From Particle-in-a-Box Thought Experiment to a Complete Quantum Theory?

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Abstract

It is an unavoidable question raised by Albert Einstein if quantum theory is complete. The wavefunctions of elements are now constructed from fitting the experimental data which has made quantum chemistry a black box of mathematical model. It is our best interest to come up with a simpler model to fit the data regardless of our wish to understand reality in a more intuitive and accurate way than classical quantum mechanics. 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 radial wavefunctions for the hydrogen atom and an ideal harmonic oscillator are then derived. Can this assumption on energy distribution and the pre-mature math in this manuscript lead to a complete quantum theory? Can the idea of energy conservation unify special relativity and quantum?

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

I had trouble explaining the 1D particle-in-a-box thought experiment to my students when I was teaching an undergraduate physical chemistry class at Ohio University 2021 during the COVID-19 pandemic. The quantum theory has been established in the past 120s 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. This thought 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 adapted an explanation from memory of reading by analogy it to the vibration of a guitar string that the two ends do not move.

![Fig. 1. The probability density function of finding a particle inside the 1D potential well with infinite high walls (A) solved with the boundary conditions and (B) a possible solution without considering the boundary conditions.](image)

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 with an infinite potential gradient slope. Thus, it makes sense to have a continuous wave function along with the whole space in the real world. In this thought 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:
\[ \imath \hbar \frac{\partial}{\partial t} \psi(x, t) = -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} \psi(x, t) + V(x)\psi(x, t) \quad (1) \]

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:

\[ \psi(x, t) = C e^{\pm iux \pm i\omega t} \quad (2) \]

where \( C, u \) and \( \omega \) are all arbitrary values. Fig. 2 shows an example free particle wave \( C e^{iux - i\omega t} \).

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 \( n = 1, 2, 3, \ldots \) is a positive integer. The normalization factor \( C = \sqrt{\frac{2}{L}} \). A comparison among the wavefunctions solved with the boundary and without the boundary conditions is shown in Fig. 3.

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. 3) 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

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**Fig. 2.** An example free particle wave (left-handed) moving towards right \( \psi(x, t) = e^{iux - i\omega t} \) (SI movie 1).
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. 1B).

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.

![Fig. 3. A few examples (n = 1, 2, 3) of the real (z-axis) and imaginary (y-axis) parts of the wavefunction at time zero of the solutions with (A) zero probability densities, and (B) equal probability densities at the boundaries vs anywhere inside the classical 1D particle-in-a-box well (x-axis from 0 to L). The probability density function is the square modulus of the two curves where the left yields a probability density curve with nodes (Fig. 1A) and the right yields a flat line along the x-axis (Fig. 1B) inside the well. See attached a movie created using MATLAB and a video converting code. Time evolution is shown in SI Movie 2.](image)

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 my JChen equation:

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

(3)

Where the potential energy \( V \) and total energy \( E \) is complex. Or

\[-\frac{\hbar^2}{2m} \left( \frac{\partial \psi^*(x,t)}{\partial x} \right) \left( \frac{\partial \psi(x,t)}{\partial x} \right) + V_r(x) = E_r \]  

(4)
where the potential energy $V_r(x)$ is a real distribution, $E_r$ is a real constant, and $\Psi^*$ is the conjugate wavefunction.

For the particle in a box problem the potential energy is zero in the well. We can still use the original equation to quantize the energy levels. Put Equation 2 into Equation 3 or 4, we got the stationary state energy density distribution to be:

$$E_n = \frac{\hbar^2 k_n^2}{2mL} e^{\pm i k_n x} \quad (5)$$

Where $k_n = \frac{n \pi}{L}$. Equation 5 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.

If we want to recreate a standing wave over the space and time to mimic the traditional solutions of the particle-in-a-box problem, then the solution of the time-dependent equation become a combination of a wave and its reflection:

$$\psi(x, t) = \psi_L(x, t) + \psi_R(x, t) = C_L e^{i k_n x + i\omega t} + C_R e^{-i k_n x + i\omega t} \quad (6)$$

Or

$$\psi(x, t) = \psi_L(x, t) + \psi_R(x, t) = C_R e^{i k_n x - i\omega t} + C_L e^{-i k_n x - i\omega t} \quad (7)$$

Where $C_L = C_R = \sqrt{\frac{1}{2L}}, k_n = \frac{n \pi}{L}, \omega_n = \frac{\hbar k_n^2}{2m}$, which yield energy density distribution along the well $E_n = \frac{\hbar^2 k_n^2}{4 m L} (e^{i k_n x + i\omega t} + e^{-i k_n x - i\omega t} + i\pi)$. This result is confusing because the energy distribution now has nodes, probably because the two waves are not orthogonal. This energy distribution is against my early assumption that the energy density over space is uniform, and I don’t know why.

For the rigid free rotator problem, the Hamiltonian becomes,

$$-\frac{\hbar^2}{4mR^2} \left[ \left( \frac{\partial \psi(\theta, \varphi, t)}{\partial \theta} \right)^2 + \left( \frac{\partial \psi(\theta, \varphi, t)}{\partial \varphi} \right)^2 \right] + V(\theta, \varphi, t) \psi(\theta, \varphi, t) = E \psi(\theta, \varphi, t) \quad (8)$$

where $R$ is the radius of the rotator, $\theta$ and $\varphi$ are the rotation angles, and $V = 0$. The rotational energy is assumed equally distributed in the two rotational 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:

$$\psi_{j,k}(\theta, \varphi) = e^{\pm ij \theta} e^{\pm ik \varphi} \quad (9)$$

Where $j$ and $k$ are 0, 1, 2, 3...
\[ E_{j,k} = \frac{(j^2+k^2)\hbar^2}{4mR^2} e^{\pm i j \theta} e^{\pm i k \phi} \quad (10) \]

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. 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. 4, and Fig. 5 with the time evolution shown in the SI Movie 3 and Movie 4 respectively. Larger quantum numbers give more structures with an example of \( j = \pm 2 \) and \( k = \pm 2 \) shown in Movie 5.

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 \( \pi \), 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. 5) 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. 4).
Fig. 4. Example classical solutions of rigid rotator free rotation wave functions with angular quantum number 1 at time zero (SI Movie 3).
Fig. 5. Example solutions of rigid rotator free rotation new energy density function with angular quantum numbers (1, 0), (1, 1), and (1, -1) (SI Movie 4).

In the external global reference frame, there should be three rotational angles. If we add the third rotation angle and ignore all the degeneracy among some redundant rotational freedoms in the global reference frame. The free rotation equation can be,

$$\frac{-\hbar^2}{4mR^2} \left[ \left( \frac{\partial \psi(\theta_1, \theta_2, \theta_3, t)}{\partial \theta_1} \right)^2 + \left( \frac{\partial \psi(\theta_1, \theta_2, \theta_3, t)}{\partial \theta_2} \right)^2 + \left( \frac{\partial \psi(\theta_1, \theta_2, \theta_3, t)}{\partial \theta_3} \right)^2 \right] = E\psi(\theta_1, \theta_2, \theta_3, t)$$  \hspace{1cm} (11)

And

$$\psi(\theta_1, \theta_2, \theta_3, t) = e^{\pm i j_1 \theta_1} e^{\pm i j_2 \theta_2} e^{\pm i j_3 \theta_3} e^{\pm i \omega t}$$  \hspace{1cm} (12)

Where $\theta_1$, $\theta_2$, $\theta_3$, are the three rotation angles on surfaces $yz$, $zx$, $xy$ along axes $x$, $y$, and $z$ respectively (right hand rule, all $\theta$s $0$-$2\pi$ for each cycle with a lot of degeneracies), and $j = 0, 1, 2, ...$ are associated quantum numbers, and $\omega$ is a three-dimensional matrix with frequency associated with each rotation angle. The above 2 angle version (Equations 8-10) is a special case when fixed $j_3 = 0$. And

$$E_j = \frac{(j_1^2 + j_2^2 + j_3^2)\hbar^2}{4mR^2} e^{\pm i j_1 \theta_1} e^{\pm i j_2 \theta_2} e^{\pm i j_3 \theta_3} e^{\pm i \omega t}$$  \hspace{1cm} (13)
For the hydrogen electron problem on the radial wavefunction, force $F = -k/x^2$ where $k = \frac{q_e^2}{4\pi\varepsilon_0}$ is the force constant of the Coulombic electric attraction and $x$ is the radius away from the sphere and $x > 0$, we have the new Hamiltonian:

$$-\frac{\hbar^2}{2m} \left( \frac{\partial \psi(x,t)}{\partial x} \right)^2 + E_V \psi(x, t) = E \psi(x, t) \quad (14)$$

Where $E_V$ is the distribution of potential energy. This equation splits the potential energy with the wave like kinetic energy. The distribution of the potential energy can be both real and imaginary, which is better to adapt the following form (Equation 4) if we want to ignore the complex composition of the potential energy:

$$-\frac{\hbar^2}{2m} \left( \frac{\partial \psi^*(x,t)}{\partial x} \right) \left( \frac{\partial \psi(x,t)}{\partial x} \right) = E_r - \frac{k}{x} \quad (15)$$

Where $x > \frac{k}{E_r}$. That is, if we stick to the three-dimensional formula (two real and one imaginary) for this one-dimensional problem, the wave is confined in the potential well to be a wavelet. An alternative solution can be placing the potential vector in the fourth imaginary dimension which will involve additional vector or quaternion calculations.

Solving this equation, and discard the positive $\sqrt{k}$ solution for now that causes infinity, we get,

$$\psi(x) = e^{\frac{\sqrt{2m}}{\hbar}(-2\sqrt{kx} \pm i\sqrt{E_r}x))} \quad (16)$$

Where $E_r$ is a positive real value, if $E_r$ is negative, $1i$ is not needed. Put the electric constant for hydrogen atom between proton and electron into the above equation with electron mass $m = 9.109 \times 10^{-31}$ kg, $k = 2.307 \times 10^{-28}$ J m, and various $E_r$, we can see a set of wavefunctions shown in Fig. 6. This model shows simple structure below \~10 eV with the maximum imaginary distribution at \~25 pm which is smaller than the Bohr radius at 53 pm. The minimum real wavefunction is found at 127 pm which is coincident with the van der Waals radius of hydrogen at 120 pm. At higher energy, the wavefunctions start to show fine structure at smaller distances. When energy is >1000 eV, the structures of both real and imaginary waves become not-very-interesting exponential decay of quasi-symmetric waves over space.
Harmonic oscillation is also tried,

$$-\frac{\hbar^2}{2m} \left( \frac{\partial \psi^*(x,t)}{\partial x} \right) \left( \frac{\partial \psi(x,t)}{\partial x} \right) = E_r - \frac{kx^2}{2} \quad (17)$$

Yielding a wavefunction,

$$\psi(x) = e^{\sqrt{2m} \left( \frac{\sqrt{E_r}}{\hbar} \right) \left( \frac{-\sqrt{k}}{4} \pm i\sqrt{E_r}x \right)} \quad (18)$$

Which is a Gaussian wavelet as expected but it is unclear what boundary condition to choose to quantize the energy. Significant tunnelling is observed for lower energy and over confinement is observed for higher energy, because the Gaussian width does not expend over larger energy which seems nonphysical. The thought experiment on harmonic oscillator could suggest this JChen model still has limitations in representing reality.

Using Albert Einstein’s special relativity summation formulas (Lorentz transformation) of 1D relative velocity between object A and B using A as the reference object:

$$v_{BA} = \frac{v_B - v_A}{1 - \frac{v_B v_A}{c^2}} \quad (19)$$

We can guess an energy wave equation that is constructed similarly by square the velocities to represent the speed limitation of exchanging information between the potential energy and the kinetic energy, and ignore the limit on exchanging real and imaginary energy:

$$\frac{\hbar^2}{2m} \left( \frac{\partial \phi(x,t)}{\partial x} \right)^2 \left( \frac{\partial \phi(x,t)}{\partial x} \right)^2 + V(x) - i\hbar c \sqrt{\frac{2V(x)\phi(x,t)}{m}} = \frac{mc^2}{\hbar c^2} \psi(x, t) \quad (20)$$
Of course, this guess is meant to be funny and nonsense, and I have no intention to make any sense of it. It is just an echo of Einstein's question about whether quantum mechanics can be considered complete.

The idea of energy conservation can be used to solve classical mechanical problems such as a pendulum on earth (Fig. 7, SI Fig. S1). Pick a reference point at -l (Fig. 7A), the angular momentum of the pendulum is fully distributed at the imaginary dimension using the coding equation (Fig. 7B, 7D, 7E). The decoding equation can be used to calculate the kinetic energy and potential energy at any angle within the boundaries (Fig. 7C, 7F-7H) and a movie that makes sense in the real world can be generated using the initial information provided in Fig. 7A. Choosing different reference heights significantly changes the coded functions, thus care is needed in choosing the reference height (SI Fig. S1).

**Fig. 7.** Solving a classical pendulum problem using the same idea of energy conservation. The equations seem to work outside of the boundaries if no extra restrictions are applied. A careful pathway must be chosen to regenerate a movie to reflect the real motion of the pendulum.

In summary, rethinking the boundary conditions in the classical-quantum mechanical problems that have been established >100 years ago inspiring super surprising results. Till now the Schrödinger equation can only calculate the wavefunctions of hydrogen and maybe helium while the wavefunctions of the rest elements are all fitted from experimental data, making the Schrödinger equation rather an empirical reflection of reality. As such, other equations to code reality can be tried equally as the Schrödinger equation and I have provided such a try that is surprisingly simple to construct wavefunctions of systems of interest. The idea is to code the reality into the model equation and use the opposite operation to decode and pull out the coded information. The main new idea in this report is that energy is equally distributed in space with a new energy distribution wavefunction proposed (Equation 3 and Equation 4) to replace the classical Schrödinger equation. If we just use the conservation of the momentum of the electromagnetic field within each cycle, we can quantize the energy and 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 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, i.e., a simpler approximation of reality.
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.

Fig. S1. Scheme of $\frac{\partial \theta}{\partial t}$ vs $\theta$ function a classical pendulum using different reference heights (A-E). The sign of the kinetic energy changes when picking different reference heights. The distribution of kinetic energy in the real and imaginary dimensions changes with the selection of reference height. The real $\left(\frac{\partial \theta}{\partial t}\right)^2$ always calculate the kinetic energy correctly even out of the boundary while $\left|\frac{\partial t}{\partial t}\right|^2$ fails sometimes. Picking a reference height below the minimum allocates all the kinetic energy in the imaginary dimension which is fully separated from the potential energy. This choice maximizes the application region of $\left|\frac{\partial t}{\partial t}\right|^2$ in calculating kinetic energy. The equations can be extrapolated beyond the boundary but there is no physical meaning of negative kinetic energy in the classical world. All reference heights have the complete set of information to generate the same swing movie of the pendulum, but care should be taken to choose the signs, the equations, and the time paths along the two solutions of this method.