C/CS/Phys 191 Planck-Einstein relation, Time Dep. Schrodinger Eq., Position/Momentum representation, deBroglie Relation
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Planck-Einstein Relation $E = h\nu$

This is the equation relating energy to frequency. It was the first 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 $\times 10^{-34}$ 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!)

Time evolution of real quantum systems

Given the three postulates relating the mathematical framework of quantum to physical systems and the Planck-Einstein relation above, we can now 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 (I) , this time evolution must be characterized by a linear transformation in the Hilbert space:

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

Conservation of probability tells us that

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

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

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

If the time origin is not important, U depends only the 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 $\delta t = t/N \to 0$, $U(\delta t) \to 1$. 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 lets 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, lets 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 $N \to \infty$ to derive the exponential form $exp[-iHt/\hbar]$ or, more simply, we 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, 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 $\left|\Psi;t_0\right\rangle$, we find

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

which is equivalent to

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

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

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 $\left|H\right\rangle$ and $\left|V\right\rangle$. 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

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

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

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

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

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

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 $\sim$ 1800 times lighter than the proton, so to a first approximation the electron can be regarded as moving around a stationnary 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 $E_n \sim -1/n^2$, $n = 1,2,3,.....$ The energy eigenvectors $\left|n\right\rangle$ 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 lets consider the effect of the measurement operator corresponding to a location $\mathbf{r}$ in configuration space. The measurement operator is

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

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

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

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 the following pictorial manner:

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

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

$$\begin{aligned} \int d\mathbf{r} \langle\mathbf{r}| |\mathbf{r}\rangle &= 1(completeness) \\ \langle\mathbf{r}| |\mathbf{r}'\rangle &= \delta(\mathbf{r}-\mathbf{r}'), \end{aligned}$$

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

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

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 Gausssians 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.

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:

$$\begin{aligned} \langle\phi| |\psi\rangle &= \int d\mathbf{r} \langle\phi| |\mathbf{r}\rangle \langle\mathbf{r}| |\psi\rangle \\ &= \int d\mathbf{r} \phi^*(\mathbf{r}) \psi(\mathbf{r}). \end{aligned}$$

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 position 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 $|\psi\rangle$:

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

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.

The de Broglie relation $\mathbf{p} = \hbar\mathbf{k}$

This relation expresses the duality between wave and particle nature. It applies to both particles with finite mass, and photons (which have zero mass). For photons, $E = pc$, the wavelength λ is related to the frequency

ν and speed c by $\lambda\nu = c$, and the wave vector k is given by $k = 2\pi/\lambda$. Combining these three relations with the Planck-Einstein relation for quantization of light, $E = h\nu$, immediately yields $p = \hbar k$. Note also that for photons $\omega = ck$ where $\omega = 2\pi\nu$ is the angular frequency, i.e., there is a linear relation between frequency and wave vector (dispersion relation).

For particles with finite mass, we can derive the de Broglie relation by constructing a wave packet to represent the motion of the particle. Recall that a monochromatic plane wave $\psi(\mathbf{r}) = e^{i(\mathbf{k}\cdot\mathbf{r}-\omega t)}$ represents an amplitude modulation of wavelength $\lambda = 2\pi/k$ traveling in the direction of the wave vector $\mathbf{k}$ with constant velocity given by $v_\phi = \omega/k$. v_ϕ is referred to as the"group velocity" and is the velocity of propagation of points of constant phase on the wave.

The Planck-Einstein relation tells us that $E = \hbar\omega$, so that this plane wave is associated with a definite energy. To establish how the wave vector relates to the particle momentum we need to associate the particle with a wave of limited extent so that a connection to the particle energy $E = p^2/2m$ may be made. We do this by constructing a packet of plane waves possessing a range of wave vectors and of associated frequencies (we cannot assume a linear dispersion relation as for photons). We present the argument for simplicity here in one dimension - you can easily generalize to more dimensions.

Construct the wave packet

$$\psi(x,t) = \int f(k')e^{i(k'x-\omega(k')t)}dk'$$

where $f(k') = A(k')e^{i\alpha(k')}$ is a complex-valued coefficient with real amplitude $A(k')$ and complex phase $\alpha(k')$. The integral is then

$$\psi(x,t) = \int A(k')e^{i(\alpha(k')+k'x-\omega(k')t)}dk'$$

which is an integral of an oscillatory function times $A(k')$. $A(k')$ may be assumed to be smoothly varying for non-pathological particles.

For any given value of x the major contribution to the integral will then derive from values of k' where the phase $\phi(k') = \alpha(k') + k'x - \omega(k')t$ is constant with respect to k', i.e., the points of "stationnary phase". These are given by

$$x - \left(\frac{d\omega}{dk}\right)t + \left(\frac{d\alpha}{dk}\right) = 0.$$

The stationnary phase point $x_0 = \left(\frac{d\omega}{dk}\right)t - \left(\frac{d\alpha}{dk}\right)$ is thus a point that moves with uniform motion at velocity $v_g = \frac{d\omega}{dk}$. This velocity, referred to as the "group velocity", therefore provides the corresponding observable to a classical particle velocity and must be identified with the latter, i.e., with $v = \frac{dE}{dp}$ (check you can get this from $E = \frac{p^2}{2m}$).

Hence

$$dp = \frac{1}{v}dE = \left(\frac{dk}{d\omega}\right)dE = \left(\frac{dE}{d\omega}\right)dk = \hbar dk$$

where we have used i) the group velocity definition, and ii) the Planck-Einstein relation. Integrating, we arrive at the wave-matter duality for a particle with finite mass,

$$p = \hbar k = \frac{h}{\lambda}.$$
