How Wave Interference May Help Explain Wavefunctions and Energy Quantization

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ABSTRACT Illustrations based on the use of radiative waves and oscillating strings are suggested to help explain the physical essence and develop intuitive understanding of the basic principles of quantum mechanics, such as quantization, shape of wavefunctions, and their fundamental features. The proposed approach is based on interference of time-independent or stationary waves, which statistically represent effective quantum mechanical particles. The physical significance of this principle is emphasized by tracing its origin back to the fundamental ideas of E. Schrödinger. The suggested explanations are suitable for chemistry undergraduate students and are compatible with covering optics and Fourier-transform spectroscopy in analytical chemistry classes.

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INTRODUCTION

Students' fear of quantum mechanics is well-known. Their common perception is that this discipline is abstract and purely mathematical, so it cannot be comprehended by using common sense and prior background in chemistry or physics. This unfortunate perception may be further exacerbated by the extensive use of calculus if the essential mathematics is not complemented by common-sense-based physics. If this notion persists, intuitive understanding of the subsequent topics, e.g., spectroscopy, becomes difficult to achieve.[1]

This problem appears to be more pronounced among chemistry majors as compared to physics students because chemistry majors tend to demand pictures and illustrations, rather than calculus-based mathematical formulas, for understanding the basic concepts of their discipline.[2] Thus, traditional coverage of quantum mechanics, starting with a highly mathematical list of postulates, may not be the optimal approach for this group of students.

In this article, I suggest an approach targeting the achievement of intuitive, physics-based (as opposed to mathematics-based) understanding of the most essential quantum mechanical phenomena. I shall show how quantum mechanics may be *qualitatively* introduced by using simple physical, algebraic, and trigonometry considerations. The treatment may be combined

with covering optics and Fourier-transform spectroscopy in analytical chemistry classes.

Coupling a Quantum Mechanical Particle (an "Effective Wave") and Its Time-Independent Wavefunction

My approach is based on the inherent connection of quantum mechanical particles to waves and on explaining their basic features by using easily comprehensible systems, e.g., oscillating flexible strings and radiative waves. Many textbooks and papers illustrate the basic quantum phenomena by using these well-known classical analogies.[3–6] However, a direct connection between quantum mechanical particles and waves is never provided. This vagueness, intentional rather than accidental, is based on an important physical reason, which is explained in the historical review in the Appendix.

In a nutshell, Schrödinger's original attempt to describe quantum particles as waves (Ψ, continuous in time) was found to be inadequate, in part, due to own subsequent work.[7] By contrast, the statistics-only treatment, involving the use of $\Psi^*\Psi$ distribution function, has been shown to be correct. Its essence can be summarized in Feynman's concise statement that "wavefunctions cannot be viewed as "smeared" electrons but used only in a probabilistic sense. Wherever the electron is located, it is a point charge."[8]

A Way to Reformulate the Wavefunction's Definition

However, the current definition of Ψ as a mathematical function completely describing particle's physical properties assumes that a wavefunction can be of any form (not necessarily wave-like), as long as it complies with the required properties (being single-valued, square-integrable, continuous, etc.). This definition implicitly states that the particle's wave function *per se* bears no *physical* significance except for being a part of the probability distribution function, $\Psi^*\Psi$.

Yet, this definition can be reconciled with that of Schrödinger (though only for time-independent waves) without conflicting with the above-quoted statement of Feynman. The objection to equalizing the quantum particle and its wavefunction can be lifted if a time-independent wavefunction is con-sidered as an *effective* stationary representation of the corresponding quantum particle. This principle can be traced back to the fundamental ideas of E. Schrödinger who proposed an "ergodic" hypothesis for Ψ, looking for an analogy with Boltzmann's statistical description of microstates.[7] An *effective* electron or other particle with a significant de Broglie's wavelength is to be considered in a probabilistic sense, i.e., in the frequency domain rather than in the time domain. A combination of its spatial "snapshots" given infinite time (thus, producing a continuous function in space) is sufficient to present a "statistical," time-independent *stationary* wave to be considered henceforth.

For a physicist, this definition may look trivial because, at first glance, it implicitly defines a real time-independent wavefunction as a square root of its $\Psi\Psi$ product for real functions. The reason for using this definition lies more in education than in physics because it visualizes wavefunctions as *waves* and provides common-sense-based explanations of several abstract concepts, as shown below. The next section sets a goal of building the $\Psi\Psi$ product and showing its physical significance starting with the wave function.

The Particle-in-a-Box and Phase Orthogonality

Bearing in mind the statistical nature of wavefunctions, let us consider the simplest quantum mechanical problem, a particle in a one-dimensional "box" having a zero potential energy within the box and infinite potential energy outside it. In more general terms, such a quantum mechanical particle (having the wavelength significantly exceeding its dimension, e.g., an electron) represents a *wave* confined (snuggly fitting) into a box. This problem is a subset of a more general (yet abstract) case of an unrestricted standing wave spanning through the entire Cartesian space. Henceforth, these two related quantum-mechanical problems will be considered along with their corresponding classical analogs, the oscillating string and radiative wave, respectively.

A wave (if not distorted by potential energy) is described by one of the periodic trigonometric functions, either a sine or a cosine. Given the boundary conditions for the particle in the box (the wave cannot exist, having a zero value, on the box boundaries), it must be

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a sine for the particle-in-a-box spatial component; the time component is defined by initial conditions.

The Oscillating String

The oscillating motion of a string is described by a continuum of time-dependent functions taking consecutively all of the values between the amplitude positions as shown in Fig. 1 (all figures in this paper were generated using Mathematica©, Wolfram Research, Champaign, IL). The number of maxima or minima in this picture varies by the different ways in which a string is pinched.[3,4] The string's oscillation is due to the superposition (interference) of two *traveling* or *progressing* waves:[19]

$$\xi(x; t) = \xi_{max} \sin(wt - kx) + \xi_{max} \sin(wt + kx) \quad (1)$$

where ξ is the time-dependent location (displacement) on the ordinate axis, ξ_{max} is the amplitude value, and w and k are the frequency and wave number, respectively. The cosine wave can also be selected to account for the oscillation in time between the amplitude waves (this complementary description is provided in the Appendix). As a result of these waves' *constructive* interference, a *standing* wave can be presented using a well-known trigonometric transform called the sine expansion:[19]

$$\xi(x; t) = 2\xi_{max} \sin(kx) \cos(wt) \quad (2)$$

The Particle in a Box as a Time-Independent Analog of the Oscillating String

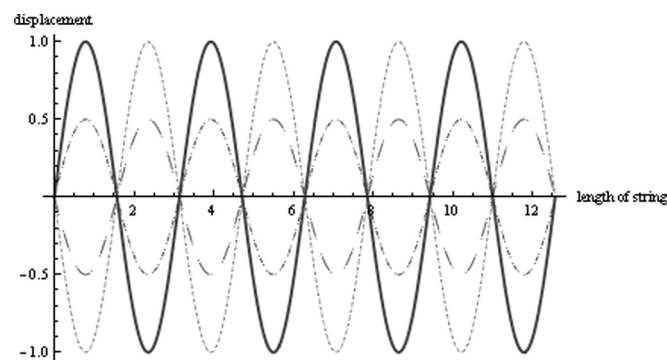In contrast with classical waves, only the amplitude waves are applicable for quantum-mechanical

FIGURE 1 Standing waves on an oscillating string. Solid and dotted lines mark the amplitude waves; dashed lines show the string shapes between the amplitude positions at a certain moment of time.

particles to meet the requirements set by the uncertainty principle as discussed above (see the Appendix for more detail). If time is removed from consideration (as stressed by the use of the lower case for ψ), Eq. (3) is obtained:

$$\psi = A \sin(kx) \quad (3)$$

Unlike Eq. (2) for the oscillating string, the wavefunction in Eq. (3) does not define the displacement, $\xi(x;t)$, at each location and each moment of time, thus satisfying the uncertainty principle. Figure 2A-D shows the first four wavefunctions for the particle in a box. This figure also demonstrates that the mirror image of the wave function represented by Eq. (1) with respect to the x-axis (dashed lines), namely,

$$\psi = -A \sin(kx) \quad (4)$$

satisfies the problem's boundary conditions (as well as the other conditions, i.e., being an equally eligible solution of Schrödinger's equation as Eq. (3)). Of course, regardless of the wavefunction's sign, the $\psi\psi$ product is positive.

The functions shown in Eqs. (3)–(4) may be called *real* conjugate wavefunctions because they are similar to complex conjugate wavefunctions. In both cases, conjugate functions are mirror images of the original functions with respect to a given axis (x); the axis of interest, orthogonal to x, may be either real (y) or imaginary (*i*). Both of these states are essential for the system's continuity in the 3D space; the likelihood of the electron taking one of them is $\frac{1}{2}$.

The connection of the quantum particle in a box and a classical oscillating string is, thus, provided using Fig. 2. It is the combination of a "traditional" time-independent wavefunction with its real conjugate that provides two amplitudes for the string oscillating in time.

Interference of Radiative Waves

The problem of wave enhancement or cancelation upon interference (superposition) can be considered for *radiative waves*.[19] As a result of a trigonometric analysis (the details are provided in the Appendix), the superposition of two waves is described as

$$I = I_1 + I_2 = (< Z/2 >)(A^2 + B^2 + 2AB \cos \phi) \quad (5)$$

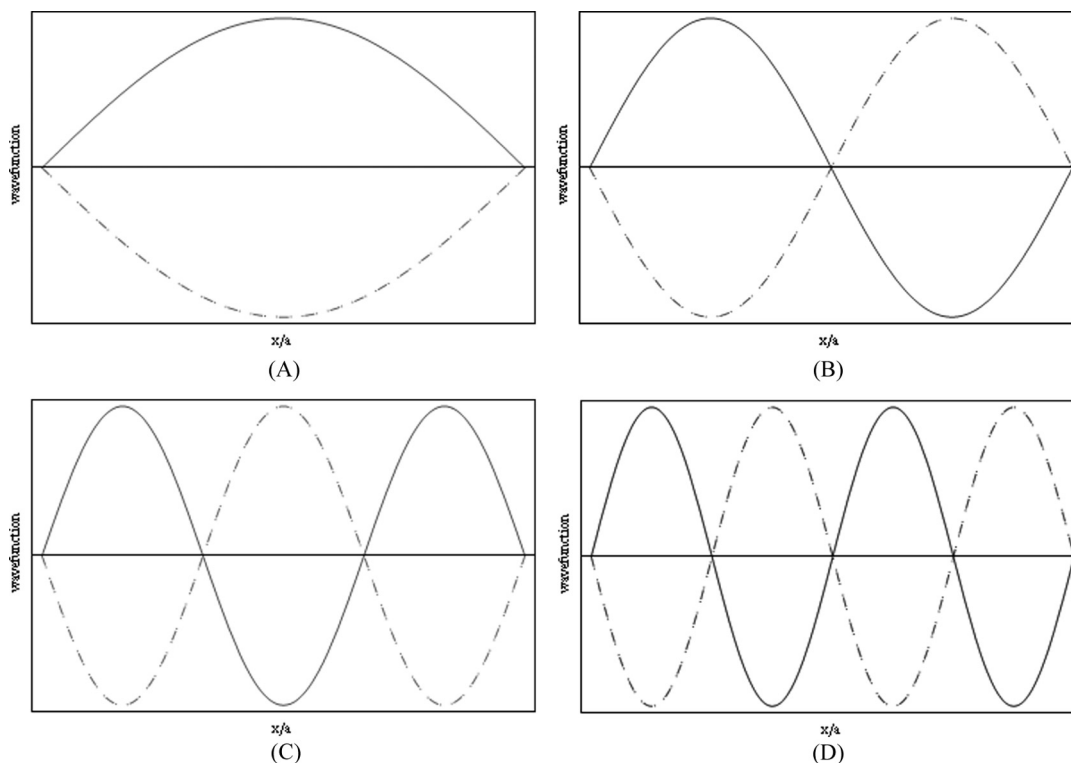where A and B are two waves' amplitudes; $Z = p/\xi$, the momentum (p) or displacement ratio called

FIGURE 2 The wavefunctions of the particle in a box shown in solid lines for n = 1–4 (A–D, respectively). The "real conjugates" of these wavefunctions (mirror images with respect to the x-axis) are shown as dashed lines.

"impedance," periodically oscillating in time, is present in Eq. (5) as its average value over the complete cycle; I designates the wave intensity; and ϕ is the phase difference between the interfering waves. Thus, it is the *product* of two amplitudes multiplied by the phase difference factor, $\cos\phi$, that defines whether two waves would interfere constructively or destructively.

Physical Significance of the $\psi\psi$ Product Besides Probability

Equation (5) is fully applicable for time-independent waves including periodical wavefunctions, ψ_n and ψ_m, where n and m are quantum numbers. Their product, $\psi_n\psi_m$, according to Eq. (5), is key to the magnitude of the statistical waves' enhancement upon interference.

Based on Eq. (5), the amplitude of the resulting standing wave will be maximal if $\phi = 0$, i.e., when two interfering wave functions of the same amplitude coincide or, in other words, when a given wavefunction, ψ_n, interferes *with itself* to yield the product, $\psi_n\psi_n$ (Fig. 3A). By contrast, if the phase difference $\phi = \pi$, two periodic waves are real

conjugates (ψ_n and $-\psi_n$), so they interfere destructively to cancel each other out (Fig. 3B).

The most interesting case, $\phi = \pi/2$, is presented in Fig. 3C. The two wave functions neither enhance nor cancel each other. Figuratively speaking, they "do not notice" each other, even though they occupy the same area of space. The word "orthogonal" captures the spirit of this phenomenon. This 90° phase difference between ψ_n and ψ_m, where m $\neq$ n, may be called "phase orthogonality." An example of "phase-orthogonal" functions is a sine and a cosine. The product of two such wavefunctions, as an average value over a complete cycle (or as an integral over a complete cycle for normalized functions), is equal to zero.

Application of the Kronecker Delta

If the mutual lineup of a wavefunction with itself is not perfect, i.e., if their corresponding maxima or minima do not occur at the same value of x (i.e., $\cos\phi$ is between zero and $\pi/2$), the maximum positive interference cannot be achieved. A *partial* enhancement would yield a lower amplitude of the resulting standing wave. However, any nonzero lower amplitude is impossible, as pointed out by
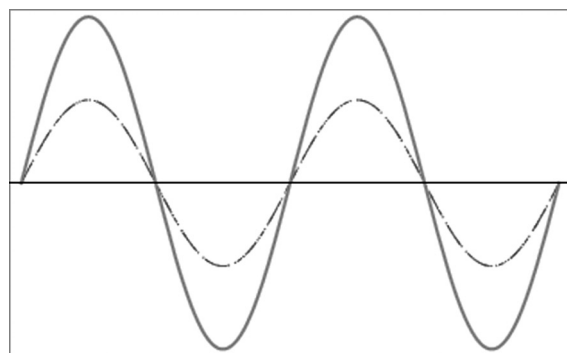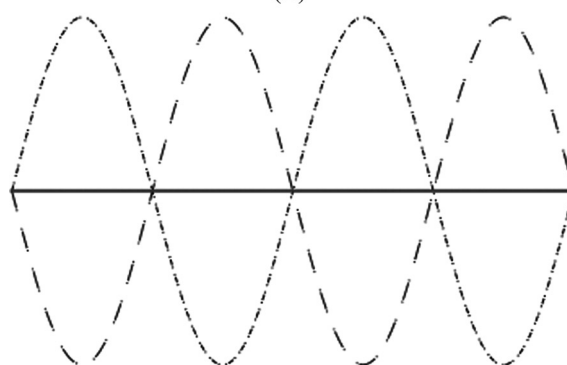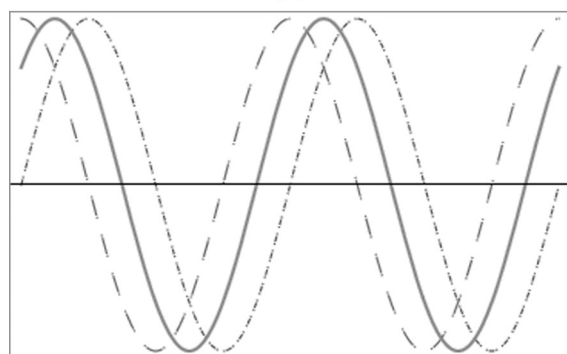
FIGURE 3 Interference of radiative waves with the phase differences of (A) zero; (B) π; and (C) $\pi/2$. The original waves are shown as dashed lines, whereas the standing waves resulting from their interference are shown as bold solid lines (the horizontal line in Part B).

Schrödinger[10,7] because this would necessitate the application of work for the wave to keep its energy constant (i.e., similar to friction in mechanical systems). Such a wave would not be stable in time by itself.

The phenomenon of "quantum friction," i.e., instability of a system in time, is well-known to modern physics.[11–13] For *infinite* time, i.e., for most of the problems relevant to teaching quantum mechanics and spectroscopy for chemistry students, quantum friction has to be zero.

Note that the solutions of all basic quantum mechanical problems considered in physical chemistry are eligible for this consideration because they are time-independent, i.e., statistically or effectively achieved by the corresponding systems. This approach is fully applicable to spectroscopy only for "long-time" solutions. Most of the spectroscopic measurements are done on such a long time-scale that, given the inherently high frequency of electronic, vibrational, or rotational motion, infinite time is a good approximation. Significant "noise" shows up on a shorter time scale, e.g., NMR in the time domain; then, of course, time cannot be ignored unless the data are transferred into the frequency domain by applying Fourier transforms.

Thus, only two options (described by the Kronecker delta) are possible for two wavefunctions occupying the same area of space: it is either a perfect enhancement (yielding the maximum amplitude), or orthogonality, with nothing in between. This is the physical essence of the $\Psi^*\Psi$ product and the explanation of the necessity of its integration over the entire cycle.

The *statistical* consideration of time-independent wavefunctions necessitates the integration of this product over the entire cycle for periodical functions. If the system's wavefunction is normalized, it concomitantly yields the particle's distribution function. In a historical perspective, Born, being influenced by Schrödinger's papers, specifically pointed out that the $\Psi^*\Psi$ product reflects the *amplitudes* of Schrödinger's time-dependent "matter waves," i.e., referring to the case shown in Figs. 1 and 2.[14] This integral is, thus, equal to the Kronecker delta for two identical normalized wavefunctions ($\delta = 1$) or orthogonal wavefunctions ($\delta = 0$), depending on whether m and n in the $\psi_m^*\psi_n$ product are equal to each other or not, respectively.

Both "phase" orthogonality and "spatial" orthogonality (e.g., p_x, p_y, and p_z orbitals) reflect, essentially, the same phenomenon: lack of enhancement of stationary, statistical waves by each other, which is mandatory for achieving positive interference.

Orthogonality: Expansion to Quantum Mechanical Problems

General

The principle of a wavefunction's maximum enhancement upon its self-interference, with orthogonality as the only alternative (for different quantum

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numbers) can be expanded to basic quantum mechanical problems. The only adjustment required is that the $\psi_m^* \psi_n$ product is to be integrated over the entire allowed space rather than over a complete cycle. A complete cycle, i.e., 2π, defines the entire available "angular space"; thus, this extension is justified.

For periodic functions, e.g., a particle in a box, the entire allowed space contains $n/2$ cycles. For non-periodic functions (e.g., hydrogen atom, harmonic oscillator), trigonometric considerations are not applicable. Even for a particle in a box, the concept of phase difference is not applicable anymore because the wave functions with different quantum numbers contain different amounts of cycles. Yet, when the "box" becomes circular, as for a particle on a ring, phase orthogonality is valid. The connection between the linear and circular boxes, essential for the expansion of the entire cycle to the entire space, is stressed in the rest of the paper.

Thus, a limitation of the suggested approach is that the $\psi_m^* \psi_n$ product's physical significance may be illustrated only by using either space-unrestricted or circular stationary waves. *Phase* orthogonality cannot be shown for nonperiodic cases, to be replaced with just "orthogonality."

The Physical Significance of Complex Functions

The superposition of a complex function, $a+ib$, and its conjugate, $a-ib$, results in vanishing of the complex component, just as a wave and its real conjugate cancel each other out (Fig. 3B). This treatment allows for having time in quantum mechanical equations as a complex exponential function; it vanishes upon its interference with a conjugate, leaving just the real trigonometric component, which is time-independent.

The $\psi_m^* \psi_n$ product of a complex function and its conjugate, equal to $a^2 + b^2$, is real. Thus, the essential choice between the wave functions' enhancement or orthogonality depends on the integration of this function over the entire allowed space, just as for the above-considered real functions. Note that the b^2 term "extracts" the physical essence of the complex variable and contributes to the mutual enhancement by complex conjugate functions in their projection to the real space. The use of complex functions is the mathematical embodiment of the uncertainty principle; even

though one cannot define a real wavefunction at any given moment of time, its *statistical* picture is real and valid.

Applications

Energy Quantization

Figure 2A-D shows that, for a particle in a box, one, two, three, etc., half-waves (which I figuratively call "bumps" to students) perfectly fit into a given box. At first glance, this phenomenon may be due to satisfying the boundary conditions (the wavefunction cannot have a nonzero value at the box's edge). Similarly, the necessity of fitting n half-waves into a *circular* box was demonstrated in the seminal paper of de Broglie[15,16] because otherwise the wavefunction would not remain single-valued upon subsequent revolutions around the circle.

To complement this mathematical reason, the need for quantization may be alternatively shown through the interference of statistical circular waves. Perfect matching of nodes is mandated by the necessity of maximum positive interference (i.e., exact matching of the wavefunction's maxima and minima, as in Fig. 3A), while an imperfect match would create multiple conjugate functions with nonmatching nodes.

Due to imperfect enhancement, the product of these mismatched waves cannot anymore yield the unity upon integration over the full circle (due to the nonzero phase difference). However, then, as shown in the section on Kronecker's delta, the only alternative is that it has to be equal to zero, i.e., Fig. 3B. Thus, the primary reason for fitting n bumps into a box, either linear or circular, is due to the necessity of matching the wavefunctions' maxima or minima rather than merely satisfying the boundary conditions. This important principle will be used in the next three subsections.

Finding Energy Values

Barrow demonstrated how the principle of fitting n half-waves of a certain wavelength, λ, into a linear box of a certain length (a) can illustrate quantization.[17] He showed that just assuming this principle allows one to calculate the system's quantized energies without solving the Schrödinger equation.

The underlying idea, using the analogy with an oscillating string, is fitting n bumps into the box's

length:

$$n\lambda/2 = a \qquad (6)$$

Then, the wavelength is expressed through momentum using de Broglie's relation, $\lambda = h/(mv)$. Combining these formulas yields the following equation, after a few algebraic steps:

$$mv^2/2(\text{kinetic energy}, E) = n^2h^2/(8ma^2) \qquad (7)$$

This is the expression for energy of a quantum particle unaffected by potential energy.

A similar treatment was provided by Barrow for a particle on a ring, resulting in the following equation: $mv^2/2$ (kinetic energy) $= n^2h^2/(8\pi^2ma^2)$.[17] Of course, solving the pertinent differential Schrödinger's equation yields exactly the same solution, thus providing a verification of this approach.

The Harmonic Oscillator

Fitting a whole number of half-waves into the entire allowed space can be readily expanded to any other common quantum mechanical problem including the harmonic oscillator and hydrogen atom. Of course, in any of these cases a simple *algebraic* way of finding a solution of the Schrödinger equation, demonstrated in the previous subsection, is impossible. However, the qualitative shape of the corresponding wavefunctions can still be predicted because n alternating maxima and minima are generated. These maxima and minima should be centered around the source of potential energy, e.g., classical turning points for the harmonic oscillator or the origin for the hydrogen atom. Symmetry considerations should be applied as well.

The harmonic oscillator must exhibit a *single* maximum for the ground state, energy level 1 (Fig. 4). Given that there is only one maximum, it must be located, out of symmetry considerations, at $x = 0$. Note the qualitative similarity of the shape of ground-state wavefunctions for the particle in a box and harmonic oscillator. The allowed space (i.e., the "box") in the harmonic oscillator stretches from minus infinity to plus infinity. For the first excited state (energy level 2), there is one minimum and one maximum located between the origin and two classical turning points symmetrically situated around the origin. The introduction of potential energy at the classical turning points results in a
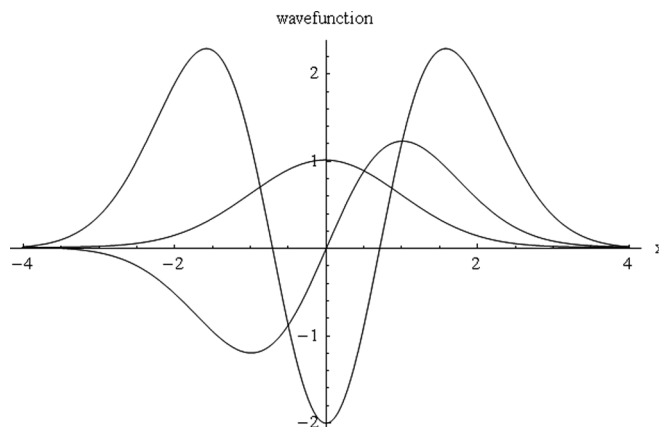

FIGURE 4 Sketches of wavefunctions for the first three energy levels of the harmonic oscillator. The labels are I, II, and III for the first, second, and third energy levels, respectively.

distortion of the original sine function to yield a non-periodic function, yet retaining a wave-like shape.

For the third quantum level, the combined number of maxima and minima (i.e., bumps) must be three, located between the origin and classical turning points (Fig. 4). The positions of these multiple crowded maxima and minima should be moving closer to the turning points for increasing quantum numbers, which is shown in many textbooks. Note that the real conjugates of the functions provided in Fig. 4 are equally valid, so the maxima and minima switch if $-\psi_n$ functions are considered.

The Hydrogen Atom

The n-bumps principle is also applicable to the hydrogen atom; although, for a valid comparison, one needs to distinguish between *s, p, d*, etc. orbitals, i.e., select and set a certain orbital or azimuthal quantum number, ℓ. Given this, positive radial wavefunctions for the lowest-level 1*s*, 2*p*, and 3*d* orbitals must all have one maximum; the wavefunctions for next quantum levels, e.g., 2*s*, 3*p*, and 4*d*, must have one maximum and one minimum, etc. (as shown in Fig. 5 for 2*s* and 3*p*). Any wavefunctions with $\ell > 0$ start from the origin to account for the forbidden area of angular space (Θ).

Mathematically, n bumps in the wavefunctions of higher quantum levels are created by the multiplication of pertinent ground state wavefunctions, with $n = 1$ [$\exp(-x^2)$ for the harmonic oscillator and $\exp(-x)$ for the hydrogen atom], by the pertinent polynomials of (n-1)-th power (Legendre and LaGuerre polynomials, respectively). Note that the
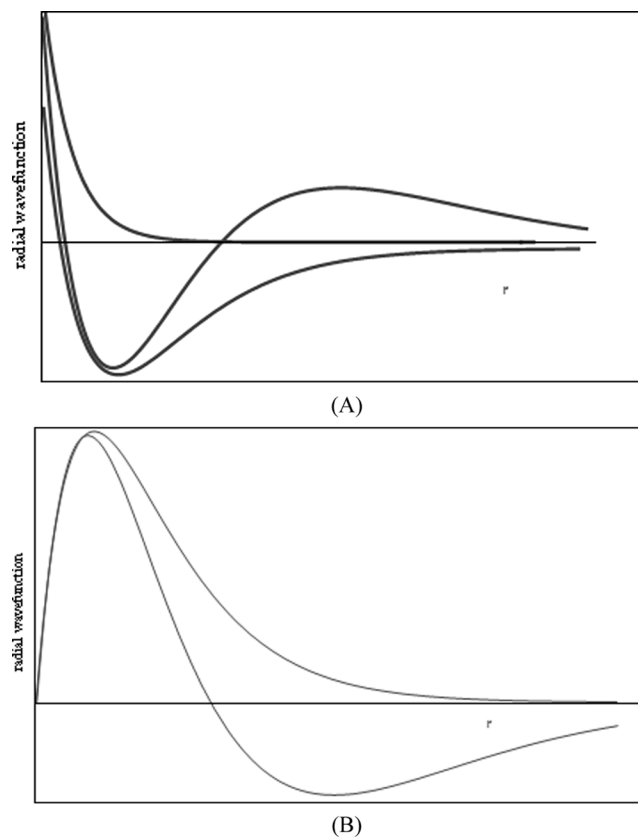
FIGURE 5 Sketches of the nonnormalized wavefunctions for low-lying energy levels of the hydrogen atom, radial component only: (A) 1*s*, 2*s*, and 3*s* orbitals; and (B) 2*p* and 3*p* orbitals. The labels are I, II, and III for the first, second, and third energy levels, respectively.

"wavy" shape of any of these functions is consistent with the consideration of a particle's wavefunction (or its conjugate) as an effective or statistical representation of the corresponding quantum particle. Thus, such wavefunctions may be viewed as periodical trigonometric functions (sine or cosine) *distorted* by the potential energy specific for each quantum mechanical problem.

Other Applications

One more use of the oscillating string analogy was provided by Silbey et al. who showed that the mathematical expression of the p_x operator can be obtained from the differential equation of string oscillation.[18]

Another application of *sound* waves explaining the fundamental principle of linear combinations was suggested by Mortimer.[4] The same musical notes obtained on different musical instruments produce slightly different sounds, due to the small instrument-specific contributions of harmonics, i.e., waves with higher quantum numbers:

$$\xi(x; t) = \Sigma[b_n A_n \sin(n\pi x/a) \sin(wt)] \qquad (8)$$

where b_n is a contribution of a sound with a given n, the number of standing half-waves fitting into the string.

Applied to statistical waves, this principle leads to simple basis sets, linear combinations of wavefunctions (orbitals for atoms or molecules) with unequal and variable (under changing conditions) contributions. It may also be applied to linear combinations of two different wavefunctions with equivalent participation (e.g., orbital hybridization); the principle of harmony of two different sounds is well-known in music. Of course, then, in order to generate normalizable statistical distribution functions, the sum of squares of the coefficients in front of the superimposed wavefunctions in Eq. (8) has to be equal to 1, i.e., satisfying one of the fundamental postulates of quantum mechanics.

CONCLUSION

The source of energy quantization is interference of time-independent or stationary waves (wavefunctions), which statistically represent effective quantum mechanical particles. Depending on the product of interfering time-independent wavefunctions, either maximum enhancement (for self-interference) or no enhancement (orthogonality for two different wavefunctions) occurs. The shape of wavefunctions and their fundamental features (symmetry, number, and tentative location of maxima or minima) may be intuitively understood by using the proposed principle of fitting n half-waves into the entire allowed space and considering the distortion of trigonometric waves by potential energy, which is specific for a given problem.

ACKNOWLEDGMENTS

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