Old quantum theory or Quantum Mechanics: a look at the spectrum of the hydrogen atom

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Abstract: The article compares the derivation of the principal energy states in the hydrogen atom as it is done in Quantum Mechanics and in old quantum theory. The method in old quantum physics makes a lot more sense. Section 3 explains why Schrödinger's momentum substitution only works in one dimension and there it is basically the same as Bohr's quantization rule for the angular momentum, which is the same as de Broglie's hypothesis in the application where this hypothesis works. The conclusion of the article is that Quantum Mechanics and Quantum Field Theory incorrectly have generalized Schrödinger's one-dimensional momentum substitution to a many dimensional momentum substitution.

Keywords: Hydrogen atom spectrum, Quantum Mechanics, old quantum theory, Schödinger equation.

1. The spectrum of hydrogen in Quantum Mechanics

The Schrödinger equation for a hydrogen atom is

$$\hat{H}\Psi = E\Psi \tag{1}$$

$$\left(-\frac{\hbar^2}{2\mu}\nabla^2 - \frac{e^2}{4\pi\varepsilon_0 r}\right)\Psi = E\Psi \tag{2}$$

where μ is the reduced mass of an electron. We can write $\mu = m_e$ with sufficient precision. Let us calculate the lowest energy level. It is on the first S-state, which is spherically symmetric and we can set

$$\Psi = \Psi(r). \tag{3}$$

The Schrödinger equation gives

$$\nabla^2\Psi(r) + \frac{\hbar^2}{2m_e}\left(\frac{e^2}{4\pi\varepsilon_0 r} + E\right)\Psi(r) = 0 \tag{4}$$

$$\frac{1}{r^2}\frac{d}{dr}r^2\frac{d}{dr}\Psi(r) + \frac{\hbar^2}{2m_e}\left(\frac{e^2}{4\pi\varepsilon_0 r} + E\right)\Psi(r) = 0 \tag{5}$$

$$\Psi'' + \frac{2}{r}\Psi' + \frac{\hbar^2}{2m_e}\left(\frac{e^2}{4\pi\varepsilon_0 r} + E\right)\Psi = 0. \tag{6}$$

Let us try the form

$$\Psi(r) = e^{-\frac{1}{2}ar} \tag{7}$$

for no other reason that that it is the wavefunction of the first S-level in Quantum Mechanics (apart of normalization). Inserting Ψ the equation gives

$$\frac{1}{4}a^2\Psi + -\frac{a}{r}\Psi + \frac{\hbar^2}{2m_e}\frac{e^2}{4\pi\varepsilon_0 r}\Psi + \frac{\hbar^2}{2m_e}E\Psi = 0. \tag{8}$$

Thus

$$\frac{\hbar^2}{2m_e}E = -\frac{1}{4}a^2 \qquad a = \frac{\hbar^2}{2m_e}\frac{e^2}{4\pi\varepsilon_0} \tag{9}$$

and

$$E = -\frac{1}{4}\frac{\hbar^2}{2me}\left(\frac{2m_e e^2}{4\pi\varepsilon_o\hbar^2}\right)^2 = -\frac{m_e e^4}{8\varepsilon_0^2\hbar^2}. \tag{10}$$

This is the correct energy level for the first S-state. Bohr's radius is also obtained correctly: the average potential energy over one wavelength is from the virial theorem and the Coulomb potential at the Bohr radius a_0

$$< V >= 2E = -\frac{m_e e^4}{4\varepsilon_0^2\hbar^2} = -\frac{e^2}{4\pi\varepsilon_0 a_0} \tag{11}$$

$$a_0 = \frac{4\pi\epsilon_0\hbar^2}{m_e e^2}. \tag{12}$$

The only question with this calculation is what is the reason to insert the wavefunction

$$\Psi(r) = e^{-\frac{1}{2}ar} = e^{-\frac{r}{a_0}}. \tag{13}$$

A free electron moves as a particle along a definite orbit, as can be seen in a cathode-ray tube: electrons do hit the screen in a very controlled way. An electron has mass, it does not dissolve into a wave when being in the electron belt of an atom. It must circulate the nucleus, else it falls to the nucleus. The wavefunction does not show any of the expected behavior of the electron. It is also not a description of the probability of finding the electron: this wavefunction has the maximum at the origin, i.e., if it is a probability of an electron to be at some place, then the electron is most likely to be at the nucleus, which is not what can happen.

In order to find solutions to higher S-levels, and to levels where the electron has azimuthal and magnetic quantum numbers l and m, the solution to the Schrodinger equation in Quantum Mechanics is calculated by trying a separating solution

$$\Psi(x, \theta, \phi) = R(r)Y(\theta, \phi). \tag{14}$$

The equation for $Y(\theta, \phi)$ is obtained by noticing that

$$r^2\nabla RY = Rr^2\nabla Y + Yr^2\nabla R + \frac{2m_e}{\hbar^2}rR(r) + \frac{2m_e}{\hbar^2}r^2ERY = 0 \tag{15}$$

separates to a part with only r and a part with θ and ϕ. Dividing by RY gives

$$\frac{1}{Y(\theta,\phi)}r^2\nabla^2 Y(\theta, \phi) = -C \tag{16}$$

and

$$\frac{1}{R(r)} r^2 \nabla^2 R(r) + \frac{2m_e}{\hbar^2} r R(r) + \frac{2m_e}{\hbar^2} r^2 E R(r) = C. \tag{17}$$

The constant C coming from separating r and θ, ϕ functions turns out to be $l(l+1)$. The solution for Y is directly generalized sperical harmonics. The solution for R is found by the trial

$$R(r) = e^{-\frac{1}{2}ar} (ar)^l L(ar). \tag{18}$$

Inserting this trial gives

$$0 = \left(l(l+1) + \frac{1}{4} a^2 r^2 - a(l+1)r \right) R \tag{19}$$

$$+ e^{-\frac{1}{2}ar} (ar)^l a^2 r^2 L''(ar). \tag{20}$$

$$+ e^{-\frac{1}{2}ar} (ar)^l \left(2(l+1)ar - a^2 r^2 \right) L'(ar) \tag{21}$$

Equation (19) has the term $C = l(l+1)$ that cancels with the term from the Y equation (16). The second term in (19) is $\frac{1}{4}a^2 r^2$. It gives the equation with the energy E term as in (9). But (19) has the term $-a(l+1)r$, which is a problem because it contains l. This l does not appear in the energy levels, we must move it somewhere. In order to do that we add and subtract a term bar, where b is a number to be determined, and move $-a(l+1)r$ away from the first term. Thus, we write

$$0 = \left(l(l+1) + \frac{1}{4} a^2 r^2 - bar \right) R \tag{22}$$

$$+ e^{-\frac{1}{2}ar} (ar)^l a^2 r^2 L''(ar). \tag{23}$$

$$+ e^{-\frac{1}{2}ar} (ar)^l \left(2(l+1)ar - a^2 r^2 \right) L'(ar) \tag{24}$$

$$+ e^{-\frac{1}{2}ar} (ar)^l \left(bar - a(l+1)r \right) L(ar). \tag{25}$$

Setting

$$a^2 r^2 L''(ar) + \left(2(l+1)ar - a^2 r^2 \right) L'(ar) + \left(bar - a(l+1)r \right) L(ar) = 0 \tag{26}$$

reduces the equation to

$$0 = \left(l(l+1) + \frac{1}{4} a^2 r^2 - bar \right) R. \tag{27}$$

First we look at (26) Let us write $x = ar$ and divide by x, then (26) is

$$x L''(x) + (2l + 1 + 1 - x) L'(x) + (b - l - 1) L(x) = 0. \tag{28}$$

This is the equation for generalized Laguerre polynomials

$$x L''(x) + (\alpha + 1 - x) L'(x) + n L(x) = 0. \tag{29}$$

where $n = b - l - 1$ and $\alpha = 2l + 1$. The solution is $L(x) = L^{2l+1}_{b-l-1}(ar)$. This means that b must be an integer and $b - l - 1 \geq 0$.

Like (8), equation (27) gives two equations that must be satisfied

$$\frac{\hbar^2}{2m_e}E = -\frac{1}{4}a^2 \qquad ba = \frac{\hbar^2}{2m_e}\frac{e^2}{4\pi\varepsilon_0}. \tag{30}$$

In the solution $L(x) = L^{2l+1}_{b-l-1}(ar)$ the number b must be an integer and $b-l-1 \geq 0$. It is natural to set $b = n$ and with this value of b we get correctly all S-state energy levels

$$a = \frac{\hbar^2}{2m_e}\frac{e^2}{4\pi\varepsilon_0}\frac{1}{n} \tag{31}$$

$$E = -\frac{m_e e^4}{8\varepsilon_0^2\hbar^2}\frac{1}{n^2}. \tag{32}$$

This solution of Quantum Mechanics may look impressive but it is only a slight variation of the solution to the Laplace equation

$$\nabla^2\Psi = 0 \tag{33}$$

which has a separating solution

$$\Phi = R(r)Y^{\theta,\phi} \tag{34}$$

where $R(r) = r^l$ and $Y(\theta, \phi)$ is spherical harmonics. $R(r)$ is modified in order to get the Coulomb potential term and the energy term.

The problem with this solution is the same problem that already was mentioned for the first S-state, all S-states have wavefunctions that do not seem to correspond to anything. The first three S-states seem to be (ignoring normalization)

$$\Phi_{1,0,0} = e^{-\frac{r}{a_0}} \tag{35}$$

$$\Phi_{2,0,0} = e^{-\frac{r}{2a_0}}\left(2 + \frac{r}{2a_0}\right) \tag{36}$$

$$\Phi_{3,0,0} = e^{-\frac{r}{3a_0}}\left(\left(\frac{r}{a_0}\right)^2 - \frac{7}{4}\frac{r}{a_0}\right). \tag{37}$$

What can these possibly mean physically? The electron does circulate the proton in the hydrogen atom.

The advantage of this solution seems initially to be that it includes the quantum numbers l and m, but the way it includes them is problematic. In chemistry there is the periodic table. The location in the periodic table to a certain degree predicts chemical properties of an atom and chemical properties depend on the electron belt, mainly from the outer electrons. We should see the rectangular shape of the periodic system in l and m corresponding to n, but the number of l and m states on a given n-state grows fast. It does not seem to fit to the periodic table structure.

2. The spectrum of hydrogen in old quantum theory

The energy levels of S-states and the Bohr radius from old quantum theory are derived as follows. Setting the centrifugal force equal the Coulomb force on the smallest circular radius $r = a_0$ gives

$$F = \frac{m_e v^2}{a_0} = \frac{e^2}{4\pi\varepsilon_0 a_0^2} \tag{38}$$

$$a_0 = \frac{e^2}{4\pi\varepsilon_0 m_e v^2}. \tag{39}$$

In a more precise calculation, the mass should be μ, but we will use m_e as it is customary and does not make a measurable error. The average kinetic energy $< K >$ (average over one round) and the average potential energy relate by the virial theorem as

$$< V >= -2 < K >= -m_e v^2. \tag{40}$$

In the old quantum theory quantization is made with quantization rules. The quantization rule in this case is

$$- < V >= h\nu \tag{41}$$

where

$$\nu = \frac{v}{\lambda} = \frac{v}{2\pi a_0}. \tag{42}$$

Here $\lambda = 2\pi a_0$, the length of of one round at the radius a_0. Then

$$m_e v^2 = h\nu = h\frac{v}{2\pi a_0} = \hbar\frac{v}{a_0} \tag{43}$$

and

$$v = \frac{\hbar}{m_e a_0}. \tag{44}$$

Inserting v into

$$a_0 = \frac{e^2}{4\pi\varepsilon_0 m_e v^2} = \frac{4\pi\varepsilon_0\hbar^2}{m_e e^2} \tag{45}$$

gives the correct value of Bohr's radius. The lowest energy level is correctly obtained

$$E_1 = - < K >= -\frac{1}{2}m_e v^2 = -\frac{1}{2}m_e\frac{\hbar^2}{m_e^2 a_0^2} = -\frac{m_e e^4}{8\varepsilon_0^2 h^2}. \tag{46}$$

Energy levels of higher S-states are also obtained correctly, and they are on circular orbits

$$r = na_0 \qquad E_n = -\frac{1}{2}m_e\frac{\hbar^2}{m_e^2(na_0)^2} = -\frac{m_e e^4}{8\varepsilon_0^2 h^2}\frac{1}{n^2}. \tag{47}$$

It should not be surprising that Bohr's radius and energy levels of S-states of the hydrogen atom are correctly obtained from old quantum theory because that is how they were originally derived. Notice that Bohr chose $r_n = n^2 a_0$ and then his atomic model could not explain the Zeeman effect because the S-states had $L = n\hbar$. With the above definition all S-states have $L = \hbar$. There is a catch to this choice: then all higher states are unstable because the centrifugal force is not sufficient to balance the Coulomb force for anything than the lowest state.

The adhoc part of old quantum theory is the quantization rules. The rule that is used above agrees with two other quantization rules of old quantum theory, de Broglie wavelength

$$\lambda = \frac{h}{p} = \frac{h}{m_e v} \tag{48}$$

where the momentum is not the relativistic or apparent momentum, and Bohr's quantization rule for angular momentum on a circular orbit

$$L = m_e v r = \hbar. \tag{49}$$

From these rules we get with $\lambda = 2\pi r = 2\pi a_0$

$$\lambda = 2\pi r = \frac{h}{m_e v} \quad \rightarrow \quad L = m_e v r = \hbar \tag{50}$$

$$\lambda = \frac{h}{m_e v} \quad \rightarrow \quad < V >= m_e v^2 = h\frac{v}{\lambda} = h\nu. \tag{51}$$

In order to get the azimuthal quantum number, we have to go to Sommerfeld's atomic theory where orbits are elliptic. Sommerfeld discovered the fine structure constant α and derived the correct fine structure spectrum for hydrogen, apart of the spin magnetic number. Sommerfeld did not yet address the spin, but he did include the azimuthal quantum number. Old quantum theory was obsolated by Quantum Mechanics, but very possibly it could be refined to give all quantum numbers. The advantages of this semi-classical theory are greater than the drawbacks. Though it did lead to some paradoxes, it is also true that Quantum Mechanics and Quantum Field Theory has several paradoxes, of much worse kind, see [1][2].

Some of the arguments used against a semi-classical atomic model are simply wrong. One of them is that a circulating electron radiates and therefore loses energy and will finally fall to the nucleus. This is not the case. A circulating charge does radiate and the field undulates but an undulating field does not make any work itself, it has to be loaded by charged masses that are moved by the field. In the case of an electron circulating the nucleus, the electron cannot move to a smaller orbit and release energy that could do work, because the electron can only be in orbits that agree with the quantization rule. Therefore the field, though undulating, cannot do any work. This means that the field cannot even be measured. But undulation of the field can be mathematically shown. If the field is loaded with something requiring work, this imposes a boundary condition on the field and with the boudary conditions the undulations are not possible.

The following section explains my main critizism against Quantum Mechanics and Quantum Field Theory: the use of the three or four dimensional Laplacian in the momentum substitution.

3. Laplacian or one-dimensional second-order partial derivative?

Consider the case of a particle moving on a straight line, like an electron in a cathode-ray tube. It is accelerated in the direction of movement, but it does not change the direction. Let there be a one-dimensional coordinate system where the r-axis is at the direction of movement of the particle. Let us investigate a function $f(r)$ of r. Let us embed this one-dimensional coordinate system into a 3-dimensional coordinate system (x, y, z) so that the r-axis is the line $y = (2/3)x$, $z = 0$. What is the second derivative of $f(r)$ in coordinates x,y and z? In order to make this simple, let $f(r) = r^3$. Then

$$\frac{d^2}{dr^2} f(r) = 6r. \tag{52}$$

If we assume that there is also a time coordinate, i.e., $f(r, t) = r^3$, we can write for any $f = f(r, t)$

$$\frac{d^2}{dr^2} f = \frac{\partial^2}{\partial r^2} f. \tag{53}$$

The one-dimensional second-order partial derivative cannot be generalized into n-dimensional partial derivative in the following way:

$$\frac{\partial^2}{\partial r^2} \quad \to \quad \sum_{i=1}^{n} \frac{\partial^2}{\partial x_i^2}. \tag{54}$$

At least, if such a generalization is done, it must be very carefully motivated because these expressions do not give the same result. Let us do the calculation with $f(r) = r^3$, $n = 3$:

$$\sum_{i=1}^{n} \frac{\partial^2}{\partial x_i^2} f(r) = \sum_{i=1}^{n} \frac{\partial^2}{\partial x_i^2} \left(\sum_{j=1}^{n} x_j^2 \right)^{\frac{3}{2}} \tag{55}$$

$$= \sum_{i=1}^{n} \frac{\partial}{\partial x_i} \left(\frac{\partial}{\partial x_i} \left(\sum_{j=1}^{n} x_j^2 \right)^{\frac{3}{2}} \right) \tag{56}$$

$$= \sum_{i=1}^{n} \frac{\partial}{\partial x_i} \left(3x_i \left(\sum_{j=1}^{n} x_j^2 \right)^{\frac{1}{2}} \right) \tag{57}$$

$$= \sum_{i=1}^{n} \left(3 \left(\sum_{j=1}^{n} x_j^2 \right)^{\frac{1}{2}} + 3x_i^2 \left(\sum_{j=1}^{n} x_j^2 \right)^{-\frac{1}{2}} \right) \tag{58}$$

$$= \sum_{i=1}^{n} \left(3r + 3\frac{x_i^2}{r} \right) = 3(n+1)r. \tag{59}$$

Especially, if $n = 3$, we get

$$\sum_{i=1}^{3} \frac{\partial^2}{\partial x_i^2} f(r) = 12r. \tag{60}$$

This is what we should get because what we used is the Laplacian in Cartesian coordinates

$$\sum_{i=1}^{3} \frac{\partial^2}{\partial x_i^2} f(r) = \nabla^2 f(r) \tag{61}$$

and in spherical coordinates the Laplacian for $f = f(r)$ is simply

$$\nabla^2 f(r) = \frac{1}{r^2} \frac{d}{dr} r^2 \frac{d}{dr} f(r) = \frac{1}{r^2} \frac{d}{dr} 3r^4 = 12r. \tag{62}$$

Clearly, if the particle moves in a direction that does not change, the one-dimensional second-order partial derivative is not replaced with a Laplacian. The correct formula is below with a proof:

$$\frac{\partial^2}{\partial r^2} = \frac{1}{n} \sum_{i=1}^{n} \frac{x_i^2}{r^2} \frac{d^2}{dx_i^2}. \tag{63}$$

The proof is as follows. Since the direction does not change

$$\frac{x_i}{r} = \frac{dx_i}{dr} = \frac{x_{i,0}}{r_0} \tag{64}$$

is always a constant, therefore

$$\frac{1}{n} \sum_{i=1}^{n} \frac{x_i^2}{r^2} \frac{d^2}{dx_i^2} f(r) = \frac{1}{n} \sum_{i=1}^{n} \frac{x_{i,0}^2}{r_0^2} \frac{d}{dx_i} \left(\frac{dr}{dx_i} f'(r) \right) \tag{65}$$

$$= \frac{1}{n} \sum_{i=1}^{n} \frac{x_{i,0}^2}{r_0^2} \frac{d}{dx_i} \left(\frac{r_0}{x_{i,0}} f'(r) \right) = \frac{1}{n} \sum_{i=1}^{n} \frac{x_{i,0}^2}{r_0^2} \frac{r_0}{dx_{i.0}} \frac{d}{dx_i} f'(r) \tag{66}$$

$$= \frac{1}{n} \sum_{i=1}^{n} \frac{x_{i,0}}{r_0} \frac{dr}{dx_i} f''(r) = \frac{1}{n} \sum_{i=1}^{n} \frac{x_{i,0}}{r_0} \frac{dr_0}{x_{i,0}} f''(r) = f''(r). \tag{67}$$

Generalizing Schrödinger's one-dimensional momentum substitution to a Laplacian is not in any way a straigth-forward step. This generalization is done in

Quantum Mechanics and in Quantum Field Theory. An example of this is in Section 1, the Schrödinger equation for the hydrogen atom has an Laplacian. The next section discusses this issue.

4. What is Schrödinger's momentum substitution?

The momentum substitution in Schröringer's equation comes from the usage of de Broglie's hypothesis in old quantum theory. We saw in Section 2 de Broglie's hypothesis in the atomic model for hydrogen in old quantum theory. In that usage de Broglie's hypothesis is the same as Bohr's quantization rule for angular momentum. When an electron is on a circular orbit of radius r, one round of the orbit has the length $2\pi r$. This is set to be the wavelength λ and

$$\lambda = 2\pi r = \frac{h}{p} \quad \to \quad m_e v r = \hbar. \tag{68}$$

The standing wave

$$\Psi = e^{ikx} \tag{69}$$

is on the circle of fixed radius r and x is the one-dimensional length coordinate on the circle, ranging from zero to $2\pi r$. It is in the same units as x in the Cartesian coordinates, but it changes the direction and always points to the tangent of the circle. Then

$$\frac{\partial}{\partial x}\Psi = ik\Psi = i\frac{2\pi}{\lambda}\Psi = \text{\ss}\frac{2\pi p}{h}\Psi = i\frac{p}{\hbar}\Psi \tag{70}$$

where we used de Broglie's hypothesis (i.e., Bohr's quantization rule). The above equation can be written as

$$\hat{p} = -i\hbar\frac{\partial}{\partial x}. \tag{71}$$

This is a valid motivation for Schrödinger's substitution. The substitution is the same as Bohr's quantization rule for angular momentum and de Broglie's hypothesis as used in the analysis of the hydrogen atom spectrum. This substitution is one-dimensional. It does not generalize to the Laplacian substitution that is seen in Section 1 equation (2).

A free electron must not quantized in this way. For instance, a free electron moving in a cathode-ray tube from the cathode to the anode in a straight line is modelled with an Euler-Lagrange equation. The electron accelerates and it cannot be modelled as a wave. The Dirac equation models a free electron as a spinor field, I think it is an incorrect approach in many respect. The wave-particle dualism paradigm is false.

The wave aspect comes when an electron is circulating the nucleus. The orbit is closed, at least in Borh's atomic model, and the solution is stationary. In such a situation there is some unknown reason why something is like a wave and must have a stationary solution. Neither the old quantum theory, nor Quantum Mechanics, nor Quantum Field Theory have explained why the solutions must be quantized, but there is some reason and it has something to do with stationary waves.

The valid use of the momentum subsitution in the Schrödinger equation is in a one-dimensional wave along a circular or an elliptic orbit, probably the orbit needs to be closed. In Quantum Mechanics and especially in Quantum Field Theory the wave equation is generalized to several dimensions in a way where the one-dimensional second-order partial derivative is replaced by a three or four dimensional Laplacian. Additionally, momentum and space coordinates are considered as conjugate coordinates. I think this all should be reconsidered.

5. References

[1] Jormakka, J., "Three fatal errors in quantum physics", ResearchGate, 2025

[2] Jormakka, J., "A critical view on quantum physics", ResearchGate, 2026.