ATOMIC STRUCTURE

Wave Theory of an Atom (Wave-Particle Duality)

Einstein's photons of light were individual packets of energy having many of the characteristics of particles. Recall that the collision of an electron (a particle) with a sufficiently energetic photon can eject a *photoelectron* from the surface of a metal. Any excess energy is transferred to the electron and is converted to the kinetic energy of the ejected electron. Einstein's hypothesis that energy is concentrated in localized bundles, however, was in sharp contrast to the classical notion that energy is spread out uniformly in a wave. We now describe Einstein's theory of the relationship between energy and mass, a theory that others built on to develop our current model of the atom.

The Wave Character of Matter

Einstein initially assumed that photons had zero mass, which made them a peculiar sort of particle indeed. In 1905, however, he published his special theory of relativity, which related energy and mass according to the following equation:

$$E = h\nu = h\frac{c}{\lambda} = mc^2$$

According to this theory, a photon of wavelength λ and frequency ν has a nonzero mass, which is given as follows:

$$m = \frac{E}{c^2} = \frac{h\nu}{c^2} = \frac{h}{\lambda c}$$

That is, light, which had always been regarded as a wave, also has properties typical of particles, a condition known as wave–particle duality. Depending on conditions, light could be viewed as either a wave or a particle.

In 1922, the American physicist Arthur Compton (1892–1962) reported the results of experiments involving the collision of x-rays and electrons that supported the particle nature of light. At about the same time, a young French physics student, Louis de Broglie (1892–1972), began to wonder whether the converse was true: Could particles exhibit the properties of waves? In his PhD dissertation submitted to the Sorbonne in 1924, de Broglie proposed that a particle such as an electron could be described by a wave whose wavelength is given by:

$$\lambda = \frac{h}{mv}$$

where *h* is Planck's constant, *m* is the mass of the particle, and *v* is the velocity of the particle. This revolutionary idea was quickly confirmed by American physicists Clinton Davisson (1881–1958) and Lester Germer (1896–1971), who showed that beams of electrons, regarded as particles, were diffracted by a sodium chloride crystal in the same manner as x-rays, which were regarded as waves. It was proven experimentally that electrons do exhibit the properties of waves. For his work, de Broglie received the Nobel Prize in Physics in 1929.

If particles exhibit the properties of waves, why had no one observed them before? The answer lies in the numerator of de Broglie's equation, which is an extremely small number. It is important to note that Planck's constant (6.63×10^{-34} J·s) is so small that the wavelength of a particle with a large mass is too short (less than the diameter of an atomic nucleus) to be noticeable. ***Therefore, objects such as a baseball or a neutron have such short wavelengths that they are best regarded primarily as particles. In contrast, objects with very small masses (such as photons) have large wavelengths and can be viewed primarily as waves. Objects with intermediate masses, such as electrons, exhibit the properties of both particles and waves.*** Although we still usually think of electrons as particles, the wave nature of electrons is employed in an *electron microscope*, which has revealed most of what we know about the microscopic structure of living organisms and materials. Because the wavelength of an electron beam is much shorter than the wavelength of a beam of visible light, this instrument can resolve smaller details than a light microscope can.

Exercise 1

Calculate the wavelength of a baseball, which has a mass of 149 g and a speed of 100 mi/h.

Given: mass and speed of object

Asked for: wavelength

Strategy:

A Convert the speed of the baseball to the appropriate SI units: meters per second.

B Substitute values into λ = *h*/*mv* and solve for the wavelength.
Answer = 9.95×10^{-35}m

(You should verify that the units cancel to give the wavelength in meters.) Given that the diameter of the nucleus of an atom is approximately 10^{-14} m, the wavelength of the baseball is almost unimaginably small).

Exercise 2

Calculate the wavelength of a neutron that is moving at 3.00×10^3 m/s.

Answer: 1.32 Å, or 132 pm

The Heisenberg Uncertainty Principle

Because a wave is a disturbance that travels in space, it has no fixed position. One might therefore expect that it would also be hard to specify the exact position of a *particle* that exhibits wavelike behavior. A characteristic of light is that is can be bent or spread out by passing through a narrow slit. You can literally see this by half closing your eyes and looking through your eye lashes. This reduces the brightness of what you are seeing and somewhat fuzzes out the image, but the light bends around your lashes to provide a complete image rather than a bunch of bars across the image. This is called diffraction.

This behavior of waves is captured in Maxwell's equations (1870 or so) for electromagnetic waves and was and is well understood. Heisenberg's uncertainty principle for light is, if you will, merely a conclusion about the nature of electromagnetic waves and nothing new

DeBroglie's idea of wave particle duality means that particles such as electron which all exhibit wave like characteristics, will also undergo diffraction from slits whose size is of the order of the electron wavelength.

This situation was described mathematically by the German physicist Werner Heisenberg (1901–1976; Nobel Prize in Physics, 1932), who related the position of a particle to its momentum. Referring to the electron, Heisenberg stated that "at every moment the electron has only an inaccurate position and an inaccurate velocity, and between these two inaccuracies there is this uncertainty relation." Mathematically, the Heisenberg uncertainty principle states that the uncertainty in the position of a particle (Δx) multiplied by the uncertainty in its momentum [$\Delta(mv)$] is greater than or equal to Planck's constant divided by 4π:

$$(\Delta x)\,(\Delta\,[mv]) \geqslant \frac{h}{4\pi}$$

Because Planck's constant is a very small number, the Heisenberg uncertainty principle is important only for particles such as electrons that have very low masses. These are the same particles predicted by de Broglie's equation to have measurable wavelengths.

If the precise position x of a particle is known absolutely ($\Delta x = 0$), then the uncertainty in its momentum must be infinite:

$$(\Delta\,[mv]) = \frac{h}{4\pi\,(\Delta x)} = \frac{h}{4\pi\,(0)} = \infty$$

Because the mass of the electron at rest (m) is both constant and accurately known, the uncertainty in $\Delta(mv)$ must be due to the Δv term, which would have to be infinitely large for $\Delta(mv)$ to equal infinity. That is, the more accurately we know the exact position of the electron (as $\Delta x \to 0$), the less accurately we know the speed and the kinetic energy of the electron ($1/2\ mv^2$) because $\Delta(mv) \to \infty$. Conversely, the more accurately we know the precise momentum (and the energy) of the electron [as $\Delta(mv) \to 0$], then $\Delta x \to \infty$ and we have no idea where the electron is.

The Heisenberg Uncertainty Principle is an application of deBroglie's wave particle duality to wave diffraction.

Bohr's model of the hydrogen atom violated the Heisenberg uncertainty principle by trying to specify simultaneously both the position (an orbit of a particular radius) and the energy (a quantity related to the momentum) of the electron. Moreover, given its mass and wavelike nature, the electron in the hydrogen atom could not possibly orbit the nucleus in a well-defined circular path as predicted by Bohr. You will see, however, that the *most probable radius* of the electron in the hydrogen atom is exactly the one predicted by Bohr's model.

Exercise 1

Calculate the minimum uncertainty in the position of the pitched baseball from the exercise 1 above that has a mass of exactly 149 g and a speed of 100 ± 1 mi/h.

Given: mass and speed of object

Asked for: minimum uncertainty in its position

Strategy:

A Rearrange the inequality that describes the Heisenberg uncertainty principle $(\Delta x)[\Delta(mv)] = h/4\pi$ to solve for the minimum uncertainty in the position of an object (Δx).

B Find Δv by converting the velocity of the baseball to the appropriate SI units: meters per second.

C Substitute the appropriate values into the expression for the inequality and solve for Δ*x*.

Answer: $\Delta x \geqslant 7.92 \pm \times 10^{-34}$m

This is equal to 3.12×10^{-32} inches. We can safely say that if a batter misjudges the speed of a fastball by 1 mi/h (about 1%), he will not be able to blame Heisenberg's uncertainty principle for striking out.

Exercise 2

Calculate the minimum uncertainty in the position of an electron traveling at one-third the speed of light, if the uncertainty in its speed is ±0.1%. Assume its mass to be equal to its mass at rest.

Answer: 6×10^{-10} m, or 0.6 nm (about the diameter of a benzene molecule)

Exercise 3

1. How much heat is generated by shining a carbon dioxide laser with a wavelength of 1.065 µm on a 68.95 kg sample of water if 1.000 mol of photons is absorbed and converted to heat? Is this enough heat to raise the temperature of the water 4°C?
2. Show the mathematical relationship between energy and mass and between wavelength and mass. What is the effect of doubling the;

a. mass of an object on its energy?

b. mass of an object on its wavelength?

c. frequency on its mass?

3. What is the de Broglie wavelength of a 39 g bullet traveling at 1020 m/s ± 10 m/s? What is the minimum uncertainty in the bullet's position?
4. What is the de Broglie wavelength of a 6800 tn aircraft carrier traveling at 18 ± 0.1 knots (1 knot = 1.15 mi/h)? What is the minimum uncertainty in its position?
5. Calculate the mass of a particle if it is traveling at 2.2×10^{6} m/s and has a frequency of 6.67×10^{7} Hz. If the uncertainty in the velocity is known to be 0.1%, what is the minimum uncertainty in the position of the particle?
6. Determine the wavelength of a 2800 lb automobile traveling at 80 mi/h ± 3%. How does this compare with the diameter of the nucleus of an atom? You are standing 3 in. from the edge

of the highway. What is the minimum uncertainty in the position of the automobile in inches?

Answers

1. E = 112.3 kJ, ΔT = 0.3893°C, over ten times more light is needed for a 4.0°C increase in temperature
2.
3. 1.7×10^{-35} m, uncertainty in position is $\geq 1.4 \times 10^{-34}$ m
4.
5. 9.1×10^{-39} kg, uncertainty in position ≥ 2.6 m
6.

Atomic Orbitals and Their Energies

The paradox described by Heisenberg's uncertainty principle and the wavelike nature of subatomic particles such as the electron made it impossible to use the equations of classical physics to describe the motion of electrons in atoms. Scientists needed a new approach that took the wave behavior of the electron into account. In 1926, an Austrian physicist, Erwin Schrödinger (1887–1961; Nobel Prize in Physics, 1933), developed *wave mechanics*, a mathematical technique that describes the relationship between the motion of a particle that exhibits wavelike properties (such as an electron) and its allowed energies. In doing so, Schrödinger's theory today is described as quantum mechanics. It successfully describes the energies and spatial distributions of electrons in atoms and molecules.

Although quantum mechanics uses sophisticated mathematics, you do not need to understand the mathematical details to follow our discussion of its general conclusions. We focus on the properties of the *wave functions* that are the solutions of Schrödinger's equations. The Schrödinger equation is similar in form to equations for the propagation of waves, which is why originally quantum mechanics was called wave mechanics, but there are significant differences between quantum wave functions and those that describe real waves. Therefore, at this point it would be best to lean only lightly on the standing wave analogy.

Wave Functions

A wavefunction (Ψ), Ψ is the uppercase Greek letter psi, is a mathematical expression that can be used to calculate any property of an atom. In general, wavefunctions depend on both time and position. For atoms, solutions to the Schrödinger equation correspond to arrangements of the electrons, which, if left alone, remain unchanged and are thus only functions of position.

Wavefunctions for each atom have some properties that are exact, for example each wavefunction describes an electron in quantum state with a specific energy. Each of these exact properties is associated with an integer. The energy of an electron in an atom is associated with the integer *n*, which turns out to be the same *n* that Bohr found in his model. These integers are called quantum numbers and different wavefunctions have different sets of quantum numbers. The important point about quantum numbers is that they are countable integers, not continuous variables like the number of points on a line. In the case of atoms, each electron has four quatum numbers which determine its wavefunction.