# Topic 1. From Newton and Maxwell to Schrödinger

## A. What is Quantum Mechanics?

Starting in the late 1800's, experimental physicists began to make observations that challenged the "classical" equations of physics.[1] What emerged was quantum mechanics. Quantum mechanics unifies and supersedes the theories of classical Newtonian mechanics and classical Maxwellian electromagnetism.

In classical physics, radiation and matter are inherently different: radiation and matter are governed by different physical laws and modeled with different equations. Quantum mechanics abolishes the inherent difference between radiation and matter. Radiation—e.g., light—has properties (a well-defined energy and momentum) that are associated with matter. Matter—e.g., an electron—has properties (a wavelength) that are associated with radiation.

The wave-like-ness of matter immediately leads to something called quantization. Matter is "chunky." There is no such thing as "half an electron." One always has an integer number of elementary particles. So if I give you a system containing some number of electrons, you can safely say that the total mass of the system is

$$m_{total} = n_e m_e \tag{1}$$

where $m_e$ is the mass of the electron and $n_e$ is a nonnegative integer. Using mass-energy equivalence, this means that the energy of these electrons should also be discrete,

$$E_{total} = n_e m_e c^2 \tag{2}$$

where $c$ is the speed of light.

Waves, however, do not seem to be "chunky." If I want to put more energy into a wave, I can increase its amplitude or increase its frequency (by an integer amount). So it would seem possible to make waves with any amount of energy. It was Max Planck, in 1900, that proposed that there should also be a "quantization" of radiation, and that radiation should come in integer chunks, with the energy proportional to the frequency of the radiation:

$$E_{total} \propto n_{ph} \nu_{ph} \tag{3}$$

the proportionality constant is Planck's constant,

$$E_{total} = h\left(n_{ph}\nu_{ph}\right) \tag{4}$$

$$h = 6.626069 \times 10^{-34} \ \mathrm{J \cdot s}$$

$$. \ = 6.626069 \times 10^{-34} \ \tfrac{\mathrm{kg \cdot m^2}}{\mathrm{s}} . \tag{5}$$

$$= 6.626069 \times 10^{-34} \ \tfrac{\mathrm{V \cdot s}}{\mathrm{C}}$$

Planck proposed Eq. (3) as a mathematical trick to provide a model for blackbody radiation. In 1905, Einstein interpreted this trick in the most literal possible way, proposing the quantization of light. This interpretation led to an interpretation of the photoelectric effect, which eventually earned Einstein the Nobel Prize in Physics. Planck also won the Nobel Prize in physics.

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[1] By "classical physics" we mean the physics that can be explained by Newton's equations (for matter) and/or Maxwell's equations (for radiation).

## B. How Was Quantum Mechanics Discovered?

It is impossible to fully explain the historical foundations of quantum mechanics in a course like this one. Instead, I will try to give you a very brief overview of four experiments that changed physics.

### 1. Blackbody Radiation: Light is "Chunky"

An inflammable object that does not transmit or absorb light is called a black body. Because it is totally opaque and absorbs all light that falls upon it, a black body at zero Kelvin is the very definition of black. However, when you heat a blackbody, it glows. A good (but not perfect) example of a black body is a red-hot poker. An even better example is the sun. Blackbody radiation has been observed by humans for millennia (or even longer): lava flows, molten glass, molten metal, and many other materials can be considered blackbodies. So it was extremely embarrassing to 19th-century physicists that they could not predict the spectrum—that is, which wavelengths of light occur with what intensity—of a blackbody.

Blackbody radiation should be easy to explain with classical mechanics:

- the equipartition of energy principle from classical thermodynamics indicated that every mode of the oscillator should contain equal energy, $kT$, where $T$ is the temperature and $k$ is Boltzmann's constant.[2]

- The number of modes with frequencies between $v$ and $v + dv$ is given by the formula,

$$\rho(v)\,dv \propto \frac{V}{c^2}v^2\,dv. \qquad (6)$$

 The constant of proportionality depends on the shape of the cavity.

- The frequency spectrum for a given temperature, per unit volume, should then be

$$\rho_T(v)\,dv \propto \frac{kT}{c^3}v^2\,dv. \qquad (7)$$

- Converting the frequency to wavelength,[3] one has

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[2] When you learned the equipartition of energy principle in thermodynamics, you learned that the amount of energy in each mode for carrying energy was $kT/2$. However, the modes we are considering here are *oscillators* (essentially vibrations of the black body), and the oscillators store, on average, $kT/2$ of kinetic energy and $kT/2$ in potential energy. This is the same result you used when you derived the contribution of a single vibrational mode to the (temperature-dependent) heat capacity.

[3] A useful mneumonic for the link between frequency and wavelength is to remember the equation from classical mechanics: $(\text{distance}) = (\text{velocity})(\text{time})$. For light, the analogue to distance is wavelength and the analogue of time is the period, $T = v^{-1}$. So

$$\lambda = cT = \frac{c}{v}$$

$$v = \frac{c}{\lambda}$$

$$\begin{pmatrix} \text{number of modes with wavelengths} \\ \text{between } \lambda \text{ and } \lambda+d\lambda \end{pmatrix} = \begin{pmatrix} \text{number of modes with frequencies} \\ \text{between } v(\lambda) \text{ and } v(\lambda+d\lambda) \end{pmatrix}$$

$$= \begin{pmatrix} \text{number of modes with frequencies} \\ \text{between } \tfrac{c}{\lambda} \text{ and } \tfrac{c}{\lambda}-\left(\tfrac{c}{\lambda^2}\right)d\lambda \end{pmatrix} \quad (8)$$

$$\rho_T(\lambda)d\lambda = \rho_T(v)\left(\frac{dv}{d\lambda}\right)d\lambda$$

$$\propto \frac{kT}{\lambda^4}d\lambda$$

But this does not agree with experiment: it says that there should be an infinite amount of radiation at zero wavelength, with huge amounts of small-wavelength radiation. If this were true, everything on earth would be cooked to a crisp by the intense gamma-ray, X-ray, and ultraviolet radiation from the sun. In fact, the Wien displacement law says that the spectrum from a blackbody has a maximum at a wavelength inversely proportional to the temperature,

$$\lambda_{\max} \propto \frac{1}{T}. \quad (9)$$

In Eq. (8), $\lambda_{\max} = 0$. Because the predicted spectrum of a black body has many more low-wavelength (high-frequency) modes than the prediction in Eq. (8), but the prediction in Eq. (8) is sometimes accurate in the infrared and visible region, this contradiction of experiment is termed the "ultraviolet catastrophe."

Max Planck decided that the problem was that the equipartion of energy was incorrect. Instead, he supposed, maybe not all of the modes of the black body had equal energy and, in fact, the high-energy modes (responsible for the low-wavelength light) were not active. He proposed that energy came in discrete chunks, with energy proportional to the frequency, as in Eq. (3). Working with this expression, he derived a new Boltzmann law, in which the amount of energy contained in the mode with frequency $v$ was

$$\frac{hv}{e^{\frac{hv}{kT}}-1} \quad (10)$$

This gives the revised prediction for the energy density per unit volume of a black body,

$$\rho_T(v)dv = \frac{8\pi hv^3}{c^3\left(e^{\frac{hv}{kT}}-1\right)}dv \quad (11)$$

or

$$\rho_T(\lambda)d\lambda = \frac{8\pi hc}{\lambda^5\left(e^{\frac{hc}{\lambda kT}}-1\right)}d\lambda \quad (12)$$

In these questions I have included the constant of proportionality that is appropriate for a cubic black body.

The agreement between Planck's radiation law, Eqs. (11)-(12) and experiment is excellent.
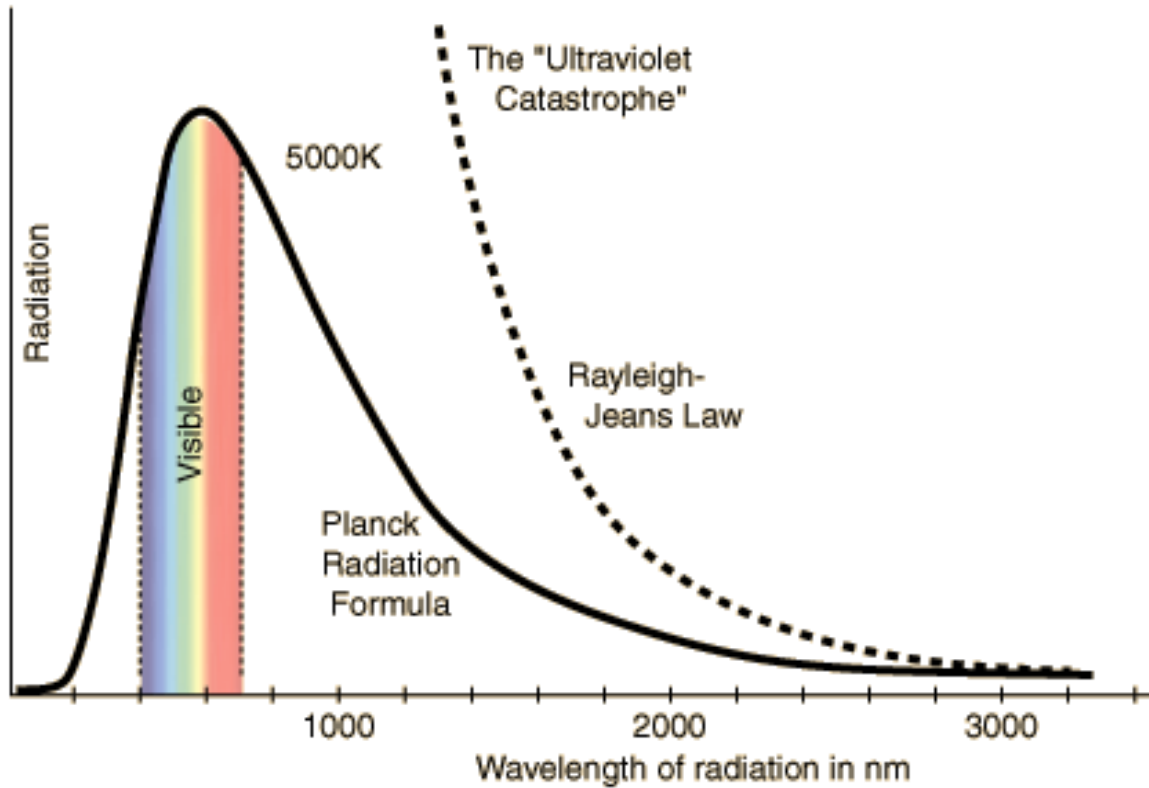
**Figure:** **The Planck law and the Raleigh-Jeans law agree at long wavelengths (high frequency). This is the predicted spectrum for the sun.**

## 2. Photoelectric Effect: the "energy" of light

The
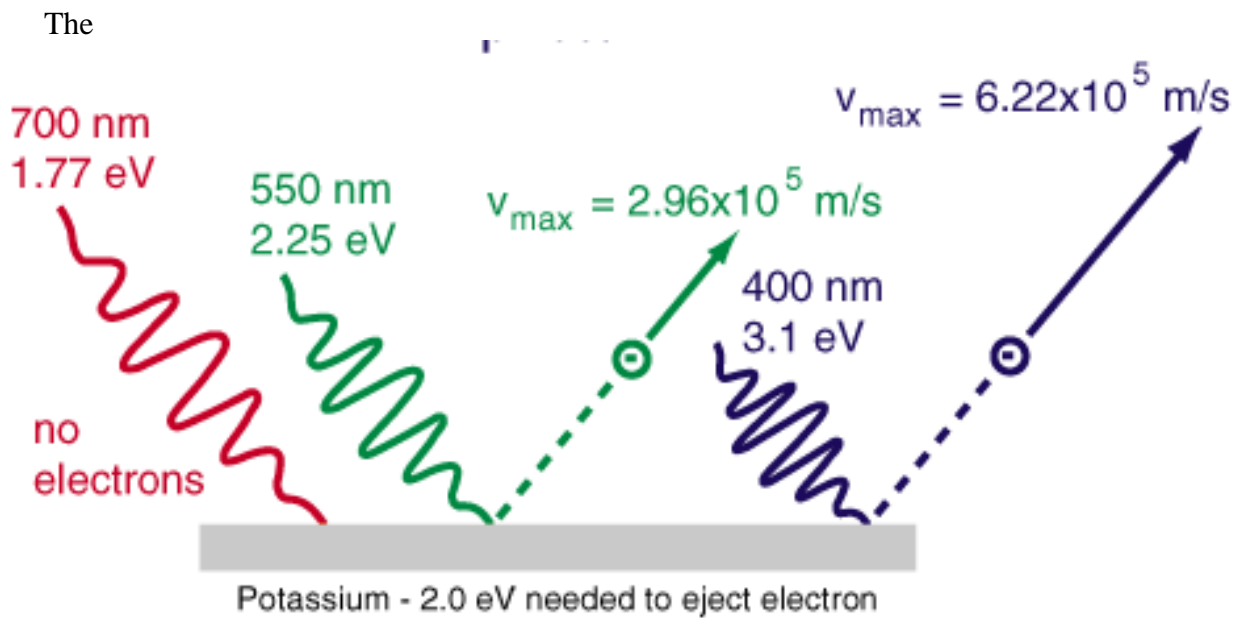


Potassium - 2.0 eV needed to eject electron

**Figure. The Photoelectric Effect.**

### 3.  Compton Effect:  the "momentum" of light

### 4.  Davisson-Germer Experiment:  Electrons are wavelike

### 5. Rydberg Formula:  Particles have "resonances"

## C.  The Schrödinger Equation

At this stage you should be convinced that division between radiation ("light") and matter ("particles") that was made in classical physics is arbitrary.  Matter shares properties with radiation; radiation shares properties with matter.  The difference between matter and radiation is merely one of perspective.

But how does one describe this "new stuff" mathematically.  In classical physics, radiation was described with Maxwell's equations and matter was described with Newton's equations.  We need a new type of equation that subsumes both Newton's equations and Maxwell's equations, which can describe quantum mechanical phenomena.  The key equations were developed, independently, by Heisenberg and Schrödinger in 1925-26.  In chemistry, we use mainly the "Schrödinger picture."

### 1.  Motivation for the Schrödinger Equation

Just like Newton's equations or Maxwell's equations, the Schrödinger equation is a law of nature:  it cannot be "derived."  Instead, it must be postulated, and then tested by experiment.  However, just as Newton's equations can be justified insofar as they encapsulate the "laws of motion" formulated by Galileo and Newton, and Maxwell's equations can be justified insofar as they encapsulate the "laws of electromagnetism" formulated by Gauss, Faraday, Coulomb, etc., Schrödinger equation can be justified by observing that it encapsulates the "laws" of Planck and De Broglie, namely that

- (Planck) The energy of a body is related to its frequency by
$$E = h\nu$$
$$= \hbar\omega \tag{13}$$

- (De Broglie) The momentum of a body is related to its frequency/wavelength
$$p = \frac{h\nu}{c} = \frac{h}{\lambda}$$
$$= \hbar k \tag{14}$$

In these formulas I have introduced $\hbar$ ("$h$-bar"), which is defined as Planck's constant divided by $2\pi$,
$$\hbar = \frac{h}{2\pi}$$
$$h = 2\pi\hbar \tag{15}$$

and also the angular frequency,
$$\omega = 2\pi\nu \tag{16}$$

and the wave number (the number of wavelengths that can fit into a given length),
$$k = \frac{2\pi}{\lambda}. \tag{17}$$

These quantities are useful because when one is dealing with waves, one is dealing with periodic functions. It is easier to include the factors of $2\pi$ in the variables than to keep track of them throughout.

Using this new notation, the equation for a traveling wave, moving in the $x$ direction, is

$$\psi(x,t) = Ae^{i(kx-\omega t)}$$
$$= A\big(\cos(kx-\omega t) + i\sin(kx-\omega t)\big) \tag{18}$$

where $A$ is the amplitude of the wave, $k$ is its wave number, and $\omega$ is its angular frequency. Since $\psi(x,t)$ is the equation for a wave, we call it the "wavefunction." Eq. (18), from electromagnetism, should give us the essential information that we need to describe the "waviness of particles." We need a second equation that will allow us to describe the "particulateness of waves." Since the energy of a wave is proportional to $\omega$ and the momentum of a wave is proportional to $k$, one obvious candidate is the equation for the conservation of total energy, namely,

$$E = T + V(x,t)$$
$$= \frac{p^2}{2m} + V(x,t) \tag{19}$$

which states that (a) the total energy is the sum of the kinetic and potential energies and (b) the kinetic energy is equation to momentum squared divided by twice the particle mass.[4]
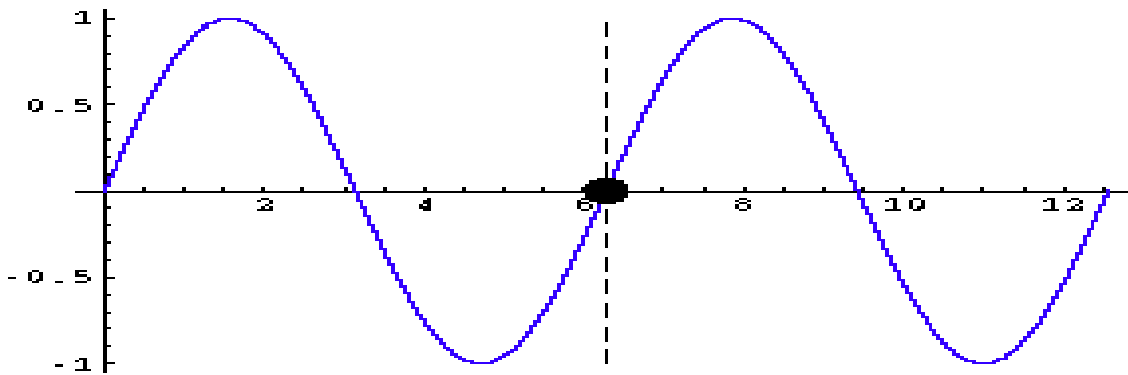


**Figure. Travelling Wave.**

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[4] Using the standard equation for the kinetic energy, $T = \frac{1}{2}mv^2$ and the standard equation for the momentum,

$p = mv$, $T = \frac{p^2}{2m} = \frac{(mv)^2}{2m} = \frac{1}{2}mv^2$.

Now we need to find a way to combine Eq. (18) and Eq. (19), using Planck's and De Broglie's laws. To do this, we differentiated Eq. (18), first with respect to the time, obtaining

$$\frac{\partial \psi(x,t)}{\partial t} = (-i\omega) A e^{i(kx-\omega t)} = -i\omega \psi(x,t) \tag{20}$$

We can combine this equation with Planck's law by multiplying both sides by $i\hbar$, to obtain

$$i\hbar\left(\frac{\partial \psi(x,t)}{\partial t}\right) = (i\hbar)(-i\omega)\psi(x,t) = \hbar\omega\psi(x,t)$$
$$= E\psi(x,t) \tag{21}$$

Differentiating Eq. (18) with respect to position, twice, gives:

$$\frac{\partial \psi(x,t)}{\partial x} = (ik) A e^{i(kx-\omega t)} = (ik)\psi(x,t)$$

$$\frac{\partial^2 \psi(x,t)}{\partial x^2} = (ik)^2 A e^{i(kx-\omega t)} = (ik)^2 \psi(x,t)$$
$$= -k^2\psi(x,t) \tag{22}$$

This can be combined with De Broglie's law by multiplying both sides by $-\hbar^2$, obtaining

$$-\hbar^2 \frac{\partial^2 \psi(x,t)}{\partial x^2} = (-\hbar^2)(-k^2)\psi(x,t) = (\hbar k)^2 \psi(x,t)$$
$$= p^2\psi(x,t) \tag{23}$$

We want to use Eqs. (19), (22) and (23) to construct a quantum mechanical equation of motion. First multiply both sides of Eq. (19) with $\psi(x,t)$,

$$E\psi(x,t) = \frac{p^2}{2m}\psi(x,t) + V(x,t)\psi(x,t) \tag{24}$$

and then insert Eqs. (21) and (22)

$$i\hbar\left(\frac{\partial \psi(x,t)}{\partial t}\right) = -\frac{1}{2m}\left(\frac{\partial^2}{\partial x^2}\psi(x,t)\right) + V(x,t)\psi(x,t) \tag{25}$$

This is the Schrödinger equation. Taking the complex conjugate of both sides gives the equivalent equation,

$$-i\hbar\left(\frac{\partial \psi^*(x,t)}{\partial t}\right) = -\frac{1}{2m}\left(\frac{\partial^2}{\partial x^2}\psi^*(x,t)\right) + V(x,t)\psi^*(x,t) \tag{26}$$

There biggest limitations of the Schrödinger equation is that it was derived using the nonrelativistic expression for the kinetic energy of a particle, $T = \frac{1}{2m}p^2$. For this reason, the Schrödinger equation is not valid for particles that are moving at a substantial fraction of the speed of light (where relativistic effects are important) or for light itself. Quantum mechanics can be extended to such cases, and relativistic quantum mechanics is quite important for the heavier atoms in the periodic table. (Typically relativity is neglected for atoms up to Zinc (Z=30) or Krypton (Z=36), and the included past that. However there are a few molecules containing lighter elements—e.g., the Sulfur dimer, where there are chemically (or at least spectroscopically) interesting relativistic effects.) The full relativistic treatment of quantum

mechanics leads to "quantum electrodynamics," which is a rich and interesting subject that we, alas, will not have time to cover.

## 2. The Hamiltonian

An equation like Schrödinger's may seem mysterious to us now, but at the time it was derived it seemed very natural. A top-rate physicist like Schrödinger had a rich background in classical physics, and he would have understood that there were many results, from classical physics, that suggested that the equations for radiation and for matter could be combined. One of the strongest such suggestions came from two principles: "Fermat's principle of least time" and the "Hamilton-Lagrange principle of least action." Fermat's principle says that a ray of light goes from point A to point B in the fastest possible way, and can be used to derive all of classical optics. The Hamilton-Lagrange principle says that a particle goes from point A to point B in a way that makes minimizes its action (the product of its momentum and its change in position) along the path. Schrödinger would have noticed that Planck's constant had units of action, and then quickly ascertained that laws of quantum mechanics might be governed by an equation similar to the Hamilton-Jacobi equation for the action,

$$\frac{1}{2m}\left(\frac{dS}{dx}\right)^2 + V(x,t) = \left(\frac{\partial S}{\partial t}\right) \tag{27}$$

or

$$S\left(-\frac{1}{2m}\left(\frac{d^2 S}{dx^2}\right)\right) + V(x,t) = \left(\frac{\partial S}{\partial t}\right) - \frac{1}{2m}\frac{d^2(S^2)}{dx^2} \tag{28}$$

The last term on the right-hand-side will integrate to zero in most cases.

In fact, the Schrödinger equation can be derived from the (quantum mechanical) principle of least action, and this observation won Feynman and Schwinger the Nobel Prize. Quantum electrodynamics is based on the formulation of quantum mechanics through the principle of least act, not the Schrödinger equation.

Equation (25) is usually rewritten in the form

$$\left(\frac{-1}{2m}\frac{\partial}{\partial x^2} + V(x,t)\right)\psi(x,t) = i\hbar\left(\frac{\partial \psi(x,t)}{\partial t}\right) \tag{29}$$

The term in blue is called the *Hamiltonian operator*. (In classical mechanics, the Hamiltonian operator is exactly the expression, $\frac{1}{2m}p^2 + V(x,t)$, that we started with in Eq. (19).) Equation (29) is often rewritten as:

$$\hat{H}(x,t)\psi(x,t) = i\hbar\left(\frac{\partial \psi(x,t)}{\partial t}\right) \tag{30}$$

The Hamiltonian is the quantum-mechanical operator for the energy. Every observable quantity has an operator that it corresponds to in quantum mechanics. For example, the kinetic energy operator is clearly (cf. Eq. (23))

$$\hat{T}(x) = \frac{-\hbar^2}{2m}\frac{d^2}{dx^2} \tag{31}$$

My father, an organic chemist, always says that he knew quantum mechanics was going to be a difficult course when the professor wrote Eq. (30) on the board at the end of the first

lecture. He still refers to $\psi$ as "Satan's pitchfork" and "$\hat{H}$" as the "hell operator." Most people call $\hat{H}$ the Hamiltonian and $\psi$ the wavefunction.

### 3. The Time-Independent Schrödinger Equation

In much of chemistry, the Hamiltonian operator is not time-dependent. For examples, the electrons in a molecule feel a fixed (time-independent) attraction to the nuclei in the molecule and, to a first approximation, the (very small) motion of the nuclei can be neglected. Similarly, in the absence of a time-varying external field, a molecule as a whole (containing both electrons and nuclei) does not feel a time-varying potential.

If the Hamiltonian is time-independent, then replacing $\hat{H}(x,t)$ with $\hat{H}(x)$ gives

$$\hat{H}(x)\psi(x,t) = i\hbar\left(\frac{\partial\psi(x,t)}{\partial t}\right) \tag{32}$$

We would like to "solve" this equation. Whenever you can "divide" a multidimensional differential equation into a sum of two terms, each of which has an explicit dependence on only a subset of the variables, you can simplify the differential equation by a technique called "separation of variables," where you assume the solution can be written as a product of the a function of the "variables in the first part" and a function of the "variables in the second part." In this case we have

$$\left[\underbrace{\hat{H}(x)}_{\text{depends only on } x} - \underbrace{i\hbar\left(\frac{\partial}{\partial t}\right)}_{\text{depends only on } t}\right]\psi(x,t) = 0 \tag{33}$$

and so we hypothesize a form of the wavefunction like

$$\psi(x,t) = \Psi(x)\phi(t). \tag{34}$$

Substitute Eq. (34) into Eq. (32) (or Eq. (33)),

$$\phi(t)\hat{H}(x)\Psi(x) = \left(i\hbar\left(\frac{d\phi}{dt}\right)\right)\Psi(\mathbf{x}) \tag{35}$$

Divide both sides by $\phi(t)\Psi(x)$. We obtain:

$$\frac{\hat{H}(x)\Psi(x)}{\Psi(x)} = \left(\frac{i\hbar}{\phi(t)}\left(\frac{d\phi}{dt}\right)\right) \tag{36}$$

The left-hand-side depends only on $x$; the right-hand-side depends only on $t$. However, the equation must hold for *all x* and *t*, which can happen only if Eq. (36) is a constant.[5] So we have:

$$\frac{\hat{H}(x)\Psi(x)}{\Psi(\mathbf{x})} = (\text{constant}) = \left(\frac{i\hbar}{\phi(t)}\left(\frac{d\phi}{dt}\right)\right) \tag{37}$$

or

$$\hat{H}(x)\Psi(x) = (\text{constant})\Psi(\mathbf{x}) \tag{38}$$

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[5]    Because $\hat{H}(x)$ is the operator for the energy, it is reasonable to expect that the constant is equal to the energy. But we will not assume this quite yet.

$$\left(\frac{d\phi}{dt}\right) = \frac{1}{i\hbar}\left(\text{constant}\right)\phi(t) \tag{39}$$

We can solve the ordinary differential equation in Eq. (39) by explicit integration,

$$d\phi = \frac{\left(\text{constant}\right)}{i\hbar}\phi(t)\,dt$$

$$\int\frac{1}{\phi(t)}\,d\phi = \left(\frac{-i}{\hbar}\right)\left(\text{constant}\right)\int dt \tag{40}$$

$$\ln\left(\phi(t)\right) = \frac{-i\left(\text{constant}\right)}{\hbar}t + \left(\text{const. of integration}\right)$$

$$\phi(t) = \left(\text{const. of integration}\right)e^{-\frac{i\left(\text{constant}\right)t}{\hbar}}$$

It is obvious that the if $\psi(x,t)$ is a solution to the Schrödinger equation, then any multiple of the wavefunction, $c\psi(x,t)$, is also. So we can ignore the constant of integration in Eq. (40).

What is the "constant" in Eq. (40) and (38)? Since $\hat{H}$ is the quantum mechanical operator for the energy, then clearly the constant is equal to the energy of the system. We write our equations, more explicitly, as

$$\phi(t) = e^{-\frac{iEt}{\hbar}} \tag{41}$$

and

$$\hat{H}(x)\Psi(x) = E\Psi(x)$$

$$\left(-\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + V(x)\right)\Psi(x) = E\Psi(x) \tag{42}$$

Equation (42) is the time-independent Schrödinger equation. We need to find all the possible values of $E$ that solve this equation. There are almost always very may different values of $E$ that work and, for this reason, we usually label the solutions to the equation as

$$\left\{\hat{H}(x)\Psi_k(x) = E_k\Psi_k(x)\right\}_{k=0}^{\infty}$$

$$\left\{\left(-\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + V(x)\right)\Psi_k(x) = E_k\Psi_k(x)\right\}_{k=0}^{\infty} \tag{43}$$

This course is largely about the "art" of solving Eq. (43).

There are some cases where we cannot use the time-independent Schrödinger equation because we want to understand how a molecule responds to a time-dependent external field. This is particularly important in spectroscopy.

**References:**

Wikipedia has excellent articles on many topics related to fundamental quantum mechanics. You are encouraged to "surf around" on wikipedia:  you'll learn stuff. Some particular articles of particular utility are:

**On General Quantum Mechanics:**
>Introduction to quantum mechanics
>Quantum Mechanics
>Mathematical formulation of quantum mechanics
>Basic concepts of quantum mechanics
>Planck's constant
>Wave-particle duality

**Black Body Radiation:**
>Black body
>Ultraviolet catastrophe
>Rayleigh-Jeans law
>Planck's law
>Wien's displacement law

**Photoelectric Effect:**
>Photoelectric effect

**Compton Scattering:**
>Compton scattering
>De Broglie wavelength

**Davisson-Germer Experiment:**
>Davisson–Germer experiment
>Electron diffraction
>Electron crystallography
>Electron Microscopy
>Transmission Electron Microscope

**Spectral Lines in Simple Atoms:**
>Franck-Hertz Experiment
>Balmer Formula
>Rydberg Formula
>Spectral Lines
>Atomic Spectral Lines

**Schrödinger Equation:**
>Schrödinger Equation
>Theoretical Justification
>Momentum Operator

**My favorite source for this material is the introductory sections of:**
R. Eisberg and R. Resnick, Quantum Physics of Atoms, Molecules, Solids, Nuclei, and Particles (Wiley, New York, 1974)
R. Dumont, An Emergent Reality, Part 2: Quantum Mechanics (Chapters 1 and 2).