

Rethinking the Boundary Conditions in the Particle-in-a-Box Mind Experiment

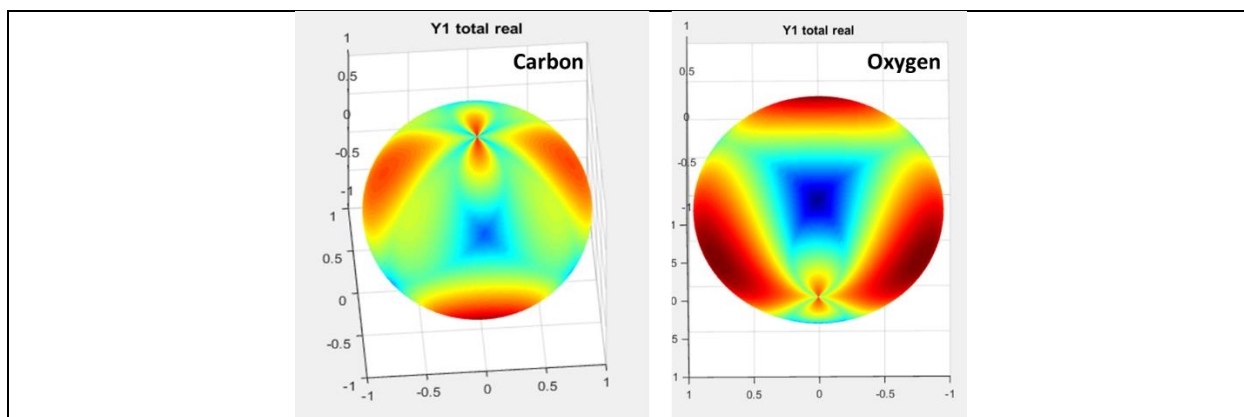
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Abstract

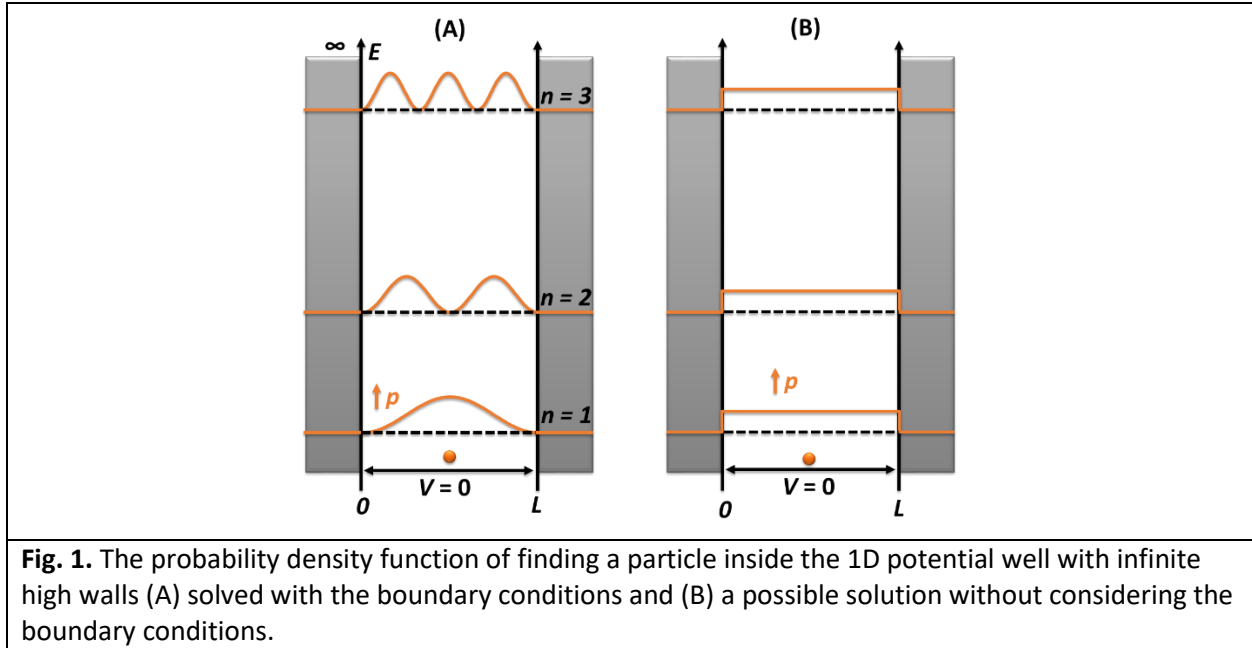
In this manuscript, I speculated that the energy density distributions along space and time in a quantum system are uniform according to the 1st law of thermodynamics. Thus, the complementary energy contributions are added to the classical solutions of the 1D particle in a box problem, making the energy density a complex distribution function over space and time. Then the concept is extended to the free rotation problem with a Hamiltonian slightly different than the classical Schrödinger equation. The picturized energy distribution functions and associated time evolution are described in movies for comparison between example classical wave functions and the energy density functions. The wave functions for the hydrogen atom are then guessed based on the historical solutions.



TOC: Guessed energy density function shapes (absolute) of carbon-like and oxygen-like atoms.

I had trouble explaining the 1D particle-in-a-box mind experiment to my students when I was teaching an undergraduate physical chemistry class at Ohio University. The field has been established in the past 121 years by the greatest physicists in our history, for example, Max Planck, Albert Einstein, Niels Bohr, Louis de Broglie, Max Born, Paul Dirac, Werner Heisenberg, Wolfgang Pauli, Erwin Schrödinger, Richard Feynman, and many others. The experiment states that there is a space of zero potential energy sandwiched between two walls with infinite potentials and a particle say an electron, is put inside the potential well.¹ The wavefunction of this particle must satisfy the continuous assumption as a well-behaved curve thus for the ground state, the probabilities of seeing this particle approaching zero near the walls and maximized at the center of the well. The excited-state wavefunctions have maximums and nodes yielding a probability density function over the space shown in **Fig. 1A**. A student asked during my lecture, why was the probability near the walls zero? I suddenly lost the reason to answer this question due to my limited knowledge of quantum mechanics. So, I said that the wavefunction “should” be

continuous and made up an explanation by analogy it to the vibration of a guitar string that the two ends do not move.



But in fact, I was not sure about my answer. The problem lies in that for a real-world experiment, we will never have a potential well to have walls with infinite potentials that break the continuity of space and time along the x -axis. Thus, it makes sense to have a continuous wave function along with the whole space in the real world. In this mind experiment, we break the continuity of space and time but still expect that the wave function is continuous. This expectation seems not physical.

What if we give up the continuity requirement of the wave function for this special case and instead assume uniform energy density over space and time? Different boundary conditions suddenly open, specifically, the space and time outside of the wall still give a wavefunction of zero but binary values at the wall. If these breaking points are allowed to compensate for our irrational assumption of the existence of potential walls with infinite values, we should expect a probability density function shown in **Fig. 1B**. If we want, we can even assume that a single Planck length from a wall is needed for the wavefunction to jump from a value to zero to enforce its continuity.

So I give it a try to solve the time-dependent Schrödinger equation with the no-boundary assumption:

$$i\hbar \frac{\partial}{\partial t} \psi(x, t) = -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} \psi(x, t) + V(x)\psi(x, t) \quad (1)$$

where the imaginary number $i = \sqrt{-1}$, \hbar is the reduced Planck constant, m is the mass of the particle, $\psi(x, t)$ is the wave function, and $V(x)$ is the potential profile. Without the boundary restriction, all wavefunctions of a free particle in space satisfy this equation:

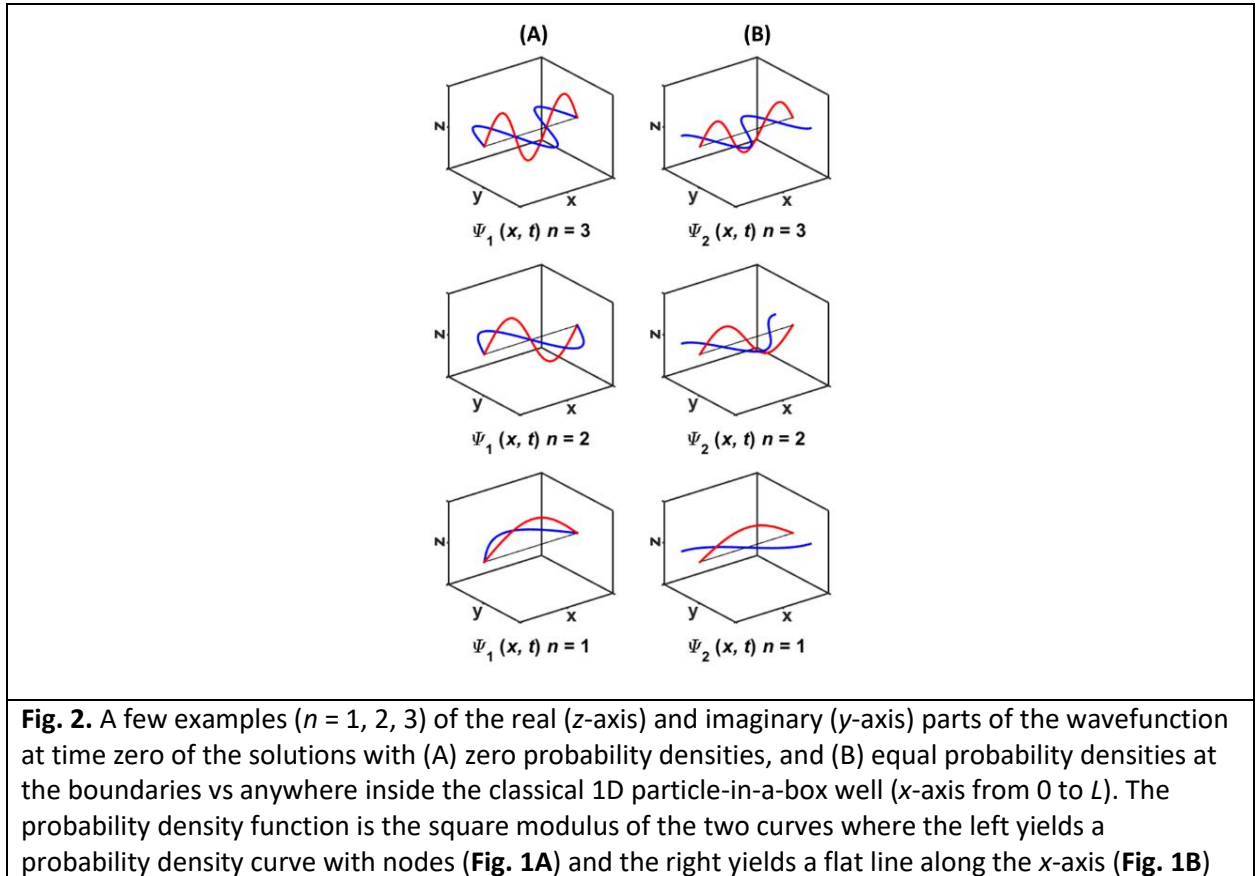
$$\psi(x, t) = \frac{1}{L} e^{\pm iux \pm i\omega t} \quad (2)$$

where u and ω are both arbitrary values.

To meet the experimental observation that energy level is quantized, symmetry argument is required to restrict the values the same as the original arguments in history. Let's assume that the left and right of the well have an identical probability in any given time to have the same amplitude of momentum, i.e. at a resonant state. This argument shrinks the solutions to $u_n = \frac{n\pi}{L}$ and $\omega_n = \frac{n^2\pi^2\hbar}{2mL^2}$ where $n = 1, 2, 3, \dots$ is a positive integer. A comparison among the wavefunctions solved with the boundary and without the boundary conditions is shown in **Fig. 2**.

The energy solutions converge to the classical solutions in the textbooks. However, we see a very different shape of the wavefunctions $\psi(x, t)$ (**Fig. 2**) and probability density functions $|\psi(x, t)|^2$ (**Fig. 1**). There is an interconversion between the real part and the imaginary part of the wavefunction which maintains the modulus of the wavefunction constant across the well (**Fig. 1B**), i.e. it is now equally possible to observe a particle at anywhere of the well. I assume that the real part can be the electric field and the imaginary part can be the magnetic field of the particle in the well that resonant and maintain the energy of the particle for a measurable period (**Fig. 2B**).

At any given time, the sum of the "momentum" in the magnetic field is zero, and/or the sum of the "momentum" of the electric field is zero. I guess any non-resonant frequency decays to the energy levels by radiating electromagnetic waves when the product of the two sums is not zero that breaks the conservation law. After all, the whole energy equation is Maxwell's electromagnetic wave function. Since the wavefunctions belong to a subset of the free-space matter-waves, the Heisenberg uncertainty principle still holds and the two sets of the solutions are entangled together in the momentum space.



inside the well. See attached a movie created using MATLAB and a video converting code.² Time evolution is shown in **SI video 1**.

We can add back the missing energy in the original Schrödinger equation to make the energy density equals everywhere in space and time. We can also modify the stationary differential equation to

$$-\frac{\hbar^2}{2m} \left(\frac{\partial \psi(x,t)}{\partial x} \right)^2 + V(x) \psi(x,t) = E \psi(x,t) \quad (3)$$

We can still use the original equation to quantize the energy levels. Put Equation 2 into Equation 3, we got the stationary-state energy to be:

$$E_n = \frac{\hbar^2 k^2}{2mL^2} e^{\pm i k x} \quad (4)$$

Where $k_n = \frac{n\pi}{L}$. Equation 4 says that the energy density is evenly distributed in the 1D well. However, there is an interconversion between the real energy and the imaginary energy that follows a complementary symmetry and obeys the energy conservation law.

For the rigid free rotator problem, the Hamiltonian becomes,

$$-\frac{\hbar^2}{4mR^2} \left[\left(\frac{\partial \psi(\theta, \varphi, t)}{\partial \theta} \right)^2 + \left(\frac{\partial \psi(\theta, \varphi, t)}{\partial \varphi} \right)^2 \right] + V(\theta, \varphi, t) \psi(\theta, \varphi, t) = E \psi(\theta, \varphi, t) \quad (5)$$

where R is the radius of the rotator, θ and φ are the rotation angles, and $V = 0$. The rotational energy is assumed equally distributed in the two rational degrees of freedom. The third degree of freedom is the axis rotation which does not carry angular momentum, the same argument as in the classical equations. Based on the solutions on Equation 1, I guess a set of stationary wave functions:

$$\psi_{j,k}(\theta, \varphi) = e^{\pm i j \theta} e^{\pm i k \varphi} \quad (6)$$

Where j and $k = 0, 1, 2, 3 \dots$ And

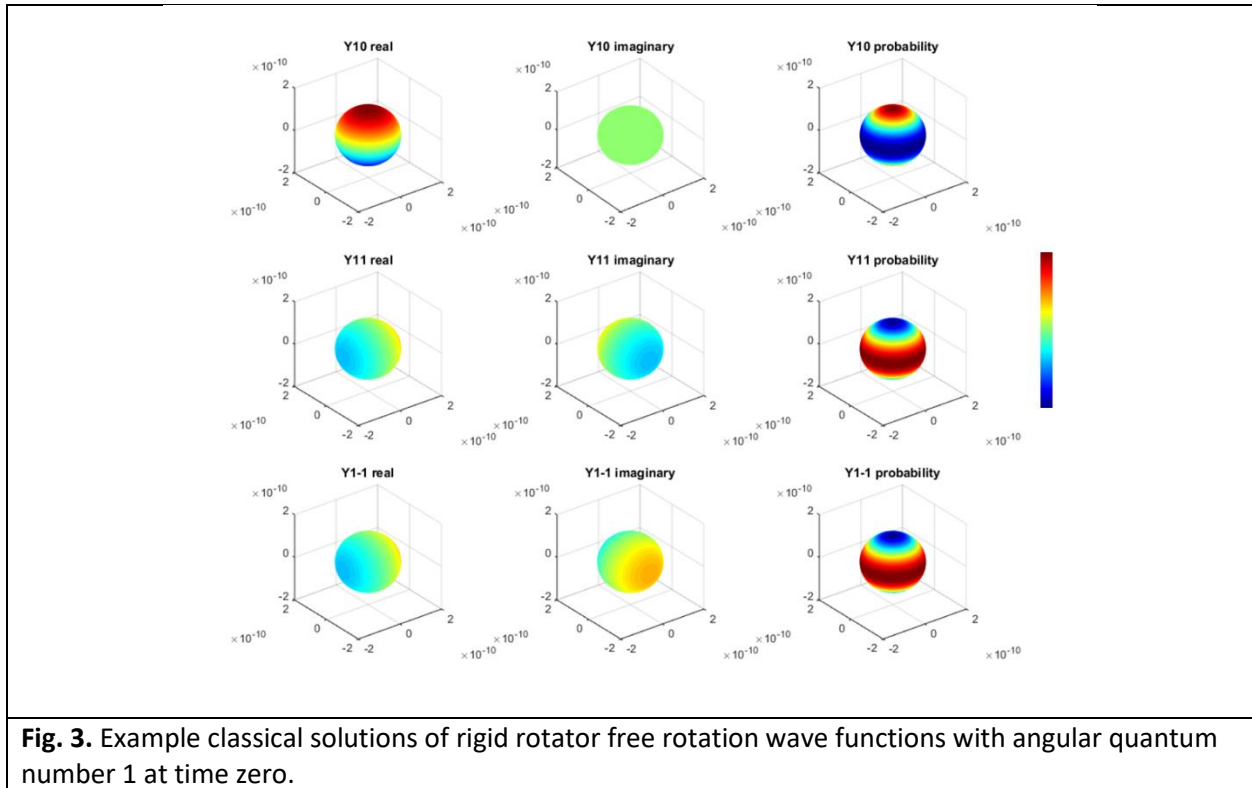
$$E_{j,k} = \frac{(j^2 + k^2) \hbar^2}{4mR^2} e^{\pm i j \theta} e^{\pm i k \varphi} \quad (7)$$

There is a difference between these solutions and the classical solutions. The classical solutions are $E_j = J(J+1) \hbar^2 / (2mR^2)$. The energy is assumed only dependent on one rotational angle and is independent on the other angle, which is a confusing assumption. This assumption yields an energy spacing jumping from J to $J+1$ state $(2J+2) \hbar^2 / (2mR^2)$ that has been experimentally confirmed with rotational spectra of molecules such as hydrogen chloride.³ In order to get the identical answer, the new solutions will need to adapt a selection rule ($\Delta J = \pm 2, \Delta k = 0$) or ($\Delta J = 0, \Delta k = \pm 2$), instead of $\Delta J = \pm 1$. A comparison between shapes of the classical solutions and the new solutions are shown in **Fig. 3**, and **Fig. 4** with the time evolution shown in the **SI video 2** and **video 3** respectively. Larger quantum numbers give more structures with an example of $j = \pm 2$ and $k = \pm 2$ shown in **video 4**.

The new solutions also have different node structures than the classical probability density functions. I speculate that the real part of the energy density function is electric field energy, and the imaginary part of the energy density function is magnetic field energy or vice versa. The distribution and strength in the

real and imaginary parts are set to equal now and I expect it to be variable depending on the systems. Importantly, these equations resemble Maxwell's equation of electromagnetic waves of massless photons. We still have nodes for the electric part and the magnetic part of the wave function that are orthogonal to each other, which can be tested by measuring the nodes with electric and magnetic methods. A problem is over time the real part and the imaginary part both evolve into chiral structures for these solutions when both j and k are none zero, whose physical meaning is unclear.

Both Pauli's exclusion principle and spin can be explained by these new wave functions. When the phase of these solutions is shifted π , a perfectly complementary wave function shows up. If this new phase-shifted function is simply added back to the original function, both the electric momentum and magnetic momentum are canceled over all space and time. This perfectly explains the Pauli exclusive principle. The left-handed and right-handed chiral structures in the wavefunction (**Fig. 4**) naturally explain the spin of the magnetic field thus we don't need to introduce additional spin as in the classical solutions when no chiral structure is observed (**Fig. 3**).



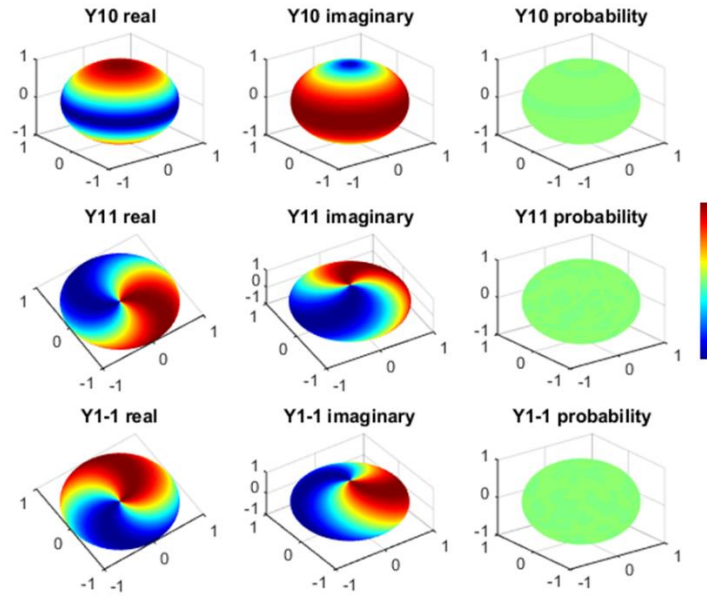


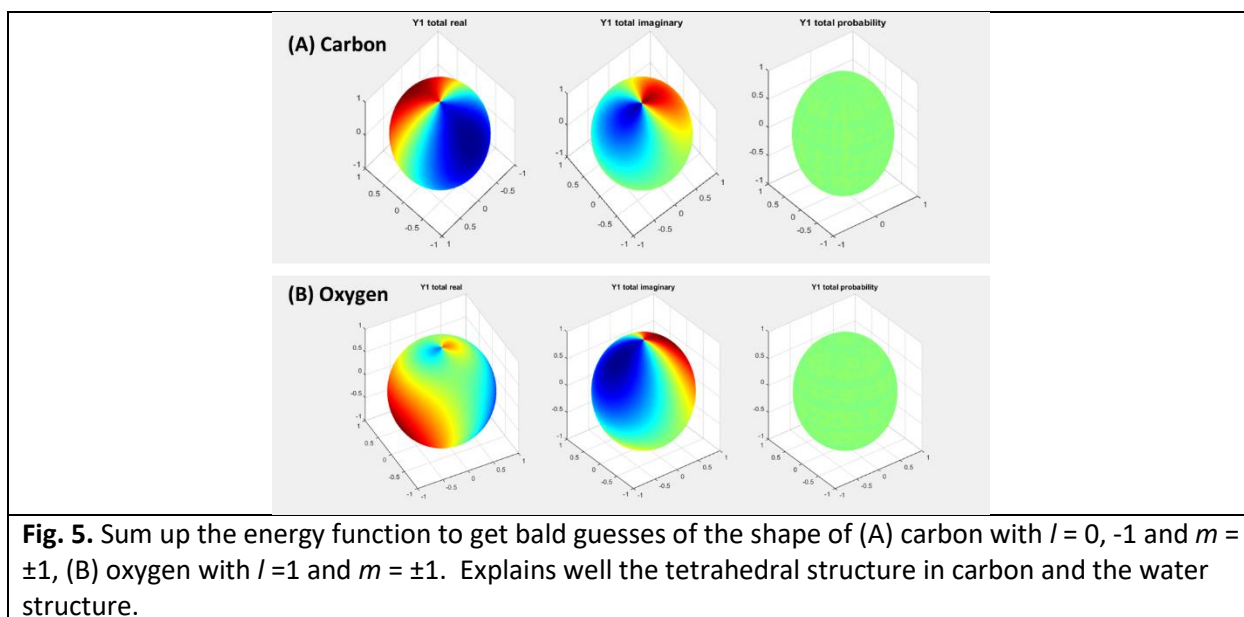
Fig. 4. Example solutions of rigid rotator free rotation new energy density function with angular quantum numbers (1, 0), (1, 1), and (1, -1).

Based on the above theory, I then give it a random guess on the new wavefunctions of atoms. For the hydrogen atom, based on the historically established solutions, I guess an un-normalized solution as

$$\psi_{n,l,m}(r, \theta, \varphi, t) = H_n(r) e^{\pm \frac{ir}{na_0}} e^{\pm il\theta} e^{\pm im\varphi} e^{\pm i\omega t} \quad (8)$$

Where $H_n(r)$ is the Hermite polynomial, and a_0 is the first Bohr radius. We can see that this solution will both satisfies the new wave equation and provide the same energy solutions with the complementary imaginary part to make the energy evenly distributed over space.

One advantage is this wave function is much easier to calculate than the classical solutions. **Fig. 5** showing consistent shapes of the energy functions for atoms such as carbon-like and oxygen-like atoms by simply adding the wave functions together.



In summary, I hope you agree that rethinking the boundary conditions in the classical-quantum mechanical problems that have established over 100 years ago inspires super surprising results. The main new idea is that energy is equally distributed in space a new wave function is proposed (**Equation 3**) to replace the classical Schrödinger equation. If we just use the conservation of the momentum of the electromagnetic field within each cycle, we can further free up the phase restriction for free particles, making a free particle really “free”. This wave equation works consistently with the classical equation and

offers the consistent energy equations with a lot of “spookiness” vanishes in the new model. It has the opportunity to be the missing piece of “incomplete” quantum mechanics that Einstein and others have been looking for over the past 100 years.

Supporting information

Videos and MATLAB source codes are attached to the supporting information.

References

Note: Too many giants have contributed to this field. Historical named references are not listed again here.

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2. Lindner M. AVI to GIF convertor. 2021.
3. Plyler EK, Tidwell ED. The Rotational Constants of Hydrogen Chloride. *Zeitschrift für*

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