

Time dependence in quantum mechanics

Notes on Quantum Mechanics

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Department of Chemistry, Boston University, Boston MA 02215

■ Time-dependent Schrödinger equation

We have learned that the Schrödinger equation

$$H \psi_j(x) = E_j \psi_j(x)$$

allows us to determine the physically acceptable wavefunctions, $\psi_j(x)$, and their energy, E_j , in terms of the number of loops in the wavefunction. The wavefunctions tell us the *spatial* distribution of the probability density,

$$\rho_j(x) = \psi_j(x)^* \psi_j(x).$$

To learn about the *temporal* variation of wavefunctions and so of probability density, we need a more general *time-dependent* Schrödinger equation. (The equation we have been using until now is called the *time-independent* Schrödinger equation.) There are several such equations, but the one most helpful in applications to chemistry is

$$i \hbar \frac{\partial}{\partial t} \Psi_j(x, t) = H \Psi_j(x, t).$$

In this equation we use an upper case symbol, $\Psi_j(x, t)$, for the time dependent wavefunction, to distinguish it from the spatial-only wavefunction, $\psi_j(x)$.

A way to make sense out of the time-dependent Schrödinger equation is to take advantage of the very common circumstance that the hamiltonian operator, H , does not depend on time. This will be true provided the potential energy part of H does not depend on time, and this is true for any isolated atom or molecule.

The most important situation in which this is not the case is when light interacts with matter, since the oscillating electric (and magnetic) fields of light contribute a time-dependent part to the potential energy experienced by the atom or molecule, but we will see that this can be handled in terms of the solutions to the time-dependent Schrödinger equation that ignore this time-varying contribution.

Assuming, then, that the hamiltonian operator does not depend on time, we can separate the time and spatial variation of the wavefunction. The way we do this is to express the time-dependent wavefunction as a product of spatial and temporal parts,

$$\Psi_j(x, t) = \psi_j(x) \theta_j(t).$$

When we substitute this into the time-dependent Schrödinger equation we can rearrange the equation as

$$\frac{i \hbar}{\theta_j(t)} \frac{d\theta_j(t)}{dt} = E_j.$$

Fill in the steps of this rearrangement.

This equation can be further rearranged to read

$$\frac{d\theta_j(t)}{\theta_j(t)} = -\frac{i E_j}{\hbar} dt,$$

In this form it is easy to integrate both sides from $t = 0$ to t to get

$$\ln \left\{ \frac{\theta_j(t)}{\theta_j(0)} \right\} = -\frac{i E_j}{\hbar} (t - 0).$$

and then exponentiating both sides, we get

$$\theta_j(t) = \theta_j(0) e^{-i E_j t / \hbar}.$$

This result means that, for a time-independent hamiltonian operator, the time-dependent wavefunction is

$$\Psi_j(x, t) = \psi_j(x) \theta_j(0) e^{-i E_j t / \hbar}.$$

The factor $\theta_j(0)$ is usually assumed to have been absorbed into the wavefunction, so that we can write finally

$$\Psi_j(x, t) = \psi_j(x) e^{-i E_j t / \hbar}.$$

Show that if the spatial part of the time-dependent wavefunction, $\psi_j(x)$, is normalized, then the time-dependent wavefunction, $\Psi_j(x, t)$, is normalized.

Show that the time-dependent wavefunction

$$\Psi(x, t) = \sqrt{.4} \psi_1(x) e^{-i E_1 t / \hbar} + \sqrt{.6} \psi_2(x) e^{-i E_2 t / \hbar},$$

expressed in terms of a combination of time-dependent normalized spatial eigenfunctions, $\psi_j(x)$, is normalized.

This form of the time-dependent wavefunction is a very important result, for it means we can add time dependence to any eigenfunction of a time-independent hamiltonian operator simply by multiplying it by the factor $e^{-i E_j t / \hbar}$.

Sign of the time phase factor

The negative sign in the time exponential traces to the stationary phase condition of wave motion, in the following sense. A mathematical wave of wavelength λ and frequency ν ,

$$\psi = a \sin \{2 \pi(x / \lambda - \nu t)\},$$

moves toward positive value of x for increasing values of t .

Show that this is true. Hint: Recall the stationary phase condition for determining the phase velocity of a wave.

Now, consider a "matter wave"

$$\psi = a e^{i k x} e^{-i E t / \hbar} = a e^{(i/\hbar)(p x - E t)},$$

where in the second equality we have used the fact that the wave has momentum eigenvalue $p = \hbar k$.

Verify that this is so.

For positive values of momentum (particles moving toward positive x), the phase factor $p x - E t$ is stationary for increasing x when t increases. That is, the negative sign in the time phase factor insures the correspondence between positive momentum and rightward motion.

Show that if the value of momentum is negative, than motion is toward negative x .

Effect of time phase factor on normalization

Because this factor has a squared modulus of 1,

$$e^{-i E_j t / \hbar} e^{i E_j t / \hbar} = e^{-i E_j t / \hbar + i E_j t / \hbar} = e^0 = 1,$$

the presence of the time factor has no effect on the probability amplitude of any eigenfunction of H !

Show that this statement is true.

Show that the time-dependent wavefunction

$$\Psi(x, t) = \sqrt{.4} \psi_1(x) e^{-i E_1 t / \hbar} + \sqrt{.6} \psi_2(x) e^{-i E_2 t / \hbar},$$

expressed in terms of a combination of time-dependent normalized spatial eigenfunctions, $\psi_j(x)$, is not an eigenfunction of H unless $E_1 = E_2$.

In our derivation of the time factor $e^{-i E t / \hbar}$ we assumed that the wavefunction was an eigenfunction of H , that is, an energy eigenstate. If this is not the case, namely, if the wavefunction is a superposition of wavefunctions of *different* energy, then we cannot assign a single overall time factor, since there is not a single value of E to use; instead, we must assign time factors separately to each of the components of the superposition.

Show that the probability density is not independent of time for any wavefunction expressed as a linear combination of normalized eigenfunctions that have different eigenvalues. Hint: Use as example

$$\Psi(x, t) = \sqrt{.4} \psi_1(x) e^{-i E_1 t / \hbar} + \sqrt{.6} \psi_2(x) e^{-i E_2 t / \hbar},$$

and assume the spatial functions $\psi_j(x)$ are normalized and that their eigenvalues are different. We will see that this behavior is the origin of quantum motion, and so of all change.

This last question shows that unless a wavepacket is formed only from degenerate states (that is, ones with the same energy), the resulting probability density will oscillate in time. The frequency of the oscillations will be $(E_j - E_k) / \hbar$, that is, proportional to the *energy differences* of the states that compose the wavepacket.

Show that the total probability is independent of time for any wavefunction expressed as a linear combination of normalized eigenfunctions that have different eigenvalues. Hint: Use as example

$$\Psi(x, t) = \sqrt{.4} \psi_1(x) e^{-i E_1 t/\hbar} + \sqrt{.6} \psi_2(x) e^{-i E_2 t/\hbar},$$

and assume the spatial functions $\psi_j(x)$ are normalized and that their eigenvalues are different.

This question shows that while a system evolves in time, it does so in a way that conserves its total probability.

Understanding the Planck-Einstein-Bohr analysis of spectra

Now, we know from the Planck-Einstein-Bohr analysis of spectra that the frequency of light that interacts with matter undergoing a change between states of energy E_j and E_k is precisely this same value, $(E_j - E_k)/h$. We have mentioned that this dependence on energy differences is nonsensical from a classical point of view, that is, that it does not at all correspond to the classical picture of matter an electron in an atom, say, orbiting the nucleus with a particular frequency.

Now, we can at last understand why light frequency should be related to matter energy differences: The matter energy differences tell us the frequencies at which the probability density of the matter is able to oscillate, and light-matter interaction occurs when the frequency of the oscillations of the electric field of the light match up with the frequencies of the oscillation of the probability density of the matter!

Time evolution and the Heisenberg uncertainty principle

Now that we know the way time evolution works, we can understand why large uncertainty in momentum means that a short time later we will not know where the particle will be.

In the analysis of wavepackets we have seen that to represent a localized particle, many different wavelengths—and so, many different momenta—need to be combined. That is, there is an inverse relationship,

$$\delta x \delta p \geq \hbar/2.$$

between the rms deviation in position, δx , and the rms deviation in momentum, δp . This so-called Heisenberg uncertainty principle means that there is a fundamental limitation on how precisely we can localize a particle. If we are very precise in the localization, then there is a very large uncertainty in the momentum of the particle.

If many different momenta contribute, then correspondingly many different energies contribute. This means that in turn many different energy *differences* will contribute to the probability density. Since the time evolution of probability density is proportional to the size of the energy differences in the time factors, a large range of energy differences means a correspondingly large range of time evolutions contributing to the probability density. The larger this range, the more rapidly the probability density will spread out, that is, the more rapidly the particle will be delocalized away from its point of initial localization.

Here we have considered the Heisenberg uncertainty principle as a consequence of wavepacket composition and evolution. In fact, it is more general, in that ultimately it is a consequence of the position-momentum commutation relation, $x p - p x = i \hbar$. This means that even for a single eigenstate of energy, the uncertainty product $\delta x \delta p$ must always be no smaller than $\hbar/2$.

Why does it not make sense to apply this time-evolution analysis of the Heisenberg uncertainty principle to a wavepacket composed of degenerate states?

Why does it not make sense to apply this time-evolution analysis of the Heisenberg uncertainty principle to a single eigenstate of energy?

Let's verify the Heisenberg uncertainty principle for the eigenstates of a particle of mass m in a one-dimensional infinite potential well of dimension L . Recall that the rms deviation can be computed as

$$\delta x = \sqrt{\langle x^2 \rangle - \langle x \rangle^2},$$

where $\langle \dots \rangle$ denotes the mean of the enclosed quantity, that is, as the square root of difference between the mean of the squared scores and the square of the mean of the scores. Here are the expectation values for in terms of the number of loops in the wavefunction:

$$\langle x \rangle = \int_0^L \psi_j(x) x \psi_j(x) dx = \frac{L}{2},$$

$$\langle x^2 \rangle = \int_0^L \psi_j(x) x^2 \psi_j(x) dx = \frac{L^2}{6} \left(2 - \frac{3}{j^2 \pi^2} \right),$$

$$\langle p \rangle = \int_0^L \psi_j(x) p \psi_j(x) dx = 0,$$

$$\langle p^2 \rangle = \int_0^L \psi_j(x) p^2 \psi_j(x) dx = \frac{j^2 \pi^2 \hbar^2}{L^2}.$$

The general expression for the infinite well uncertainty product, in units of h , is

$$\delta x \delta p / h = \frac{\sqrt{j^2 \pi^2 - 6}}{4 \pi \sqrt{3}}.$$

The Heisenberg uncertainty principle requires that this be no less than $1 / (4 \pi) = 0.0796$. The value for $j = 1$ is 0.0904 and the values for higher j grow linearly. This shows that the Heisenberg uncertainty principle is satisfied.

Where there is life there is *inevitable* change

Perhaps the most profound consequence of the role of time in quantum mechanics is that in order for anything to *happen*, that is, in order for there to be any change, then that change must be ceaseless. The reason is that in order for a quantum system to change with time, it must correspond to a superposition of parts with different energies so that the probability density of the system evolves with time. But once a system is formed that has a any time evolution, this evolution must continue forever.

The only way to have a system that does not change is for all of its components to have the same energy. The only way this is possible is for the components to be degenerate. But since degenerate states have identical wave properties, any superposition of degenerate components will have constructive or destructive interference and so *no localization*.

Now, if by life we mean at the very least *localized* matter *interacting* with its environment, then quantum mechanics tell us that life requires superposition of non-degenerate (due to interactions with

the world) components and so ceaseless change. Thus, *change is an inevitable consequence of life itself.*

■ Time evolution of expectation values and conservation laws

The presence of the time-dependent component of the wavefunction also does not affect expectation values, provided the operator does not depend on time. This is the origin of energy conservation in isolated quantum systems experiencing only time-independent interactions.

Show that the expectation value of H for the time-dependent wavefunction $\psi_j(x) e^{-i E_j t/\hbar}$ is the same as that for its normalized spatial component $\psi_j(x)$.

Show that the expectation value of H for the time-dependent wavefunction

$$\Psi(x, t) = \sqrt{.4} \psi_1(x) e^{-i E_1 t/\hbar} + \sqrt{.6} \psi_2(x) e^{-i E_2 t/\hbar},$$

expressed in terms of a combination of time-dependent normalized spatial eigenfunctions, $\psi_j(x)$, is the same as that for the corresponding time-independent wavefunction

$$\Psi(x, 0) = \sqrt{.4} \psi_1(x) + \sqrt{.6} \psi_2(x).$$

The time independence of the energy of an isolated system (one whose hamiltonian operator is independent of time) is the origin of energy conservation in quantum mechanics. More generally, expectation values of operators other than the hamiltonian *may* change with time. It turns out that whether an expectation value of an operator Q depends on time is determined by the value of its commutator with the hamiltonian operator. The general expression is

$$\frac{d\langle Q \rangle}{dt} = -i \langle [Q, H] \rangle / \hbar.$$

where we have used the commutator abbreviation

$$[Q, H] = QH - HQ.$$

You can confirm this relation by writing $\langle Q \rangle = \int \Psi(x, t)^* Q \Psi(x, t) dx$, etc., carrying out the time differentiation, using the assumed time independence of H , and using the time-dependent Schrödinger equation.

The simplest example is

$$\frac{d\langle H \rangle}{dt} = i \langle [H, H] \rangle / \hbar = 0$$

since H commutes with itself,

$$[H, H] = HH - HH.$$

A more interesting example is that the time dependence of the expectation value of momentum is

$$\frac{d\langle p \rangle}{dt} = i \langle [p, H] \rangle / \hbar = -\langle dV/dx \rangle$$

Confirm this relation by evaluating the commutator $[p, H]$ for the hamiltonian operator $H = -(\hbar^2/2m) d^2/dx^2 + V(x)$

In classical physics the negative of the gradient of the potential is the force experienced by a particle, and force in turn is equal to the time variation of momentum,

$$-\frac{dV}{dx} = F = ma = m \frac{dv}{dt} = \frac{d(mv)}{dt} = \frac{dp}{dt}.$$

The time-dependence of the expectation value of momentum,

$$\frac{d\langle p \rangle}{dt} = \langle F \rangle = -\langle dV/dx \rangle.$$

mirrors the classical result, provided we interpret classical quantities as corresponding to quantum expectation values (that is, as values averaged over the probability distribution of the quantum system).