

Hydrogen atom

Heisenberg and his collaborators came up with a correct theory of quantum mechanics called “matrix mechanics” in 1925. The next year Schrödinger came up with “wave mechanics” also a correct theory of quantum mechanics, equivalent to matrix mechanics, but with a different approach. Schrödinger showed that his wave mechanics was correct by solving his Schrödinger equation for hydrogen atom and showing that the result coincides with experiments. This is what we will do in this article.

Recall that in our earlier article “Planet’s motion around the Sun,” we changed the three-dimensional problem to one-dimensional problem by using the fact that angular momentum is conserved. We reproduce our earlier formula here for convenience:

$$E = \frac{1}{2}m\dot{r}^2 + \frac{L^2}{2mr^2} - \frac{GMm}{r} \quad (1)$$

The energy of hydrogen atom, which consists of a proton and an electron, is very similar to the system composed by the Sun and a planet, since both Coulomb force and gravitational force are inversely proportional to the square of distance. Replacing the gravitational potential energy to the Coulomb analog, the Hamiltonian (i.e. energy) of hydrogen atom is given as follows:

$$H = \frac{p_r^2}{2m} + \frac{L^2}{2mr^2} - \frac{ke^2}{r} \quad (2)$$

where p_r is the radial momentum, and m is the mass of the electron (precisely speaking, the reduced mass of the electron and the proton.) Considering that L^2 is quantized as $\hbar^2 l(l+1)$, Schrödinger equation becomes:

$$\left(\frac{p_r^2}{2m} + \frac{\hbar^2 l(l+1)}{2mr^2} - \frac{ke^2}{r}\right)\psi = E\psi \quad (3)$$

Therefore, we need to know how p_r can be expressed. Since we know that p_x is given by $-i\hbar\frac{\partial}{\partial x}$, we can guess that $p_r = -i\hbar\frac{\partial}{\partial r}$. However, this turns out not to be the case, as p_r can be shown not to be Hermitian. To explain this point, let me digress into the wave function in 3d space.

Recall that in 1d, the inner product between two vectors $|\psi_1\rangle$ and $|\psi_2\rangle$ is given as follows:

$$\langle \psi_2 | \psi_1 \rangle = \int dx \langle \psi_2 | x \rangle \langle x | \psi_1 \rangle = \int dx \psi_1(x) \psi_2^*(x) \quad (4)$$

By analogy, it is easy to see that the following must be satisfied in 3d:

$$\langle \psi_2 | \psi_1 \rangle = \int \int \int dx dy dz \psi_1(x, y, z) \psi_2^*(x, y, z) \quad (5)$$

In spherical coordinate, $dx dy dz$ the volume form for 3d Cartesian coordinate must be appropriately replaced by the spherical coordinate analog, as follows:

$$\langle \psi_2 | \psi_1 \rangle = \int \int \int r^2 \sin \theta dr d\theta d\phi (\psi_1(r, \theta, \phi) \psi_2^*(r, \theta, \phi)) \quad (6)$$

Now, let's check whether $p_{r0} = -i\hbar \frac{\partial}{\partial r}$ is Hermitian. If we use the notation $d\Omega = \sin \theta d\theta d\phi$, we have:

$$\langle \psi_2 | p_{r0} | \psi_1 \rangle = -i\hbar \int dr d\Omega \left(r^2 \frac{\partial \psi_1}{\partial r} \psi_2^* \right) \quad (7)$$

$$\begin{aligned} \langle \psi_2 | p_{r0}^\dagger | \psi_1 \rangle &= i\hbar \int dr d\Omega \left(r^2 \psi_1 \frac{\partial \psi_2^*}{\partial r} \right) \\ &= -i\hbar \int dr d\Omega \left(\frac{\partial (r^2 \psi_1)}{\partial r} \psi_2^* \right) \\ &= -i\hbar \int dr d\Omega \left(\left(r^2 \frac{\partial \psi_1}{\partial r} + 2r \psi_1 \right) \psi_2^* \right) \\ &= -i\hbar \int dr d\Omega \left(r^2 \left(\frac{\partial \psi_1}{\partial r} + \frac{2}{r} \psi_1 \right) \psi_2^* \right) \end{aligned} \quad (8)$$

Therefore, we see that p_{r0} is not Hermitian since (7) is not equal to (8). So, how can we construct a Hermitian operator from p_{r0} ? Notice that $\frac{1}{2}(p_{r0} + p_{r0}^\dagger)$ is Hermitian since:

$$\left(\frac{1}{2}(p_{r0} + p_{r0}^\dagger) \right)^\dagger = \frac{1}{2}(p_{r0}^\dagger + p_{r0}) \quad (9)$$

Therefore, this can be and is actually p_r . Let's obtain its explicit formula. From (7) and (8) we have:

$$\begin{aligned} \langle \psi_2 | p_r | \psi_1 \rangle &= -i\hbar \int dr d\Omega \left(r^2 \left(\frac{\partial \psi_1}{\partial r} + \frac{\psi_1}{r} \right) \psi_2^* \right) \\ &= -i\hbar \int dr d\Omega \left(r^2 \left(\frac{1}{r} \frac{\partial (r \psi_1)}{\partial r} \right) \psi_2^* \right) \end{aligned}$$

which implies:

$$p_r = \frac{1}{r} \frac{\partial}{\partial r} r \quad (10)$$

Therefore, (3) becomes:

$$\left[-\frac{\hbar^2}{2m} \left(\frac{1}{r} \frac{\partial^2(r\psi)}{\partial r^2} \right) + \frac{\hbar^2 l(l+1)}{2mr^2} - \frac{ke^2}{r} \right] \psi = E\psi \quad (11)$$

If we say, $u = r\psi$, the above equation becomes:

$$\left(-\frac{\partial^2}{\partial r^2} + \frac{l(l+1)}{r^2} - \frac{2m ke^2}{\hbar^2 r} - \frac{2mE}{\hbar^2} \right) u = 0 \quad (12)$$

By being careful that E is negative since we are considering the case that electron is bound by the proton (i.e roughly speaking, orbiting around the proton), let's introduce the following notation:

$$\frac{\hbar^2 \kappa^2}{2m} = -E, \quad \rho = 2\kappa r \quad (13)$$

$$a_0 = \frac{\hbar^2}{mke^2}, \quad \text{Ry} = \frac{\hbar^2}{2ma_0^2} \quad (14)$$

$$\lambda^2 = \left(\frac{1}{\kappa a_0} \right)^2 = \frac{\text{Ry}}{-E} \quad (15)$$

Here, Ry is called the Rydberg unit of energy and a_0 is called the Bohr radius. Then, the above equation is simplified as follows:

$$\frac{d^2 u}{d\rho^2} - \frac{l(l+1)}{\rho^2} u + \left(\frac{\lambda}{\rho} - \frac{1}{4} \right) u = 0 \quad (16)$$

For large ρ , this equation reduces to:

$$\frac{d^2 u}{d\rho^2} - \frac{u}{4} = 0 \quad (17)$$

which implies

$$u \sim Ae^{-\rho/2} + Be^{\rho/2} \quad (18)$$

As u cannot be infinitely big for large ρ , we set $B = 0$, so

$$u \sim e^{-\rho/2} \quad (\rho \rightarrow \infty) \quad (19)$$

when ρ is very small, (16) reduces to:

$$\frac{d^2 u}{d\rho^2} - \frac{l(l+1)}{\rho^2} u = 0 \quad (20)$$

To solve this equation, let's try a solution $u = \rho^q$, then we have:

$$q(q-1)\rho^{q-2} - l(l+1)\rho^{q-2} = 0 \quad (21)$$

which implies $q = -l, l + 1$. Therefore, we have:

$$u \sim A\rho^{-l} + B\rho^{l+1} \quad (22)$$

As u cannot be infinity when $r = 0$, we must set $A = 0$. Therefore, we have

$$u \sim \rho^{l+1} \quad (\rho \rightarrow 0) \quad (23)$$

With these two asymptotic forms, we are ready to solve (16) through a polynomial expansion as follows. Solution in the following form

$$u(\rho) = e^{-\rho/2} \rho^{l+1} F(\rho) \quad (24)$$

$$F(\rho) = \sum_{i=0}^{\infty} C_i \rho^i \quad (25)$$

with F finite everywhere satisfy (19) and (23). Plugging (24) to (16), we obtain (**Problem 1.**):

$$\left[\rho \frac{d^2}{d\rho^2} + (2l + 2 - \rho) \frac{d}{d\rho} - (l + 1 - \lambda) \right] F(\rho) = 0 \quad (26)$$

Plugging (25) into the above equation and equating coefficients of equal powers in ρ yields (**Problem 2.**):

$$C_{i+1} = \frac{(i + l + 1) - \lambda}{(i + 1)(i + 2l + 2)} C_i \quad (27)$$

In the limit that $i \rightarrow \infty$, this relation reduces to

$$C_{i+1} \sim \frac{C_i}{i} \quad (28)$$

Now, notice that this is also the ratio of coefficients obtained from the following expansion:

$$e^\rho = \sum C_i \rho^i = \sum \frac{\rho^i}{i!} \quad (29)$$

$$\frac{C_{i+1}}{C_i} = \frac{i!}{(i + 1)!} = \frac{1}{i + 1} \sim \frac{1}{i} \quad (30)$$

Therefore, for large ρ , we have $F(\rho) \sim e^\rho$ which implies:

$$u(\rho) \sim e^{-\rho/2} \rho^{l+1} e^\rho = e^{\rho/2} \rho^{l+1} \quad (31)$$

which diverges for large ρ , which doesn't make sense, since it would imply that electrons orbiting inside hydrogen atom would be strongly distributed for the regions infinitely far away from the proton, the nucleus of hydrogen

atom. To make sense, the recursion relation (27) must terminate by vanishing at some finite value of i , which we denote i_{max} . By looking at the numerator of (27), we see that this is possible, if

$$i_{max} + l + 1 = \lambda \quad (32)$$

In other words, if this equation is satisfied F is finite since Taylor expansion terminates at i_{max} power of ρ , which in turn implies u is also finite. Since i_{max} and l are integer, we see that λ is also an integer, which we call “principal quantum number” and denote by n as follows:

$$n = i_{max} + l + 1 \quad (33)$$

Given this, using (15) we conclude:

$$E_n = -\frac{\text{Ry}}{n^2} \quad (34)$$

This is exactly the formula found by Rydberg. We have obtained this final result using (2), but this was not the method Schrödinger used. Nor is it the method most textbooks present. In the rest of the article, I will briefly explain the method. Since it reduces to (11), one can take afterwards the same step as presented in our article.

Notice that in 3d, Schrödinger equation can be expressed as follows:

$$\frac{\hbar^2}{2m} \nabla^2 \psi + V(x, y, z) \psi = E \psi \quad (35)$$

where Laplacian “ ∇^2 ” is defined as follows:

$$\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \quad (36)$$

In the spherical coordinate, it can be shown that Laplacian can be expressed as follows:

$$\nabla^2 f = \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial f}{\partial r} \right) + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial f}{\partial \theta} \right) + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2 f}{\partial \phi^2} \quad (37)$$

For a derivation, see M. Boas, *Mathematical Methods in the Physical Sciences*, Chapter 10, section 9. Therefore, Schrödinger equation becomes:

$$-\frac{\hbar^2}{2m} \left[\frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial \psi}{\partial r} \right) + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial \psi}{\partial \theta} \right) + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2 \psi}{\partial \phi^2} \right] + V(r) \psi = E \psi \quad (38)$$

where we assumed that the potential only depends on r . Actually, this is the whole point of solving problems in spherical coordinate. Now, let’s look for solutions of following form:

$$\psi(r, \theta, \phi) = R(r)Y(\theta, \phi) \quad (39)$$

Plugging this, we obtain:

$$\frac{Y}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial R}{\partial r} \right) + \frac{R}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial Y}{\partial \theta} \right) + \frac{R}{r^2 \sin^2 \theta} \frac{\partial^2 Y}{\partial \phi^2} = \frac{2m}{\hbar^2} (V(r) - E) R Y \quad (40)$$

Dividing the both-hand sides by RY/r^2 and rearranging, we obtain:

$$\frac{1}{Y} \left(\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial Y}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2 Y}{\partial \phi^2} \right) = \frac{2mr^2}{\hbar^2} (V(r) - E) - \frac{1}{R} \frac{\partial}{\partial r} \left(r^2 \frac{\partial R}{\partial r} \right) \quad (41)$$

Notice that the left-hand side is the function of θ and ϕ only, while the right-hand side is the function of r only. As the left-hand side is equal to the right-hand side we conclude that the both-hand sides should be merely a constant, which never depends on θ , ϕ and r . Therefore, we can separately solve the differential equations for the left-hand side and the right-hand side. We will not solve them explicitly, but present solutions.

Actually, it turns out that we have following formulas for angular momentum in terms of spherical coordinate:

$$L_x = i\hbar \left(\sin \phi \frac{\partial}{\partial \theta} + \cot \theta \cos \phi \frac{\partial}{\partial \phi} \right) \quad (42)$$

$$L_y = i\hbar \left(-\cos \phi \frac{\partial}{\partial \theta} + \cot \theta \sin \phi \frac{\partial}{\partial \phi} \right) \quad (43)$$

$$L_z = -i\hbar \frac{\partial}{\partial \phi} \quad (44)$$

These can be derived by using chain-rules. For example,

$$\begin{aligned} L_x &= -i\hbar \left[y \frac{\partial}{\partial z} - z \frac{\partial}{\partial y} \right] \\ &= -i\hbar \left[y \left(\frac{\partial r}{\partial z} \frac{\partial}{\partial r} + \frac{\partial \theta}{\partial z} \frac{\partial}{\partial \theta} + \frac{\partial \phi}{\partial z} \frac{\partial}{\partial \phi} \right) - z \left(\frac{\partial r}{\partial y} \frac{\partial}{\partial r} + \frac{\partial \theta}{\partial y} \frac{\partial}{\partial \theta} + \frac{\partial \phi}{\partial y} \frac{\partial}{\partial \phi} \right) \right] \end{aligned}$$

For more detail, see Problem (9.14) of *Introductory Quantum Mechanics* by Richard L. Liboff. In any case, (42), (43) and (44) yield:

$$L^2 = -\hbar^2 \left(\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right) \quad (45)$$

Compare this with the left-hand side of (41). As we have

$$\begin{aligned} L^2 R Y &= l(l+1) \hbar^2 R Y \\ L^2 Y &= l(l+1) \hbar^2 Y \end{aligned} \quad (46)$$

the left-hand side of (41) becomes $-l(l+1)$. Plugging this back in, and using the following fact which can be easily checked:

$$\frac{1}{r} \frac{\partial^2(r\psi)}{\partial r^2} = \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial \psi}{\partial r} \right) \quad (47)$$

we recover (11) as advertised.

So, why was the wave function of the form (39) the solution to the Schrödinger equation? Was it a coincidence?

No. Let me explain the reason why. To this end, remember that the angular momentum is preserved in our case, as there is rotational symmetry. Upon rotation, the Coulomb potential doesn't change, as the distance to the center doesn't change upon rotation. The kinetic energy doesn't change either, as the kinetic energy is same whether one measures it in a system S or in a system S' rotated from the system S .

Actually, we can say the same thing a little bit more mathematically; the angular momentum commutes with the Hamiltonian. Let's check the potential term first. The Coulomb potential is given by $-ke^2/r$. Then, from (42), (43), and (44), one can easily check

$$[L_x, -\frac{ke^2}{r}] = [L_y, -\frac{ke^2}{r}] = [L_z, -\frac{ke^2}{r}] = 0 \quad (48)$$

as the Coulomb potential doesn't depend on θ and ϕ .

Now, let's check the kinetic term. We can easily check (**Problem 3.**)

$$[L_x, P_x^2 + P_y^2 + P_z^2] = 0 \quad (49)$$

Similarly, $[L_y, P_x^2 + P_y^2 + P_z^2] = [L_z, P_x^2 + P_y^2 + P_z^2] = 0$. Thus, we get

$$[L_x, H] = [L_y, H] = [L_z, H] = 0 \quad (50)$$

where

$$H = \frac{P_x^2 + P_y^2 + P_z^2}{2m} - \frac{ke^2}{r} \quad (51)$$

From (50), we conclude

$$[L^2, H] = [L_x^2 + L_y^2 + L_z^2, H] = 0 \quad (52)$$

Therefore, L^2 and H are simultaneously diagonalizable. Thus, we can write the eigenfunction of Hamiltonian in (39), where $Y(\theta, \phi)$ as well as $R(r)Y(\theta, \phi)$ are the eigenfunctions of L^2 .

Now, let's think about what l (i.e. j in our earlier article "Angular momentum in quantum mechanics") can be if the electron in an hydrogen atom is in state n . Let's look at state $n = 1$ first. (33) shows that the only way this can happen is when $l = 0$ since i_{max} can't be negative. Therefore when $n = 1$ there is no orbital angular momentum for the electron. This

contradicts Bohr's model in which $n = 1$ state has angular momentum \hbar which is nonzero. This shows that Bohr's derivation of Rydberg formula was a "fluke," even though it played an important role for the construction of correct quantum theory.

For other n as well, the possible values for l can be easily obtained from (33). The result is:

$$l = 0, 1, 2, \dots, n-2, n-1 \quad (53)$$

Furthermore, if you remember our earlier article "Angular momentum in quantum mechanics," we have:

$$m = -l, -l+1, \dots, l-1, l \quad (54)$$

Also, we know that an electron can have spin up and spin down. Let's call this s . For example, $s = 1/2$ for spin up, and $s = -1/2$ spin down.

Summarizing, an arbitrary electron orbiting inside hydrogen atom can have certain n, l, m, s . These numbers are called quantum numbers. You may be familiar with this if you learned what is called "orbital" in chemistry. The same structure of quantum numbers exists for atoms other than the hydrogen atom as well. However, what is different is that the energy of the electrons can be different if l is different even if n is same. Remember that in our hydrogen atom case (34) only depends only on n and not l . (However, even in hydrogen atom, the energy depends on l if one considers relativistic effect, but this effect is very tiny.) This is due to the fact that there are multiple numbers of electrons in non-hydrogenic atoms; notice that Schrödinger equation must contain extra terms for the Coulomb force between electrons, which change the eigenvalues for the energy matrix. Anyhow, we cannot solve Schrödinger equation for such atoms analytically; we can only do it numerically, with an aid of supercomputer. Many chemists use supercomputers to solve Schrödinger equation to find out the properties of atoms and molecules. Maybe more so than physicists.

Finally, a comment on Pauli's exclusion principle. If you remember our earlier article, you know that two fermions cannot occupy the same state. This is true for electrons orbiting inside atoms as an electron is a fermion. In other words, two electrons cannot have all the same n, l, m, s .

Let's examine its consequences. How many states are there given n ? When $n = 1$, we call it "K shell." There are two states in K shell. $n = 1, l = 0, m = 0, s = 1/2$ and $n = 1, l = 0, m = 0, s = -1/2$. Therefore, there can be no more than two electrons in K shell because of Pauli's exclusion principle. How many electrons can be in $n = 2$ called "L shell?" 8 electrons. You can check this yourself. (**Problem 4.**)

So, a total of 8 states. It actually turns out atoms are more chemically less reactive if shells they have are completely filled. For example, Helium, which has two electrons, can fill K shell. Neon, which has ten electrons,

can fill both K shell and L shell. It is really amazing that all the properties of atoms and molecules can be reduced to a simple law called “quantum mechanics.” (Remember our first article “A short introduction to the history of physics, and string theory as a ‘Theory of Everything’ ”)

Problem 5. Find the relation between the Rydberg unit of energy and the Rydberg constant introduced in our earlier article “Rydberg formula.”

Problem 6. Find the normalized wave function for the ground state (i.e. $n = 1$) and calculate the probability that an electron in the ground state will be found at position $r < a_0$. (Hint¹)

Summary

- If you solve the Schrödinger equation for hydrogen atom, the radial part and the angular part are completely separated. It’s because the angular momentum commutes with the Hamiltonian.
- The energy of the hydrogen atom is given by $E_n = -\frac{\text{Ry}}{n^2}$. Ry is the Rydberg constant, and n is the principal quantum number, which is a positive integer.
- Given n , l ranges from $0, 1, 2, \dots, n - 1$ where l denotes the quantum number for the orbital angular momentum (i.e. the orbital angular momentum is given by $\sqrt{l(l+1)}\hbar$.)
- Given l , m ranges from $-l, -l+1, \dots, l-1, l$. m denotes the quantum number for the L_z .
- An electron can have either spin up ($s = 1/2$) or spin down ($s = -1/2$).
- Pauli’s exclusion principle says that two fermions cannot occupy the same state. Therefore, two electrons in a same hydrogen cannot have all the same n, l, m, s .

¹When $l = 0$ $L_x Y = L_y Y = L_z Y = 0$ which implies Y is a constant that doesn’t depend on θ and ϕ .