341 Project Schrodinger's Equation

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1 Introduction

The Schrodinger's equation is derived by German physicist Erwin Schrodinger, one of the preeminent founders of modern quantum physics, in 1925 and is published in the following year

$$i\hbar\frac{\partial}{\partial t}\Psi(\boldsymbol{r},t) = [\frac{-\hbar^2}{2m}\nabla + V(\boldsymbol{R},t)]\Psi(\boldsymbol{r},t).$$

This (non-relativistic) equation is structured to be a differential linear equation based on classical energy conservation, and consistent with the relations in quantum mechanics. The solutions of Schrodinger's represent the displacement of matter and electromagnetic wave. Ever since its discovery, physicists are enabled to develop theories governing the behavior of quantum particles mathematically; this equation explains the atomic structures, such as shapes of orbitals and orientations of atoms, which profoundly puts forward the field of quantum physics; as we will see later, the solution of the equation governs the quantized properties of quantum mechanics systems. Because the Schrodinger's equation is a PDE, we can solve it with the techniques we have developed and make connection between the solutions and their physical properties.

2 Mathematical Analysis

A simplest atom can be described by the PDE

$$i\hbar u_t = \frac{\hbar^2}{2m}\Delta u + \frac{e^2}{r}u$$

where h is the Planck constant, m is the mass of the particle and the potential energy of the particle in a confined region, and e^2/r, is a variable coefficient. We can simplify this by taking particle to a free space, where the potential goes to 0, and set h and m to be 1

$$-i\frac{\partial u}{\partial t} = \frac{1}{2}\Delta u$$

Notice that this equation is reminiscent to the diffusion equation $u_t = ku$ where k is a real constant. In fact, if we multiply the both side of the Schrodinger's equation, the only difference of the two will be that in the Schrodinger's equation the constant $k = i/2$ is complex. We will see later the imaginary constant implies the solutions are "wave like". With the initial condition be $u(\boldsymbol{x}, t) = \phi(\boldsymbol{x})$, we will be able to construct the solutions. First consider the 1D case. Since we would like to have a $S(x,t)$ such that the convolution

$$\lim_{t \longrightarrow 0} \int S(x - x', t)\phi(x')dx' = \phi(x)$$

where we use x' as a dummy variable, running over all of x domain. We can construct $S(x,t) = \frac{1}{(4\pi(i/2)t)^{1/2}}e^{-x^2/4(i/2)t}$. We observe that

$$\frac{\partial S}{\partial t} = \frac{x^2}{4(i/2)t^2}\frac{1}{(4\pi(i/2)t)^{1/2}}e^{-x^2/4(i/2)t}$$

$$= (i/2)\frac{x^2}{4(i/2)^2t^2}\frac{1}{(4\pi(i/2)t)^{1/2}}e^{-x^2/4(i/2)t} = i^2\frac{\partial^2 x}{\partial x^2} = (i/2)\Delta S.$$

We can see S is a solution of the complex diffusion initial condition but we actually want S is a fundamental solution of the complex diffusion equation since if we substitute $p = \frac{x}{4\pi(i/2)t}$ and $dp = dx/(4\pi(i/2)t)$ then

$$\int S(x,t)\partial x = \int \frac{1}{(4\pi(i/2)t)^{1/2}}e^{-x^2/4(i/2)t}\partial x = \frac{1}{\sqrt{\pi}}\int e^{-q^2}dq = 1.$$

The plot is the magnitude of complex function S and x (see Figure 1). With a small

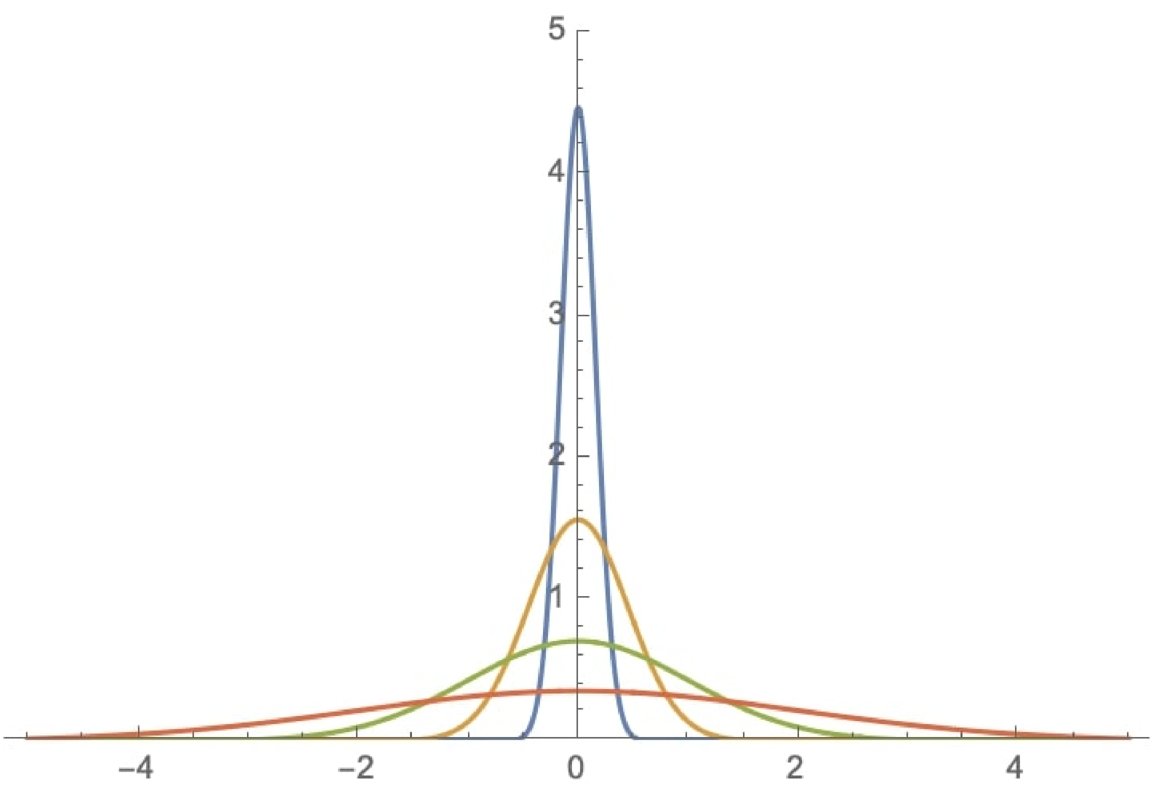

Figure 1: The vertical axis is the magnitude of S and the horizontal axis is the spatial variable x. Plotted over different t.

t, S will have a high and narrow peak, and as time goes, the probability distribution is more spread out. Now we come back to the general case when $\boldsymbol{x} = (x, y, z, ...)$ is a spatial vector. To show the same result as the one dimensional case, we denote $\boldsymbol{S}(x, y, z, ..., t) = S(x,t)S(y,t)S(,z,t)...$ be the product of one dimensional functions we have worked with. We can easily show the results from the one dimensional case holds; the initial condition is now $\boldsymbol{S}(\boldsymbol{x}, 0) = \Phi(\boldsymbol{x} = (\phi(x))(\phi(y))(\phi(z)...)$

$$\frac{\partial \boldsymbol{S}}{\partial t} = \frac{\partial S}{\partial t}(x,t) * S(y,t) * S(z,t) * ... + \frac{\partial S}{\partial t}(y,t) * S(x,t) * S(z,t) * ...$$
$$+\frac{\partial S}{\partial t}(z,t) * S(x,t) * S(y,t) * ... + (\text{ more similar terms})$$

From the relation from the one dimensional demonstration,

$$= (i/2)\frac{\partial^2 S}{\partial x^2}(x,t) * S(y,t) * S(z,t) * ... + (i/2)\frac{\partial^2 S}{\partial y^2}(y,t) * S(x,t) * S(z,t) * ...$$
$$+(i/2)\frac{\partial^2 S}{\partial z^2}(z,t) * S(x,t) * S(y,t) * ... + (\text{ more similar terms})$$

Here we can bring forth the common multiples and the linear operator,

$$= (i/2)(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2})(S(x,t)S(y,t)S(,z,t)..) = (i/2)\Delta \boldsymbol{S}$$

as we expect. We notice that also

$$\int\int\int ... \int \boldsymbol{S}(\boldsymbol{x}, t) = (\int S(x,t)dx)(\int S(y,t)dy)(\int S(z,t)dz)... = 1 * 1 * 1 * ... = 1.$$

With the initial condition, we will have the convolutional equation

$$\int\int\int ... \int \boldsymbol{S}(\boldsymbol{x} - \boldsymbol{x'}, t)d\boldsymbol{x'} = [\int S(x - x', t)dx'][\int S(y - y', t)dy'][\int S(z - z', t)dz']$$

same as before,

$$\lim_{t \xrightarrow{0}} \int\int\int ... \int \boldsymbol{S}(\boldsymbol{x} - \boldsymbol{x'}, t)\Phi(\boldsymbol{x'}d\boldsymbol{x'}$$
$$= \lim_{t \xrightarrow{0}} [\int S(x - x', t)dx'][\int S(y - y', t)dy'][\int S(z - z', t)dz']$$

$$= \Phi(\boldsymbol{x} = (\phi(x))(\phi(y))(\phi(z)...)$$

$$= \Phi(\boldsymbol{x})$$

We now can conclude

$$u(\boldsymbol{x}, t) = \int\int\int ... \int \boldsymbol{S}(\boldsymbol{x} - \boldsymbol{x'}, t)\Phi(\boldsymbol{x'})d\boldsymbol{x'}.$$

We can get the explicit formula for $\boldsymbol{S}$ by substitute in S for each spatial term.

$$\boldsymbol{S}(\boldsymbol{x}, t) = [\frac{1}{(4\pi(i/2)t)^{1/2}}e^{-x^2/4(i/2)t}][\frac{1}{(4\pi(i/2)t)^{1/2}}e^{-y^2/4(i/2)t}][\frac{1}{(4\pi(i/2)t)^{1/2}}e^{-z^2/4(i/2)t}]...$$

If $\boldsymbol{x}$ is nth dimensional, the formula becomes

$$\frac{1}{(4\pi(i/2)t)^{n/2}}e^{-(x^2+y^2+z^2+...)/4(i/2)t}$$

Although we have a general solution to the simplified Schrodinger equation with initial condition, we still need to check its convergence, which can be carried out quite easily, thus not the focus of this paper. One thing worth noting is that the solution of this complex equation is wave-like. If we separate the spatial and temporal factors, $\boldsymbol{u}(\boldsymbol{x}, t) = v(\boldsymbol{x})w(t)$.

$$-i\frac{\partial vw}{\partial t} = 1/2\Delta(vw)$$

can be rearranged to

$$-i\frac{w'}{w} = 1/2\frac{v''}{v} = \lambda.$$

Solving $w' = i\lambda w$ gives $w(t) = e^{i\lambda t} = cos\lambda t + isin\lambda t$, which has oscillatory behavior. This matches our observation of wave-like behaviors of free particles. Additionally, we always assume that for large $|\boldsymbol{x'}|$, the initial value $\Phi(\boldsymbol{x'})$ vanishes, with the assumption that the function is finite. This conclusion is not always true for any finite functions. In fact, there are handful functions, piece-wise or smooth, serve as counter examples. However, it is not the case in physics. In real life, the solutions to the Schrodinger's equation are wave functions. The real part of that is the probability amplitude of the particle, the inner product of which is the probability density at (x, t). Furthermore, since the probability of the particle is 1 over all space, the function of probability density is finite, and in turn, the solution of the Schrodinger's equation is finite. This is actually one hidden boundary condition which, for instance, forbids the solutions oscillating at infinite.

Solving the Schrodinger equation of particles in free space is a good demonstration but it lacks physical meanings, as the particles are rarely free of external force fields. On the other hand, if we introduce a new term in the simplified equation to take potential force into consideration, this equation will have a lot more physical meanings. The hydrogen atom, consisting of an electron and a proton, is a two-particle system in which their motion is around the center of mass. Since the mass of the proton is far greater than that of the electron, we say the center of mass of the system is that of the proton. we can model the system with the Schrodinger's equation

$$i\hbar u_t = -\frac{\hbar^2}{2m}\Delta u - \frac{e^2}{r}u$$

where r is the radius of the radial distance of the two particles and e is charge. In comparison to the free particle scenario, this equation is more realistic and predicts non-relativistic hydrogen atom in great accuracy.

To make the equation more friendly while not losing generality, we look at the example when

$e = m = \hbar = 1$

$$iu_t = -\frac{1}{2}\Delta u - \frac{1}{r}u.$$

If the equation is in space $\boldsymbol{x} = (x, y, z, ...)$ we can express $r = (x^2 + y^2 + z^2 + ...)^{1/2}$. Similarly, for the solution to have physical meanings, we need be able to normalize the probability of the particle to be 1. From the argument above for free particle, it forces the $u(\boldsymbol{x}, t)$ to be finite. Thus we have

$$\int\int\int |u(\boldsymbol{x}, t)|^2 d\boldsymbol{x} < \infty.$$

Relating to our earlier discuss, this is equivalent of condition of vanishing at infinity. We can separate the variables to obtain

$$u(\boldsymbol{x}, t) = T(t)v(\boldsymbol{x}).$$

The Schrodinger's equation becomes

$$iT'(t)v(\boldsymbol{x}) = -\frac{1}{2}T(t)\Delta v(\boldsymbol{x}) - \frac{1}{r}T(t)v(\boldsymbol{x}).$$

We have

$$2i\frac{T'}{T} = \frac{-\Delta v - (2/r)v}{v} = \lambda$$

where the equations equal to a constant. Solving $2iT' = \lambda T$ gives us $T(t) = e^{-i\lambda t/2}$ and $u = v(\boldsymbol{x})e^{-i\lambda t/2}$. ;we also have $-\Delta v - \frac{2}{r}v = \lambda t v$ which is cumbersome to solve.

It is appropriate in this case to do a change of variable to spherical coordinates to simplify the computation due to the r and the nature of the system. We could consider the other cases but we will focus on the spherically symmetric solutions: $v(\boldsymbol{x} = R(r))$. Due to the length of the paper, I will also omit some algebra in the change of variables and instead focusing on analyzing the result. We can reduce it to an ODE

$$-R_{rr} - (2/r)R_r - (2/r)R = \lambda R$$

with the condition at infinity that $\int_0^\infty |R(r)|^2 r^2 dr < \infty$ and $R(0)$ is finite, which are expected. With another change of variable, we have

$$(1/2)rw_{rr} - \beta r w_r + w_r + (1-\beta)w = 0$$

where $w(r) = e^{\beta r}R(r)$ and $\beta = \sqrt{-\lambda}$ so the solutions vanish at infinity. We want to manipulate the equation further to a nicer form. When $r = 0$, we have $(1/2)r = 0$ in the first term. This gives us that it is a regular singular point at $r = 0$. By theorem in Partial Differential Equation by Strauss (A.4), we can substitute the power series form $w(r) = \sum_{k=0}^\infty a_k r^k$ in the equation to get

$$(1/2)\sum_{k=0}^{\infty} k(k-1)a_k r^{k-1} - \beta \sum_{k=0}^{\infty} k a_k r^k + \sum_{k=0}^{\infty} k a_k r^{k-1} + (1-\beta)\sum_{k=0}^{\infty} a_k r^k = 0.$$

The key observation here is that $\sum_{k=0}^\infty a_k r^k = \sum_{k=1}^\infty a_{k-1} r^{k-1}$ because k is a dummy variable. This allows us to combine the terms with such change of variable for the second and forth terms

$$\sum_{k=0}^{\infty}[\frac{1}{2}k(k-1) + k]a_k r^{k-1} + \sum_{k=1}^{\infty}[-\beta(k-1) + (1-\beta)]a_{k-1} = 0.$$

because we need to have the constants $\frac{k(k-+1)}{2}a_k - (\beta k - 1)a_{k-1}$'s that will make the sum vanish for any r, the only choice is to take all $\frac{k(k+1)}{2}a_k - (\beta k - 1)a_{k-1} = 0$ or $\frac{k(k+1)}{2}a_k = (\beta k - 1)a_{k-1}$. Here we have a expression of each constant a_k in sequence. Taking $b = 1/k$ will kill the term a_k which in turn kills the following terms in the sequence. Thus the sequence will terminate for such β's. Keep in mind we have $v(\boldsymbol{x}) = R(r) = e^{-\beta r}w(r)$.

First Few Solutions				
n	β	λ	w(r)	v($\boldsymbol{x}$)
1	1	-1	1	e^{-r}
2	1/2	-1/4	1-(1/2)r	$e^{-r-(1/2)r}$
3	1/3	-1/9	1-(2/3)r + (2/27)r^2	$e^{-r-(1/2)r+(2/27)r^2}$
4	1/4	1/16	...	...

We want to make sure the boundary condition to still hold, namely, as $r \to \infty$, $v(\boldsymbol{x})$ will approach zero for the finite function $R(r)$. As we can see, $e^{-\beta r}$ tends to zero so surely it does. This is actually the mathematical interpretation of Niels Bohr's observation that the energy level of the electron in a hydrogen atom occurs at special values related to the squares of integers. Its energy is $\lambda = -\beta = -1/n^2$. The energy levels are:

$$-1, -\frac{1}{4}, -\frac{1}{9}, ...$$

Also, the lowest energy state or the ground state is when $n = 1$ and so on. From the plot (see Figure 2), we see that $v(x)$ has no node(zero crossing) in the ground state(blue), one node when $n = 2$(red),and two nodes when $n = 3$(green). In general, there are $n - 1$ nodes. That tells us the probability of the electron to be at those distance is zero. In conclusion, we discover that the discrete solutions are actually accurate modelling of the energy states of the hydrogen atom.

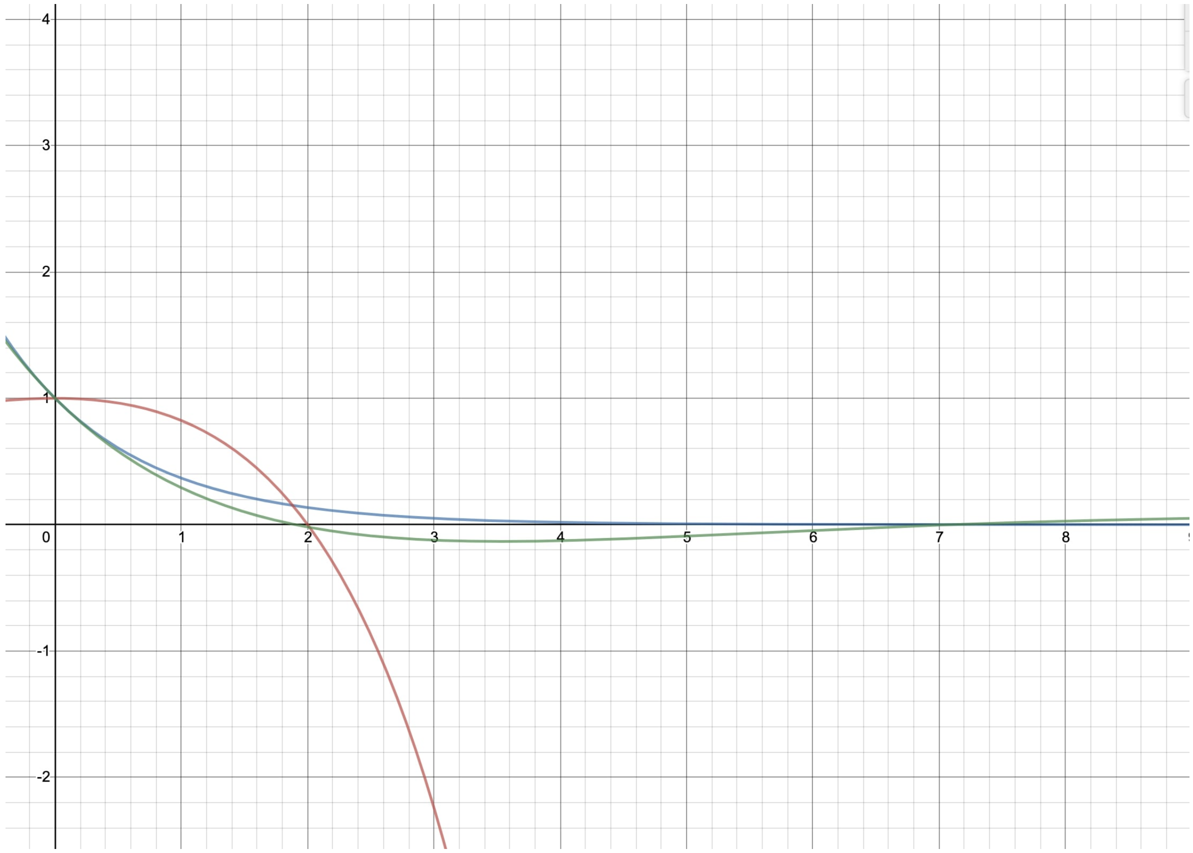

Figure 2: The vertical axis is $v(x)$. The horizontal axis is x

3 Application

Directly from the result of the Schrodinger equation for a hydrogen atom, we find out that the electron has discrete energy levels corresponding to different n. Since when an electron goes from an excited state to a ground state will release the energy in the form of a photon. The photon of such energy has frequency $v = E/h$ where E is the energy and the wavelength $\lambda = c/v$. Since the energy of the photon is the difference of the two energy states, we can find the energy of the photon and also the wavelength. With appropriate energy states,the light emitted is within observable wavelength. We obtain the equation

$$\frac{1}{\lambda} = R(\frac{1}{n_1^2} - \frac{1}{n_2^2}),$$

where $R = 1.097e7(1/\text{m})$ is a constant, and n_1 is the final energy state and n_2 is the initial energy state.

For instance, if we take $n_1 = 2$ and $n_2 = 1$ then $\lambda = 121.5$ is not within the visible light spectrum. But if we take $n_1 = 2$ and $n_2 = 3$ we will have $\lambda = 656.3$, which is a red light. With some trial and error, we will find all the visible light wavelengths (See Figure 3).

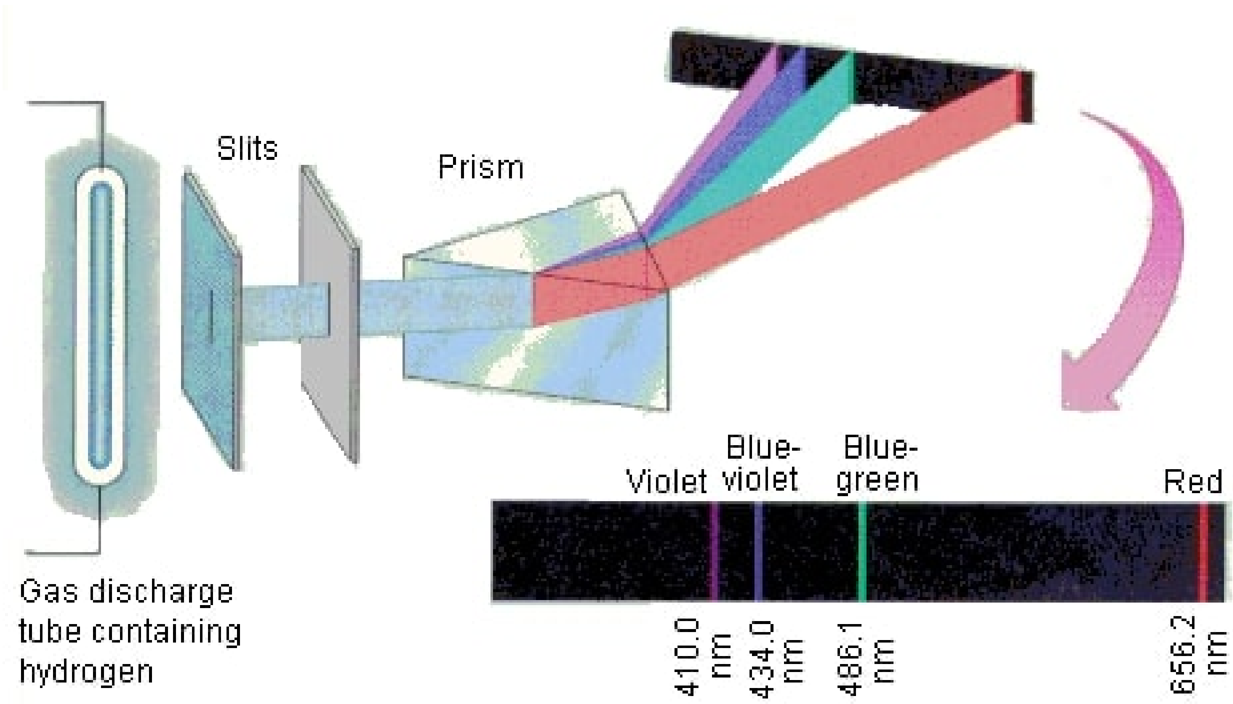

Figure 3: From Development of Current Atomic Theory

4 Further Discussions

We have solved Schrodinger's equation for free particles and hydrogen atoms. One observation is that in both cases, we rely on separation of variables to separate out each spatial term or to break apart temporal and spatial variables. It is also important that there is a hidden boundary condition that the the solutions are finite and vanishes when $\boldsymbol{x}$ or r is large. This effectively eliminates some non-convergence cases. Lastly, the presence of the potential term in hydrogen model induced the discrete solutions which are spherically symmetric. Naturally, the discrete solutions of the Schrodinger equation for hydrogen make us suspect that it arises from Fourier transformation. Indeed, we can solve the Schrodinger's equation using Fourier transformation. For instance, in free space, the equation is

$$-i\frac{\partial u}{\partial t} = \frac{1}{2}\Delta u.$$

Solving with Fourier Transformation

$$i\frac{\partial}{\partial t}\int \frac{dk}{2\pi}e^{ikx}\hat{u}(k,t) = -\frac{1}{2}\int \frac{dk}{2\pi}e^{-1kx}\hat{u}(k,t).$$

This gives us the easy ODE

$$0 = i\frac{\partial}{\partial t}\hat{u}(k,t) - \frac{1}{2}\hat{u}(k,t).$$

Then we can solve the ODE and transform it back to get the solution for $u(x,t)$. Furthermore, we can derive the Heisenberg uncertainty principle with the Fourier transformation. This uncertainty principle is a fact about Fourier transformation, but in the Schrodinger's equation, it has more physical meanings, namely, the relation of position and momentum of one object. This would be my next investigation.

References

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