Revisiting Schrödinger Equation

Rohan Biswas
Dept. of Computer Science and Engineering ,
Tezpur University,India

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Abstract

Schrödinger Equation, given by Erwin Schrödinger in 1926 is fundamental in quantum mechanics. The equation revolutionizes our understanding of behavior of particles at a microscopic level, providing an elegant mathematical framework to predict probabilities of different outcomes. The equation was first published in 1926 as '*Quantisierung als Eigenwertproblem*'(Translation : Quantization as an Eigenvalue Problem) in the Journal '*Annalen der Physik*'.

1 Introduction

Schrödinger Equation has a wide range of applications from Physics and Chemistry to Biology , Finance and others.
Here in this paper we will derive the equation using the original method used by Schrödinger in the *Erste Mitteilung* (First Communication) of his paper using Hamilton- Jacobi's equation .The equation is given as :

$$-\frac{\hbar^2}{2m}\nabla^2\psi + V\psi = E \tag{1}$$

Then we will see how Schrödinger used his equation for Hydrogen Atom .
We, then would see how the Non-Linear Schrödinger equation came into existence.The Non-Linear Schrödinger equation is given as :

$$i\frac{\partial\psi}{\partial t} + \frac{\partial^2\psi}{\partial x^2} + 2|\psi|^2\psi = 0 \tag{2}$$

2 Deriving the Schrödinger Equation

Schrödinger used the case of Hydrogen atom (non-relativistic and unperturbed , just like he mentioned).
It all starts with Hamilton-Jacobi Equation used in Analytical Mechanics :

$$H\left(q, \frac{\partial S}{\partial q}\right) = E \tag{3}$$

where S is action-functional and q is just generalised coordinate.
Now, Schrödinger considers,

$$S = K \log \psi$$

Thus equation (3) neglecting relativistic mass variations becomes :

$$H\left(q, \frac{K}{\psi}\frac{\partial \psi}{\partial q}\right) = E \tag{4}$$

Now since he considered particle in a conservative field . The Hamiltonian can be written as :

$$H = \frac{1}{2}p^2 + U$$

Thus, Formation of variational equations using regular cartesian coordinates gives :

$$\left(\frac{\partial \psi}{\partial x}\right)^2 + \left(\frac{\partial \psi}{\partial y}\right)^2 + \left(\frac{\partial \psi}{\partial z}\right)^2 - \frac{2m}{K^2}\left(E + \frac{e^2}{r}\right)\psi^2 = 0 \tag{5}$$

where e is charge, m is the mass of the electron, and $r^2 = x^2 + y^2 + z^2$.
Our variation problem then goes like:

$$\delta J[\psi] = \delta \iiint_{\mathbb{R}^3} F(\psi, \nabla\psi, x, y, z)\, dx\, dy\, dz = 0 \tag{6}$$

where F is a functional.
Now, we get:

$$\delta J[\psi] = \delta \iiint_{\mathbb{R}^3} dx\, dy\, dz \left[\left(\frac{\partial \psi}{\partial x}\right)^2 + \left(\frac{\partial \psi}{\partial y}\right)^2 + \left(\frac{\partial \psi}{\partial z}\right)^2 - \frac{2m}{K^2}\left(E + \frac{e^2}{r}\right)\psi^2\right] = 0 \tag{7}$$

or

$$\delta J[\psi] = \delta \iiint_{\mathbb{R}^3} dx\, dy\, dz \left[|\psi|^2 - \frac{2m}{K^2}\left(E + \frac{e^2}{r}\right)\psi^2\right] = 0 \tag{8}$$

where

$$|\psi|^2 = \left(\frac{\partial \psi}{\partial x}\right)^2 + \left(\frac{\partial \psi}{\partial y}\right)^2 + \left(\frac{\partial \psi}{\partial z}\right)^2$$

Using Integration by parts we find ,

$$\frac{1}{2}\delta J = \int df\, \delta\psi \frac{\partial \psi}{\partial n} - \iiint dx\, dy\, dz\, \delta\psi \left[\nabla^2\psi + \frac{2m}{K^2}\left(E + \frac{e^2}{r}\right)\psi\right] = 0 \tag{9}$$

Here, df is element of infinite closed surface over which integral is taken.
and so we find that :

$$\nabla^2\psi + \frac{2m}{K^2}\left(E + \frac{e^2}{r}\right)\psi = 0, \tag{10}$$

and

$$\int df\, \delta\psi \frac{\partial \psi}{\partial n} = 0 \tag{11}$$

Schrödinger in his paper stated that discrete spectrum obtained by the variation problem corresponds to the Balmer terms of Hydrogen atom and for numerical agreement :

$$K = \frac{h}{2\pi} = \hbar$$

.

$$\boxed{\nabla^2\psi + \frac{2m}{\hbar^2}\left(E + \frac{e^2}{r}\right)\psi = 0} \tag{12}$$

This is the equation that Schrödinger derived as the equation (5) in First communication. We will just rearrange this to get :

$$\nabla^2\psi = -\frac{2m}{\hbar^2}\left(E + \frac{e^2}{r}\right)\psi \tag{13}$$

We then generalize it for any potential to get the schrödinger equation we know about ,

$$\boxed{-\frac{\hbar^2}{2m}\nabla^2\psi + V\psi = E\psi} \tag{14}$$

3 Applying Schrödinger Equation to Hydrogen Atom

We have equation (12) that can be written as :

$$-\frac{\hbar^2}{2\mu}\nabla^2\psi - \frac{e^2}{r}\psi = E\psi \tag{15}$$

where, $r = \sqrt{x^2 + y^2 + z^2}$ and μ is the reduced mass. Equation(15) can be written as :

$$\frac{\partial^2\psi}{\partial x^2} + \frac{\partial^2\psi}{\partial y^2} + \frac{\partial^2\psi}{\partial z^2} + \frac{2\mu}{\hbar^2}\left(E + \frac{e^2}{r}\right)\psi = 0 \tag{16}$$

So, for ease we are gonna be using separation of variables method after converting this entire thing to spherical coordinate system .
Then, the wavefunction ψ would look something like :

$$\psi(r,\theta,\phi) = \chi(r)Y_l^m(\theta,\phi)$$

where $Y_l^m(\theta,\phi)$ is a spherical hsarmonic and the radial equation is thus :

$$\frac{d^2\chi(r)}{dr^2} + \frac{2}{r}\frac{d\chi(r)}{dr} + \left(\frac{2\mu E}{\hbar^2} + \frac{2\mu e^2}{\hbar^2 r} - \frac{l(l+1)}{r^2}\right)\chi(r) = 0 \tag{17}$$

Here, l is the orbital angular momentum quantum number and l=0,1,2,3,...
This equation has singularities in complex plane at $r = 0$ and $r = \infty$.
Since, $\chi(r)$ vanishes faster as $r \to 0$ than $r \to \infty$ which is a requirement for Hilbert spaces.

Examining the singularity at $r = 0$, the indicial equation is :

$$\rho(\rho - 1) + 2\rho - l(l + 1) = 0 \tag{18}$$

The roots of this equation are : $\rho_1 = l$, and $\rho_2 = -(l + 1)$, and we neglect the second term due to negative nature.

Schrödinger then writes $\chi(r)$ as :

$$\chi(r) = r^{\alpha} U \tag{19}$$

such that $\alpha = l$ and is chosen in such a way that $1/r^2$ term drops out.
We substitute this in equation (17) to get :

$$\frac{d^2U}{dr^2} + \frac{2}{r}(\alpha + 1)\frac{dU}{dr} + \frac{2\mu}{K^2}\left(E + \frac{e^2}{r}\right) U = 0 \tag{20}$$

where equation(20) is called Laplace's equation. We can write all these as :

$$U" + \left(\delta_0 + \frac{\delta_1}{r}\right) U' + \left(\epsilon_0 + \frac{\epsilon_1}{r}\right) U = 0 \tag{21}$$

where $\delta_0 = 0$, $\delta_1 = 2(\alpha + 1)$, $\epsilon_0 = \frac{2mE}{K^2}$, and $\epsilon_1 = \frac{2m\mu^2}{K^2}$

This will be easier to handle because now we are gonna be applying Laplace's transformation.
Thus, we get :

$$U = \int_L e^{zr}(z - c_1)^{\alpha_1 - 1}(z - c_2)^{\alpha_2 - 1} dz \tag{22}$$

which is a solution of equation (21) for a path of integration L, for which

$$\int_L \frac{d}{dz}[e^{zr}(z - c_1)^{\alpha_1}(z - c_2)^{\alpha_2}] dz = 0 \tag{23}$$

The constants $c_1, c_2, \alpha_1, \alpha_2$ have following values and also c_1 and c_2 are roots of quadratic equation :

$$z^2 + \delta_0 z + \epsilon_0 = 0 \tag{24}$$

and

$$\alpha_1 = \frac{\epsilon_1 + \delta_1 c_1}{c_1 - c_2}, \alpha_2 = -\frac{\epsilon_1 + \delta_1 c_2}{c_1 - c_2}$$

Putting the values of δ_1, ϵ_1 and solving we get :

$$c_1 = \sqrt{\frac{-2\mu E}{\hbar^2}}, c_2 = -\sqrt{\frac{-2\mu E}{\hbar^2}}$$

$$\alpha_1 = \frac{\mu e^2}{\hbar\sqrt{-2\mu E}} + l + 1, \alpha_2 = -\frac{\mu e^2}{\hbar\sqrt{-2\mu E}} + l + 1$$

Now , Schrödinger says to exclude the cases where α_1 and α_2 are real numbers. This happens when

$$\frac{\mu e^2}{\hbar\sqrt{-2\mu E}} \in \mathbb{R}$$

So, we gotta assume that this criteria shouldn't be met.
r becomes infinite through real positive values characterized by behavior of two linearly independent solutions , U_1 and U_2 that are obtained by specializations of path of integration L .
In each case he lets z come from inifity in such a direction that :

$$\lim_{z\to\infty} e^{zr} = 0$$

i.e., $\mathbb{R}(zr)$ is to become negative and infinite.
In one case let z make a circuit once round the point c_1 to get solution U_1 and once c_2 to get solution U_2.
Now, for very large values of r these two solutions are represented (in the sense used by Poincaré) as :

$$\begin{aligned} U_1 &\sim e^{c_1 r} r^{-\alpha_1} (-1)^{a_1} (e^{2\pi i \alpha_1} - 1)\Gamma(\alpha_1)(c_1 - c_2)^{\alpha_2 - 1}, \\ U_2 &\sim e^{c_2 r} r^{-\alpha_2} (-1)^{a_2} (e^{2\pi i \alpha_2} - 1)\Gamma(\alpha_2)(c_1 - c_2)^{\alpha_1 - 1}. \end{aligned} \tag{25}$$

Since $c_1 > 0$, $U_1(r)$ diverges for $r \to \infty$ We now see the case when α_1 and α_2, are real integers. So we see,

$$\frac{\mu e^2}{\hbar\sqrt{-2\mu E}} = l \tag{26}$$

where n is principal quantum number having positive inter values.So , Energy :

$$E_n = -\frac{\mu e^4}{2\hbar^2 n^2} \tag{27}$$

we note that in the case where $\alpha_{1,2}$ are integers, the integrand in equation(22) is not multivalued anymore, but becomes single valued because it is raising the complex monomials $z - c_1$ and $z - c_2$ to integer powers, namely:

$$U = \int_L e^{zr}(z - c_1)^{n+l}(z - c_2)^{-n+l} dz \tag{28}$$

We solve it to find the value of χ as :

$$\begin{aligned} \chi(x) &= x^l e^{-x} L_{n-l-1}^{(2l+1)}(2x), \\ \text{with} \quad x &= c_1 r = \frac{\sqrt{-2\mu E}}{\hbar} r \end{aligned} \tag{29}$$

Here , L is Laguerre polynomial given as :

$$L_n^\alpha(x) = \sum_{k=0}^{n} \frac{(-x)^k}{k!} \binom{n+\alpha}{n-k} \tag{30}$$

So , we form our final hydrogen wavefunction as :

$$\boxed{\chi(x) = x^l e^{-x} \sum_{k=0}^{n-l-1} \frac{(-2x)^k}{k!} \binom{n+l}{n-l-1-k}} \tag{31}$$

which is exactly the form Schrödinger wrote in the original paper in 1926 (except for our interchanging of the integers n and l according to modern nomenclature).

4 Non-Linear Schrödinger Equation

The Non-Linear Schrödinger Equation (NLSE) models an evolution equation for slowly varying envelope dynamics of a weakly nonlinear quasi-monochromatic wave packet in dispersive media.

The NLSE is significant in areas like quantum mechanics, Bose-Einstein condensates, and nonlinear optics. It predicts phenomena such as solitons—stable, localized wave packets with applications in optical communications . Despite its challenging analytical solutions, numerical methods help researchers study its diverse applications in fields like plasma physics and condensed matter systems.

We will derive it from Maxwell's and Helmholtz's equations.
So, Maxwell's equations for medium (Here, optical fibres) are given as :

$$\begin{aligned} \nabla \times E &= -\partial_t B, \\ \nabla \times H &= J + \partial_t D, \\ \nabla \cdot D &= \rho, \\ \nabla \cdot B &= 0 \end{aligned} \tag{32}$$

where,

$$D = \epsilon_0 E + P$$

$$B = \mu_0 H + M$$

and **P** and **M** are induced electric and magnetic polarizations.

We now take curl of the first equation in (32) to get :

$$\nabla \times \nabla \times E + \frac{1}{c^2} \partial_t^2 E = -\mu_0 \partial_t^2 P \tag{33}$$

Thereby eliminating B and D .
Here c is the speed of light given as $1/c^2 = \mu_0 \epsilon_0$ in vacuum.

We now write the Electric polarisation P as sum of Linear and Non-Linear terms : $P(\mathrm{r},t) = P_L(\mathrm{r},t) + P_{NL}(\mathrm{r},t)$ where,

$$P_L(\mathrm{r},t) = \epsilon_0 \int_{-\infty}^{t} \chi^{(1)}(t-t_0)E(\mathrm{r},t)dt_0 \tag{34}$$

$$P_{NL}(\mathrm{r},t) = \epsilon_0 \int_{-\infty}^{t}\int_{-\infty}^{t}\int_{-\infty}^{t} \chi^{(3)}(t-t_1,t-t_2,t-t_3)E(\mathrm{r},t_1)E(\mathrm{r},t_2)E(\mathrm{r},t_3)dt_1dt_2dt_3 \tag{35}$$

where $\chi^{(j)}$ is a tensor of rank j+1 , the j-th order of susceptibility.
Now consider the Non-linear term to be zero. Then we write the Fourier transform of E($\mathbf{r}$,t) as :

$$\hat{E}(\mathbf{r},\omega) = \int_{-\infty}^{+\infty} E(\mathbf{r},t)e^{i\omega t}dt \tag{36}$$

and let $\hat{\chi}^{(1)}(\omega)$ be Fourier transform of $\chi^{(1)}(t)$. So equation(33) can be written as :

$$\nabla \times \nabla \times \hat{E} = \epsilon(\omega)\frac{\omega^2}{c^2}\hat{E}(\mathbf{r},t) \tag{37}$$

such that : $\epsilon(\omega) = 1 + \hat{\chi}^{(1)}(\omega) = (n + i\alpha c/(2\omega))^2$ is the frequency dependent dielectric constant and it's real and imaginary parts are related to refractive index $n(\omega)$ and absorption coefficient $\alpha(\omega)$.

Due to low optical loses in optical fibres within wavelength region of interest , $\epsilon(\omega) = n^2(\omega)$. and $\nabla \cdot D = 0$.
So, we finally arrive at Helmholtz equation :

$$\nabla^2\hat{E} + n^2(\omega)\frac{\omega^2}{c^2}\hat{E} = 0 \tag{38}$$

Including the nonlinear effect modifies the above equation as :

$$\nabla^2\hat{E} + \epsilon(\omega)k_0^2\hat{E} = 0 \tag{39}$$

where $k_0 = \omega/c$ and the dielectric constant $\epsilon(\omega) = 1 + \hat{\chi}^{(1)} + \frac{3}{4}\frac{d^4\chi^{(3)}}{dx^4}|E(\mathbf{r},t)|^2$.
We solve using variable separation method here,

$$\hat{E}(\mathbf{r},\omega-\omega_0) = \hat{A}(z,\omega-\omega_0)B(x,y)e^{i\beta_0 z} \tag{40}$$

where $\hat{A}(z,\omega)$ is a slowly varying function of z and β_0 is a wavefunction that needs to be determined. After solving we get these two equations:

$$2i\beta_0\partial_z\hat{A} + (\hat{\beta}^2 - \beta_0^2)\hat{A} = 0 \tag{41}$$

$$\nabla^2 B + [\epsilon(\omega)k_0^2 - \hat{\beta}^2]B = 0 \tag{42}$$

The wavelength $\hat{\beta}$ is determined by solving the eigenvalue equation using the first-order perturbation theory. We see :

$$\hat{\beta}(\omega) = \beta(\omega) + \Delta\beta \tag{43}$$

where,

$$\Delta\beta = \frac{\omega^2}{c^2}\frac{n(\omega)}{\beta(\omega)}\frac{\int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty}\Delta n(\omega)|B(x,y)|^2 dxdy}{\int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty}|B(x,y)|^2 dxdy} \tag{44}$$

Also we have to know that $\hat{\beta}^2 - \beta_0^2 \approx 2\beta_0(\hat{\beta} - \beta_0)$, the Fourier transform $\hat{A}$ can be written as :

$$\partial_z \hat{A} = i[\beta(\omega) + \Delta\beta(\omega) - \beta_0]\hat{A} \tag{45}$$

Expanding $\beta(\omega)$ and $\Delta\beta(\omega)$ about carrier frequency ω_0 we get :

$$\beta(\omega) = \beta(\omega_0) + \beta'(\omega_0)(\omega - \omega_0) + \frac{1}{2}\beta"(\omega_0)(\omega - \omega_0)^2 ... \tag{46}$$

$$\Delta\beta(\omega) = \Delta\beta(\omega_0) + \Delta\beta'(\omega_0)(\omega - \omega_0) + \frac{1}{2}\Delta\beta"(\omega_0)(\omega - \omega_0)^2 ... \tag{47}$$

Replacing $\omega - \omega_0$ with the differential operator $i\partial_t$ and taking inverse Fourier transform of $\hat{A}$ we get :

$$i\partial_z A + i\beta'(\omega_0)\partial_t A - \frac{1}{2}\beta"(\omega_0)\partial_t^2 A + \Delta\beta(\omega_0)A = 0 \tag{48}$$

Using $T = t - \beta'(\omega_0)z$ and considering non-linearlity we obtain the NLSE

$$\boxed{i\partial_z A - \frac{1}{2}\beta"(omega_0)\partial_T^2 A + \gamma|A|^2 A = 0} \tag{49}$$

where the non-linear coefficient γ is :

$$\gamma(\omega_0) = -\frac{\omega_0}{c}n_2(\omega_0)\frac{\int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty}|B(x,y)|^4 dxdy}{(\int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty}|B(x,y)|^2 dxdy)^2} \tag{50}$$

For a single-mode fiber, the modal distribution B(x, y) corresponds to the fundamental fiber mode, given by one of the following expressions:

$$B(x,y) = \begin{cases} J_0(p\sqrt{x^2+y^2}), & \sqrt{x^2+y^2} \le a \\ \frac{\sqrt{a}}{\sqrt[4]{x^2+y^2}} J_0(pa) e^{q\sqrt{x^2+y^2}-a}, & \sqrt{x^2+y^2} > a \end{cases} \tag{51}$$

or

$$B(x,y) = e^{-\frac{-(x^2+y^2}{w^2}} \tag{52}$$

Here, J_0 is Bessel function of first kind of order zero, a is the radius of fiber core, w is the width parameter , and the quantities $p = \sqrt{n_1^2 k_0^2 = \beta^2}$ and $q = \sqrt{\beta^2 - n_c^2 k_0^2}$.

We got everything but we want it in the form we promised above .So for that we will make some assumptions like:

$$A(z, T) = \psi(x, t)e^{i\alpha z}$$

where $x = \alpha z$ and $t = \beta T$
We substitute this in equation (49) to get :

$$\boxed{i\frac{\partial\psi}{\partial t} + \frac{\partial^2\psi}{\partial x^2} + 2|\psi|^2\psi = 0} \tag{53}$$

5 Conclusion

In conclusion, the Schrödinger Equation, derived through Hamilton-Jacobi's equation, is a foundational element in quantum mechanics with broad applications in physics, chemistry, biology, and finance. Schrödinger's application to the hydrogen atom demonstrated its predictive power, unraveling complex atomic behaviors.
The evolution into the Non-Linear Schrödinger Equation extended its utility, particularly in describing nonlinear wave dynamics in various systems. From subatomic particles to complex structures, both equations remain pivotal in understanding natural phenomena.
Schrödinger's legacy persists, guiding ongoing research and technological advancements. The Schrödinger Equation, in its linear and nonlinear forms, continues to shape our understanding of the quantum world, inspiring discoveries that impact diverse scientific disciplines.

6 References

1. Schrödinger ,E.,1926, '*Quantisierung als Eigenwertproblem*' *Annalen der Physik* 79,361.

2. Agrawal, Govind P. 2012. Nonlinear Fiber Optics, Fifth Edition. Burlington,MA: Academic Press.

3. Ablowitz, Mark J., David James Kaup, Alan C. Newell, and Harvey Segur. 1974. 'The inverse scattering transform-Fourier analysis for nonlinear problems'. Studies in Applied Mathematics 53, no. 4: 249–315.

4. Chiao, Raymond Y., E. Garmire, and Charles H. Townes. 1964. 'Self-trapping of optical beams'. Physical Review Letters 13, no. 15: 479–482.