# Using Quantum Mechanics To Facilitate the Introduction of a Broad Range of Chemical Concepts to First-Year Undergraduate Students

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Ⓢ *Supporting Information*

ABSTRACT: A first-year undergraduate course that introduces students to chemistry through a conceptually detailed description of quantum mechanics is outlined. Quantization as arising from the confinement of a particle is presented and these ideas are used to introduce the reasons behind resonance, molecular orbital theory, degeneracy of electronic states, quantum mechanical tunneling, and band structure in solids and quantum dots.
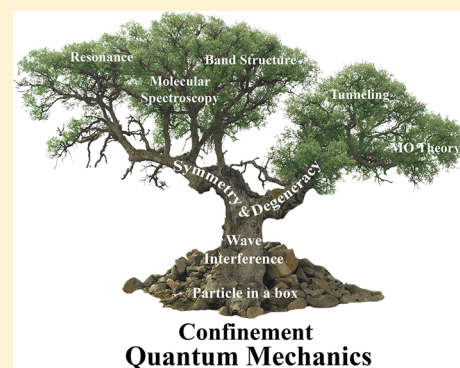
The nurturing of a nascent scientist during the undergraduate years is a delicate matter. Studies indicate that the number of students who take advanced placement (AP) courses and examinations is growing significantly.[1] Measured by the metric of their successful completion of advanced placement chemistry, an increasing number of students are entering the university "well prepared". This trend presents a unique opportunity to attract good students to the field beginning in the first year of undergraduate studies. Nevertheless, first-year university courses are generally perceived to reiterate much of what the students have already learned in high school, even if at greater depth and with more nuance. Consequently, these courses, even honors courses, are often underappreciated by the students. Many develop the opinion that chemistry is boring and are drawn toward other fields. In response to the change in student preparedness, along with other factors, a number of approaches have been implemented. For example, one curriculum revision has implemented an Organic-first approach.[2] In this article, we propose an alternate approach, namely, a physically oriented course stressing the fundamental concepts that underlie chemistry. There are two main advantages in this approach. In a traditional curriculum, students often first encounter quantum mechanics in their final year. They often become lost in the mathematics and consequently lose sight of the physical result. By presenting chemical concepts through a quantum mechanical description in the first year, faculty teaching the course are forced not to rely principally on mathematics and thus can focus on how the quantum world behaves. When students re-encounter quantum mechanics more formally as upperclassmen, they already have an exposure to the fundamental concepts. A second advantage

in this approach is that students who are inclined toward the more physical side of our discipline become interested early on. There is considerable evidence that the number of U.S.-born students pursuing the physical sciences is declining,[3] an alarming trend for our society. A quantum principles-first approach works to address this deficiency. In this article, an honors introductory chemistry course that has evolved at Indiana University over the past decade is described. It developed organically, driven not by any grand design at curriculum revision but by the desire of a couple of research faculty to teach advanced concepts, fundamental to an understanding of chemistry, at the introductory level.

◼ THE STUDENT POPULATION

Students enrolling in the main general chemistry sequence are required to take both chemistry and mathematics placement tests. Upon the basis of their performance on these tests, a cohort is selected. This group (approximately the upper 5%) is invited to enroll in the honors version of introductory chemistry, which is entitled "Principles of Chemistry and Biochemistry". The remaining students register for the regular class. At an introductory meeting prior to the first scheduled class, the professors teaching the honors class invite the prospective students to enroll in this challenging course. At this meeting, the faculty stress that the course will not be a rehash of AP Chemistry. Each year approximately 48 highly motivated students elect to enroll in the honors course. The average mathematics SAT scores for the honors students is 736 and
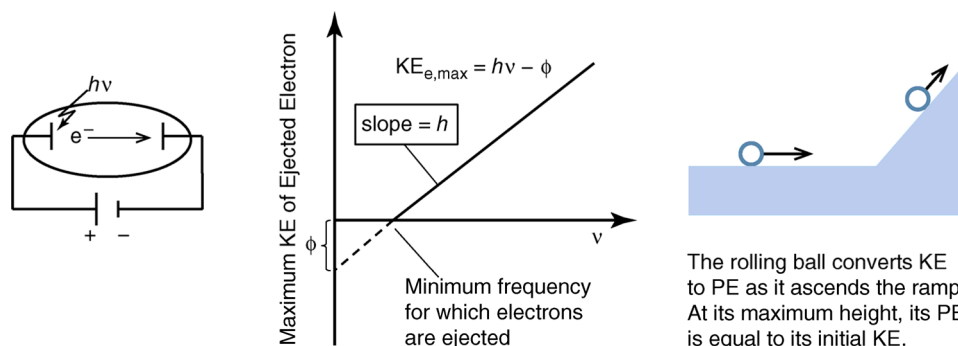
Figure 1. Cartoon illustrating the experimental setup of the photoelectric effect. By using retarding potentials, the dependence of the maximum kinetic energy of the ejected electron on the frequency of the incident light is established. A classical depiction of a retarding potential is included.

their average ACT score is 32.8. The majority of these students have taken AP chemistry in high school and earned a score of 4 or 5 on the exam. Most of them, though not all, have had a year of physics and a year of calculus in high school.

■ COURSE LOGISTICS

This particular general chemistry course consists of both laboratory and lecture portions. For the lecture portion of the course, students meet with the faculty member for three 50 min lectures weekly. For the laboratory section of the course, students meet with a faculty member for one 50 min lecture in which both the theory underpinning the particular laboratory exercise and the experimental details are described. In addition to this interaction with the faculty member, the students are each assigned to a discussion section. This discussion section, which is also 50 min in duration, is conducted by a graduate student teaching assistant. The final component of the course is the 3-h long laboratory that the students attend weekly. During the course, four in-term exams and a cumulative final are administered. These exams are conducted in the evenings to provide sufficient time for the students to demonstrate their understanding of the material presented. Each exam is 2 h in duration. Although a textbook is utilized in this course,[4] it is only loosely followed, as a suitable textbook has not been found that is consistent with the organization or depth of presentation as described below. A syllabus for this course can be found in the Supporting Information.

■ THE PHOTOELECTRIC EFFECT AND RETARDING POTENTIALS: AN EXAMPLE THAT CONVEYS THE NEED FOR A QUANTUM MECHANICAL THEORY

We begin the course by describing the fundamental experiments conducted at the onset of the 20th century that shattered the classical interpretation of the world around us. Although the students may have heard of some of these experiments such as the photoelectric effect and the interference patterns obtained in classical water waves as part of high school, they have not yet been exposed to others such as blackbody radiation and the ultraviolet catastrophe. From the outset, the depth of detail and level of understanding expected of the students is stressed. Over the years, experience demonstrates that although almost all the students in the class have learned about the photoelectric effect, this generally means they have memorized the results of the experiment and the conclusions deduced. This course is differentiated from their high school experience by a detailed description of the experiment. Consequently, students are introduced to the concept of a retarding potential. The concept

of using a retarding potential to measure the kinetic energy of a particle is new to all the students. To convey the concept, the classical analog of a ball rolling up a ramp is used. As shown in Figure 1, the students learn that measurement of the dependence of the maximum kinetic energy of the ejected electron on the frequency of the incident light yields a linear relation. This introduces them to not only to Planck's constant (the slope of the plot in Figure 1) but also the idea of the work function, which binds the electron in the metal. Finally, by showing that the retarding potential is *not* a continuous function of the applied frequency, discrete states (and hence quantization) is introduced as an experimentally observed result.

One key aspect of the lectures on the photoelectric effect is making students comfortable in moving between plots, equations, and words, all different communication modes to describe the results of the experiment. Practicing scientists employ all these modes of communication to a greater or lesser extent and it is important that students become familiar with these different means of communication early in their undergraduate experience.

■ CONFINING A PARTICLE IN ONE DIMENSION

Although many advanced texts used for general chemistry explicitly solve Schrodinger's equation for the particle in the infinite square well,[4] few focus on why the particle's behavior changes. Students are typically puzzled as to what the physical significance of the box is and why the particle "moving in the box" should behave as a standing wave. Although they follow the mathematics presented, the implications of the result elude them (Figure 2). Many wonder what the wave function is. *Some mistakenly think that the wave function is simply the square root of the probability and that the probability is the fundamental quantity.* A common source of confusion is: How does the particle travel from the left half of the box to the right half in the first excited state if there is a node in the middle? This critical point is addressed in class by presenting an analogy between the quantum mechanical wave function and classical water waves. It is stressed that the particle depicted by the wave function is simultaneously present on both sides of the box, just as is the case for water at various points on a classical wavefront. The students further recognize from the mathematics that the energy is quantized, but why? In this course it is discussed in detail how it is the behavior of the wave at the boundaries of the box (boundary conditions) that results in quantization. It is further inferred that quantization, zero-point energy, and the uncertainty principle are *all* a direct consequence of physical

$$\psi(x) = \sqrt{\frac{2}{L}} \sin\frac{n\pi x}{L} \quad E_n = \frac{n^2 h^2}{8mL^2} \quad n = 1, 2, 3, 4, \ldots$$
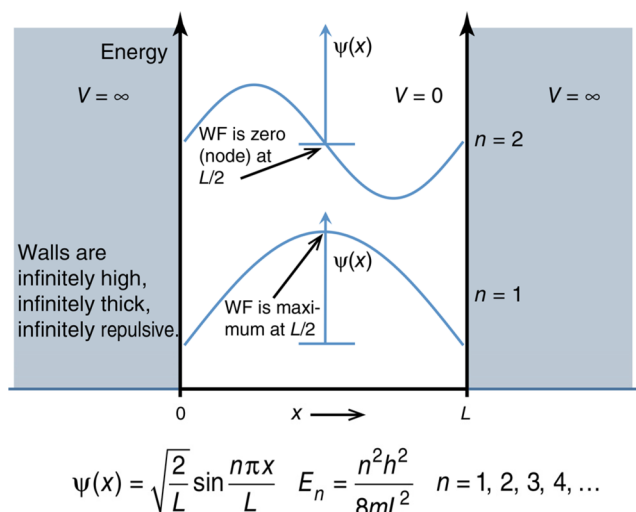
Figure 2. Behavior of a particle confined to an infinite square well. The infinitely high, infinitely repulsive, and infinitely thick walls result in the requirement that the wave function is exactly zero at the walls. Solution of Schrödinger's equation with this boundary condition reveals that the wave function must be an integer number of half-sine waves with the quantized energies indicated above. It should be noted that there are two vertical scales displayed in the figure. The energy scale indicates the potential energy in the different regions and the relative placement of the two wave functions. For a given wave function, the amplitude of the wave function is indicated by the second vertical scale designated $\psi(x)$.

confinement. This also leads the students to understand how the difference between energy levels is related to the extent of confinement (that is size of the box or spatial region where the particle is to be retained). The latter concept is particularly exciting, as a connection is then made to resonance, as discussed below.

During the course of presentation, it is emphasized that the wave function is a more fundamental quantity than the probability because the wave function has a sign (or a phase that can sometimes arise from a complex number) whereas the probability does not. This latter fact is easily illustrated to the students by asking them the question: "Which of the two following statements has more information? A number is minus four *or* the square of a number is sixteen." Appreciating the fundamental nature of the wave function is crucial not only for understanding how waves constructively and destructively interfere in molecules to make bonds but in understanding the atomic and molecular transitions involved in spectroscopy. From these lectures, the students are exposed to the basic concept that it is the confinement of the particle-in-the-box that leads to quantization. They learn that the confinement in one dimension results in one quantum number and that confinement results in a zero-point energy (and hence uncertainty between position and momentum), which cannot be removed from the particle. All these points are taught with appropriate drawings as well as with numerical formulas to stress their interdependence.

Having set the abstract tone with these discussions, it is then stressed that several important concepts in chemistry can be clearly understood from these ideas. Three such ideas are presented, namely, resonance states in conjugated polyenes, molecular orbital theory, and band structure in solids and in quantum dots. These ideas are presented by invoking concepts

learned during the treatment of the particle confined within a one-dimensional box.

■ RESONANCE

Although the phenomenon of resonance stabilization in conjugated polyenes will be presented to students in their organic chemistry course as they study aromatic molecules, their background of the particle-in-the-box presents a wonderful opportunity to convey the fundamental basis for resonance stabilization. As indicated in Figure 3, the four π electrons in
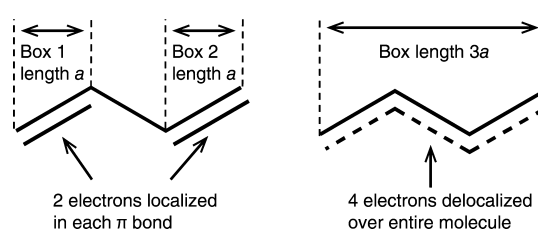
Figure 3. Schematic diagram illustrating localization and delocalization of π electrons in a conjugated diene.

the conjugated diene can either exist localized in two separate double bonds (that is two separate boxes) or can exist delocalized over the entire molecule (one larger box). The benefit of delocalization is that the box is bigger than if the electrons are confined to being just between two atoms. (By this time, the students have already been exposed to the dependence of zero-point energy and the spacing between energy levels on box-size, this connection is exploited to reinforce the concept of resonance stabilization.) The benefit of the electron wave function spreading out over the molecule can be appreciated by comparing the two scenarios. For the localized situation one has:

$$E_{\text{localized,total}} = E_{\text{box1}} + E_{\text{box2}} = 2\frac{h^2}{8ma^2} + 2\frac{h^2}{8ma^2}$$
$$= 4\frac{h^2}{8ma^2}$$

where the factor of 2 for each term arises from that fact that there are two electrons occupying each energy level. In contrast, for the delocalized situation one has:

$$E_{\text{delocalized,total}} = 2\frac{h^2}{8m(3a)^2} + 2\frac{2^2 h^2}{8m(3a)^2} = \frac{10}{9}\frac{h^2}{8ma^2}$$

Because $(10/9) < 4$, clearly the delocalized configuration corresponds to a lower-energy configuration and is more stable! This basic fact of the stabilization of the wave function by spreading out over a larger box is the fundamental factor driving of all resonance in molecules. (Also see refs 5 and 6 for an interesting discussion on the topic of resonance.)

Box 1 contains two questions given during an exam. Clearly the questions gauge the understanding of the concepts involved in resonance stabilization. It is, however, useful to note that these concepts are not only accessible to the honors level students, but also to many in the broader first-year general chemistry class. To illustrate this, the performance of students for similar questions in the general chemistry class that is accessible to all students has been tracked. Their performance is presented in Figure 4. Clearly evident is that their performance in these questions is reasonably good indicating their

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Box 1. Example of Exam Questions

RESONANCE We have learned in class and during discussion how the particle-in-a-box is a concept that can be used to understand resonance stabilization in double bonded systems. Consider the following structure, where the particle-in-a-box has helped in understanding why the delocalized system is more stable.
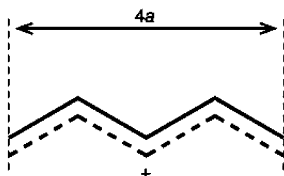
This system now contains four electrons inside a box of length 4a. If an electron in the highest occupied orbital in this box were to be excited using external radiation, what would be the largest wavelength absorbed by the system? (Use the particle-in-a-box and $E = h\nu$ hc/λ; $= 6.63 \times 10^{-34}$ J s; $= 3 \times 10^8$ m/s; m = mass of the electron = 9.1×10^{-31} kg. Assume $a = 1.0$ Angstrom)

a. $\left[\dfrac{1}{c}\dfrac{5}{16}\left(\dfrac{h}{8ma^2}\right)\right]^{-1}$; 1055.8 Angstroms

b. $\left[\dfrac{1}{c}\dfrac{4}{16}\left(\dfrac{h}{8ma^2}\right)\right]^{-1}$; 1319.8 Angstroms

c. $\left[\dfrac{1}{c}\dfrac{9}{16}\left(\dfrac{h}{8ma^2}\right)\right]^{-1}$; 586.6 Angstroms

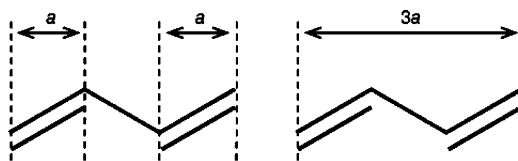d. $\left[\dfrac{1}{c}\left(\dfrac{h}{8ma^2}\right)\right]^{-1}$; 330 Angstroms

e. $\left[\dfrac{1}{c}\dfrac{10}{9}\left(\dfrac{h}{8ma^2}\right)\right]^{-1}$; 297 Angstroms

EXTRA CREDIT

Consider the following two cases we considered in class:

We were able to show how the box on the right where four electrons were delocalized all over the box was in fact more stable (lower in energy). In this problem we would like you to calculate the stabilization energy, E_s. First calculate the energy of the system on the left with two electrons in each separate box. Then calculate the energy of the system on the right where the four electrons are delocalized all over the box. Finally, calculate the difference between the energy of the picture on the right and that for the picture on the left (the stabilization energy).

a. $E_s = 4\left(\dfrac{h^2}{8ma^2}\right)$

b. $E_s = \dfrac{10}{9}\left(\dfrac{h^2}{8ma^2}\right)$

c. $E_s = \dfrac{26}{9}\left(\dfrac{h^2}{8ma^2}\right)$

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comprehension of the material presented. Apparently, this is one of the more popular concepts and one that the students are able to assimilate to a very large degree.

■ BONDING AND ANTIBONDING ORBITALS IN MOLECULAR ORBITAL THEORY AS A DIRECT CONSEQUENCE OF INTERFERENCE OF WAVES

In teaching this course for a decade, it is apparent that students arrive from high school with a good understanding of the rules for drawing Lewis dot structures and VSEPR. Though these concepts are reiterated briefly, we concentrate on a more

advanced understanding of bonding, namely, the constructive and destructive interference of the wave function that is the basis of molecular orbital theory. Depicted in Figure 5 is the situation of two hydrogen atoms approaching each other. How do the two wave functions for the two electrons (represented by boxes in the figure) add? It is clear that addition of the overlapping waves leads to an increase in the amplitude. The increased amplitude corresponds to an increased probability for the electron being located between the two hydrogen nuclei. Thus, the electrons reduce the Coulomb repulsion of the two nuclei from each other. On the other hand, subtraction (180° out-of-phase addition) leads to a node between the two nuclei.
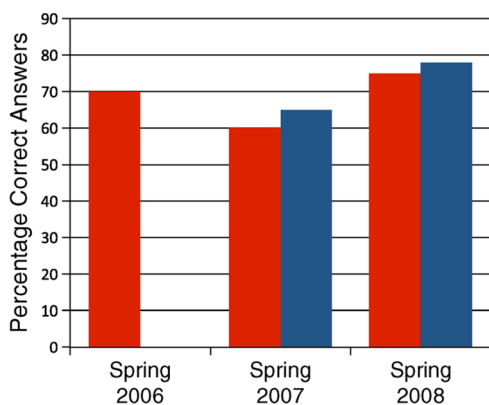
Figure 4. The concepts described in this work, slightly modified, have also been taught to the students in the main sequence course. We evaluated their understanding of the concepts of the stabilization energy that occurs due to delocalization in polyenes (blue histogram) and the concept of wave addition as the underpinning of MO theory (red histogram). The number of students in each of the three semesters ranged from a low of 418 in 2006 to a high of 491 in 2008.
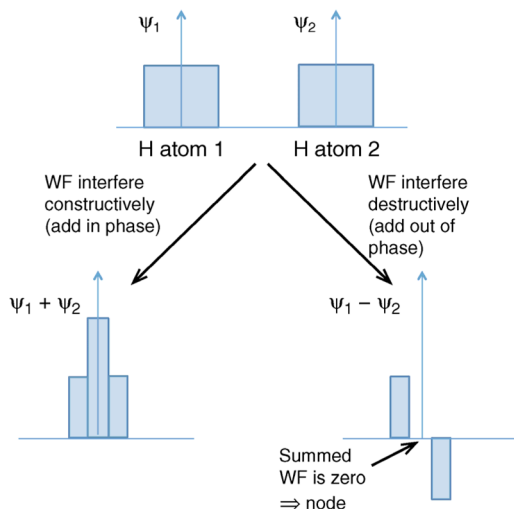
Figure 5. Constructive and destructive addition of "box" electron wave fuctions. A node results between the two atoms due to cancellation of the wave functions in the case of $\psi_1 - \psi_2$.

Both situations exist. The lack of electron density between the two nuclei means that there is more Coulomb repulsion between the two nuclei than when there is no node. Consequently, the configuration with a node is higher in energy than when there is no node. This simple illustration perfectly illustrates the existence of bonding and antibonding orbitals and the relative energies of the σ_{1s} and σ_{1s}^* molecular orbitals for H_2.

Although the students generally understand these concepts, one of the questions that remain in their minds is why do the atomic s and p orbitals only *add* and *subtract* with each other to create the new (bonding and antibonding) orbitals that belong to the molecule? To understand this tricky point, it is necessary to reiterate that waves interfere either constructively or destructively. Constructive interference of the atomic s and p orbitals yields a bonding molecular orbital, whereas destructive interference of the same atomic orbitals leads to antibonding orbitals. Petersen and co-workers[7] provide a lab-based alternative to teach molecular orbital theory using computational chemistry. Pritchard[8] presents the current situation in

teaching the concept of bonding and suggests that an IUPAC committee be formed to review the teaching of this important concept. Our goal here was to provide a conceptual basis for the topic.

■ DIMENSIONALITY, SEPARABILITY, SYMMETRY, AND DEGENERACY

With the concept of the one-dimensional infinite box firmly established, along with illustrations on resonance, molecular orbital theory and band structure (see below), the discussion is extended to the two-dimensional box. Unfortunately, this topic is often not discussed in most texts or else it is relegated to a homework problem. However, extending the 1D box to two dimensions is incredibly useful to illustrate the role of symmetry on degeneracy. Consider a particle of mass m allowed to "move" freely within a box with length L_x in the x direction and L_y in the y direction as indicated in Figure 6.
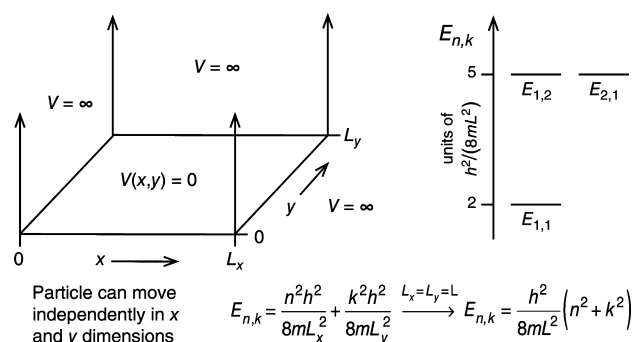
Figure 6. Illustration of how independent motion of a particle in a symmetric potential (box) results in degeneracy. The measurement of degeneracy thus provides insight into a symmetry of the confining potential.

Without any mathematics it is easy to justify that *if* the motion in the two dimensions is independent (*uncorrelated*), then the energy of the particle should be given by:

$$E_{n,k} = \frac{n^2h^2}{8mL_x^2} + \frac{k^2h^2}{8mL_y^2}$$

and the wave function should be the product of the 1D wave functions. Though initially puzzled as to why the wave function $\psi_{xy} = \psi_x\psi_y$, the students are able to understand it when asked about the probability of achieving two heads on successive coin tosses. They all recognize that for two independent coin tosses the probability of achieving two heads is the product of the probability of achieving a head on an individual toss. Because probability is the square of the wave function, if the probability associated with independent events is multiplicative, then wave functions should also be multiplicative. The link between independent motion and the nature of the wave function established for the 2D box is also useful later in the course when discussing the separability of the hydrogen wave function. Separability is inextricably linked to independence. Exposure of the students to the case of the 2D box also allows us to connect degeneracy with symmetry. It is trivial to demonstrate from the formula above that when $L_x = L_y$, degeneracy results, that is, the states with $n = 1$, $k = 2$ and $n = 2$, $k = 1$ have the same energy. Of course this is not the only type of degeneracy possible. What if $L_y = 2L_x$? The students quickly appreciate that degeneracy, a measurable quantity, always teaches us about the symmetry of

the box (potential that confines the particle). This connection is a fundamental concept often not presented at the undergraduate level.

ANOTHER BOX, THE HYDROGEN ATOM

One of the central concepts encountered in any general chemistry course is the hydrogen atom. Explicitly solving Schrodinger's equation for the hydrogen atom is beyond the mathematical ability for even the talented first-year students in an honors course. Nevertheless, building on what the students have already learned, quite a bit can be done beyond the standard treatment of the topic. First and foremost, the students are confronted with the realization that the hydrogen atom is simply a situation where the electron is confined by a different type of box. The Coulomb attraction of the electron to the nucleus results in attractive potential that falls off inversely with the distance, r, between the nucleus and the electron. This $1/r$ potential binds the electron within the atom. For this "box" one must therefore solve Schrodinger's equation resulting in the wave function, ψ, and eigenenergies, E. As the shape of the box is different from the one-dimensional square well, one does not expect that the solutions (wave functions and energies) should be the same as those in the case of the one-dimensional infinite square well previously studied. Given the symmetry of the potential, it is apparent to the students that it makes sense to express $V(x,y,z)$ in terms of the spherical coordinates (r,θ, and ϕ). When posed the question "How many quantum numbers do you expect for the electron confined in the hydrogen atom?", students are conflicted. Based upon what they have learned in the course, half the students reason correctly that as the electron is confined in three spatial dimensions one would expect to find three quantum numbers (labeled n, l, and m_l). Yet all the students know from their high school course that the electron in the hydrogen atom is characterized by *four* quantum numbers. How can they resolve this apparent conflict? Because quantum numbers arise from confinement, what other quantity is being confined? We explain to the students that it is confinement in time that causes the intrinsic spin of the electron.[9] It was only with the relativistic treatment of quantum mechanics by P.A. M. Dirac that the spin of the electron was realized.

BAND STRUCTURE IN SOLIDS AND QUANTUM DOTS

Using the concepts gleaned from one-dimensional confinement, molecular orbital theory and the hydrogen atom, the students are now in a position to tackle band-structure in solids and quantum dots. The primary concept here is the fact that a greater degree of spatial "overlap" between waves, or wave functions, yields greater interference between these waves; interference between these waves is always constructive (bonding) *and* destructive (antibonding). For example, consider a one-dimensional lattice of atoms. The overlapping $1/r$ potentials for adjacent atoms results in the periodic potential energy diagram shown in Figure 7. In this case, the quantity r represents the distance between an electron and the nucleus of an individual atom. For the orbitals buried deep inside the Coulomb well (the atomic core energy levels), the overlap between orbitals (wave functions) localized on neighboring atoms is small. This leads to a lesser degree of interference between these atomic waves on neighboring atoms. For orbitals closer to the top of the potential, on the other
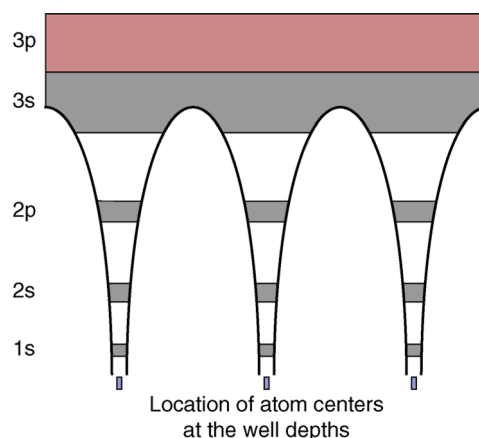
Figure 7. Potential energy diagram for a one-dimensional lattice of Na atoms. The overlapping $1/r$ potentials for each atom produce the indicated potential. The periodic, attractive potential energy experienced by the electrons due to the periodic lattice arrangement of nuclei is shown using the solid lines. The gray and light red boxes represent the band of orbitals formed due to interference between neighboring atomic orbitals that are listed on the left. The gray band represents orbitals that are occupied whereas the light red band represents unoccupied orbitals. Each band contains a combination of constructive (bonding) and destructive (antibonding) "interfered" orbitals.

hand, the overlap is greater leading to larger interference. Such interference leads to a combination of bonding and antibonding orbitals. These "interfered orbitals" yield a "band of orbitals" due to the closeness in energy of the corresponding bonding and antibonding counterparts. The relative energetic spread of these bands is directly related to the extent of overlap, and hence interference, between the atomic orbitals on neighboring atomic centers. Note, for example, that the spread of the continuum band corresponding to overlap between neighboring 3s and 3p orbitals is much greater than for the core 1s orbitals. This is due to the greater overlap and great interference between neighboring atomic 3s and 3p orbitals.

In addition, in the energetic regime corresponding to the atomic 1s orbitals, the confining potential is deep and hence in this region the wave functions are strongly bounded. What about the energetic regime corresponding to the 3s and 3p orbitals? In this region, which lies above the overlapping $1/r$ potentials, the electron is not confined or bounded by the adjacent atoms. The wave function can spread out, that is, delocalized. That is the orbitals created after interference have a greater degree of delocalization in this case. This scenario is similar to the situation within a large box where the confining potential is relatively weak.

The distinction between metals, semiconductors, and insulators comes about when the difference between energies of the occupied and unoccupied bands of orbitals is small or large with respect to room temperature. Following this presentation, the students are in a position to grasp the ideas and distinctions between semiconductors and metals.

Quantum dots are introduced as solids-chunks that are additionally confined by an infinite particle-in-a-box potential; that is, boundary conditions of confinement, similar to those seen in particle-in-a-box, are introduced over and above the band structure obtained from the periodic potential illustrated above. The connections to the particle-in-a-box are utilized to

qualitatively understand trends in the functional dependence of absorption frequency to nanoparticle size.

■ THE HARMONIC OSCILLATOR AND THE INTERATOMIC POTENTIAL

In a typical honors first-year course, students are unquestionably introduced to the interatomic potential. By teaching students about the harmonic oscillator first, one is positioned to explore the differences encountered in the asymmetric, finite potential of the interatomic potential as compared to the infinite, symmetric harmonic oscillator. The students have little difficulty in relating to the concept of the classical oscillator as depicted in Figure 8. They also appreciate that due to the

$$V(x) = \tfrac{1}{2}kx^2$$
$$F(x) = -dV/dx = -kx$$
$$\omega = (k/m)^{1/2}$$
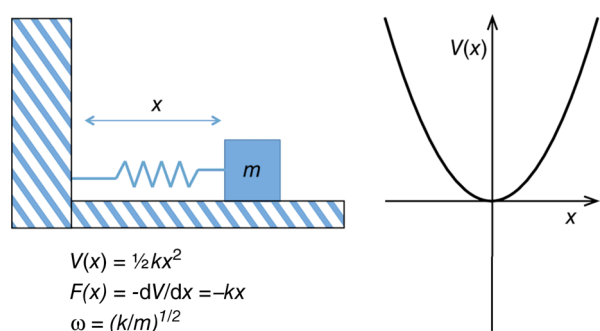
Figure 8. The potential energy diagram for a harmonic oscillator. Shown at left is the physical situation of the classical oscillator.

confinement in one dimension one should expect quantization with one quantum number. Most students can correctly sketch the wave function with the number of nodes increasing as the energy increases. The students are told that for a particle of mass m, the expression for the eigenenergies is:

$$E_n = \left(n + \frac{1}{2}\right)\hbar\omega \text{ where } n = 0, 1, 2, 3, \dots \text{ and } \omega = \sqrt{\frac{k}{m}}$$

with the strength of the spring (curvature of the parabola) given by k. For this infinite harmonic oscillator, it can be seen that the adjacent energy levels are evenly spaced apart by $\Delta E = \hbar\omega$.

The students are then engaged to realize that for the interatomic potential shown in Figure 9, the minimum of the
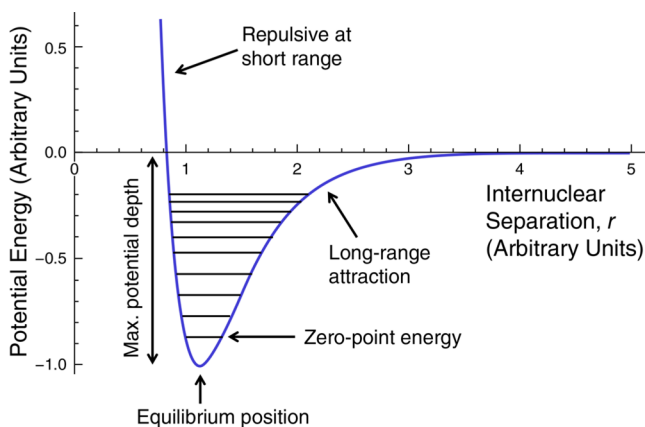
Figure 9. Variation of potential energy with separation distance between two atoms (interatomic potential). The bottom of the potential is well described by a harmonic oscillator.

potential resembles the harmonic oscillator just discussed. How though does the top of the potential differ? The finiteness and asymmetry of the potential are apparent and inevitably the students realize that the wider potential must result in quantum states that are more closely spaced as the energy (quantum number) increases. The finiteness of the potential means that for large internuclear separation the wave function is not confined (bounded). This lack of boundedness means that bonds can break and that chemical reactions can occur.

■ THE TREATMENT OF MORE ADVANCED CONCEPTS AT THE FIRST-YEAR UNDERGRADUATE LEVEL: CASE STUDY ON THE CONSEQUENCES FROM TREATMENT OF A FINITE CONFINING BOX, NEGATIVE KINETIC ENERGIES, IMAGINARY MOMENTA, AND TUNNELING

In the above analysis, it has been shown how subtle features from quantum mechanics, such as wave interference, play a direct role on (a) the creation of bonding and antibonding energy levels and (b) the presence of continuum bands in solids. In addition, the treatment of particle-in-a-box yields a conceptually elegant and complete treatment of resonance in delocalized systems. In this section, the discussion is expanded to include how the treatment of finite box potentials leads to one of several vagaries of quantum mechanics, namely, quantum mechanical tunneling. As usual, the focus here is on the conceptual understanding of these ideas, without being confounded by the mathematics that may be challenging to some. However, it should be noted at the outset that, thus far, this has only be presented at the honors level.

Before delving into these "quantum-eccentricities", their significance to chemistry was highlighted. There are several areas of chemistry where these anomalies disconcertingly manifest themselves. For example, α-particle decay is one of the first instances where this was noted.[10] The large dependence of the alpha decay half-lives on decay energy occurs only because the α particle tunnels through a finite barrier. In addition, several hydrogen transfer reactions in physical organic chemistry[11,12] display anomalous primary or secondary isotope effects; these are now believed to result from quantum mechanical tunneling. The umbrella inversion of an ammonia molecule is another example where significant population transfer occurs under the barrier and forms the basis for the ammonia maser.[13] Scanning tunneling microscopy (which the students are exposed to as part of the laboratory section of the honors course, a lab syllabus may be found in Supporting Information) is yet another example where tunneling is significant.

The fundamental definition of quantum-mechanical tunneling comes about from the following discussion. Consider a particle moving inside a binding potential. At any given temperature, the particle has high velocity at the minimum of the potential. As the particle starts to traverse higher regions of the potential, its kinetic energy decreases, and one reaches a point in the high potential region where the kinetic energy becomes zero. This point is the classical turning point; that is, this is the point where the classical particle decides that it needs to turn around. However, the quantum mechanical particle, being eccentric, keeps going further! As it goes further, the particle tunnels through the barrier. A finite box potential is used to illustrate this concept.

Imagine the situation shown in Figure 10. A particle of mass m in region 1 has a kinetic energy, K, which is greater than the
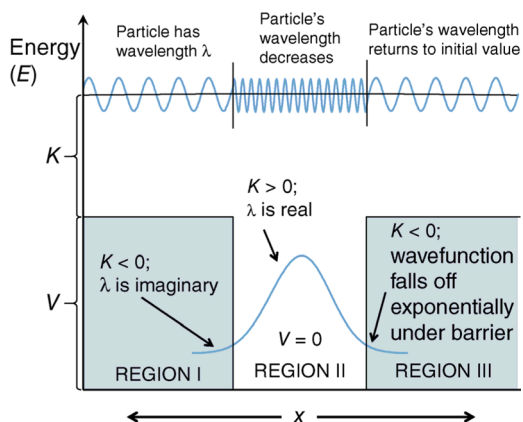
Figure 10. Behavior of a wave above and inside a finite square well. When confined to a finite square well, a particle has a finite probability of penetrating inside the wall, the phenomenon of quantum tunneling. For the wave function above the finite well, the kinetic energy is indicated by the light horizontal gray line. The variation of the wave function from this horizontal line reflects the amplitude of the wave as a function of position and not a change in its energy. The lower wave function in the figure has a smaller kinetic energy. Its amplitude as a function of position is displayed by the blue curve. The labeling of the kinetic energy, K, applies to region I and region III. In region II, as $V = 0$, K is positive.

potential energy, V. In this region the particle has a total energy $E = K + V$. Because

$$K = \frac{1}{2}mv^2 = \frac{p^2}{2m}$$

with p being the particle momentum, the momentum can be expressed as

$$p = \sqrt{2mK}$$

Consequently, the particle's de Broglie wavelength is

$$\lambda = \frac{h}{p} = \frac{h}{\sqrt{2mK}}$$

Because the mass $m > 0$ and $K > 0$, then $\lambda > 0$.

Now what happens when the particle enters region II? Its potential energy is zero in this region. Because its total energy is conserved, it remains the same as it was in region I. Thus, the particle's kinetic energy, K, must increase over what it was in region 1 which means that the de Broglie wavelength of the particle must decrease. (See equation above.) In region III the particle's wavelength returns to the original value it had in region I.

Next, consider a particle confined in region II. It has no potential energy in this region. Its total energy is simply its kinetic energy, which is less that the potential energy, V, at the walls. Because it has $K > 0$, it has a finite de Broglie wavelength. How does the particle behave in region I (or region III)? In the case of the infinite box, the particle cannot exist within the wall. However, in the case of the finite box, it can! Because the total energy of the particle must be conserved, and because $E < V$, there must be another form of energy (kinetic energy!) that needs to be added to (or subtracted from!) V to obtain conserved energy, E. It is, thus, clear that $K < 0$ in regions I and

III. The particle, thus, has a negative kinetic energy in regions I and III! Because momentum is proportional to the square root of the kinetic energy (see above), it implies that the particle has an imaginary momentum and consequently an imaginary wavelength. Although the students have encountered imaginary numbers in mathematics in high school, they have not learned of physical situations requiring imaginary numbers. This lends further credence to the notion that advanced mathematical ideas have a significant role in scientific endeavors.

But What Does Imaginary Wavelength Really Mean? Is It Really a Wave or Is It Something Else?

To address this question, the Schrodinger equation used for the infinite square well (particle in a box) problem was revisited

$$-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\psi(x) + V\psi(x) = E\psi(x)$$

which rearranges to

$$\frac{d^2}{dx^2}\psi(x) = \frac{2m(V-E)}{\hbar^2}\psi(x) = -\frac{2mK}{\hbar^2}\psi(x) = -\frac{p^2}{\hbar^2}\psi(x)$$
$$= \left(\frac{ip}{\hbar}\right)^2\psi(x) = \left(\frac{2i\pi}{\lambda}\right)^2\psi(x)$$

Based on their high school calculus, students recognize that the solution is

$$\psi(x) = e^{ax} \text{ where } a = \left(\frac{ip}{\hbar}\right)$$

which is an exponential decay function inside the barrier (regions I and III). In these regions $V > E$, which means $(V - E) > 0$, and consequently quantity, ip is real. Hence, the momentum p (and wavelength) is imaginary under the barrier.

However, when $V < E$ (above the barrier), p is real, the solution then is $\psi(x) = e^{[ip/\hbar]x}$. How does one reconcile this new realization with the result earlier in the course that the wave function for the particle in the infinite square well is an integer number of half-sine waves, namely,

$$\psi(x) = \sqrt{\frac{2}{L}}\,\sin\left(\frac{n\pi x}{L}\right)$$

The answer lies in the Euler relations. Consequently, on-the-fly, the students can be exposed, albeit briefly, to the idea that "advanced" mathematics (imaginary numbers!) is used in chemistry and enable them to make a connection in the process.

To conclude, the physical consequence of this situation is that the wave function under the finite barrier is an exponential decay; it is not zero. This means that there is a probability for the wave function to exist in this classically forbidden region. This result is not just an abstract concept. All of the students have learned in high school of the spontaneous emission of α particles (^{4}He nuclei) from radioactive ores. They are surprised to learn that α decay only occurs because of quantum mechanical tunneling. However, α decay is not the only occurrence of quantum tunneling. As previously stated, isomerization reactions at low temperatures and several hydrogen transfer reactions in physical organic chemistry provide other examples.

◼ SUMMARY

We have developed a first-year undergraduate honors course that teaches students fundamental quantum concepts that underlie chemistry and biochemistry. This material is presented in a manner that is intrinsically different from the mathematically intensive route typically encountered in an upper-level undergraduate course. Introducing the concepts in this way allows us to focus on the physical situation rather than the mathematics. This approach clearly establishes a high level of intellectual engagement of the students with the subject matter. Despite the rigor of the course, many students, not only upon finishing the course but later in their undergraduate experience, comment favorably on their experience and what they learned.

◼ ASSOCIATED CONTENT

Ⓢ Supporting Information

Syllabus for the lecture course; syllabus for the lab course; course evaluations. This material is available via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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