

Lecture 16—learning outcomes

- Understand how we can use the Schrödinger Equation in a simple situation to find the form of the wave function.
- Understand the derivation of the formula for energy levels of electrons in infinitely deep wells.
- Be able to calculate the wavelength of light absorbed or emitted as an electron moves between energy levels.
- Be able to explain how we can model the hydrogen atom with the Schrödinger equation.
- Recall basic features of the Pauli exclusion principle.

Textbook chapters: 38.8–9, 39.1–2, 39.5, 40.4

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Schrödinger's equation—review of last lecture

Here is the 1D non-relativistic Schrödinger's equation

$$-\frac{\hbar^2}{2m} \frac{\partial^2 \Psi(x, t)}{\partial x^2} + U(x, t) \Psi(x, t) = i\hbar \frac{\partial \Psi(x, t)}{\partial t}.$$

Simplifying to the case $U = U(x)$, we can separate variables $\Psi(x, t) = \psi(x)\phi(t)$ and write

$$\frac{d^2 \psi}{dx^2} + \frac{8\pi^2 m}{h^2} [E - U(x)].$$

Simplifying again, now to a constant U ,

$$\frac{d^2 \psi}{dx^2} + k^2 \psi = 0,$$

where k is

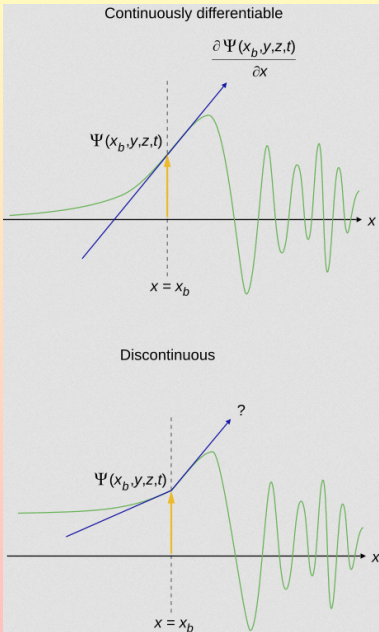
$$k = \frac{2\pi \sqrt{2m(E - U)}}{h} \quad (\text{the angular wave number}).$$

The general solution of this special case of Schrödinger's equation is

$$\psi(x) = Ae^{ikx} + Be^{-ikx},$$

in which A and B are constants.

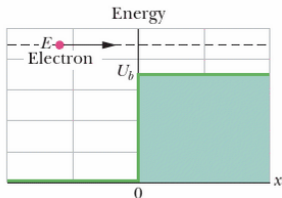
Schrödinger's equation—application to connected regions of constant U



- It turns out that we can make lots of interesting progress with the greatly simplified Schrödinger's equation from the last slide.
- We will examine several examples of particles moving between regions of different (but constant) U . Specifically,
 - a step jump in U ,
 - a potential barrier, and
 - an infinitely deep potential well.
- In order to find solutions, we will (1) require the wave function to be continuously differentiable (see figure) at the interface of the regions (with the exception that if one region has an infinite potential, then we do not require the derivative to be smooth), and (2) set A or B to zero if we know that there is no wave heading in the particular direction.

Schrödinger's equation—a step jump in U

Classically, the electron has too much energy to be reflected by the potential step.



When $x < 0$, U is zero, the angular wave number is

$$k = \frac{2\pi\sqrt{2mE}}{h}, \quad (1)$$

and the general space-dependent solution to Schrödinger's equation is

$$\psi_1(x) = Ae^{ikx} + Be^{-ikx}, \quad (x < 0).$$

When $x > 0$, the potential energy is U_b , the angular wave number is

$$k_b = \frac{2\pi\sqrt{2m(E - U_b)}}{h}, \quad (x > 0), \quad (2)$$

and the general solution is

$$\psi_2(x) = Ce^{ik_b x} + De^{-ik_b x}, \quad (x < 0).$$

Since there is no electron source off to the right in the figure, there can be no electrons moving to the left in region $x > 0$, so, we set $D = 0$, and we have

$$\psi_2(x) = Ce^{ik_b x}, \quad (x > 0).$$

Next, we use the continuously differentiable requirement at $x = 0$ to establish boundary conditions

$$A + B = C \quad (\text{matching of values}), \quad (3)$$

and

$$Ak - Bk = Ck_b \quad (\text{matching of slopes}). \quad (4)$$

Our end goal here is to find the probability that electrons reflect at the barrier. Recall that probability density is proportional to $|\psi|^2$. We can relate the probability density in the reflection (which is proportional to $|B|^2$) to the probability density in the incident beam (which is proportional to $|A|^2$) by defining a reflection coefficient R :

$$R = \frac{|B|^2}{|A|^2}. \quad (5)$$

Eliminating C from eqns 3 and 4, we have

$$A \left(1 - \frac{k}{k_b}\right) = -B \left(1 + \frac{k}{k_b}\right)$$

and substituting into eqn 5 and finding the ratio k/k_b from dividing eqn 1 by eqn 2,

$$R = \left(\frac{1 - \sqrt{\frac{E}{E - U_b}}}{1 + \sqrt{\frac{E}{E - U_b}}} \right)^2$$

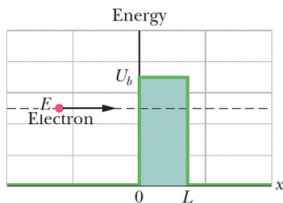
The following table shows some example reflection coefficients,

$E/(E - U_b)$	R (Schrödinger)	R (Classical)
1000	88%	0%
100	67%	0%
10	27%	0%
2	3%	0%
1	0%	0%

You can see that the difference between the quantum and classical results is quite significant, e.g., when the electron has twice the energy of the barrier, it has a 3% chance of being reflected, compared with no chance classically.

Schrödinger's equation—tunneling through a barrier

Classically, the electron lacks the energy to pass through the barrier region.



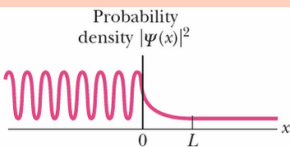
- A particularly interesting application of Schrödinger's equation is to calculate the transmission through a potential barrier that classically is impossible.
- The figure shows an electron heading towards a barrier that is higher than the electron's kinetic energy (shown by the dashed line). Classically the electron would be reflected, but quantum mechanically there is a finite probability that it would make it to the other side of the barrier and continue off to the right with its original energy.
- To calculate the probability we follow a similar approach to the step jump. Now we have three regions to worry about, two interfaces to reflect from and match boundary conditions at. The mathematics is somewhat laborious so we will just give the results, which have the appearance shown in the figure at bottom left.
- The wave in the region $x < 0$ is due to interference between the oncoming electron and the reflection from the barrier at $x = 0$. Then follows an exponential decay within the barrier, with a small probability of the electron making it to $x > L$.
- The end result is that the transmission probability T is

$$T \approx e^{-2bL}$$

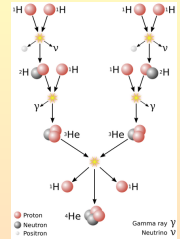
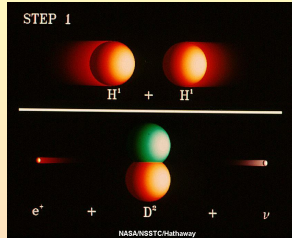
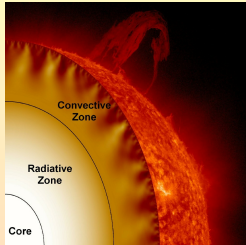
where

$$b = \sqrt{\frac{8\pi^2 m (U_b - E)}{h^2}}$$

- The exponential term makes transmission rare if $2bL \gg 1$, but rapidly more likely as E approaches U_b .



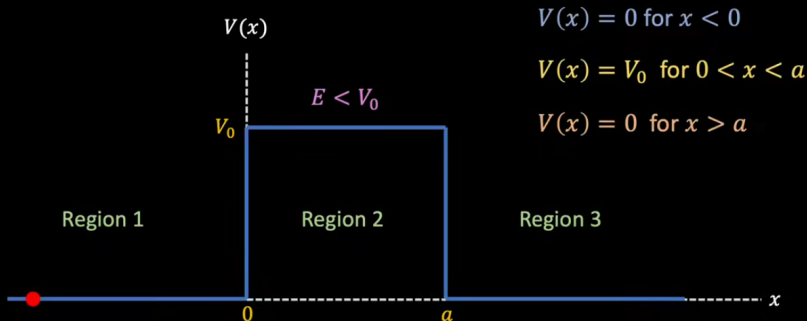
Tunneling through a barrier—fusion in the core of the Sun



- The Sun obtains its energy through fusion of hydrogen nuclei (protons) into helium nuclei. This happens in the core, where the temperature and pressure are sufficiently high.
- The predominant reaction pathway is the proton-proton chain, shown in the figure on the right. This begins with two protons colliding (middle figure) and overcoming the enormous coulomb potential barrier. Even then, in most cases the two protons separate again, but a small fraction of the time β decay turns one proton into a neutron, and a stable deuterium nucleus is formed.
- A typical proton in the core of the Sun collides with another one 10^{12} times per second. It still takes about a billion years for two protons in the core to collide and form deuterium.
- Once deuterium is formed, it takes only about a second to form helium-3, and another 400 years for two helium-3 nuclei to form helium-4.
- The energy created in the core of the Sun is $\sim 100 \text{ Wm}^{-3}$, about the same as a compost heap. The immense size of the core compensates for the low-energy density.

Quantum tunneling by Physics Explained

Solving the Schrödinger Equation



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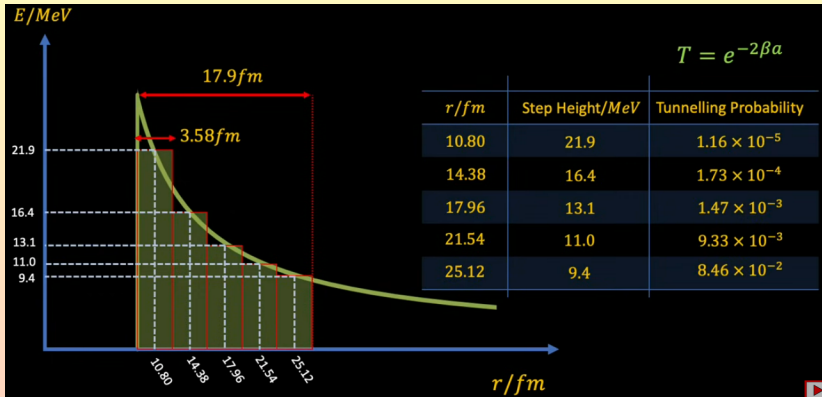
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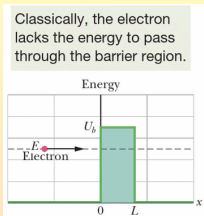
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α decay of radioactive elements—an example of quantum tunneling



An α particle consists of 2 protons and 2 neutrons bound together—it is the nucleus of a helium atom. It is also emitted by some radioactive elements such as polonium 212, which has a half-life of $0.3 \mu\text{s}$. The α particle is normally held tightly within the nucleus by the short-range strong nuclear force, but occasionally escapes the nucleus with an energy of 8.78 MeV. Probing the nucleus by firing α particles at it reveals that the Coulomb potential reaches 26.2 MeV, which is the barrier that an α particle in the nucleus must surmount. Classically this is impossible, but quantum tunneling permits it, and it is possible to make a good estimate of the polonium half-life using the knowledge that we now have. See the video from the last slide for the details.

Problem—barrier tunneling by matter waves



Suppose that the electron in the figure, having a total energy E of 5.1 eV, approaches a barrier of height $U_b = 6.8$ eV and thickness $L = 750$ pm.

- (a) What is the approximate probability that the electron will be transmitted through the barrier, to appear (and be detectable) on the other side of the barrier?
- (b) What is the approximate probability that a proton with the same total energy of 5.1 eV will be transmitted through the barrier, to appear (and be detectable) on the other side of the barrier?

Solution

Barrier tunnelling by matter wave

Suppose that the electron in figure 38.17, having a total energy E of 5.1 eV, approaches a barrier of height $U_b = 6.8$ eV and thickness $L = 750$ pm.

(a) What is the approximate probability that the electron will be transmitted through the barrier, to appear (and be detectable) on the other side of the barrier?

KEY IDEA

The probability we seek is the transmission coefficient T as given by equation 38.38 ($T \approx e^{-2bL}$), where

$$b = \sqrt{\frac{8\pi^2 m (U_b - E)}{h^2}}.$$

Calculations

The numerator of the fraction under the square-root sign is

$$(8\pi^2) (9.11 \times 10^{-31} \text{ kg}) (6.8 \text{ eV} - 5.1 \text{ eV}) \\ \times (1.60 \times 10^{-19} \text{ J/eV}) = 1.956 \times 10^{-47} \text{ J} \cdot \text{kg}.$$

Thus,

$$b = \sqrt{\frac{1.956 \times 10^{-47} \text{ J} \cdot \text{kg}}{(6.63 \times 10^{-34} \text{ J} \cdot \text{s})^2}} = 6.67 \times 10^9 \text{ m}^{-1}.$$

The (dimensionless) quantity $2bL$ is then

$$2bL = (2)(6.67 \times 10^9 \text{ m}^{-1})(750 \times 10^{-12} \text{ m}) = 10.0$$

and, from equation 38.38, the transmission coefficient is

$$T \approx e^{-2bL} = e^{-10.0} = 45 \times 10^{-6}. \quad (\text{Answer})$$

Thus, of every million electrons that strike the barrier, about 45 will tunnel through it, each appearing on the other side with its original total energy of 5.1 eV. (The transmission through the barrier does not alter an electron's energy or any other property.)

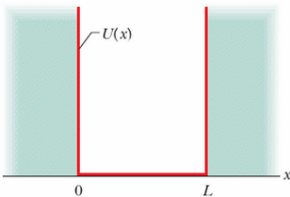
(b) What is the approximate probability that a proton with the same total energy of 5.1 eV will be transmitted through the barrier, to appear (and be detectable) on the other side of the barrier?

Reasoning: the transmission coefficient T (and thus the probability of transmission) depends on the mass of the particle. Indeed, because mass m is one of the factors in the exponent of e in the equation for T , the probability of transmission is very sensitive to the mass of the particle. This time, the mass is that of a proton (1.67×10^{-27} kg), which is significantly greater than that of

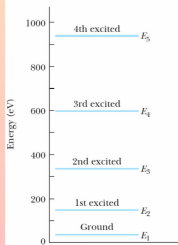
the electron in (a). By substituting the proton's mass for the mass in (a) and then continuing as we did there, we find that $T \approx 10^{-186}$. Thus, although the probability that the proton will be transmitted is not exactly zero, it is barely more than zero. For even more massive particles with the same total energy of 5.1 eV, the probability of transmission is exponentially lower.

Schrödinger's equation—an electron in an infinite well

An electron can be trapped in the $U = 0$ region.



These are the lowest five energy levels allowed the electron. (No intermediate levels are allowed.)



- The figure at top left shows an infinite well of width L , within which an electron can be trapped.
- By analogy with a standing wave on a string between two fixed supports, L must be an integer number of half-wavelengths

$$L = \frac{n\lambda}{2}, \quad \text{for } n = 1, 2, 3, \dots \quad (1)$$

where λ is the de Broglie wavelength of the electron

$$\lambda = \frac{h}{p} = \frac{h}{\sqrt{2mE}} \quad (2)$$

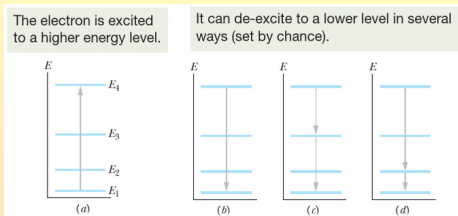
where we have used the nonrelativistic expression for momentum in terms of the electron's kinetic energy E . Substituting the expression for λ from eqn 2 into eqn 1 we have

$$E_n = \left(\frac{h^2}{8mL^2} \right) n^2, \quad \text{for } n = 1, 2, 3, \dots$$

n is known as the quantum number of the state.

- The electron can only have energies corresponding to the quantum states.
- The state $n = 1$ is called the **ground state**, and shows that there is a minimum energy that the electron can have (if the energy were zero, this implies that the wavefunction in the well is everywhere zero, i.e., there is no electron in the well). The state $n = 2$ is the **first excited state**.

Schrödinger's equation—1D infinite well—energy transitions



- Electrons can be excited to a higher energy level from a lower one by absorbing a photon of energy

$$hf = \frac{fc}{\lambda} = \Delta E = E_{\text{high}} - E_{\text{low}}.$$

- Once excited, the electrons want to return to the ground state. In doing so, they emit one or more photons depending on the path they take (e.g., panels b, c, and d above). In all cases the energy of each photon is given by the energy difference between the states.
- While this discussion has been about 1D infinite wells, the broad approach applies to 3D finite wells such as atoms.

Problem—energy levels in a 1D infinite potential well

An electron is confined to a one-dimensional, infinitely deep potential energy well of width $L = 100 \text{ pm}$.

- (a) What is the smallest amount of energy the electron can have?
- (b) How much energy must be transferred to the electron if it is to make a quantum jump from its ground state to its second-excited state?
- (c) If the electron gains the energy for the jump from energy level E_1 to energy level E_3 by absorbing light, what light wavelength is required?

Solution—part 1

Energy levels in a 1D infinite potential well

An electron is confined to a one-dimensional, infinitely deep potential energy well of width $L = 100$ pm.

(a) What is the smallest amount of energy the electron can have? (A trapped electron cannot have zero energy.)

KEY IDEA

Confinement of the electron (a matter wave) to the well leads to quantisation of its energy. Because the well is infinitely deep, the allowed energies are given by equation 39.4 ($E_n = (h^2/8mL^2)n^2$), with the quantum number n a positive integer.

Lowest energy level: Here, the collection of constants in front of n^2 in equation 39.4 is evaluated as

$$\frac{h^2}{8mL^2} = \frac{(6.63 \times 10^{-34} \text{ J} \cdot \text{s})^2}{(8)(9.11 \times 10^{-31} \text{ kg})(100 \times 10^{-12} \text{ m})^2} = 6.031 \times 10^{-18} \text{ J.} \quad (39.1.1)$$

The smallest amount of energy the electron can have corresponds to the lowest quantum number, which is $n = 1$ for the ground state of the electron. Thus, equations 39.4 and 39.1.1 give us

Solution—part 2

$$E_1 = \left(\frac{h^2}{8mL^2} \right) n^2 = (6.031 \times 10^{-18} \text{ J}) (1^2) \\ \approx 6.03 \times 10^{-18} \text{ J} = 37.7 \text{ eV.} \quad (\text{Answer})$$

(b) How much energy must be transferred to the electron if it is to make a quantum jump from its ground state to its second excited state?

KEY IDEA

First a caution: note that, from figure 39.3, the second excited state corresponds to the *third* energy level, with quantum number $n = 3$. Then if the electron is to jump from the $n = 1$ level to the $n = 3$ level, the required change in its energy is, from equation 39.5,

$$\Delta E_{31} = E_3 - E_1. \quad (39.1.2)$$

Upward jump: The energies E_3 and E_1 depend on the quantum number n , according to equation 39.4. Therefore, substituting that equation into equation 39.1.2 for energies E_3 and E_1 and using equation 39.1.1 lead to

$$\Delta E_{31} = \left(\frac{h^2}{8mL^2} \right) (3)^2 - \left(\frac{h^2}{8mL^2} \right) (1)^2 \\ = \frac{h^2}{8mL^2} (3^2 - 1^2) \\ = (6.031 \times 10^{-18} \text{ J}) (8) \\ = 4.83 \times 10^{-17} \text{ J} = 301 \text{ eV.} \quad (\text{Answer})$$

(c) If the electron gains the energy for the jump from energy level E_1 to energy level E_3 by absorbing light, what light wavelength is required?

KEY IDEAS

(1) If light is to transfer energy to the electron, the transfer must be by photon absorption. (2) The photon's energy must equal the energy difference ΔE between the initial energy level of the electron and a higher level, according to equation 39.6 ($hf = \Delta E$). Otherwise, a photon cannot be absorbed.

Wavelength: Substituting c/λ for f , we can rewrite equation 39.6 as

$$\lambda = \frac{hc}{\Delta E}. \quad (39.1.3)$$

For the energy difference ΔE_{31} we found in (b), this equation gives us

$$\lambda = \frac{hc}{\Delta E_{31}} \\ = \frac{(6.63 \times 10^{-34} \text{ J} \cdot \text{s}) (2.998 \times 10^8 \text{ m/s})}{4.83 \times 10^{-17} \text{ J}} \\ = 4.12 \times 10^{-9} \text{ m.} \quad (\text{Answer})$$

(d) Once the electron has been excited to the second excited state, what wavelengths of light can it emit by de-excitation?

KEY IDEAS

1. The electron tends to de-excite, rather than remain in an excited state, until it reaches the ground state ($n = 1$).
2. If the electron is to de-excite, it must lose just enough energy to jump to a lower energy level.
3. If it is to lose energy by emitting light, then the loss of energy must be by emission of a photon.

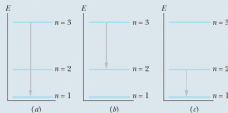
Downward jumps: Starting in the second excited state (at the $n = 3$ level), the electron can reach the ground state ($n = 1$) by either making a quantum jump directly to the ground-state energy level (example 39.1 figure 1a) or by making two separate jumps by way of the $n = 2$ level (example 39.1 figures 1b and c).

The direct jump involves the same energy difference ΔE_{31} we found in (c). Then the wavelength is the same as we calculated in (c) — except now the wavelength is for light that is emitted, not absorbed. Thus, the electron can jump directly to the ground state by emitting light of wavelength

$$\lambda = 4.12 \times 10^{-9} \text{ m.} \quad (\text{Answer})$$

EXAMPLE 39.1 FIGURE 1

De-excitation from the second excited state to the ground state either directly (a) or via the first excited state (b, c).



Following the procedure of part (b), you can show that the energy differences for the jumps of example 39.1 figures 1b and c are

$$\Delta E_{32} = 3.016 \times 10^{-17} \text{ J} \quad \text{and} \quad \Delta E_{21} = 1.809 \times 10^{-17} \text{ J}.$$

From equation 39.1.3, we then find that the wavelength of the light emitted in the first of these jumps (from $n = 3$ to $n = 2$) is

$$\lambda = 6.60 \times 10^{-9} \text{ m,} \quad (\text{Answer})$$

and the wavelength of the light emitted in the second of these jumps (from $n = 2$ to $n = 1$) is

$$\lambda = 1.10 \times 10^{-8} \text{ m.} \quad (\text{Answer})$$

Wave functions in an infinite well—part 1 (text from Dr. Michael Schmidt)

Consider an infinitely deep potential well described by the piece-wise constant potential

$$U(x) = \begin{cases} 0 & \text{for } 0 \leq x \leq L \\ \infty & \text{otherwise} \end{cases}$$

We solve the Schrödinger equation each of the three regions separately and then combine the solutions by demanding continuity. Starting with the region $U(x) = 0$, we use the solution we found earlier for a free particle

$$\psi(x) = Ae^{ikx} + Be^{-ikx}$$

where $k^2 = 2m/\hbar^2 E$. In regions outside the central well, the potential is infinitely high and thus the wave function has to vanish ($\psi(x) = 0$) in order to satisfy the Schrödinger equation, i.e., the particle cannot enter these regions. In particular we have the boundary conditions $\psi(0) = \psi(L) = 0$.

In a second step we have to combine the three solutions and demand that they are continuous. Using the result that $\psi(0) = \psi(L) = 0$ outside the well, we find when equating it to the solution in the well

$$0 = \psi(0) = A + B \quad 0 = \psi(L) = Ae^{ikL} + Be^{-ikL}$$

From the first equation, we find $B = -A$ and the second equation results in

$$0 = Ae^{ikL} + Be^{-ikL} = A(e^{ikL} - e^{-ikL}) = 2iA \sin(kL),$$

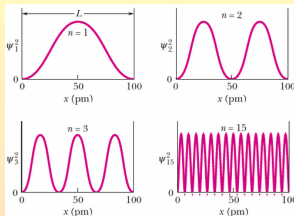
which only vanishes for $A = 0$ (which is trivial) or the quantisation of k . We find $k_n L = n\pi$ where n is an integer. From the wave number we can calculate the energy of the different solutions

$$E = \frac{\hbar^2 k_n^2}{2m} = \frac{\hbar^2}{8mL^2} n^2$$

Thus the solution is given by

$$\psi(x) = 2iA \sin(kx)$$

Wave functions in an infinite well—part 2



Finally, we have to find the value of A by requiring that the $|\psi(x)|^2$ can be interpreted as a probability density, i.e., the total probability to find the particle anywhere adds up to 1

$$1 = \int_0^L dx |\psi_n(x)|^2 = 4|A|^2 \int_0^L \sin^2(kx) = 2|A|^2 L$$

and thus the final solution is

$$\psi_n(x) = \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi}{L}x\right).$$

Note that as the probability depends on the absolute magnitude square of the wave function, the phase of the wave function is not measurable and we thus used this freedom to remove the factor i that we had earlier.

Let us summarise the main steps to solve the Schrödinger equation:

1. we solve the Schrödinger equation for each region separately, then
2. we combine the solutions by demanding the solution to be continuous (and differentiable), and finally
3. we normalise the wave function $\psi(x)$ such that it can be interpreted as probability amplitude $\int |\psi(x)|^2 = 1$.

Problem—detection probability in a 1D infinite potential well

A ground-state electron is confined to a one-dimensional, infinitely deep potential energy well of width $L = 100$ pm.

- (a) What is the probability that the electron can be detected in the left one-third of the well?
- (b) What is the probability that the electron can be detected in the middle one-third of the well?

Solution

Detection probability in a 1D infinite potential well

A ground-state electron is trapped in the one-dimensional infinite potential well of figure 39.2, with width $L = 100$ pm.

(a) What is the probability that the electron can be detected in the left one-third of the well ($x_1 = 0$ to $x_2 = L/3$)?

KEY IDEAS

(1) If we probe the left one-third of the well, there is no guarantee that we will detect the electron. However, we can calculate the probability of detecting it with the integral of equation 39.10. (2) The probability very much depends on

which state the electron is in — that is, the value of quantum number n .

Calculations

Because here the electron is in the ground state, we set $n = 1$ in equation 39.10. We also set the limits of integration as the positions $x_1 = 0$ and $x_2 = L/3$ and set the amplitude constant A as $\sqrt{2/L}$ (so that the wave function is normalised). We then see that

$$\left(\begin{array}{c} \text{probability of detection} \\ \text{in left one-third} \end{array} \right) = \int_0^{L/3} \frac{2}{L} \sin^2 \left(\frac{1\pi x}{L} \right) dx.$$

We could find this probability by substituting 100×10^{-12} m for L and then using a graphing calculator or a computer math package to evaluate the integral. Here, however, we shall evaluate the integral 'by hand'. First we switch to a new integration variable y :

$$y = \frac{\pi}{L}x \quad \text{and} \quad dx = \frac{L}{\pi}dy.$$

From the first of these equations, we find the new limits of integration to be $y_1 = 0$ for $x_1 = 0$ and $y_2 = \pi/3$ for $x_2 = L/3$. We then must evaluate

$$\text{probability} = \left(\frac{2}{L} \right) \left(\frac{L}{\pi} \right) \int_0^{\pi/3} (\sin^2 y) dy.$$

Using integral 11 in appendix E, we then find

$$\text{probability} = \frac{2}{\pi} \left(\frac{y}{2} - \frac{\sin 2y}{4} \right)_0^{\pi/3} = 0.20.$$

Thus, we have

$$\left(\begin{array}{c} \text{probability of detection} \\ \text{in left one-third} \end{array} \right) = 0.20. \quad (\text{Answer})$$

That is, if we repeatedly probe the left one-third of the well, then on average we can detect the electron with 20% of the probes.

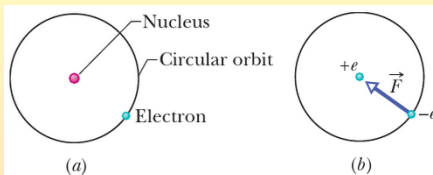
(b) What is the probability that the electron can be detected in the middle one-third of the well?

Reasoning: We now know that the probability of detection in the left one-third of the well is 0.20. By symmetry, the probability of detection in the right one-third of the well is also 0.20. Because the electron is certainly in the well, the probability of detection in the entire well is 1. Thus, the probability of detection in the middle one-third of the well is

$$\left(\begin{array}{c} \text{probability of detection} \\ \text{in middle one-third} \end{array} \right) = 1 - 0.20 - 0.20 = 0.60. \quad (\text{Answer})$$

Bohr's model of the hydrogen atom—part 1

Classically, the orbiting electrons in atoms should continuously emit EM radiation since they are accelerating. This should cause them to spiral in to the nucleus. Bohr's model



Bohr's model for hydrogen resembles the orbital model of a planet around a star.

for the hydrogen atom looked into what happens if we just assume that the angular momentum of the electron is quantised. Now, the proton and electron in the atom attract each other via the Coulomb force, and for a given distance r , the potential difference is described by the Coulomb potential

$$U(r) = -\frac{e^2}{4\pi\epsilon_0 r}.$$

Before the description of the hydrogen atom using quantum mechanics, Niels Bohr developed a model of the hydrogen atom, based on two assumptions:

- (1) The electron in the hydrogen atom orbits the nucleus like the Earth the Sun, and
- (2) The magnitude of the angular momentum is quantized $L = n\hbar$ with n being an integer.

From those two assumptions, we can derive the energy levels of the hydrogen atom. We start by equating the Coulomb force with the centripetal force

$$-\frac{1}{4\pi\epsilon_0} \frac{e^2}{r^2} = ma = m \left(-\frac{v^2}{r} \right).$$

The quantisation of the angular momentum implies quantisation of the velocity of the electron in the potential well of the proton.

$$n\hbar = L = mvr \Rightarrow v = \frac{n\hbar}{mr}.$$

Bohr's model of the hydrogen atom—part 2

Then, replacing the velocity in the centripetal force equation with this quantised velocity we find

$$\frac{1}{4\pi\epsilon_0} \frac{e^2}{r^2} = \frac{m}{r} \frac{n^2 \hbar^2}{m^2 r^2},$$

which can be solved for the distance r_n between the electron and the proton which is also quantized

$$r_n = \frac{4\pi\epsilon_0 \hbar^2}{me^2} n^2 \equiv a_B n^2$$

where we defined the Bohr radius

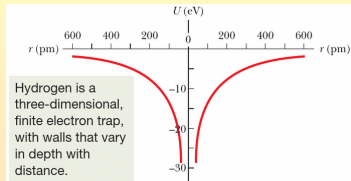
$$a_B = \frac{4\pi\epsilon_0 \hbar^2}{e^2 m} \approx 52.92 \text{ pm}$$

which sets the characteristic length scale of the hydrogen atom. From here we find the quantized energy of the hydrogen atom

$$E_n = \frac{1}{2} m v_n^2 + U(r_n) = -\frac{e^2}{8\pi\epsilon_0 a_B} \frac{1}{n^2} \approx -\frac{13.61 \text{ eV}}{n^2}.$$

Although the assumptions of the Bohr model are unjustified, they lead to the correct Bohr radius and energy levels.

Schrodinger's equation and the hydrogen atom



Solving Schrödinger's equation for the hydrogen atom is more complex than our one-dimensional infinite potential well calculation, but it shares many of its characteristics.

A proper quantum mechanical treatment shows that the wave function depends on three quantum numbers:

- (1) the principal quantum number $n = 1, 2, 3, \dots$
- (2) the orbital angular momentum quantum number $\ell = 0, 1, \dots, n - 1$, and
- (3) the orbital magnetic quantum number $m_\ell = -\ell, -(\ell - 1), \dots, 0, \dots, \ell - 1, \ell$.

Each set of three quantum numbers (n, ℓ, m_ℓ) identifies the wave function of a particular quantum state. n defines the energy of the state (unless the atom is in a magnetic field, in which case the Zeeman effect causes the other quantum numbers to shift the energy level slightly).

Due to the quantisation of the energy in the hydrogen atom, the emission and absorption of light is quantized

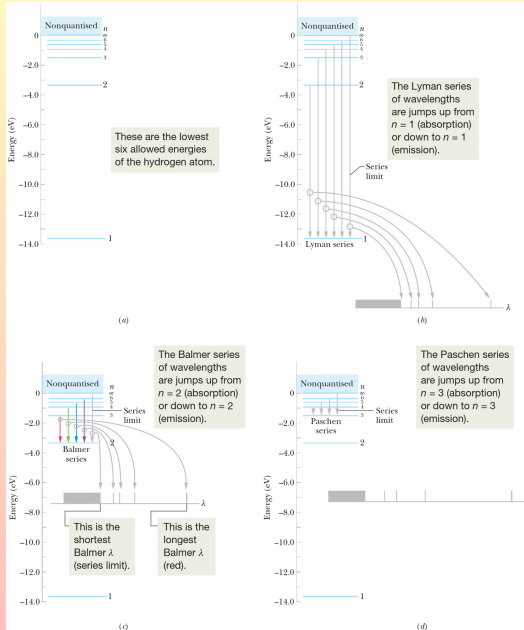
$$E = hf = \frac{hc}{\lambda} = E_{\text{high}} - E_{\text{low}}$$

and the wavelength of the light is given by

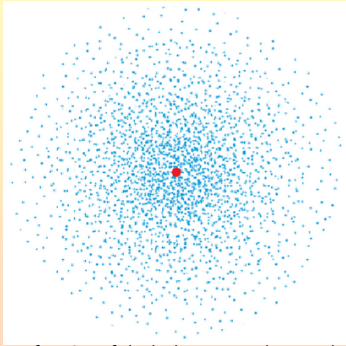
$$\frac{1}{\lambda} = R \left(\frac{1}{n_{\text{low}}^2} - \frac{1}{n_{\text{high}}^2} \right)$$

where the Rydberg constant $R = me^4/8\epsilon_0^2 h^3 c \approx 1.0974 \times 10^7 \text{ m}^{-1}$. The emitted light can be grouped into series, as illustrated in the next slide.

The energy-level diagram of a hydrogen atom



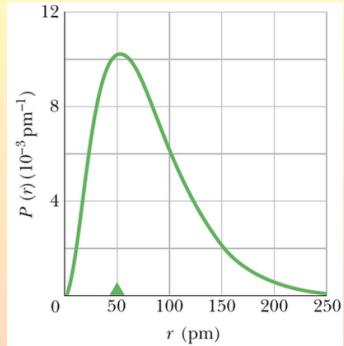
The ground state probability density of a hydrogen atom



The wave function of the hydrogen atom's ground state can be solved using the 3D Schrödinger equation, with the result

$$\psi(r) = \frac{1}{\sqrt{\pi a^{3/2}}} e^{-r/a} \quad (\text{ground state}),$$

where $a = 5.291772 \times 10^{-11} \text{ m}$ is the Bohr radius. This radius is loosely taken to be the effective radius of a hydrogen atom and turns out to be a convenient unit of length for other situations involving atomic dimensions. As with other wave functions, $\psi^2(r)$ gives the probability density—the probability

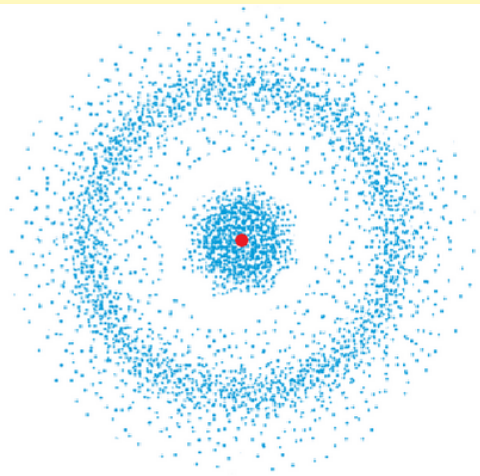


per unit volume—that the electron can be detected. Specifically, $\psi^2(r)dV$ is the probability that the electron can be detected in any given (infinitesimal) volume element dV located at radius r from the centre of the atom. $\psi^2(r)$ is shown as a dot plot in the figure at the left. Given the spherical symmetry of the ground state, it makes sense to use the volume between spherical shells as our dV . This leads to the probability of detection between r and $r + dr$ as

$$P(r) = \frac{4}{a^3} r^2 e^{-2r/a}$$

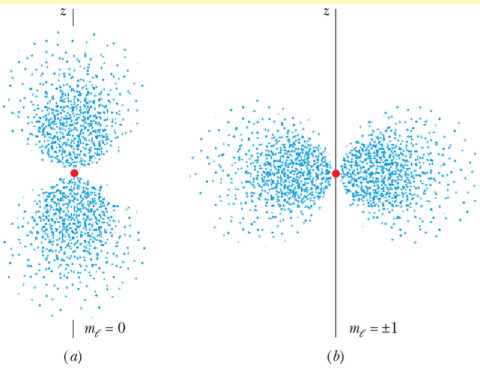
and is plotted in the figure on the right.

The $n = 2, \ell = 0, m_\ell = 0$ probability density of a hydrogen atom



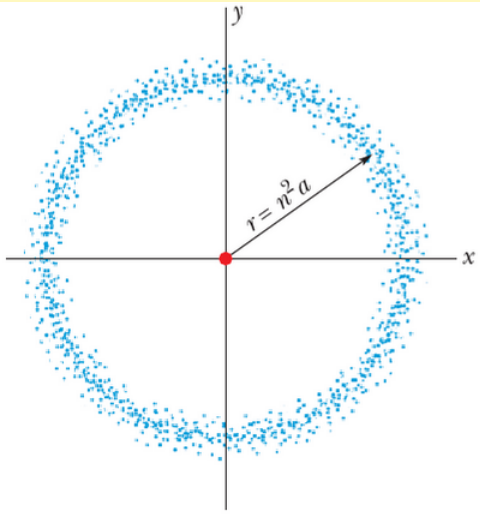
- Schrödinger's equation can be solved for all combinations of the three quantum numbers.
- Whenever $\ell = 0$, the result is spherical symmetry such as the first excited state shown in the figure. This agrees with the interpretation of ℓ as the angular momentum quantum number: a spherically symmetric distribution has no preferred axis, and so has zero angular momentum.
- Note that there is a gap in the distribution in the figure, where the wave function is zero.

The $n = 2, \ell = 1, m_\ell = 0, \pm 1$ probability density of a hydrogen atom



With $\ell = 1$, we have a preferred axis, such as shown in the figure. These distributions have the same energy as the $\ell = 0$ state from the last slide.

The $n = 45, \ell = n - 1 = 44$ probability density of a hydrogen atom



The figure shows a state with a high n quantum number, and the maximum allowed angular momentum $\ell = n - 1$. This isn't a spherical shell, but a torus, somewhat reminiscent of a planetary orbit.

Problem—radial probability density for the electron in a hydrogen atom

Show that the radial density probability density for the ground state of the hydrogen atom has a maximum at $r = a$.

Solution

Radial probability density for the electron in a hydrogen atom

Show that the radial probability density for the ground state of the hydrogen atom has a maximum at $r = a$.

KEY IDEAS

1. The radial probability density for a ground-state hydrogen atom is given by equation 39.37,

$$P(r) = \frac{4}{a^3} r^2 e^{-2r/a}.$$

2. To find the maximum (or minimum) of any function, we must differentiate the function and set the result equal to zero.

Calculation

If we differentiate $P(r)$ with respect to r , using derivative 7 of appendix E and the chain rule for differentiating products, we get

$$\begin{aligned}\frac{dP}{dr} &= \frac{4}{a^3} r^2 \left(\frac{-2}{a} \right) e^{-2r/a} + \frac{4}{a^3} 2r e^{-2r/a} \\ &= \frac{8r}{a^3} e^{-2r/a} - \frac{8r^2}{a^4} e^{-2r/a} \\ &= \frac{8}{a^4} r(a - r) e^{-2r/a}.\end{aligned}$$

If we set the right side equal to zero, we obtain an equation that is true if $r = a$, so that the term $(a - r)$ in the middle of the equation is zero. In other words, dP/dr is equal to zero when $r = a$. (Note that we also have $dP/dr = 0$ at $r = 0$ and at $r = \infty$. However, these conditions correspond to a *minimum* in $P(r)$, as you can see in figure 39.17.)

Problem—probability of detection of the electron in a hydrogen atom

It can be shown that the probability $p(r)$ that the electron in the ground state of the hydrogen atom will be detected inside a sphere of radius r is given by

$$p(r) = 1 - e^{-2x} (1 + 2x + 2x^2)$$

in which x , a dimensionless quantity, is equal to r/a .

Find r for $p(r) = 0.90$.

Solution

Probability of detection of the electron in a hydrogen atom

It can be shown that the probability $p(r)$ that the electron in the ground state of the hydrogen atom will be detected inside a sphere of radius r is given by

$$p(r) = 1 - e^{-2x} (1 + 2x + 2x^2),$$

in which x , a dimensionless quantity, is equal to r/a . Find r for $p(r) = 0.90$.

KEY IDEA

There is no guarantee of detecting the electron at any particular radial distance r from the centre of the hydrogen atom. However, with the given function, we can calculate the probability that the electron will be detected *somewhere* within a sphere of radius r .

Calculation

We seek the radius of a sphere for which $p(r) = 0.90$. Substituting that value in the expression for $p(r)$, we have

$$0.90 = 1 - e^{-2x} (1 + 2x + 2x^2)$$

or

$$10e^{-2x} (1 + 2x + 2x^2) = 1.$$

We must find the value of x that satisfies this equality. It is not possible to solve explicitly for x , but an equation solver on a calculator yields $x = 2.66$. This means that the radius of a sphere within which the electron will be detected 90% of the time is $2.66a$. Mark this position on the horizontal axis of figure 39.17. The area under the curve from $r = 0$ to $r = 2.66a$ gives the probability of detection in that range and is 90% of the total area under the curve.

Problem—light emission from a hydrogen atom

- (a) What is the wavelength of light for the least energetic photon emitted in the Lyman series of the hydrogen atom spectral lines?
- (b) What is the wavelength of the series limit for the Lyman series?

Solution

Light emission from a hydrogen atom

(a) What is the wavelength of light for the least energetic photon emitted in the Lyman series of the hydrogen atom spectrum lines?

KEY IDEAS

1. For any series, the transition that produces the least energetic photon is the transition between the home-base level that defines the series and the level immediately above it.
2. For the Lyman series, the home-base level is at $n = 1$ (figure 39.16b). Thus, the transition that produces the least energetic photon is the transition from the $n = 2$ level to the $n = 1$ level.

Calculation

From equation 39.27 the energy difference is

$$\Delta E = E_2 - E_1 = -(13.60 \text{ eV}) \left(\frac{1}{2^2} - \frac{1}{1^2} \right) = 10.20 \text{ eV}.$$

Then from equation 39.6 ($\Delta E = hf$), with c/λ replacing f , we have

$$\begin{aligned} \lambda &= \frac{hc}{\Delta E} = \frac{(6.63 \times 10^{-34} \text{ J} \cdot \text{s}) (3.00 \times 10^8 \text{ m/s})}{(10.20 \text{ eV}) (1.60 \times 10^{-19} \text{ J/eV})} \\ &= 1.22 \times 10^{-7} \text{ m} = 122 \text{ nm} \quad (\text{Answer}) \end{aligned}$$

Light with this wavelength is in the ultraviolet range.

(b) What is the wavelength of the series limit for the Lyman series?

KEY IDEA

The series limit corresponds to a jump between the home-base level ($n = 1$ for the Lyman series) and the level at the limit $n = \infty$.

Calculation

Now that we have identified the values of n for the transition, we could proceed as in (a) to find the corresponding wavelength λ . Instead, let's use a more direct procedure. From equation 39.30, we find

$$\begin{aligned} \frac{1}{\lambda} &= R \left(\frac{1}{n_{\text{low}}^2} - \frac{1}{n_{\text{high}}^2} \right) \\ &= 1.097\,373 \times 10^7 \text{ m}^{-1} \left(\frac{1}{1^2} - \frac{1}{\infty^2} \right), \end{aligned}$$

which yields

$$\lambda = 9.11 \times 10^{-8} \text{ m} = 91.1 \text{ nm}. \quad (\text{Answer})$$

Light with this wavelength is also in the ultraviolet range.

Pauli's exclusion principle

- Suppose you had a bare oxygen nucleus (8 protons, 8 neutrons) and you started adding electrons to it one by one.
- If the electrons all went into the ground state they would repel each other vigorously, resulting in an increase in the potential energy.
- It turns out that **Pauli's exclusion principle** forbids electrons from occupying the same quantum state. Every electron must have a unique quantum state, which is defined by the three numbers in an atom (n, ℓ, m_ℓ) with addition of the **electron spin** m_s which can be either $+1/2$ or $-1/2$, making a total of four quantum numbers.
- Pauli's exclusion principle is more general than just electrons, it applies to all **fermions**, i.e., particles with spin equal to an integer $+1/2$, although only fermions with spin $\pm 1/2$ are currently known.
- Electrons with the same n are said to be in the same **shell**. If they have the same n and ℓ they are in the same **subshell**.
- Pauli's exclusion principle guides how electrons fit into shells and subshells as they are added to successive elements in the periodic table, as shown in the next slide.

Electron spin—what is it?

Electron Spin



Do Electrons Really Have "Intrinsic" Angular Momentum?



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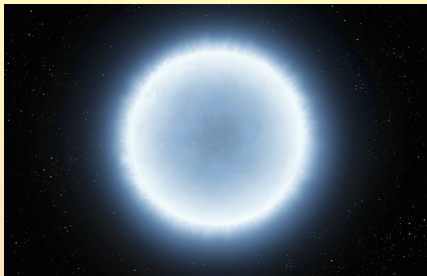
Electron configurations and the periodic table

$\ell \rightarrow$ $n \downarrow$	0	1	2	3	4	5	6	
Orbital	s	p	d	f	g	h	i	Capacity of shell
1	1s							2
2	2s	2p						8
3	3s	3p	3d					18
4	4s	4p	4d	4f				32
5	5s	5p	5d	5f	5g			50
6	6s	6p	6d	6f	6g	6h		72
7	7s	7p	7d	7f	7g	7h	7i	98
Capacity of subshell	2	6	10	14	18	22	26	

1 H																	2 He	2x1 = 2 elements 1s
3 Li	4 Be										5 B	6 C	7 N	8 O	9 F	10 Ne	2x(1+3) = 8 elements 2s 2p	
11 Na	12 Mg										13 Al	14 Si	15 P	16 S	17 Cl	18 Ar	2x(1+3) = 8 elements 3s 3p	
19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr	2x(1+3+5) = 18 elements 4s 3d 4p
37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe	2x(1+3+5) = 18 elements 5s 4d 5p

Conventionally, the angular momentum quantum number is identified using the letters s, p, d, f, g, h, i as shown in the top table. The electron configuration of an atom is shown using the shorthand $n\ell^{\#}$, where n is the principal quantum number, ℓ is the letter for the angular momentum, and $\#$ is the number of electrons in the m_{ℓ} states. E.g., hydrogen has the configuration $1s$, carbon is $1s^2 2s^2 2p^2$ and sodium is $1s^2 2s^2 2p^6 3s$.

White dwarf stars— an extreme example of Pauli's exclusion principle



- White dwarfs are one of the end stages of stellar evolution (the Sun will evolve into a white dwarf in about 5 billion years).
- They have masses up to 1.4 times that of the Sun, and are about the same size as the Earth. Their densities are therefore huge, about 1 tonne per cubic centimetre.
- At the densities and temperatures inside a white dwarf, atoms are completely ionised, and the star is only supported by collapse against gravity by **electron degeneracy pressure**.
- If more mass is added to a white dwarf (which can easily happen by accretion from a binary companion star), the electrons have to occupy higher and higher energy states, due to Pauli's exclusion principle.
- Eventually, at the Chandrasekhar limit, the energy required of the newly added electrons becomes relativistic. Electron degeneracy pressure can no longer halt the collapse into a neutron star with a radius 12 km, supported by neutron degeneracy pressure. The density of a neutron star is $\sim 4 \times 10^{10}$ times greater than that of a white dwarf.
- Further accretion of mass can eventually lead to the formation of a black hole.