

1 Planck-Einstein Relation $E = h\nu$

This is the equation relating energy to frequency. It was the earliest equation of quantum mechanics, implying that energy comes in multiples (“quanta”) of a fundamental constant h . It is written as either

$$E = h\nu$$

or

$$E = \hbar\omega$$

where $\hbar = h/2\pi$. ν is linear frequency and ω is angular frequency. The fundamental constant h is called Planck’s constant and is equal to 6.62608×10^{-34} Js ($\hbar = 1.05457 \times 10^{-34}$ Js, or 1.05457×10^{-27} erg s).

This relation was first proposed by Planck in 1900 to explain the properties of black body radiation. The interpretation was that matter energy levels are quantized. At the time this appeared compatible with the notion that matter is composed of particles that oscillate. The discovery that the energy of electrons in atoms is given by discrete levels also fitted well with the Planck relation. In 1905 Einstein proposed that the same equation should hold also for photons, in his explanation of the photoelectric effect. The light incident on a metal plate gives rise to a current of electrons only when the frequency of the light is greater than a certain value. This value is associated with the energy required to remove an electron from the metal (the “work function”). The electron is ejected only when the light energy matches the discrete electron binding energy. Einstein’s proposal that the light energy is quantized just like the electron energy was more radical at the time: light quantization was harder for people to accept than quantization of energy levels of matter particles. (The word “photon” for these quantized packets of light energy came later, given by G. N. Lewis, of Lewis Hall!)

2 Time evolution of real quantum systems

Given the postulates relating the mathematical framework of quantum to physical systems, together with the Planck-Einstein relation, we can make a heuristic derivation of the time dependent Schrodinger equation. One simple but critical leap of “analogy” to classical mechanics will be required.

Time evolution is characterized by a continuous parameter t . Because of superposition, this time evolution must be characterized by a linear transformation in the Hilbert space:

$$|\Psi;t\rangle = L_t|\Psi;0\rangle$$

Conservation of probability tells us that

$$\langle\Psi;t|\Psi;t\rangle = \langle\Psi;0|\Psi;0\rangle$$

Hence we conclude that $L_t^\dagger L_t = 1$, i.e., L_t is unitary, so write as $U(t)$. More precisely then,

$$|\Psi;t'\rangle = U(t',t)|\Psi;t\rangle$$

If the time origin is not important, U depends only on the time difference, i.e., $U(t' - t)$. We also want U to obey the composition law

$$U(t_2)U(t_1) = U(t_2 + t_1).$$

Then we obtain

$$U(t) = [U(t/N)]^N.$$

Now consider what happens as we make the time interval infinitesimal. As $\delta t = t/N \rightarrow 0$, $U(\delta t) \rightarrow 1$. We can write an expression for this that is unitary to first order as

$$U(\delta t) = 1 - i\Delta(\delta t),$$

where the operator Δ is Hermitian. What physical operator might Δ correspond to? Here comes the physical leap of analogy. First look at what the units of Δ are; they are time^{-1} , i.e., the units of frequency. What physical observable has units of frequency? The Planck-Einstein relation says that $E = \hbar\omega$ where ω is frequency and $\hbar = h/2\pi$, with h the fundamental Planck constant. So let's choose our operator Δ to correspond to energy divided by \hbar . Now we know that in classical mechanics that the energy is given by the Hamiltonian operator $H = KE + PE$ and that this operator generates the time evolution. So in a simple leap of analogy, let's take $\hbar\Delta$ to be equal to the quantum mechanical Hamiltonian operator that corresponds to the total energy of the quantum system, i.e., a sum of kinetic and potential energy operators. Then we have

$$U(\delta t) = 1 - \frac{i}{\hbar}H\delta t.$$

The rest is plain sailing. We can either take the limit as $N \rightarrow \infty$ to derive the exponential form $\exp[-iHt/\hbar]$ or, more simply, we use the composition law to write

$$\begin{aligned} U(t + \delta t) - U(t) &= [U(\delta t) - 1]U(t) \\ &= -i\frac{\delta t H}{\hbar}U(t). \end{aligned}$$

Rewriting and taking the limit $\delta \rightarrow 0$, we obtain

$$i\hbar\frac{\partial U}{\partial t} = HU(t).$$

This is the Schrodinger equation for the time evolution operator $U(t)$. Rewriting the evolution operator in its full form as $U(t, t_0)$ and multiplying on the right by $|\Psi; t_0\rangle$, we find

$$i\hbar\frac{\partial U(t, t_0)}{\partial t}|\Psi; t_0\rangle = HU(t, t_0)|\Psi; t_0\rangle,$$

which is equivalent to

$$i\hbar\frac{\partial |\Psi; t\rangle}{\partial t} = H|\Psi; t\rangle.$$

So we have arrived at the time dependent Schrodinger equation for the time evolution of the wave function of a quantum system.

3 Position Representation of Quantum State Function

We will motivate this using the framework of measurements. Consider first the simpler example of a photon. The polarization of the photon can be either horizontal (H) or vertical (V), from which we have a discrete basis of two states $|H\rangle$ and $|V\rangle$. We can measure the polarization by passing the photon through a polarizer crystal, which passes either H or V light depending on its orientation. The measurement operators for this simple 2-state basis are

$$M_H = |H\rangle\langle H|, M_V = |V\rangle\langle V|.$$

A single measurement on an arbitrary state $|\psi\rangle$ will collapse $|\psi\rangle$ onto one of the two orthonormal basis vectors. For example, if the H measurement is made, the state after measurement will be

$$|H\rangle \left(\frac{\langle H|\psi\rangle}{\sqrt{\langle\psi|H\rangle\langle H|\psi\rangle}} \right).$$

If the measurement is repeated many times, this state will be obtained with probability

$$P_H = |\langle H|\psi\rangle|^2.$$

Now consider a particle in a quantum state, e.g., the energy level of a hydrogen atom. The hydrogen atom consists of 1 positively charged proton in the nucleus and 1 negatively charged electron. The electron is ~ 1800 times lighter than the proton, so to a first approximation the electron can be regarded as moving around a stationary proton. The possible energy levels for this electronic motion form a discrete, infinite set of levels of negative total energy (indicating overall binding to the proton), and are given by the relation $E_n \sim -1/n^2$, $n = 1, 2, 3, \dots$. The energy eigenvectors $|n\rangle$ formed by these energy levels form an infinite dimensional Hilbert space. Now what if we want to observe the electron? It is moving in configuration space, so let's consider the effect of the measurement operator corresponding to a location \mathbf{r} in configuration space. The measurement operator is

$$P_{\mathbf{r}} = |\mathbf{r}\rangle\langle\mathbf{r}|$$

and a measurement on the ket $|\psi\rangle$ collapses this onto the state $|\mathbf{r}\rangle\langle\mathbf{r}|\psi\rangle$, with probability

$$|\langle\mathbf{r}|\psi\rangle|^2 = |\psi(\mathbf{r})|^2.$$

So $|\psi(\mathbf{r})|$ is the probability amplitude of finding an electron at \mathbf{r} , i.e., “the wave function in the position representation”. Note that the state after measurement is the position ket $|\mathbf{r}\rangle$.

We can understand this in a pictorial manner by imagining a basis consisting of a very densely spread set of delta functions: the wave function is the amplitude of the expansion of the quantum state in this basis.

$$\begin{aligned} |\psi\rangle &= \sum_i \alpha_i |\mathbf{r}_i\rangle \\ \langle\mathbf{r}|\psi\rangle &= \sum_i \alpha_i \langle\mathbf{r}|\mathbf{r}_i\rangle \\ &= \alpha_i \delta(\mathbf{r} - \mathbf{r}_i) \\ &= \psi(\mathbf{r}). \end{aligned}$$

The position representation is defined by the continuous set of basis vectors $|\mathbf{r}\rangle$, satisfying

$$\int d\mathbf{r} |\mathbf{r}\rangle \langle \mathbf{r}| = 1 \text{ (completeness)}$$

$$\langle \mathbf{r} | \mathbf{r}' \rangle = \delta(\mathbf{r} - \mathbf{r}'),$$

where $\delta(\mathbf{r} - \mathbf{r}')$ is the Dirac delta function. This is defined by the relation (shown here for 1D)

$$\int_{-\infty}^{+\infty} f(x') \delta(x - x') dx' = f(x).$$

Setting $f(x) = 1$ shows that the integral under the delta function is equal to unity. The three dimensional delta function is given by

$$\delta(\mathbf{r} - \mathbf{r}') = \delta(x - x') \delta(y - y') \delta(z - z').$$

We can regard the Dirac delta function as the limit of a sequence of functions possessing unit norm, e.g., a sequence of Gaussians with variable width λ :

$$f_\lambda = \frac{1}{\lambda \sqrt{2\pi}} \exp^{-(x-x')^2/2\lambda^2}.$$

Note that the norm of the basis states $|r\rangle$ is ill-defined, unless one agrees to implicitly integrate over the position coordinate and make use of the delta function property.

To summarize, the ket $|\psi\rangle$ can be expanded in the position representation as

$$|\psi\rangle = \int d\mathbf{r}' |\mathbf{r}'\rangle \langle \mathbf{r}' | \psi \rangle$$

The inner product between two state $|\psi\rangle$ and $|\phi\rangle$ can be expressed in terms of the corresponding wave functions in the position representation:

$$\langle \phi | \psi \rangle = \int d\mathbf{r} \langle \phi | \mathbf{r} \rangle \langle \mathbf{r} | \psi \rangle$$

$$= \int d\mathbf{r} \phi^*(\mathbf{r}) \psi(\mathbf{r}).$$

Now the norm is well-behaved

$$\langle \psi | \psi \rangle = \int \psi^*(\mathbf{r}) \psi(\mathbf{r}) d\mathbf{r} = 1.$$

This implies we can choose a set of functions $\phi_n(\mathbf{r})$ satisfying

$$\int \phi_n^*(\mathbf{r}) \phi_m(\mathbf{r}) d\mathbf{r} = \delta_{mn}$$

which is just the orthonormality condition between $|\phi_n\rangle$ and $|\phi_m\rangle$. We can make this set of functions a basis for the Hilbert space spanned by the energy eigenstates $|n\rangle$. This basis of wave functions in position representation has a well behaved norm

$$||\phi_n||^2 = \int |\phi_n(\mathbf{r})|^2 d\mathbf{r} = 1.$$

These functions are therefore a set of square integrable functions, often also called L^2 functions.

Similar arguments lead to the definition of the momentum representation. The ket $|\psi\rangle$ can be expanded in the momentum representation as

$$|\psi\rangle = \int d\mathbf{p}' |\mathbf{p}'\rangle \langle \mathbf{p}' | \psi \rangle$$

where $\langle \mathbf{p}' | \psi \rangle = \psi(\mathbf{p}')$ is the probability amplitude to find the particle with momentum \mathbf{p}' . It is the wave function in the momentum representation. Note that equivalently, it can be understood as the expansion coefficient in the expansion in momentum eigenstates $|\mathbf{p}'\rangle$.

Projecting this expansion into the position representation yields the basic equation relating position and momentum representations of a quantum state $|\psi\rangle$:

$$\psi(\mathbf{r}) = \langle \mathbf{r} | \psi \rangle = \int d\mathbf{p}' \langle \mathbf{r} | \mathbf{p}' \rangle \psi(\mathbf{p}').$$

Note that using the Dirac notation we are correct in writing ψ on both right and left hand sides of this equation. However, the two functions may have very different dependence on their respective variables \mathbf{r} and \mathbf{p} . To avoid confusion, one usually gives these different names, e.g., $\psi(\mathbf{r})$ and $\tilde{\psi}(\mathbf{p})$.

Transformation between position and momentum representations

What is the transformation element $\langle \mathbf{r} | \mathbf{p}' \rangle$ in the above equation? If we set this equal to $e^{i\mathbf{p}'\cdot\mathbf{r}}$ then the equation looks like a Fourier transform of the wave function in momentum space, $\tilde{\psi}(\mathbf{p})$, i.e.,

$$\psi(\mathbf{r}) = \int d\mathbf{p} e^{i\mathbf{p}\cdot\mathbf{r}} \tilde{\psi}(\mathbf{p}).$$

This is not quite a Fourier transform, since we have momentum p rather than wave vector k in the integral. However, p and k satisfy the *de Broglie* relation,

$$\mathbf{p} = \hbar \mathbf{k}$$

which leads to the Fourier transform relation

$$\psi(\mathbf{r}) = \int d\mathbf{k} e^{i\mathbf{k}\cdot\mathbf{r}} \tilde{\psi}(\mathbf{k})$$

where we have omitted factors of \hbar and 2π .

4 The Hamiltonian

What is the Hamiltonian operator? Classically, the Hamiltonian is the energy operator, $H = \frac{p^2}{2m} + V(x)$. Quantum mechanically, we would like to use either the position or momentum basis to represent the operator since then either x or p will be diagonal, and consequently also any corresponding functions of these operators that occur in the Hamiltonian. Thus in a position representation $V(x)$ is diagonal, while in a momentum representation $\frac{p^2}{2m}$ is diagonal. E.g.,

$$\begin{aligned} \hat{V} &= \int dx dx' |x\rangle \langle x| V |x'\rangle \langle x'| \\ &= \int dx dx' |x\rangle V(x) \delta(x-x') \langle x| \\ &= \int dx |x\rangle V(x) \langle x| \end{aligned}$$

We usually have a more complicated potential energy term than kinetic term, so prefer to work in the position representation - will illustrate with an example below. So, we need to express $\hat{p}^2/2m$ in the position representation. The definition of the momentum operator in position representation is

$$\hat{p} = \frac{\hbar}{i} \nabla.$$

For the derivation see "Quantum Mechanics", vol. 1, page 149, by Cohen-Tannoudji; "Modern Quantum Mechanics", page 54, by Sakurai; "Quantum mechanics", chapter 4, by Dirac.

Hence the kinetic energy operator in the position representation is $\hbar^2/2m\nabla^2$.

So, what if we had used the momentum representation? Then the kinetic energy would be simple, merely the diagonal form $p^2/2m$ and we would need to evaluate x in the momentum representation. This is given by $x = i\hbar d/dp$. Now suppose we had some non-trivial potential energy, e.g., $V(x) = 1/\cosh^2(x)$. This happens. Then the potential energy would be given by $V(p) = 1/\cosh^2(i\hbar d/dp)$ which is really not something that you want to deal with in your partial differential equation for the wave function!

5 The Schrodinger Equation and its Solutions

What is the role of energy here? It is very intertwined with time dependence. Let's examine how...

First, let's consider the Schrodinger equation for a free particle, $V(x) = 0$:

$$i\hbar \frac{\partial}{\partial t} \psi(x,t) = -\frac{\hbar^2}{2m} \frac{\partial^2 \psi}{\partial x^2} \psi(x,t) \quad (1)$$

with m the particle's mass and $\hbar = \frac{h}{2\pi}$. Recall that Planck's constant has a value of $h = 6.6 \times 10^{-34} \text{ J}\cdot\text{s}$. This is a very small quantity with respect to ordinary macroscopic levels, and is the main reason why quantum effects are not usually noticeable.

If we take this Schrodinger equation and plug in our trial solution $\psi(x,t) = e^{i(kx - \omega(k)t)}$, we find that this trial solution works provided that $\omega(k) = \frac{\hbar k^2}{2m}$. This is known as the dispersion relation for a free particle. Now, notice that the most general solution is a linear superposition of such functions for many different k values:

$$\psi(x,t) = \int dk A_k e^{i(kx - \omega(k)t)} \quad (2)$$

This superposition solution is known as a *wave packet*. The velocity of a wave packet is $v = \frac{\partial \omega}{\partial k} = \frac{\partial}{\partial k} \left(\frac{\hbar k^2}{2m} \right) = \frac{\hbar k}{m}$. This is the "group velocity". We can also quickly rearrange this to note that $mv = \hbar k$. But what is "mv"? It's the momentum, p ! Therefore we conclude that $p = \hbar k$. This is a relationship between the physical momentum of a particle and the wave-vector of a wavefunction. We can illuminate this further as follows:

$$p = \hbar k = \left(\frac{h}{2\pi} \right) \left(\frac{2\pi}{\lambda} \right) = \frac{h}{\lambda} \quad (3)$$

This is known as the DeBroglie relation, and it actually predates the Schrodinger equation.

Now we will consider how to solve the Schrodinger equation in general, when there is also a non-zero potential energy term, $V(x)$ (say, due to an electric field). If there is a potential energy in the system, then the Hamiltonian becomes:

$$\hat{H} = KE + PE = -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + V(x) \quad (4)$$

To be clear about the distinction between operators and functions, we'll denote quantum mechanical operators with "hats", e.g. \hat{H} or \hat{p} .

The Schrodinger Equation

$$i\hbar \frac{\partial}{\partial t} \psi(x,t) = \hat{H} \psi(x,t) \quad (5)$$

defines the relationship between the energy of a system (through \hat{H}) and its time development. Can we understand this relationship better?

First, we note that this is a partial differential equation, which means that it is a differential equation with more than one variable (x and t in this case). We now employ a handy math trick for partial differential equations, and assume that the solution to the Schrodinger Equation can be written as the product $\psi(x,t) = \psi(x)\phi(t)$. This is called *separation of variables*. If we plug this into the Schr. Eqn. and divide both sides by $\psi(x)\phi(t)$:

$$i\hbar \psi(x) \frac{\partial}{\partial t} \phi(t) = \phi(t) \hat{H} \psi(x) \rightarrow i\hbar \frac{\frac{\partial \phi}{\partial t}}{\phi(t)} = \frac{\hat{H} \psi(x)}{\psi(x)} \quad (6)$$

The left hand side (LHS) is a function of t , and the right hand side (RHS) is a function of x . Therefore, for this solution to make sense for all possible x and t , both sides must equal a *constant*. What is that constant? Why, *energy*, of course!

So, the Schr. eqn. breaks into two equations, one in time (t) and one in space (x):

$$space : \hat{H} \psi(x) = E \psi(x) \quad (7)$$

$$time : i\hbar \frac{\partial \phi(t)}{\partial t} = E \phi(t) \quad (8)$$