

ENERGY & WAVE FUNCTIONS - A FEW THEOREMS

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Reference: Griffiths, David J. (2005), Introduction to Quantum Mechanics, 2nd Edition; Pearson Education - Problems 2.1, 1.7.

There are a few facts about the solutions to the Schrödinger equation that are useful, both from the point of view of further calculations in quantum mechanics, and for general interest.

In the time-independent case, the Schrödinger equation can be solved by separation of variables, with the result that the spatial component satisfies the equation

$$-\frac{\hbar^2}{2m} \frac{d^2\psi}{dx^2} + V(x)\psi = E\psi \quad (1)$$

The time component has the simple solution

$$\Xi(t) = e^{-iEt/\hbar} \quad (2)$$

and the complete solution, for a given value of the energy E is

$$\Psi(x,t) = \psi(x)e^{-iEt/\hbar} \quad (3)$$

First, since the energy E is a physically measurable quantity, we would expect that it has to be a real number. This is fairly easy to prove, as follows.

Suppose $E = E_0 + i\Gamma$, where E_0 and Γ are real numbers. Then $\Psi(x,t) = \psi(x)e^{-iEt/\hbar} = \psi(x)e^{-iE_0t/\hbar}e^{\Gamma t/\hbar}$. To normalize, we must have $\int |\Psi|^2 dx = 1$, so $e^{2\Gamma t/\hbar} \int |\psi|^2 dx = 1$. The normalization condition must apply at all times, so we must have $\Gamma = 0$. Thus the energy must be real.

Another useful theorem is that the energy of a particle must be greater than the minimum value of $V(x)$. This would seem to be obvious from the principle of conservation of energy, since the energy of a particle is $E = T + V$ where T is the kinetic energy, and the kinetic energy is always positive (or zero) so E can never be less than the minimum of V . However, there is another argument which shows this must be true in quantum mechanics specifically.

The spatial part 1 of the Schrödinger equation can be written as

$$\frac{d^2\psi}{dx^2} = \frac{2m}{\hbar^2}(V - E)\psi \quad (4)$$

If $E < V_{\min}$, $V - E > 0$ for all x . This means that ψ and ψ'' have the same sign everywhere. If ψ has a maximum, from the second derivative test in elementary calculus we must have $\psi'' < 0$ so at the point of the maximum ψ itself must be negative. Similarly, any minima of ψ must occur where ψ is positive. For any realistic potential function $V(x)$, Born's conditions say that ψ and its derivative ψ' must be continuous, so ψ can have either a maximum or a minimum but not both. In either case, the restriction of ψ and ψ'' having the same sign means that ψ cannot tend to 0 as $x \rightarrow \infty$ so it can't be normalized.

Now a couple of theorems on the stationary states ψ that are solutions of 1. First, there will always be a ψ that is a real function. This follows from the fact that if we have a function $\phi(x)$ that is complex and solves 1 then, since $V(x)$ and E are real, the complex conjugate $\phi^*(x)$ will also solve the equation. Since the equation is linear, linear combinations of solutions are also solutions, so $\phi + \phi^*$ and $i(\phi - \phi^*)$ are also solutions, and both these are real functions. This, of course, doesn't mean that real functions are the only ones worth considering, but it does say that if there are any solutions at all, some of them must be real.

Another theorem comes in handy for potentials that satisfy a certain condition. If the potential is even, so that $V(x) = V(-x)$, then $\psi(x)$ can be taken as even or odd. Follows by considering the Schrödinger equation with x replaced by $-x$:

$$-\frac{\hbar^2}{2m} \frac{d^2\psi(-x)}{dx^2} + V(x)\psi(-x) = E\psi(-x) \quad (5)$$

Thus $\psi(-x)$ satisfies the same equation as $\psi(x)$ for an even potential, so another pair of solutions must be (since the equation is linear) $\psi(-x) \pm \psi(x)$. Taking the + sign, we get the function $\psi_+(x) = \psi(-x) + \psi(x) = \psi_+(-x)$, which is an even function. Taking the - sign we get $\psi_-(x) = \psi(-x) - \psi(x) = -\psi_-(-x)$, which is an odd function. Thus the general solution is a linear combination of even and odd functions.

Finally, it's worth stating *Ehrenfest's theorem*, which says that expectation values (means or averages) of observable quantities in quantum mechanics obey classical laws. One example is the quantum form of the equation for a conservative force. In classical physics, any conservative force can be expressed as the gradient of a potential. From Newton's law, a force is $F = \frac{dp}{dt}$ so for a conservative force, $\frac{dp}{dt} = -\frac{dV}{dx}$ (in one dimension). The

quantum equivalent can be worked out using the usual methods of calculating expectation values.

The quantum momentum operator is $p = -i\hbar\partial/\partial x$, so the expectation value of the momentum is

$$\langle p \rangle = -i\hbar \int \Psi^* \frac{\partial \Psi}{\partial x} dx \quad (6)$$

To make the notation easier, we will denote a derivative by a subscript, so $\Psi_t = \partial\Psi/\partial t$, $\Psi_{xx} = \partial^2\Psi/\partial x^2$, etc. To work this out we need the original, time-dependent Schrödinger equation

$$-\frac{\hbar^2}{2m} \frac{d^2\Psi}{dx^2} + V(x)\Psi = i\hbar \frac{\partial\Psi}{\partial t} \quad (7)$$

The time derivative is then

$$\frac{\partial\langle p \rangle}{\partial t} = -i\hbar \int [\Psi_t^* \Psi_x + \Psi^* \Psi_{xt}] dx \quad (8)$$

$$= \int \left[\left(-\frac{\hbar^2}{2m} \Psi_{xx}^* + V\Psi^* \right) \Psi_x + \Psi^* \left(\frac{\hbar^2}{2m} \Psi_{xxx} - V_x\Psi - V\Psi_x \right) \right] dx \quad (9)$$

$$= \int \left[\left(-\frac{\hbar^2}{2m} \Psi_{xx}^* \right) \Psi_x + \Psi^* \left(\frac{\hbar^2}{2m} \Psi_{xxx} - V_x\Psi \right) \right] dx \quad (10)$$

The first line uses the product rule for derivatives on 6, and the second line uses the original time-dependent Schrödinger equation 7 twice to replace the time derivatives with spatial derivatives. The third line cancels off a pair of $V\Psi^*\Psi_x$ terms.

We can now integrate the first term by parts twice and throw away the boundary terms in both steps due to the usual assumption that the wave function and all its derivatives are zero at infinity (as required by normalization). When we do this, we are left with

$$\frac{\partial\langle p \rangle}{\partial t} = \int \left[\left(-\frac{\hbar^2}{2m} \Psi^* \right) \Psi_{xxx} + \Psi^* \left(\frac{\hbar^2}{2m} \Psi_{xxx} - V_x\Psi \right) \right] dx \quad (11)$$

$$= - \int \Psi^* V_x \Psi dx \quad (12)$$

$$= \left\langle -\frac{\partial V}{\partial x} \right\rangle \quad (13)$$

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