines the elementarization process that we pursued in order to end up to these core ideas.

A material's intensive properties are affected by its size in the nanoscale

There are many examples of metals, like gold and silver, which exhibit different colors for particles with a size of a few nanometers than their bulk counterparts. For the purpose of this study, we will refer to the term *color* as a macroscopic property that stems from excitations of electrons and the consequent energy release. Therefore, changes in this energy yield changes to the color of a compound and vice versa (causal relationship between color change and electronic excitation). The size-dependent optical properties in the nanoscale were initially attributed to a phenomenon called "quantum confinement" (QC) (Alivisatos, 1996). According to this, the reduction of size gives rise to changes in the density of electronic states of a particle. In other words, as the size of particle decreases its electrons are confined within the particle much like the "particle in the box" from elementary quantum mechanics (Serway & Jewett, 1983). A more recent theory is that the unique optical properties of a nanoparticle are related to surface plasmon resonance (SPR, Kelly, Coronado, Zhao, & Schatz, 2003). In SPR, the color change of a nanoparticle is attributed to oscillation of plasmons and the way they are affected by its size. For the purpose of the study, the optical properties of a nanoparticle will be explained in accordance with QC, since its foundation lies in classical quantum mechanics and – even though SPR explanation is a more accurate theory – it still has support within the scientific community (Sangwan & Hersam, 2020).

Size-dependent properties are embodied in Stevens et al. (2009) fifth Big Idea (Size-Dependent Properties). This Idea refers to unique properties that occur as the size of a material alters, especially between the nanoscale and the macroscale. Hence the fundamental content of this idea can be formed as: *"A material's properties are affected by its size in the nanoscale"*.

A material's properties are affected by the quantization of its energy levels

To clarify the scientific content of QC, it is necessary to examine the basic quantum principles it is based on. QC is based on the "particle in a box", which is a model that explains how the energy of a particle (an electron in this occasion) is affected when it is "trapped" within a well of infinite potential. In its simplest form ("one-dimensional box"), the particle cannot escape the "box's walls", owe to their infinite potential, meaning that at each wall its kinetic energy, and therefore its momentum, must be equal to zero. Since a quantum particle has a binary nature (De Broglie's principle), its wavefunction must be equal to zero at each wall. This creates a basic limitation in the wavelength's values, since – in order for the previous principle to stand – the particle's wavelength must be equal to an integer multiple of one half the "box's" length. Hence, a form of quantization is established in the model which, due to De Broglie's principle, leads to the quantization of particle's momentum and, by extension, its kinetic energy. In summary, the length of the "box" defines the particle's wavelength giving rise to an energy quantization (Serway, 1983). Therefore, energy quantization could be considered as the most essential part of PODB, since it is the base upon which the outcomes of QC can be deduced.

As a quantum phenomenon energy quantization is embodied in Stevens et al. (2009) fourth Big Idea (Quantum Effects) where it is included as a fundamental pillar. Additionally, energy quantization holds a special role in students' understanding of quantum mechanics and it can be argued that it is the underlying idea behind the shift from classical physics to quantum mechanics (Didis, Eryilmaz, & Erkoc, 2014). According to Didis et al. (2014), students find it difficult, even at an undergraduate level, to conceptualize that energy quantization is a natural phenomenon that particles exhibit only in confined systems. Many students describe quantization as a physical property of all particles, not only bound ones, hence it is important for this reconstruction to highlight the connection between a particle's confinement and the quantization of its energy.

The teaching sequence

A classroom intervention is proposed in the following section as a means of introducing the aforementioned fundamental concepts in a teaching learning environment. The steps of the proposed intervention follow.

Step 1: Introduction.

Aim: To introduce students to the unique optical properties of materials in the nanoscale.

Process: A small introductory discussion takes place on the use of gold in medieval times to create stained glass. The students are presented with a picture of stained glass, such as Figure 2, and are informed that the red hue in such stained glasses is derived from gold nanoparticles inside the glass (Varghese et al., 2019) which is in direct contrast with the common yellow color of gold. The students are asked to hypothesize structural differences between the nanoparticles in the glass and the macroscopic materials (like a gold bar or a silver jewel).

Step 2: Size-dependent optical properties.

Aim: To inform students about the size dependency of the optical properties of nanomaterials (CdSe nanoparticles).

Process: To further explore the unique phenomenon explored in the introduction a two-part activity is implemented. In this activity the CdSe nanoparticles are synthesized from a solution of trioctylphosphine selenide ($C_{24}H_{51}PSe$) and a solution of cadmium oxide (CdO) using oleic acid as a capping agent (Boatman, Lisensky, & Nordell, 2005).

Figure 2: An example of a medieval stained glass (as seen in https://commons.wikimedia.org/wiki/File:Vitrail_Chartres_210209_07.jpg, May 2021).

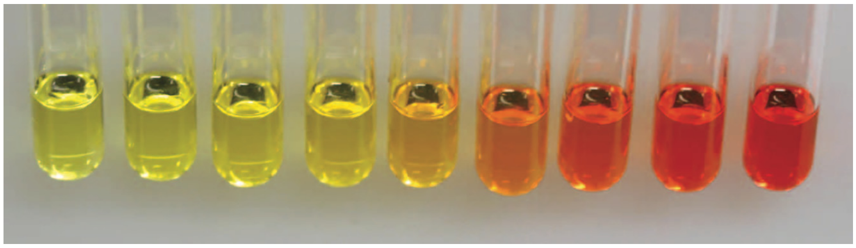

Figure 3: An example of nine samples of CdSe (Reprinted with permission Nordell K. J.; Boatman, E. M. & Lisensky, G. C. (2005), A safer, easier, faster synthesis for CdSe quantum dot nanocrystals, Journal of Chemical Education, 82 (11), 1697–1699. Copyright 2005 American Chemical Society).

In the first part a demonstration of the synthesis takes place, where the two solutions are mixed and heated to 225 °C. Since the mechanistic aspects are omitted from this activity, the two solutions are referred to as "Se solution" and "Cd solution" to the students. Due to high temperature, nanoparticles are formed and the color shifts from colorless to yellow. When this shift takes place a small amount of liquid (~0.5 mL) is transferred from the reaction pot to a 5 mL vial and it's quenched at room temperature. This transfer is repeated in quick succession until 9–10 samples are obtained (Figure 3). Due to the fact that the formation of the nanoparticles only takes place in high temperatures, at room temperature the colors of the different samples are stable and non-changing. Therefore, they can be observed by the students for the duration of the activity.

In the second part of the activity, the students are asked to discuss the difference in color of each sample, highlighting the fact that it is not only the color's intensity that changes (e.g. yellow shifts to deeper shades) but also the color itself (from yellow it shifts to red). It is pointed out that the color change takes place in the same reaction pot without the addition of any substrate or changes in the temperature of the mixture. Furthermore, it is clarified that only one reaction takes place with only one product, the CdSe nanoparticles and all these nanoparticles have the same Cd/Se ratio. After these inputs the students are tasked with hypothesizing the structural differences between the nanoparticles in each sample. The aim of this discussion is for students to reach the conclusion that the only difference among the samples is the size of the nanoparticles in them and therefore to recognize color as a size-dependent property of a nanoparticle. In this activity, students are introduced to the first part of the first fundamental concept. Specifically, they are introduced to the idea that a material's properties are not inherit to it, but are affected by its size.

Step 3: A material's energy levels are dependent on its size.

Aim: The aim of this activity is to support students in understanding how the quantization of an electron's energy levels arises from its confinement and how a particle's size correlates with the energy gap of these levels.

Process: After the students are introduced to this phenomenon by the previous activity a more direct link between size and color is attempted by the following activity. This activity is based on an online freeware called wavefiz (as seen in http://ridiculousfish.com/wavefiz/, March 2021). This simulation offers a variety of PODB models but only one (Infinite Square Well) will be part of this activity as it is the simplest form of the PODB models. At the beginning of the activity the students are reminded of the conclusions they reached during the previous activity. Subsequently they are given a scenario alongside the simulation. They are told that the simulation depicts the dissection of a metallic "nanoparticle" and that they are watching a single electron (as a wave) moving inside it (Figure 4). In this scenario the potential well represents a "nanoparticle's" diameter while the wavefunction ψ and its corresponding ψ^2 are simple representations of an electron's wave-like behavior (the "shape of the wave") and they are free to choose the former or the latter when they operate the simulation.

In the first part of this activity, students are tasked with changing the electron's energy in order to find the first four energies that are "allowed" by the "walls" of the "nanoparticle". The term "allowed" stems from the fact that the electron is confined inside the particle, therefore it cannot escape. This confinement is depicted in the simulation as a periodic wave that has its wavefunction or its squared form equal to zero at each end of the

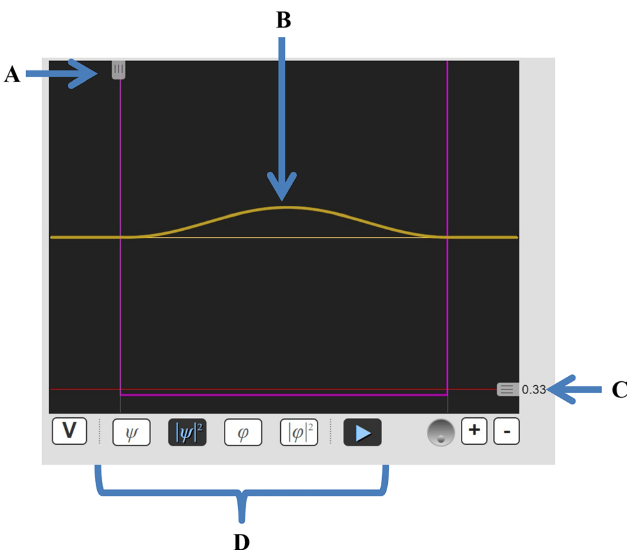

Figure 4: The simulation's interface: (A) A "button" that controls the "diameter" of the theoretical "nanoparticles" (B) The moving electron as a wave as it is depicted by its ψ^2 (C) A "button" that controls the electron's energy (D) This part of the simulation is omitted from the activity and is simply labeled as a "shape of the wave".

theoretical particle, in accordance with the PODB model (Figure 5). Students through this simulation will correlate the quantization of an electron's energy with its confinement inside a particle.

In the second part of this activity the students are tasked with experimenting with different sizes for the theoretical nanoparticle and are asked to deduce the effect of size in the particle's quantized energy levels.

Through this experimentation a correlation is expected to be drawn between the quantization of an electron's energy and its confinement, resulting in defined energy levels as it is described in the second fundamental concept. Additional students are able to rationalize how a decrease in a particle's size leads to an increase in the energy gap between the electron's energy levels and vice versa.

Step 4: The optical properties of a material are size-dependent only in the nanoscale.

Aim: To clarify to the students the concept that the size-dependency of a material's energy levels is a phenomenon inherent only to the nanoscale.

Process: It is highlighted to the students that even though the conclusions reached at Step 3 are valid they are purely qualitative in nature since the simulation offers no units of measurement neither for the energy levels or the "nanoparticles" size. Therefore, there is a need for a more quantitative approach to this phenomenon as it is described in this activity. The activity is designed around a spreadsheet, developed by the authors, where the difference between an electron's ground and first excited state is calculated according to Bruss' equation (Bruss, 1986) (equation 1). In Bruss' equation, E is the energy difference between the ground

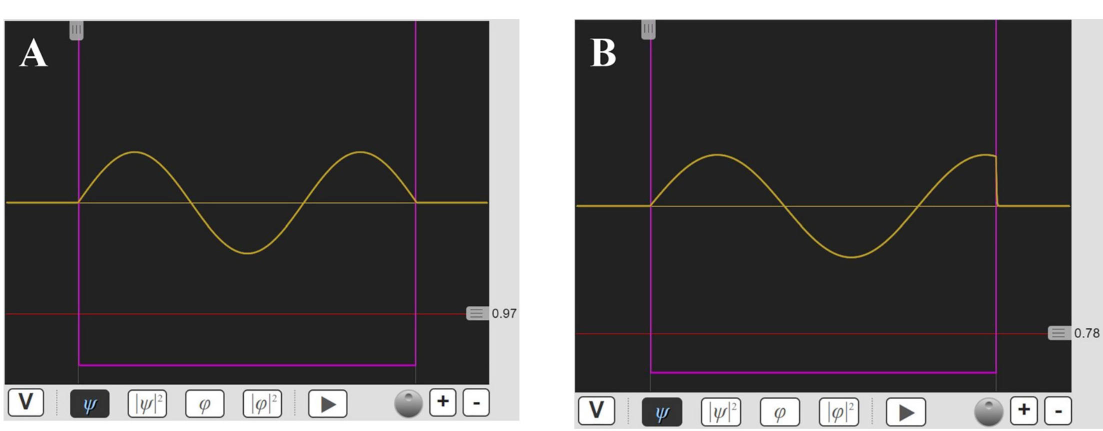

Figure 5: (A) A periodic wave, confined within the theoretical particle. (B) A non-periodical unconfined wave.

and first excited energy level, E_g the bag-gap energy of the bulk material; h is Plank's constant; L is the particles diameter; m is the semiconductor's electron reduced mass; ε' is the semiconductor's relative permittivity; ε is the semiconductor's permittivity of a vacuum and Mr is the semiconductor's mass number. Alongside the resulting energy from equation 1 its corresponding wavelength is calculated according to equation 2, where λ is emission's wavelength; h is Plank's constant; c is light speed in vacuum and E the energy calculated by equation 1. The implementation of equation 1 was done based on the theoretical calculations of Wakaoka et al. (2014) for CdSe quantum dots but with a different E_{gap} (1.17 eV instead of 1.74 eV). This change is due to the fact that equation 1 is used for theoretical calculations at the nanoscale, and not larger scales. Therefore, when applied for bulk materials, it may give implausible results (e.g. for the colorless bulk CdSe the model predicts an absorbance of 713 nm which is inaccurate). Hence an adjustment was made in order to have more realistic calculations (e.g. an absorbance of 1060 nm for bulk CdSe). These calculations are not exhibited in the spreadsheet's interface since there is an almost unanimous viewpoint that the first goal when students are introduced to quantum mechanics is a conceptual understanding, not mathematical formulation or calculation (Anupam et al., 2018; Hobson, 2005; Kalkanis et al., 2003; Müller & Wiesner, 2002). In its interface only three cells for each scale are used. One cell for the materials diameter (measured in meters, micrometers and nanometers for the macro-, micro- and nanoscale respectively) another for the energy gap (measured in eV) between the first two energy levels, the ground and the first excited one and finally a cell in which the corresponding wavelength is presented. The students can only input values in the first cell of each scale, the other values are calculated automatically.

$$E = E_g + \frac{h^2}{8mL^2} - \frac{1.786e^2}{\epsilon\epsilon' L} - 0.248\frac{13.6}{Mr^2} \quad (1)$$

$$\lambda = \frac{hc}{E} \quad (2)$$

This spreadsheet is given to the students and they are tasked with inputting different diameters (numbers 1 through 15) of theoretical materials across three different scales (macroscale, microscale and nanoscale). Through this activity they will be able to deduce that the size dependency of a material's energy levels is inherent only to the nanoscale (with the other scales yielding an almost constant absorbance wavelength) as described in the second part of the first fundamental concept. For example, the values 2, 4 and 7 yield three distinct wavelengths in the nanoscale (532, 849 and 980 nm respectively) while in the other two scales the wavelength is steady at 1060 nm. Finally, it should be noted that the mathematical formulation of Bruss's model and the calculations made by the authors in order to create the excel spreadsheet are not part of the activity, since there is an almost unanimous viewpoint that the first goal when students are introduced to quantum mechanics is a conceptual understanding, not mathematical formulation or calculation (Anupam et al., 2018; Hobson, 2005; Kalkanis et al., 2003; Müller & Wiesner, 2002).

Conclusion

In this study we proposed a novel reconstruction of the scientific content of size-dependent properties using as theoretical framework the MER and two fundamental ideas where identified. Additionally, three putative classroom activities are proposed based on the aforementioned elementarization. Surely, our educational analysis based on science education research frameworks and findings has to be empirically tested. This is a future direction to which our group is working.

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