THE SCHRÖDINGER EQUATION (A REVIEW)

We do not derive $F = ma$; we conclude $F = ma$ by induction from a large series of observations. We use it as long as its predictions agree with our experiments. As with many theories, it has limitations.

Based on experimental observations, particles are found to have wave properties. In the same manner in which we conclude (not derive) from a large series of observations the equation F = ma, we now search for a wave equation for particles that will be in agreement with our observations. The goal of this paragraph is to find (not derive) the wave equation for a non relativistic free particle. We start by assuming that the wave function for a free particle can be written as the plane wave

$$\phi(x,t) = \exp 2\pi i(x/\lambda - \nu t). \tag{1}$$

This is a wave with a constant frequency ν and a constant wavelength λ. The particles energy E and its momentum p are related to the wavelength and the frequency by $E = h\nu$ and $p = h/\lambda$. So the wave function can be written

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$$\phi(x,t) = \exp \frac{i}{\hbar}\big(px - Et\big) \tag{2}$$

where h is Plancks constant and $\hbar = h/2\pi$. This wave function is a wave with a constant energy and a constant momentum. We seek the wave equation which has the above wave function as its solution. For a free non-relativistic particle, the energy is given by $E = p^2/2m$ where m is the mass of the particle, and the hamiltonian H is equal to the energy. Notice that two derivatives of the wave function with respect to x have the effect of multiplying the wave function by $i^2p^2/\hbar^2$ and one derivative with respect to t has the effect of multiplying the wave function by $-iE/\hbar$. So guess that the wave equation takes the form

$$\frac{-\hbar^2}{2m}\frac{\partial^2\phi(x,t)}{\partial x^2} = i\hbar\frac{\partial\phi(x,t)}{\partial t}. \tag{3}$$

Substitute ϕ in the above equation and find

$$\frac{p^2}{2m}\phi(x,t) = E\phi(x,t) = H\phi(x,t). \tag{4}$$

Thus, we recover the free particle relationship, $E = p^2/2m = H$. So the assumed wave function and Eq. (3) are consistent with our knowledge of particles and waves. Eq. (3) is identified as the Schrödinger equation for a free particle. Notice that the replacement $p \to -i\hbar\,\partial/\partial x$ and $E \to i\hbar\,\partial/\partial t$ takes Eq. (4) back to Eq. (3). So operators will be associated with measurable quantities such as momentum and energy. We may also associate an operator with the hamiltonian, and write

$$H\phi(x,t) = \frac{-\hbar^2}{2m}\frac{\partial^2\phi(x,t)}{\partial x^2} = E\phi(x,t). \tag{5}$$

The goal of this paragraph is to find the wave equation for a free non-relativistic particle moving in three dimensions. We start by assuming that wave function for such a free particle can be written as the plane wave

$$\phi(\mathbf{x},t) = \exp\frac{i}{\hbar}\big(\mathbf{p}\cdot\mathbf{x} - Et\big) = \exp\frac{i}{\hbar}\big(p_x x + p_y y + p_z z - Et\big) \tag{6}$$

where $\mathbf{x} = (x, y, z)$ and $\mathbf{p} = (p_x, p_y, p_z)$. Eq. (6) is the generalization of Eq. (2) to three dimensions. Guess that the three dimensional wave equation for a free particle takes the form

$$\frac{-\hbar^2}{2m}\Big(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\Big)\phi(\mathbf{x},t) = i\hbar\frac{\partial\phi(\mathbf{x},t)}{\partial t}. \tag{7}$$

Substitution of Eq. (6) into Eq. (7) yields

$$\frac{(\mathbf{p})^2}{2m}\phi(\mathbf{x},t) = \frac{(p_x^2 + p_y^2 + p_z^2)}{2m}\phi(\mathbf{x},t) = E\phi(\mathbf{x},t) \tag{8}$$

as is required for a free particle. Eq. (8) is identified as the three-dimensional Schrödinger equation for a free particle. Notice that the replacements $p_x \to i\hbar\partial/\partial x$, $p_x \to i\hbar\partial/\partial x$, and $p_x \to i\hbar\partial/\partial x$ take Eq. (8) back to Eq. (7).

Introduce the operator

$$\nabla = \hat{\imath}\partial/\partial x + \hat{\jmath}\partial/\partial y + \hat{k}\partial/\partial z \tag{9}$$

where $\hat{\imath}, \hat{\jmath}, \hat{k}$ are the Cartesian unit basis vectors. Introduce the notation

$$\nabla^2 \equiv \nabla \cdot \nabla = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}. \tag{10}$$

Finally, the three-dimensional Schrödinger equation for a free particle can be written

$$-\frac{\hbar^2\nabla^2\phi(\mathbf{x}, t)}{2m} = i\hbar\frac{\partial\,\phi(\mathbf{x}, t)}{\partial t}. \tag{11}$$

The replacement $\mathbf{p} \to -i\hbar\,(\hat{\imath}\partial/\partial x + \hat{\jmath}\partial/\partial y + \hat{k}\partial/\partial x) = -i\hbar\nabla$ and $E \to i\hbar\,\partial/\partial t$ in Eq. (8) takes us to Eq. (11). The symbol ϕ will be used for the wave function of a free particle. So we write

$$H\phi(\mathbf{x}, t) = -\frac{\hbar^2\nabla^2\phi(\mathbf{x}, t)}{2m} = E\phi(\mathbf{x}, t). \tag{12}$$

Introduce the wave vector $\mathbf{k}$ where $|\mathbf{k}| = |\mathbf{p}|/\hbar = 2\pi/\lambda$, and intoduce the angular frequency $\omega = E/\hbar = 2\pi\nu$. So now

$$\phi(\mathbf{x},t) = \exp i\big(\mathbf{k}\cdot\mathbf{x} - \omega t\big) = \exp i\big(k_x x + k_y y + k_z z - \omega t\big) \tag{13}$$

The following normalization is often used: $\int \phi_2^* \, \phi_1 \, d^3x = \delta^3(\mathbf{k_2} - \mathbf{k_1})$. In order that this is true, set $\phi(\mathbf{x},t) = \exp i(\mathbf{k}\cdot\mathbf{x} - \omega t)/(2\pi)^{3/2}$, and recall $\int \exp(-i(\mathbf{k_2} - \mathbf{k_1})\cdot\mathbf{x}) d^3x = (2\pi)^3 \delta^3(\mathbf{k_2} - \mathbf{k_1})$. Note that $E_2 = E_1$ when $\mathbf{p_2} = \mathbf{p_1}$, or equivalently $\omega_2 = \omega_1$ when $\mathbf{k_2} = \mathbf{k_1}$, since $\omega = \hbar k^2/2m$.

A normalization that will be used in future papers is box normalization. The particle is placed in a large but finite box. First, consider a one dimensional box of length L, which is centered at the origin. Periodic boundary conditions are imposed on the wave functions, i.e., the wave function at one end of the box is equated to the wave function at the other end of the box, so $\exp(ikL/2) = \exp(-ikL/2)$. Thus, $sin(kL/2) = 0$, so $k = 2\pi n/L$ where n is an integer. The requirement $\int_{-L/2}^{+L/2} \phi_2^* \phi_1 \, d^3x = \delta_{k_2,k_1}$ is fulfilled if

$$\phi(x,t) = \frac{1}{L^{1/2}} \exp i\big(kx - \omega t\big). \tag{14}$$

Here $\delta_{k_2,k_1} = 1$ when $k_2 = k_1$, and $\delta_{k_2,k_1} = 0$ when $k_2 \neq k_1$. In three dimensions

$$\phi(\mathbf{x},t) = \frac{1}{V^{1/2}} \exp i\big(\mathbf{k}\cdot\mathbf{x} - \omega t\big) \tag{15}$$

where V is the volume of the box. So to go from the first normalization to box normalization, replace $(2\pi)^{3/2}$ by $V^{1/2}$.

When an external force, which is derivable from a potential energy $V(\mathbf{x})$, acts on the particle, then the total energy E is given by the sum of the kinetic energy and the potential energy, i.e., $E = p^2/2m + V(\mathbf{x})$. The hamiltonian is again the energy, so $H = p^2/2m + V(\mathbf{x}) = E$. Generalizing the free particle Schrödinger equation to include conservative forces, we write

$$H\psi(\mathbf{x},t) = -\frac{\hbar^2\nabla^2\psi(\mathbf{x},t)}{2m} + V(\mathbf{x})\psi(\mathbf{x},t) = i\hbar\frac{\partial\,\psi(\mathbf{x},t)}{\partial t} = E\psi(\mathbf{x},t). \tag{16}$$

This is the Schrödinger equation when conservative forces are present. Its justification and acceptance is based on agreement with experiment. The symbol ψ will be used for the wave function when the particle is subjected to forces.

To include an interaction of a charge q with an electro-magnetic field, introduce the three-dimensional vector potential $\mathbf{A}$. The potential energy is now given by $q\Phi$ where Φ is the potential. The hamiltonian is

$$H = \frac{1}{2m}\big(\mathbf{p} - \frac{q}{c}\mathbf{A}\big)^2 + q\Phi, \tag{17}$$

and the Schrödinger equation for a charged particle in an electromagnetic field is

$$H\psi = \frac{1}{2m}(-i\hbar\nabla - \frac{q}{c}\mathbf{A})\cdot(-i\hbar\nabla - \frac{q}{c}\mathbf{A})\psi + q\Phi\psi = i\hbar\frac{\partial\,\psi}{\partial t} = E\psi. \quad (18)$$

This equation is in good agreement with experiment at non-relativistic speeds.

The last subject will be eigenvalue equations. Let O be an operator associated with a measurable, physical quantity. Sometimes, the application of O to a function f results simply in the product of a number o times f. The equation $Of = of$ is called an eigenvalue equation; the number o is called the eigenvalue, and the function f is called the eigenfunction. The importance of an eigenvalue equation is that if the wave function of a particle is an eigenfunction of the operator, then a measurement of the associated physical quantity will yield the eigenvalue associated with that eigenfunction.

Consider the momentum operator $-i\hbar\,\partial/\partial x$. A non-normalized eigenfunction is $\exp{(ipx/\hbar)}$ and the eigenvalue is p since

$$-i\hbar\frac{\partial(\exp{(ipx/\hbar)})}{\partial x} = p\exp{(ipx/\hbar)}. \quad (19)$$

A particle with its wave function equal to an eigenfunction of momentum has a definite momentum. Since the value of the momentum eigenvalue p is not restricted, there are an infinite number of momentum eigenvalue equations. Each of these equations has its eigenfunction and associated eigenvalue.

The energy operator $i\hbar\,\partial/\partial t$ has eigenfunction $\exp(-iEt/\hbar)$ with eigenvalue E since

$$+i\hbar\frac{\partial(\exp(-iEt/\hbar))}{\partial t} = E\exp(-iEt/\hbar). \tag{20}$$

A particle with its wave function equal to an eigenfunction of energy has a definite energy. Similarly, the energy operator has an infinite number of eigenfunctions and eigenvalues. Now observe that the wave function of Eq. (2) is an eigenfunction of both the momentum and the energy. Also notice that Eq. (6) is the eigenfunction of the three dimensional mementum operator $-i\hbar\nabla$ with eigenvalue $\mathbf{p}$.

Particles may have a spin angular momentum. For the electron, the spin angular momentum is $\hbar/2$, and the z-component of spin angular momentum is $\pm\hbar/2$. The electron spin operator can be represented by $\mathbf{S} = (\hbar/2)\boldsymbol{\sigma}$ where $\sigma^x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}$, $\sigma^y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}$, and $\sigma^z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$. These are the Pauli matrices. The operator σ^z has eigenfunction $\begin{pmatrix} 1 \\ 0 \end{pmatrix}$ and eigenvalue $+1$ since

$$\sigma^z \begin{pmatrix} 1 \\ 0 \end{pmatrix} = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \begin{pmatrix} 1 \\ 0 \end{pmatrix} = +1 \begin{pmatrix} 1 \\ 0 \end{pmatrix} \tag{21}$$

This is referred to as a spin up electron since the z-component of spin angular momentum is $\hbar/2$. Recall $S^z = \hbar/2\,\sigma^z$. This operator has a second eigenfunction $\begin{pmatrix} 0 \\ 1 \end{pmatrix}$ with eigenvalue -1 since

$$\sigma^z \begin{pmatrix} 0 \\ 1 \end{pmatrix} = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \begin{pmatrix} 0 \\ 1 \end{pmatrix} = -1 \begin{pmatrix} 0 \\ 1 \end{pmatrix}. \tag{22}$$

This is referred to as a spin down electron since the z-component of spin angular momentum is $-\hbar/2$. Thus, S^z and σ^z each have two eigenfunctions and two eigenvalues. An arbitrary spin wave function will be a linear combination of the above two spin wave functions. The total wave function of a free electron is the product of $\phi(\mathbf{x}, t)$ and a two component spin wave function.

As pointed out earlier, all theories have limited applicability. The Schrödinger equation is not relativistic. Operators, wave functions, wave equations, eigenvalue equations, and spin are put to use in finding a relativistic wave equation, namely, the Dirac equation, which is the subject of the next review paper.