The Superformula and model quantum systems as tools for learning

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Teaser: The superformula, a simple extension of the equation describing a circle, is introduced in the context of particle-in-a-box model problems.
Abstract

Our understanding of quantum phenomena often begins with simple ‘particle-in-a-box’ style problems, the solutions of which introduce the student to foundational quantum concepts such as degeneracy and quantization. Simple model geometries of confinement afford analytic solutions, which are readily derivable, easily manipulable, and provide a unique ‘sandbox’ of exploration accessible at the undergraduate level. In the current work, these model problems are explored in a variety of ways. Firstly, through a historical lens - orienting them to the birth and development of quantum physics. Then, via an organizing syntax. This framework allows the interested student to orient the diverse multidisciplinary literature that has evolved around these problems. Finally, through consideration of the shape element of the syntax, the superformula – a simple extension of the equation describing a circle – is introduced and discussed.
1. Introduction

In May 1981 renowned physicist Richard Feynman delivered a talk entitled ‘Simulating physics with computers’, Feynman detailed his thinking on the limits of the use of classical computers to accurately describe physical systems and exhorted the development of novel computing devices which would enable the accurate simulation of the physical world, being themselves ‘quantum’ in nature\textsuperscript{1}. Around the same time, others were similarly thinking of novel quantum modes of computation, and a summary of the genesis of the field and the time since Feynman's lecture can be found here in Ref. \textsuperscript{2}.

In the years since, Quantum Computers have been realized, and the field of Quantum Computing has exploded. The use of quantum computers is being explored in a wide range of fields including finance, automotives, and the life sciences\textsuperscript{3}. Due to their broad utility, they have become an important geopolitical consideration, resulting in funding from governmental and private sectors, across the globe, of more than 35 billion USD\textsuperscript{4}. As is true of any emerging technology, the creation and sustainable delivery of a workforce equipped to develop, utilize, and further innovate is a critical consideration. Accordingly, those working in the field of quantum technology need to understand the foundational underpinnings of quantum mechanics. For many, including one of the authors of the current work, this understanding starts with the particle-in-a-box problem.

This trivially simple model manifests critical elements of quantum systems and has been used to introduce countless students to the foundational concepts of quantization and degeneracy; properties arising through the act of describing a confined particle. A robust literature exists that describes ever more sophisticated extensions of this simplest of possible problems, and one of the aims of this contribution is to provide an underlying syntax to help organize and orient the interested student.

The current work is organized as follows. In the following section the particle-in-a-box problem will be more fully introduced and contextualized historically. A syntax is then suggested that unifies the landscape of model quantum systems, and is aimed to help scientists navigate the literature, and the facets of the physics and chemistry described by the models. As will be seen, the confining shape, the ‘box’ the particle(s) are placed in, has a profound effect on their behavior. In its simplest form the box is two dimensional and the range of permissible shapes are bounded by the platonic ideals of the square and the circle. To connect these two shapes, we introduce the Superformula. This remarkably flexible mathematical construct has been used to describe biological, chemical, and physical phenomena\textsuperscript{5}, but is simple enough in its functional form to be accessible to a student with a secondary education. The use of the Superformula as a model of confinement will be similarly reviewed. Summary remarks conclude the paper.
2. The empirical foundations of quantum mechanics

The history of quantum mechanics begins with wanting to understand how atoms and molecules interact with radiation. Predictions from classical physics were incomplete, and so a different empirically oriented set of physical theories emerged that were created to fit experimental observation. This is an important point: while expressed mathematically, and ultimately validated to an extremely high level of experimental accuracy, these descriptions were arrived at not via a comprehensive understanding of underlying physical reality but more instead through determining the general shape of the mathematical boundaries such theories required.

The following line of reasoning, from Sir Nevill Francis Mott (On Teaching Quantum Phenomena⁶), is illustrative of this development of quantum theory. The observation that the specific heat of a fixed amount of a monatomic gas at a constant volume is itself constant, suggests that the specific heat of the gas is solely due to the kinetic energy of the atoms. Heating the system increases the atoms’ kinetic energy, while not seemingly transferring energy to the internal movement of the constituent components of the atoms (e.g., electrons and the nucleus). From this, it can be assumed a minimal potential and kinetic ‘ground state’ of the atom, that is separated from the next allowed ‘state’ by a finite amount that is larger than $kT$ (here $k$ is the Boltzmann constant, while $T$ is the temperature). This quantized nature is confirmed by scattering experiments wherein the scattered particles (electrons) either suffer no energy loss, or loss of a specific definite amount (i.e., enough to cause atomic ionization).

At this juncture, the following experimental observations require rationalization: the movement of electrons within the atom is quantized, while the kinetic energy of a free electron can take any value. Accordingly, Mott resolves this:

“...The answer to this is that quantization applies to any movement of particles within a confined space, or any periodic motion, but not to unconfined motion such as that of an electron moving in free space or deflected by a magnetic field. This is an experimental fact.”⁶

To account for these experimental facts, empirical rules were introduced in the earliest days of quantum theory to enable the prediction of properties. The Bohr model of the hydrogen atom, appearing in 1913, successfully predicted energies but was fundamentally flawed—giving an incorrect angular momentum of the ground state. This inconsistency resulted from his adoption of orbits to describe the observed energy quantization.

Experimental observation of the ‘wave particle’ duality of matter provides some explanation for the exploration of theories that incorporate wave-like behavior. In 1926 Erwin Schrödinger introduced his eponymous equation which permits a probabilistic view of quantum phenomena. Mathematical operators applied to a wave function (an object that encodes all the information of the system) result in the prediction of observable properties. His initial applications considered an electron in a Coulombic potential, the harmonic oscillator, and the rigid rotor⁷⁻⁹.
As noted in Ref. 7, the first appearance of the ‘particle-in-a-box’ problem appears to be in a summary textbook by Mott from 1930 10. His presentation of the infinite square well—the problem of a particle in one dimension trapped between two impenetrable ‘walls’ (representing a ‘well’)—permits a quantized set of eigenfunctions. It has a readily interpretable classical analog in a standing wave with fixed ends. This conceptual model is a tool for pedagogy and introduces the properties of confinement, quantization, and degeneracy—the understanding of all of which are requisite in navigating quantum phenomena.

It is important, however, to recall that neither Born or Schrödinger’s insights were supported by rigorous derivation. There are no simple statements from which quantum mechanics can be bootstrapped, in contrast to Einstein’s theory of relativity. As described in 11 “It’s a complex framework, but it’s also an ad hoc patchwork, lacking any obvious physical interpretation or justification”. It is outside of the scope of the current contribution, but there is a vibrant effort in theoretical physics to engage in a ‘quantum reconstruction’. This effort began in 2001, and sought to focus on probabilities, ignoring wave-particle duality, and quantization. Accordingly, it is enough to assume that any system can be described by a list of properties and their possible values, and from this much of ‘traditional’ quantum theory can be recovered 11,12.

The focus for the remainder of the current work will be the ‘particle-in-a-box’ model and its related extensions.

3. Particle-in-a-box-in-a-laboratory

In addition to its use as a model system to introduce students to the foundational concepts of quantum mechanics in the lecture hall, the ‘particle-in-a-box’ model has been utilized in a laboratory setting. Certain experimental systems, when probed spectroscopically, can be approximated as if they were ‘particle-in-a-box’ problems 13–15. Similarly, simple experiments to generate solvated electrons can also serve as accessible introductions to systems that can be modeled via particle-in-a-box strategies 16–18.

Using nanotechnology and semiconductor fabrication techniques it is possible to construct devices with a known, and well-defined, number of electrons, within a specific spatial region. These ‘quantum dot’ systems are sometimes referred to as ‘artificial atoms’ and provide an excellent introduction to both nanoscale physical systems, and their underlying quantum mechanics 19–21.

A particularly interesting nanostructure is that of CdSe nanocrystals which can be readily synthesized in a university laboratory setting. These will have the same wurtzite crystal structure as bulk CdSe but will consist of just hundreds to thousands of atoms. These structures can be grown to a desired size and as size their increases, the energy of the first excited state decreases (in qualitative agreement with the particle-in-a-box model), thus they serve as accessible experimental systems that link theory and tractable experimentation 22.
In this same vein, although currently out of the scope of a teaching laboratory, is the recent synthesis of perfluorocubane$^{23}$. This fluoridation of a cube-shaped hydrocarbon, consistent with theoretical predictions$^{24}$, results in an unpaired electron being located predominantly in the cage. A physical manifestation of a three dimensional ‘particle-in-a-box’, perfluorocubane was voted a ‘molecule of the year’ for 2022 by the editors of Chemical and Engineering News$^{25}$.

4. An organizing syntax

As was discussed in the context of the foundations of quantum mechanics, the mathematical boundaries of a theoretician’s models are shaped to help understand or rationalize experimental reality. Once understood, theoretical models are routinely extended—usually to make the model closer in its ability to describe reality (a refinement in the ability of the model to resolve the phenomena to a higher experimental precision). Sometimes though models are extended in abstract ways, these abstractions might represent mathematical tractability—such extensions afford no additional experimental insight but offer interesting mathematical excursions.

The class of problems represented by the previously introduced particle-in-a-box is no different in this regard and, in this section, as an aide to the interested student, a syntax is provided to describe the canonical elements of these types of problems and their theoretical exploration. It is our hope that such a syntax provides a unifying framework to help students successfully navigate the burgeoning literature.

The proposed syntax consists of the following elements, which are briefly described below.

A. The number of particles

How many particles are involved in the model? An explicit number (1 or 2), or a generalized amount, ‘few’, or ‘many’?

B. Mediating interaction

What physical interaction mediates the behavior of the particle(s)? Examples include infinite, finite, harmonic, or Coulombic.

C. Flavor of particle

Are the particles Fermionic or Bosonic in nature?

D. Shape of confinement

What is the confining geometric shape the particles experience?
E. Preposition

Are the particles in the shape, or on the shape?

F. Occupied space

What is the nature of the space the system is embedded in? 1-dimensional, 2-dimensional, … d-dimensional.

G. Method of solution

How is the model solved? Exactly, i.e., through an analytic description, or approximately?

To be clear, the goal with the introduction of this syntax in the current work is not to then provide a comprehensive review of the existing literature regarding the problem of confined model systems, but rather to provide a useful aide to the student interested in organizing and navigating the literature accordingly. In the next section, specific attention will be paid to the shape elements of the syntax.

E. The Platonic limits

Consider the following explanatory article describing the solution of the particle-in-a-box, and the particle-in-a-circular box problems\textsuperscript{26}. The first part of the work consists of the description of 1 particle in a ‘box’ of infinite potential in 1 dimension. The particle in a ‘rectangular box’ is then discussed (as a simple extension to 2 dimensions). The final part of the work begins, “Squares are nice, but we learn more from circles.” And proceeds to describe 1 particle in a circular box of infinite potential in 2 dimensions.

More succinctly, using the above syntax:

A. 1
B. Infinite potential boundary condition
C. Electron
D. ‘Box’, ‘Rectangular box’, ‘Circular box’
E. In
F. 1D, 2D, 2D
G. Analytic

The geometric ‘endpoints’ defined by the square and the circle have quite natural characteristics to them, representing the orthogonal and the infinitely smooth respectively. In addition there exists
an exact solution to 1 particle in an equilateral triangle\textsuperscript{27,28}, however the general polygonal case requires an approximate solution derived via a perturbation from the circle\textsuperscript{29}.

Fixing every other element of our syntax and just varying $D$ (the “Shape of Confinement”) what, if anything, can be said about the manifold of particle-in-a-box problems between the ‘endpoints’ of the circle and square? Before addressing this question, it is useful to introduce a generalization of the circle, a so-called ‘Supercircle’.

7. From Superellipses to the Superformula

Supercircles and, more generally, superellipses use a different power in the equation of a circle. They were first systematically studied by Gabriel Lamé in the early 19\textsuperscript{th} century. Superellipses are defined by the equation:

$$\left(\frac{x}{A}\right)^n + \left(\frac{y}{B}\right)^n = 1$$

(1)

where $x$ and $y$ represent the horizontal and vertical coordinates of points in the rectangular coordinate system, respectively; $A$, $B$, and $n$ are positive real numbers. Superellipses include the circle, the diamond and squares for $A = B$, and ellipses, rhombi, and rectangles for $A \neq B$\textsuperscript{30,31} for $n$ to infinity. Gabriel Lamé introduced these curves to be able to apply geometry to crystals. The absolute values ensure closed curves (Figure 1). Interest in superellipses was revived in the 20\textsuperscript{th} century through the Danish mathematician Piet Hein\textsuperscript{31-33}.

![Figure 1: Lamé curves (left, appearing in 34), and superellipses (right, appearing in 35)](image)

Figure 1: Lamé curves (left, appearing in \textsuperscript{34}), and superellipses (right, appearing in \textsuperscript{35})
The Superformula is a further generalization of superellipses, describing a much wider range of abstract and natural shapes. By transforming supercircles into polar coordinates, the superformula can deal with any symmetry by introducing a symmetry parameter $m$. Gielis modeled various ranges of more symmetrical and asymmetrical geometries found in nature. The mathematical expression of the superformula is:

$$r(\phi) = \left( \left| \frac{\cos(m\phi/4)}{A} \right|^{n_2} + \left| \frac{\sin(m\phi/4)}{B} \right|^{n_3} \right)^{-\frac{1}{n_1}}$$

(2)

where $r$ and $\phi$ are the polar radius and polar angle, respectively; $n_i$ ($i = 1, 2, 3$) and $m$ are real numbers. The mathematics community synonymously refer to the superformula as Gielis curves, surfaces, and transformation.

### 7.1 Some general geometric considerations

As remarked above, the superformula describes an infinitude of geometric variability. What follows is a summary of how recognizable shapes are recapitulated as a function of the parameters of the superformula.

The parameter $m$ divides the plane into $m$ sectors, defining superellipses for $m = 4$ (and supercircles for $A = B$). For $m = 2$, the plane is divided into two parts of $180^\circ$, for bilateral symmetrical shapes. For $m = 1$, one side is more pointed, like a teardrop. Pentagonal shapes are determined for $m = 5$ relating five sectors of $72^\circ$. (Figure 2).
The symmetry parameter $m$ can be any real number. If it is an integer, the shape closes in one turn (for $A = B$), and if $m$ is a rational number, the numerator determines the number of angles. For example $m = 5/2$ also gives five sectors, but with a spacing of $144^\circ$, giving the symmetry of the pentagram. Self-intersecting shapes result when $m$ is rational or irrational (see Figure 3 below). True polygons are defined by Equation 33 of reference\textsuperscript{38} and for close approximations, see Reference\textsuperscript{39}.

The exponents act as shape parameters and the resulting shapes can be concave or convex. The Superformula can act as a geometric transformation on planar functions. For constant functions, Equation 2 transforms the circle (Figure 2: a-f), but transformations of spirals (Figure 2: g-i) or trigonometric functions (Figure 2: j-l) are also possible. Three dimensional supershapes can be generated in spherical or cylindrical coordinates, or in parametric version, based on two perpendicular two-dimensional supershapes\textsuperscript{36}. 

\textbf{Figure 2:} Transformations of circles, spirals, and trigonometric functions (in flower and wave form)
Figure 3: Self Intersecting Gielis curves (for \( m \) rational) and polygons.

As a result of its functionality flexibility, the Superformula has been used to model a wide range of biological systems\(^{36,40,41} \). The method has been tested on the modeling of plant leaves, tree rings, bamboo culms and meristems, fruits, seeds, starfish, and avian eggs (amongst others). Recently, a software package written for the R software was made available\(^42 \). Polygrammal symmetries (Figure 3 upper row) are common plant phyllotaxis\(^36 \) and commonly occur in biomacromolecules (proteins, nucleic acids, and viruses)\(^{43-45} \).

8. **The Superformula as a confining shape**

Superellipses and Superformula can be considered as a generalization of circles and ellipses, two of the classical conic sections. In fact, all conic sections (circle, ellipse, parabola and hyperbola) are special cases of Equation 1\(^{30} \). One can then also consider the same procedure applied to the classic parabola (\( y = x^n \)), the results of which are shown in Figure 4 (left) for integer values of \( n \). The log-log plot of the superparabola is known as a power law (Figure 4, right). Using absolute values (\( y = |x^n| \)) creates shapes that are ‘open’ above, and ‘closed’ below. For \( n \to \infty \), the shape can be be considered a confining ‘box’, or infinite well.
Figure 4: Superparabola’s for positive integer values of n (left); log-log plot with same values as the left plot (right).

Table One below details the range of ground state energies, determined numerically, for an electron confined to a shape described by Equation 1 where $A = B = 1$ for a variety of values of $n^{46,47}$. The energies are reported as a function of mesh spacing ($\Delta$), where the mesh spacing refers to the fineness of the grid used to determine the numeric solutions. Analytic solutions exist for $n = 1$ (diamond), $n = 2$ (square), and $n = \infty$ (circle) and serve as useful validation of the approximate solutions.

The problem of a particle confined to a super-circular box has been considered$^{48}$ through a perturbative strategy (leveraging the analytic nature of the circular solution). Accurate eigenvalues are resolved as a function of the parameters defining the super-circular boundary conditions. Recently, an extension of this method was presented looking at the ground and 1st excited state energies and wave functions for systems of one (or two) electrons in a 2D (and 3D) potential well having a shape intermediate between a circle and a square (or a sphere and a cube for the case of 3 dimensions). A variety of literature exists exploring these generalized eigenvalue problems, and showcase a range of strategies both analytic and numeric in nature$^{49–56}$.

The original idea of Gabriel Lamé was to develop a best fit coordinate system so that the relevant boundary problems can be solved directly. Interestingly, the Gielis Transformation inspired a generalization of the Laplacian for stretchable radii so that the Fourier series solution could be extended to solve boundary value problems (i.e. those of Laplace, Poisson, wave, and Helmholtz) on arbitrary normal polar domains, including 3D domains and Riemann surfaces$^{57,58}$.

For completeness we remark that solutions to the Laplace equation are known as harmonic solutions, while solutions to the Helmholtz equation are known as meta-harmonic solutions$^{59}$. In particular, Helmholtz equations with Dirichlet and Robin conditions were solved using the Fourier projection method in 2D disk and annular domains and in 3D domains$^{38,40,57,60}$.
9. Concluding Remarks

Much like the things they describe, model quantum systems are simultaneously trivial and complex. Their continued use throughout the birth and evolution of quantum physics is a testament to these characteristics.

The current work introduces the reader to the particle-in-a-box class of problems, orienting them historically as simple expository tools of pedagogy. Experimental systems are discussed, some accessible in a laboratory setting, and others perhaps less so. All of which though, provide a physical framing for these unique mathematical models.

A syntax is introduced, one which deconstructs the canonical elements of literature presenting research on interacting particles, in a shape, in a space, of a number, and type. This is offered as an organizing framework to navigate the literature across disciplines, as these model problems, and their solutions, appear in journals throughout the mathematical and natural sciences.

Via consideration of the ‘shape’ of confinement of these problems, the Superformula is introduced. This remarkably flexible extension of a circle has found great utility in a variety of fields. As was discussed, the superformula naturally connects the ‘endpoint’ geometries with analytic solutions, and so can be used to introduce numerical simulation, approximation, and optimization techniques, all within a mathematically simple and geometrically interpretable way.

By introducing the superformula in the context of boundary value problems and the foundations of quantum mechanics, it is the authors hope to spark interest in this remarkably flexible construct amongst students of physical chemistry and chemical educators alike.

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**Table One:** Ground state energies ($E_0$, a.u.) of the single particle-in-a-box model as a function of $n$ in Equation One ($A = B = 1$) for a variety of mesh spacings ($\Delta$). Note analytic solutions for $n = 1$, $n = 2$, and $n = \infty$.
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