CHAPTER 1

What Is Light?

The fact that [Einstein] may occasionally have overshot the mark in his speculations, for example, in his hypothesis concerning light quanta, should not be counted against him too strongly. For without ever taking a risk, it is impossible to introduce real innovation. . . .

— Max Planck and others, in their nomination of Einstein for membership in the Prussian Academy of Sciences, 1913

1.1 SIGNPOST: PHOTONS

Living organisms are physical systems that can obtain information about their environment and act on it. Certainly there are other hallmarks of Life: Organisms also obtain energy from external sources and transduce it; that is, they convert it into useful motion, use it to construct their own bodies, and even use it to perform the computations needed to integrate and act on the information they receive.

The nature of light is a thread that runs through the preceding ideas:

• Good vision can give one organism a decisive fitness advantage over another, so many animals have evolved remarkably sophisticated visual systems, and dedicate significant amounts of their energy budget to them.
• Solar energy—harnessed by photosynthesis—is the primary driver of nearly all life on Earth.

Scientists are a particular class of living organisms, also involved in obtaining certain kinds of information. In that vein, we may add to our list that

• Light-based imaging has enabled much of the progress in our understanding of Life over the past three and a half centuries, including new advances right up to the present.

Light also offers us a case study of how scientists were forced to abandon a cherished physical model that was long regarded as the paragon of a successful scientific theory. This chapter begins by reviewing some of the phenomena that led to this model (the “classical wave theory” of light). Later sections will describe other phenomena, however, that forced physicists to reject this model in the early 20th century, and replace it by something quite different.

This chapter and the next ones will argue that the newer model—“quantum physics”—is needed to understand many phenomena that are directly relevant to biology, and to biophysical instruments. Chapter 4 will then return to the task of reconciling quantum physics, and its picture of light as a stream of photons, with the phenomena that appeared to demand a wave interpretation.
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Figure 1.1: [Diagram.] Part of the light spectrum, showing different names traditionally given to various ranges. Because there is no fundamental difference between any of these, this book will refer to them all generically as “light”; the colored band will be called “visible light.” Frequencies and their associated vacuum wavelengths are shown on log scales.

Along the way, we will see that light phenomena have an irreducibly random character, both in space and in time. Concepts developed in the Prologue will therefore be needed to describe light.

The Focus Question is

Biological question: Why do you need natural sunlight, not indoor artificial lighting, to generate vitamin D?

Physical idea: Sunlight contains an invisible component required for vitamin D synthesis in the skin.

1.2 LIGHT BEFORE 1905

Light can mediate interactions between two material objects. Among other effects, it can transfer energy from one object to another. Originally, “light” referred only to radiation that could stimulate our eyes, but eventually many other kinds were found—an entire light spectrum. That is, light from any source can be separated by physical means (for example, by sending it through a prism) into a continuum of different types (see Figure 1.1):

- Ordinary visible light occupies a narrow band in this spectrum, with red and orange at one end, green in the middle, and blue and violet at the other extreme.
- Adjacent to the visible on one side is the infrared (IR) region, and beyond that lie the microwave and radio regions.
- On the other side of the visible lies the ultraviolet (UV) region. Beyond it lie x rays and then gamma rays.

Within any of these ranges, light can be more finely subdivided. For example, within the visible range the various different types of light appear to our eyes to have different colors.\(^1\) More precisely, we can construct a filter that transmits any desired part of the spectrum, while blocking other parts. If the transmitted part consists of one very narrow spectral band, we call that light monochromatic.

\(^1\)There exist colors, such as magenta, that do not appear anywhere in the spectrum. Chapter 3 will discuss perceived color systematically; the present chapter considers only the physical characterization of light.
1.2.1 Basic light phenomena

Today, every part of the light spectrum is viewed as a different aspect of a single thing, because all share a suite of phenomena. We will refer to any of them as “light.”

Light can connect two objects separated by vacuum, for example, the space between Earth and the Sun. Most kinds of light also pass readily through media of very low density, such as air. Some kinds even pass through certain dense media: Visible light can pass through water or glass; x rays pass through the soft tissue in our bodies.

Light moves: That is, it takes time to get from one place to another. Unlike everyday objects, however, light in vacuum always travels at a single speed, regardless of its type or how the emitting object was moving. Because it is universal, we call this speed a constant of Nature. It’s denoted by the letter \( c \); its value is \( c \approx 3.0 \times 10^8 \text{ m/s} \).

Light generally travels in straight-line paths. Thus, a point source of light (or a large source that is very distant from us, like the Sun) can cast sharply defined shadows. When light encounters an opaque object, it can be partly absorbed; for example, it may warm the object. But some or all of the light can instead reflect (bounce) off the obstruction. If the object is smooth with a well-defined shape, the light reflects in a predictable way.

These phenomena inspired some early scientists with a metaphor from everyday life: Light appeared to be a stream of tiny material particles, like grains of sand but much smaller. They emerged from a luminous body, flew unimpeded through empty space (or partially impeded by a medium), bounced off certain kinds of obstructions, and ultimately delivered their energy by being absorbed. For example, those entering our eyes would give rise to the sensation of light, and so on.

1.2.2 Light displays wavelike behavior in many situations

However, light also exhibits some phenomena that are hard to reconcile with the material-particle metaphor, for example, diffractive effects, in which light deviates from straight-line motion. You can see such effects yourself, following an observation made by F. Hopkinson in 1785:\(^3\) Hold a piece of finely woven fabric close to your eye, and look through it at a distant point source of light, perhaps a street light at night. In addition to the main image, you’ll see other images, a “transmission grating” effect that we will study in later chapters. Hopkinson mentioned his observations to his friend D. Rittenhouse. Although it was too early to be able to explain the effect, Rittenhouse did document it in quantitative detail, constructing finely spaced, parallel arrays of human hairs in place of fabric and measuring the angular displacement of the images. These results are difficult or impossible to explain from a physical model of light as a stream of tiny material particles.

Shortly after Rittenhouse’s experiments, Thomas Young championed a metaphor for light as a wave phenomenon, in part to explain diffractive effects. Although this classical wave theory of light was eventually found to be incomplete, it does explain phenomena that the particle model cannot. Later, when we propose a third theory of light (quantum physics), we’ll need to ensure that it, too, can explain diffractive effects.

\(^2\)Abu Ali al-Hasan ibn al-Hasan ibn al-Haitham made this observation, and reported many other experiments with lenses, mirrors, refraction, and reflection, in his Kitab al-Manazir, written from 1011 to 1021CE.

\(^3\)Hopkinson was an American musician and public official; he signed the US Declaration of Independence and helped to design the first US flag in 1777.
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Any wave—for example, the sound from a flute, or ripples on the surface of water—has properties called frequency and amplitude. Because the energy carried by a wave depends on its amplitude, Young also interpreted the intensity of a light source in terms of the amplitude of a corresponding wave. As for the frequency, Young proposed that it was related to where the light fell on the spectrum. Instead of frequency $\nu$, one can equivalently characterize a wave by specifying the quantity $T = 1/\nu$ (called “the period”), or by stating the distance $\lambda$ that the wave travels in vacuum during one period:

$$\lambda = c \times (1/\nu). \quad \text{vacuum wavelength corresponding to frequency } \nu$$

(1.1)

Young then explained light diffraction by analogy to corresponding phenomena with sound or water waves: Similarly to light, each segment of a water wavefront moves on a straight-line path in open space, but will spread out after passing the edge of an obstruction. The interplay between $\lambda$ and the physical dimensions of a grating then accounted for the patterns of light and darkness seen in diffraction patterns. This connection also made sense of mysterious colors that appeared in Rittenhouse’s diffraction experiments: A grating bends each part of the spectrum of visible light by a different angle, and so can separate it. Young also noted that water and sound waves bounce when they encounter a straight wall, with the same geometry as that followed by light hitting a mirror.

Another kind of deviation from straight-line motion occurs when light passes from air into water. C. Huygens had already noted that such refraction phenomena also follow naturally from the wave theory, if we extend it by adding the assumption that light waves move more slowly in water than they do in air. When it later became possible to measure the speed of light directly, this assumption was confirmed.

For reasons like these, most scientists eventually adopted the classical wave model of light. Its triumph seemed complete when J. C. Maxwell found equations of motion for electricity and magnetism, then showed that those equations have wavelike solutions that give quantitative explanations of diffraction, refraction, and many other light phenomena. The equations also showed how the waves could be created when electric charges are set in motion, and conversely, that they could cause initially motionless charges to shake; these two processes correspond to the generation and reception of light. Shortly later, H. Hertz and others performed experiments confirming that oscillating electric currents do indeed give rise to traveling waves with all the characteristics of light (including propagation through vacuum at speed $c$, diffraction, reflection, and refraction). Around the same time, W. Röntgen also discovered x rays, which also proved to be lightlike, though with shorter wavelengths than visible light. An enormous range of phenomena thus seemed to fit comfortably into a single framework.

Section 1.2 has surveyed a physical model of light that appeared to be satisfactory up until the early 20th century. This model not only explained many phenomena; it also had an appealingly intuitive foundation.

1.3 LIGHT IS LUMPY

The classical wave model supplanted the older model of light as a stream of material particles, in part because the material-particle model gave no clear explanation of

4Chapter 4 will discuss diffraction effects, for example Figure 4.2, in detail.
1.3 Light Is Lumpy

Figure 1.2: [Experimental data.] Signals from a sensitive detector exposed to light. Top: Time series of the output from the detector exposed to dim illumination. Bottom: Even dimmer illumination. In each case, the signal consists of similar blips superimposed on a background of instrumental noise. The difference between dim and dimmer light lies in the mean rate of the blips' appearance, not in the strength of individual blips. [Data courtesy John F. Beausang, available in Dataset 2.]

diffraction phenomena. But today we can observe still other phenomena, for which the wave model gives no explanation. Thus, neither of these models is fully satisfactory.

1.3.1 The discrete aspect of light is most apparent at extremely low intensity

Many living organisms have evolved means to detect very dim light, for example starlight, or the greatly diminished sunlight available deep underwater. Light shows some surprising behavior in the regime of faint illumination.

Before we tackle the rather involved visual apparatus of living organisms, let’s begin with a less sophisticated device: a laboratory light sensor. When exposed to steady illumination, it creates a measurable signal. Reducing the illumination reduces this signal, but it does so in a surprising way. We might expect to find that, as we gradually dim the light, the signal would gradually decrease in strength, eventually disappearing into background electrical noise from the equipment. This is what happens when a friend speaks too softly over a noisy telephone connection. But it’s not what is observed with light.

A sensitive light detector in total darkness does show some noise in its output signal. But the effect of faint illumination is to superimpose distinct “blips” on the noise background (Figure 1.2). Changing the illumination level does not change the strength of each blip; what changes is the mean rate at which blips arrive.

The discrete, or “lumpy,” character of the signals in Figure 1.2 does not automatically imply anything about light itself. Following the classical wave model, we might imagine that light really is a continuous stream of energy (symbolized by water in Figure 1.3), but that some mechanism in the detector triggers a blip only after enough of this energy has been captured. One difficulty with this metaphor is that it predicts
that steady illumination would lead to blips at uniformly spaced times. Experiments show, however, that the blips instead form a random process, called shot noise.\(^5\)

You can appreciate the difference between uniformly spaced blips and shot noise by listening to the audio clips in Media 1.\(^6\) One of these contains clicks that are uniformly spaced in time. The other is an audio version of an experimental dataset (partially shown in Figure 1.2); it contains clicks at the arrival times of each of the blips. The two audio clips sound quite different, despite the fact that they have the same mean click rate.

We might at first suspect that the discrete, random character of the blips is a pathology of one particular light source or detector technology. But on the contrary, a variety of light sources (including the Sun, a candle, a hot filament, or a laser) all give random blips when reduced to extremely low intensity, regardless of how carefully we try to make them steady. Also, several different detector technologies (including an avalanche photodiode, a photomultiplier tube, or high-sensitivity photographic film) all give similar results. Nor is this randomness a byproduct of thermal motion:\(^7\) Cooling the detector, even to nearly absolute zero temperature, doesn’t affect it. Instead, \[\text{The discrete, random character of signals from a sensitive light detector is a property of light itself.} \] (1.2)

Experiments like the one just discussed also reveal another important property of light. Suppose that we construct a grid of millions of identical detectors, like the camera in a portable electronic device, then illuminate this array uniformly. The classical wave model would lead us to imagine a succession of “wavefronts” spreading from the source, arriving at a distant array of detectors, and inducing measurable signals in each of them, in unison. An analogy could be a spreading wave on water, impinging on an array of floating corks. The corks respond by all bobbing in synchrony, with similar amplitudes.

In contrast to that expectation, experiments instead show that each detector creates blips independently of the others, and that no two ever respond at exactly the same time. This behavior implies that light consists of a random stream of something that creates highly localized effects. In the wave metaphor with floating corks, the

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\(^5\)Section 1.4 will examine random processes in detail.
\(^6\)See page xx for how to obtain the Media.
\(^7\)Section 0.6 (page 17) introduced thermal motion. Cooling a detector certainly does reduce random signals not caused by light (the detector’s “dark current”).
1.3 Light Is Lumpy

observed behavior would correspond to all the corks remaining motionless, except for one, chosen at random, that somehow gets flung out of the water, at the same time stilling the wave everywhere!

Similar behavior is also observed with more complex visual scenes. Such a scene is often described as a continuously varying distribution of energy to different parts of our eye, from corresponding points in the external world. The preceding discussion, however, suggests a radically different view:

Each part of a visual scene should be regarded as supplying its own random time series of light blips to a detector, and the apparent modulation of intensity as we move over a scene is actually a variation of the mean rates of these random arrival processes. (1.3)

To explore this distinction, A. Rose created the images in Figure 1.4, by using a scanning photomultiplier apparatus he had constructed in 1948. The figure shows an intelligible image emerging gradually out of the randomness of low-number counting statistics as the exposure time gets longer, or equivalently as the illumination goes from very dim to bright. At intermediate illumination, the brighter parts of the scene show clearer detail than the dark parts because the corresponding pixels contain larger numbers of blips.8 The dim parts of the scene remain noisy until the illumination is increased still further. Images made under the microscope when observing single fluorescent molecules are also very dim, and here, too, the light is observed to arrive in discrete blips, building up gradually to form an image.

Nor is the “blip” interpretation (Idea 1.3) limited to camera images: Chapter 4 will show that even diffractive phenomena, long thought to be the decisive proof of

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8Section 0.5.3 argued that blip counts are Poisson distributed, and Equation 0.30 (page 9) says that relative standard deviation decreases with increasing mean blip count.
the wave character of light, turn out to be discrete (lumpy) at low light intensity.\(^9\) That is, their patterns of illumination, too, are found to be position-dependent mean rates for random, localized blip arrivals.

The classical wave theory cannot explain phenomena in which light displays a lumpy character. But this does not automatically imply that the older theory was right, and light is a stream of tiny material particles; after all, it remains true that light can also display diffractive (wavelike) phenomena. In fact, we now think of light via a third physical model, which is \textit{neither} classical wave nor material particle. We will explore some of the details of this model in Chapter 4. Until then, we will regard “frequency” and “vacuum wavelength” in Figure 1.1 (page 24) merely as convenient labels for the various kinds of light, equivalent to stating a position within the spectrum.\(^{10}\) Chapter 4 will explain the role of these quantities in the model.

Section 1.3.1' (page 50) discusses other kinds of randomness in physics.

1.3.2 The photoelectric effect

Modern instruments, like the one that yielded the shot noise data in Figures 1.2 and 0.3b, reveal the lumpy character of light directly. Remarkably, however, indirect experimental evidence for this proposition became available much earlier, in the late 19th century. Those early experiments also found a key detail, not visible in Figure 1.2, that proves to be essential for understanding the role of light in biology. Ironically, the first of these experiments was done by H. Hertz, in the course of experiments that (temporarily) seemed to assure the wave theory’s supremacy! The story of Hertz’s accidental discovery gives insight into the approach of a meticulous researcher when confronted with a totally unexpected result.

Hertz was studying the generation of light in the spectral range now called “radio,” but he quickly realized that this aspect of his experiment was immaterial to the new phenomenon he had discovered. So he temporarily shelved his original research and set up an apparatus designed to focus attention only on the new phenomenon (Figure 1.5).

In Figure 1.5, a high-voltage power source is applied to two metal electrodes, generating a large (up to 10 cm) “primary” spark (electrical arc) across the gap between them. The power supply also applies high voltage to a smaller, “secondary” spark gap located a distance \(L\) from the primary. Holding the primary spark fixed, Hertz gradually reduced the secondary spark gap, to find the point at which sparks just began to be created there. He recorded this critical separation as a function of several variables in the apparatus, to see which changes affected it.

The observation that Hertz found surprising was that the secondary gap’s propensity to spark seemed to depend on whether it was in a direct line of sight from the primary spark, as if some influence came out of the primary spark and traveled on straight lines. Interrupting this visual contact by an opaque screen—or even by a piece of clear window glass—greatly impeded sparking at the secondary gap. Eliminating the primary spark altogether had the same effect.

Hertz wanted to know how the primary spark was influencing the secondary. First, he found that the influence decreased in strength as the distance \(L\) was increased, qualitatively similar to the decrease in the intensity of light from a point source with

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\(^9\)See Figure 4.2 (page 147).

\(^{10}\)When light passes into a transparent medium, such as water, its wavelength changes. Nevertheless, it is traditional to identify the kind of light by the wavelength that it \textit{would have had} in vacuum (Equation 1.1, page 26). We will call this quantity vacuum wavelength, but many authors abbreviate it to simply “the wavelength.”
increasing distance. And whatever the cause of this influence, Hertz also found that it could be reflected by mirrors and bent by prisms, displaying the same reflection and refraction behavior as ordinary light. Crucially, the bending angle after passing through a prism was even larger than with visible blue light. Hertz also knew two more relevant facts: Sparks create both visible and ultraviolet light, and glass blocks ultraviolet.

For all these reasons, Hertz proposed that

\[ \text{Ultraviolet light somehow promotes spark generation when it lands on metal electrodes.} \]

This hypothesis made an experimentally testable prediction, namely, that an independent source of UV light could restore sparking, even if direct illumination from the primary was blocked. Hertz tested this prediction, and found that indeed with this arrangement the sparking was restored to the higher level seen in the original experiments. Visible light with no UV component yielded no such enhancement. Hertz documented his results carefully, but then returned to his main investigation.

In short, Hertz found that ultraviolet light falling on a metal surface can enhance the metal’s ability to initiate an electric spark—a photoelectric effect. Followup experiments by several other scientists turned up additional clues:

1. When a piece of metal in air is negatively charged, exposure to UV light can cause it to lose its excess charge. No such effect occurs with a positively charged object.

2. The ability to discharge a negative object depends on the kind of light: Blue light is more effective than red, and UV light still more effective. Each particular kind of metal has a characteristic photoelectric threshold \( \nu_* \), a cutoff point on the light spectrum below which there is no photoelectric effect.\(^{11}\)

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\(^{11}\)Most metals have a photoelectric threshold located in the ultraviolet range, though a few, such as sodium, have it in the visible.
3. The photoelectric threshold $\nu_*$ does not depend on how bright the light is. That is, increasing the intensity of light at a fixed frequency below the threshold does not result in any discharge. (Above the threshold, however, the rate of discharge does depend on the illumination intensity.)

4. The mechanism that ejects negative charges does not depend on thermal motion: Cooling the metal makes no change to its photoelectric effect.

5. If we place a second metal plate near the first one, it can collect the charge ejected from the first (Figure 1.6a). If the two plates are joined by a wire, then a continuous “photocurrent” will flow indefinitely (as long as the illumination remains on), even when no high-voltage source is present.

6. The photocurrent always begins immediately upon turning on the illumination. In particular, although the strength of the photocurrent depends on the intensity of the light, there is no delay that increases at weaker illumination.

7. For a given type of metal, we can modify the photoelectric threshold by connecting a battery between the two plates described in point 5 (Figure 1.6b). P. Lenard found that, if the illuminated plate is at a positive electric potential relative to the collection plate (a “retarding potential”), then the photoelectric threshold $\nu_*$ always increases (Figure 1.6b,c).

Other experiments also showed that negatively charged objects were being ejected from the metal, and that they were the same “electrons” that had recently been found to stream across a vacuum in cathode-ray tubes. This interpretation explained why UV light facilitated the production of sparks in Hertz’s experiment: It liberated electrons already present in the secondary electrode. These free electrons left the metal surface, ready to be driven by the electric field present at the secondary spark gap.

In Lenard’s photocurrent experiments, introducing a battery created an energy barrier, related to the retarding electric potential $\Phi$ by the formula $U = -e\Phi$, where $-e$ is the charge on an electron. Such a barrier repels electrons from the second plate, and attracts them back to the illuminated plate. Both effects impede their passage,
reducing or eliminating the photocurrent.

Physicists eventually interpreted Lenard’s results by arguing that incident light liberates electrons by giving each one a “kick,” enabling some of them to overcome the barrier. More precisely, for any given frequency \( \nu \) of incident light, we define the stopping energy \( U_{\text{stop}}(\nu) \) as the value of the potential energy barrier that is just large enough to eliminate the photocurrent when light of that frequency shines on the metal surface. Lenard found that

- The stopping energy depends on the type of metal. This result fits with point 2 above: The photoelectric threshold mentioned there is the value \( \nu_* \) at which \( U_{\text{stop}}(\nu_*) = 0 \), and it depends on the metal.
- The stopping energy does not depend on the intensity of the light (compare point 3); and
- The stopping energy is an increasing function of the frequency of the light (again see point 2).

These observations support a physical model for the photoelectric effect, in which

The maximum “kick” that light can deliver to a single electron depends only on its frequency. Brighter light can kick more electrons per second, but it gives each one the same kick as dimmer light of the same frequency.

This idea also fits with the modern data shown in Figure 1.2: Higher light intensity means more electrons getting kicked (more blips from the detector per second), but not more energy delivered to each electron (each blip’s strength is unchanged).

### 1.3.3 Einstein’s proposal

The photoelectric effect posed a serious challenge to the model of light as a classical wave. For example, the wave picture implies that, for monochromatic light, increasing the intensity amounts to increasing the amplitude of the wave. If the photoelectric effect amounted to pulling electrons off atoms and giving them kinetic energy, surely a wave of greater amplitude would deliver more energy to each electron—but Lenard’s results disproved this expectation. Moreover, the transfer from energy spread out in a wave to energy concentrated on one electron would require time, as the energy gradually built up.\(^{12}\) Thus, the wave model predicted a delay before the first electrons acquired enough energy to break loose. But no such delay was observed experimentally, even for low illumination intensity.\(^{13}\)

Albert Einstein realized that the emerging concept of light delivering a definite kick to a single electron (Idea 1.5), although incomprehensible in the classical wave model, did fit with some recent experiments concerning the light given off by red-hot objects. Max Planck had proposed a mathematical formula that described the measured spectrum of this “thermal radiation.” The formula included a new constant of Nature that we now call the “reduced Planck constant” and denote by the symbol \( \hbar \).\(^{14}\) Einstein found that Planck’s formula could be obtained by starting from the

\(^{12}\)Recall the metaphor in Figure 1.3 (page 28).

\(^{13}\)This observation was point 6 on page 32.

\(^{14}\)Pronounced “aitch-bar.” Some authors introduce the symbol \( h \) to denote the quantity that we will call \( 2\pi \hbar \). But this notation runs the risk of confusion with other quantities also named \( h \), so we will instead always express our formulas using the unique symbol \( \hbar \). Other authors introduce the “angular frequency” \( \omega = 2\pi \nu \), in terms of which Equation 1.6 says \( E_{\text{photon}} = \hbar \omega \).
hypothesis that monochromatic light consists of lumps, now called \textbf{photons}, each carrying a packet of energy equal to

\[ E_{\text{photon}} = 2\pi\hbar \nu. \]  
\textit{(1.6)}

In this formula, \( \nu \) refers to the frequency that we would have attributed to the light, under the classical wave model. For example, \( \nu \) describes where in the spectrum the light in question would fall if sent through a prism or grating.

Einstein then predicted that the \textit{same} numerical constant \( \hbar \) would also control the photoelectric effect, by setting the maximum kick that any particular kind of light could give to an electron in a collision. This physical model led to a quantitative prediction for the stopping energy: Suppose that the minimum energy cost to remove an electron is some constant \( W \), whose value is a characteristic of the particular metal used in the experiment. Therefore, the electron must expend some of its initial kick just exiting the metal, leaving at most \( 2\pi\hbar \nu - W \) to overcome any additional retarding potential imposed by the experimenter. If the kick is less than the energy required to eject an electron (that is, if \( 2\pi\hbar \nu < W \)), then the electron can’t exit the metal at all, and there’s no photocurrent even with no applied retarding potential. Otherwise, Equation 1.6 predicts that the stopping energy is the difference between \( 2\pi\hbar \nu \) and \( W \).

Because \( W \) depends only on the metal, not on the kind of incoming light, Einstein obtained a detailed prediction for the dependence of stopping energy on frequency:

\[ U_{\text{stop}}(\nu) = 2\pi\hbar \nu - W. \]  
\textit{(1.7)}

This prediction was highly falsifiable: It was quantitative, and the key quantity \( \hbar \) was not a fitting parameter—it was independently known from the spectrum of thermal radiation.\textsuperscript{15}

Einstein was out on a limb, because at the time there were no experimental results that could confirm his prediction. Definitive confirmation took another 11 years, but eventually it was found that indeed the slope in Idea 1.7 is universal: It always agrees with Planck’s value, regardless of the type of metal in the electrode, source and intensity of the light, temperature, and other adjustable parameters.

Einstein’s proposal fits with the observation of discrete blips in today’s sensitive light detectors (Figure 1.2), because they operate by a mechanism similar to the photoelectric effect. But it adds a crucial element, the dependence of the effect on frequency.

Section 1.3.3’\textsuperscript{a} (page 50) discusses more evidence for the reality of photons. Section 1.3.3’\textsuperscript{b} (page 51) discusses the momentum that they carry. Section 1.3.3’\textsuperscript{c} (page 52) discusses the link between the Einstein relation and the thermal radiation spectrum. Section 1.3.3’\textsuperscript{d} (page 53) discusses the concept of “frequency.” Appendix B discusses Planck’s discovery of his constant.

\textsuperscript{15}Section B.4 (page 442) explains how Planck determined \( \hbar \).
1.3.4 Light-induced phenomena in biology qualitatively support the Einstein relation

Einstein’s proposal meshes with some things we know about biology and light. A number of biologically and medically relevant processes require light, and indeed light with frequency greater than a certain threshold, in order to operate. For example,

- Visible light does not induce skin cancer. Only light with higher frequency (or shorter wavelength) than visible will have this biological effect.
- Similarly, UV light is required for the production of vitamin D in our skin; artificial indoor lighting, which lacks a UV component, won’t suffice.
- Exposure to blue light (phototherapy) can clear excess bilirubin in the blood of a premature infant—but red light does not work.

Each of these examples highlights a threshold dependence on frequency, not intensity, of light, consistent with Einstein’s proposal. Each will be discussed further in the following sections.

Section 1.3 has surveyed some phenomena that contradict the continuous wave model of light and seem to call for a “lumpy” model. We have also seen some hints that the lumpy aspect of light is relevant for biological phenomena. Before we propose a replacement for the wave model of light, the rest of this chapter and Chapter 2 will begin by documenting this aspect more systematically. To that end, we now pause to construct some ideas about probability that we’ll need.

1.4 BACKGROUND: POISSON PROCESSES

“Background” sections, like this one, give brief reviews of foundational material.

Figure 1.2 illustrates how the arrival times of individual photon blips are unpredictable, even for a light source that is carefully constructed to be as stable as possible. But the Prologue pointed out that no system is completely unpredictable: We characterize whatever we do know about it by stating a probability distribution. In fact, experiments showed that, for many kinds of light source, the arrival of blips on a sensitive light detector follows a simple, universal form, called a Poisson process. Many other apparently unrelated processes are also approximately Poisson in character, for example, radioactive decay, enzyme turnovers, release of neurotransmitter vesicles, and even in some cases neural signaling itself.

1.4.1 A Poisson process can be defined as a continuous-time limit of repeated Bernoulli trials

A random process is a random system whose draws are time series. For example, the blips coming from the light detector in Figure 1.2 are all identical, so the only information we need to describe the outcome of a particular trial is the series of times \( \{t_1, t_2, \ldots\} \) at which the blips occurred. If we repeat the experiment, we obtain another draw from the random process, represented by another such sequence of numbers.

One class of random processes, called Poisson processes, describes many biophysical phenomena. To define it, first imagine taking a time interval of interest and dividing

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16 You’ll study such data in Problem 1.3.
17 For vesicle release, see Figure 2.8 (page 72), Problem 2.1, and Figure 10.13 (page 338).
it into small, consecutive slices of duration $\Delta t$. Then we decide whether or not to place a blip in the middle of each time slice. A Poisson process is characterized by the properties that

1. The probability of a blip occurring in any small time slice equals $\beta \Delta t$, independent of what is happening in any other slice, and
2. We take the continuous-time limit $\Delta t \to 0$ holding $\beta$ fixed.

Thus, a Poisson process is characterized by a single parameter $\beta$. Because $\beta$ gives probability per unit time, it has dimension $T^{-1}$.

### 1.4.2 Blip counts in a fixed interval are Poisson distributed

Each draw from a random process consists of many numbers, so it is not easy to give the complete probability density function on this large sample space. For Poisson processes, however, it often suffices to know about two kinds of reduced distributions.

The first of these reductions asks, “How many blips will we observe in a fixed time interval $T_i$?” The answer is not a single number. Rather, it is a discrete probability distribution for a random variable $\ell$, and in fact the form of this distribution is familiar:

For a Poisson process with mean rate $\beta$, the probability of getting $\ell$ blips in a given time interval $T_i$ is Poisson distributed:

$$P_{\text{pois}}(\ell; \beta T_i) = \frac{1}{\ell!} e^{-\beta T_i} (\beta T_i)^\ell.$$  

### Your Turn 1A

a. Use what you know about the Poisson distribution to find the expectation of the number of blips in a fixed time interval of duration $T_i$, then divide by $T_i$ to get blips per unit time. How does this quantity depend on $\beta$ and $T_i$?
b. Normally, we don’t notice the Poisson character of light, because the photons are arriving so rapidly that we don’t register them as individual events. Show that, moreover, the relative standard deviation of the blip number $\ell$ in $T_i$ is small if $T_i$ is much greater than $\beta^{-1}$.

### 1.4.3 Waiting times are Exponentially distributed

The second reduced form of a Poisson process asks instead, “How long must I wait until the next blip arrives?” Here again, the answer is different each time; there is a continuous probability density function of waiting times. Section 0.4.2 already gave the answer:

The waiting times in a Poisson process are distributed according to the Exponential distribution, $\varphi_{\text{exp}}(t_w; \beta) = \beta e^{-\beta t_w}$, regardless of when any previous blips may have occurred.

Figure 0.3b illustrates that very dim light does follow this distribution, a hint of its underlying Poisson-process character. The intensity of the light source is related to the mean rate of the random process.

This background section has constructed a new kind of probability distribution (a random process), which will prove useful for describing light.

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18See Equation 0.41 (page 14).
For further details on Poisson processes, see the references at the end of this chapter. Section 1.4' (page 54) says more about when we can and cannot expect photon arrivals to form a Poisson process.

1.5 A NEW PHYSICAL MODEL OF LIGHT

Earlier sections described some results that seem to imply that light cannot be a stream of material particles (“grains of sand”), as well as others that seem to imply that light cannot be a classical wave:

- A monochromatic light source of uniform intensity activates a detector with a random series of discrete events.
- Uniform illumination over a broad area gives rise to independent and highly localized events. Thus, two different pixels in a sensitive camera never respond at exactly the same time. In contrast, a classical wave would spread its energy continuously over the illuminated region; if the wave were of uniform amplitude, any response would be expected to be synchronous across the region.
- In the photoelectric effect, at one fixed wavelength, fainter light ejects fewer electrons, but does not affect the stopping energy.

The rest of this chapter will focus on these three points. Chapter 4 will return to the wavelike phenomena (Section 1.2.2), and reconcile them with the discrete ones.

1.5.1 The Light Hypothesis, part 1

The phenomena described in previous sections motivate a series of related claims about light.¹⁹

**Light Hypothesis, part 1:**

- Light travels through empty space at speed $c \approx 3 \times 10^8$ m/s.
- It comes in lumps (photons). The photons from a monochromatic light source each carry the same amount of energy, determined by the light’s position in the spectrum.
- A photon interacts with matter by transferring all its energy to a single electron and disappearing (absorption). Or a photon can pass by the electron without disturbing it (or being itself changed) in any way. The choice of which option occurs is random (a Bernoulli trial). (1.11)
- Conversely, a photon can be created from nothing by a single electron, which loses an amount of energy equal to that of the new photon. Photon creation (also called “emission”) is also probabilistic; for example, a source like the Sun, while seemingly of constant intensity, actually gives off photons in a random process.

We won’t derive the Light Hypothesis from any deeper bedrock of truth. Instead, we’ll regard it as just a compact statement of a few principles, into which a large

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¹⁹Idea 1.11 is called “part 1” because Chapter 4 will extend it.
number of biophysically relevant phenomena will fit. Although physicists regard it as confirmed, we will nevertheless use the word “hypothesis,” to emphasize that it’s inherently implausible as it stands. We’ll need to examine many more phenomena before concluding that it is even promising.

The Light Hypothesis asserts that every form of light has a discrete character. However, low-frequency forms, like radio, have such small $E_{\text{photon}}$ that their discreteness is usually not observable. In contrast, high-frequency forms, like gamma rays, have such large $E_{\text{photon}}$ that their effects appear discrete in nearly every situation. Intermediate forms, such as visible light, can appear either discrete or continuous, depending on the specific situation we study. Many biophysical applications involve the visible region of the spectrum, so we will need to come to grips with the dual character of light.

1.5.2 The spectrum of light can be regarded as a probability density times an overall rate

Section 1.3.3 noted a quantitative relation between $E_{\text{photon}}$ and the apparent frequency of light: the Einstein relation $E_{\text{photon}} = 2\pi\hbar\nu$. Instead of including this observation in the Light Hypothesis, however, Chapter 4 will obtain it as a consequence of a more general principle. Until then, we will continue to think of $\nu$ as simply an abbreviation for the quantity $E_{\text{photon}} / 2\pi\hbar$; similarly, for now the vacuum wavelength is simply an abbreviation for the quantity $c/\nu$.

We can find the probability density function for the vacuum wavelength of any photon in the stream, $\wp(\lambda)$, with dimensions $L^{-1}$ appropriate to such a PDF. Equivalently, we can let $\Phi_p$ denote the total mean rate for photon arrivals of all wavelengths, and introduce the combined function $I(\lambda) = \Phi_p\wp(\lambda)$, called the spectral photon arrival rate, or simply the “spectrum” of the light. A possible choice of units for $I$ is $s^{-1}$ nm$^{-1}$. The normalization condition on $\wp(\lambda)$ then says that the total mean photon arrival rate, $\Phi_p$, is given by $\int d\lambda I(\lambda)$.

Instead of giving the photon arrival rate per wavelength interval, $I$, some authors introduce the function $(2\pi\hbar c/\lambda)I(\lambda)$. This function gives the rate of energy transfer per wavelength interval, so it has units like W nm$^{-1}$. It, too, is often called “the spectrum,” potentially leading to confusion, so this book will not use this description of light; instead we will always use the function $I$ defined in the previous paragraph. When reading other books and publications, you can see which description is being used by looking at the units.

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21 We could equally well describe the photons by their frequency or energy and find the corresponding transformed PDFs, but this book will use the more customary description, via vacuum wavelength. See Problem 3.2.
22 We will use the same word “spectrum” to denote either the actual pattern of light cast on a screen by a prism, or the mathematical function $I(\lambda)$ describing the content of a light beam. When there seems to be danger of ambiguity, the longer term “spectral photon arrival rate” can be used instead to denote $I(\lambda)$.
23 When writing your own work, you can if necessary refer to $I$ as the “actinometric spectrum” and to $(2\pi\hbar c/\lambda)I(\lambda)$ as the “radiometric spectrum.”
1.5.3 Light can eject electrons from individual molecules, inducing photochemical reactions

A lump of matter consists of a lot of positively charged atomic nuclei that attract ("bind") electrons. Each electron may be associated to a single nucleus, or the electrons may be shared. Metals are an extreme case, in which some of the electrons wander at will throughout the entire sample.

In the photoelectric effect, a photon’s energy is converted to kinetic energy of one electron (Section 1.3.2). That kinetic energy may then suffice to overcome the electron’s attraction to a metal surface. Any energy left over after this ejection is then available to overcome an additional retarding potential in the surrounding space. Similarly, even a single atom can lose an electron ("ionize") upon exposure to light with high enough frequency. Here are two related phenomena that further illustrate what the Light Hypothesis means when it says that a photon “transfers all its energy to a single electron.”

- Most materials are electrical insulators: Their electrons are locked into a rigid state with no net flow, even when we apply an electric potential difference across the sample. However, in a special class of insulators, called photovoltaics, an incoming photon can deliver energy to an electron, promoting it into a higher-energy state, in which it is mobile. Even without actually leaving the material, such “excited” electrons can then travel through it, creating a net current. This mechanism forms the basis of solar cells. More sophisticated versions (for example, charge-coupled devices found in cameras) operate on a similar principle.

- Next, consider an electron that participates in a chemical bond in a single molecule. An incoming photon can knock the electron out of its molecule altogether or just move it internally, breaking the original bond and possibly allowing a different one to form—a photochemical reaction. If the original bond was part of the structure of a strand of DNA, changing it can cause a mutation, a first step to skin cancer (Figure 1.7). That’s why ultraviolet radiation is dangerous, whereas visible light is not: Analogously to the photoelectric effect, disrupting a chemical bond requires a certain threshold energy, and therefore light of at least a threshold frequency. Similarly, many paints and inks fade in direct sunshine (they photobleach), but not in artificial light, because only sunlight contains a significant UV component.

The following sections will explore how the Light Hypothesis helps us to understand several more physical, chemical, and biological phenomena beyond the ones already discussed. These phenomena cannot be understood in the old model of light as a classical wave. We will also find some surprising behavior involving electrons: They, too, display both wavelike and particle-like behavior.

Section 1.5 has begun our exploration of a new physical model of light. Before completing our Light Hypothesis, we next look around for more phenomena that can lend it qualitative support.

Section 1.5.3’ (page 55) discusses DNA photodamage in more detail.

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24In fact, Einstein’s 1905 paper already noted that his proposal explained a related phenomenon: Exposure to light can ionize a gas (photoionization), but only if the light’s wavelength is sufficiently short. Einstein also noted that the hypothesis could explain the Stokes shift phenomenon (Section 1.6.3).
1.6 FLUORESCENCE AND PHOTOISOMERIZATION CAN OCCUR AFTER PHOTON ABSORPTION

1.6.1 The Electron State Hypothesis

A photon need not eject an electron completely from an atom, nor break a bond in a molecule, to have an effect on it. To understand such phenomena qualitatively, we must combine the Light Hypothesis with an additional set of ideas, which may be familiar to you from chemistry:

**Electron State Hypothesis:**

- The electrons bound in an isolated atom have a discrete set of allowed physical states. Each such state has a characteristic energy and spatial structure (size and shape).
- The electrons in an isolated atom tend spontaneously to revert to their lowest-energy state (the **ground state**). Those reversions are abrupt; they occur only after a randomly chosen waiting time. \(^{(1.12)}\)
- When two or more atomic nuclei come close together, the allowed states of their electrons merge into a new set of shared, or “molecular,” states. The electron energy in each allowed state depends on the relative positions of the nuclei.

The electron energy mentioned in Idea 1.12 includes the kinetic energy of the electrons as well as the potential energies of their mutual repulsion and their attraction to the nuclei. We’ll denote the nuclear positions collectively by a symbolic variable \(y\).

Because electrons are much less massive than nuclei, their motions are faster; they rearrange themselves to account for slow changes in the nuclear positions, maintaining a fixed excitation level (ground or “excited” state). So it makes sense to think of the electron state energy as simply a function of \(y\), effectively a kind of potential energy for the nuclear positions. Combining it with the nuclear mutual repulsion energy then gives a total effective potential energy \(U_\alpha(y)\) that depends on nuclear positions and also on the discrete excitation level \(\alpha\). Thus, there are many such functions. We will give the special name \(U_0(y)\) to the one associated with the electron ground state. For
any excitation level, the nuclei tend to choose a spatial arrangement \( y \) that minimizes the effective potential energy.

Section 1.6.1’ (page 56) mentions some fine points about the Electron State Hypothesis applied in a water solution. The discreteness of electron energy levels can actually be derived, starting from ideas similar to the ones describing light; see Chapter 12.

1.6.2 Atoms have sharp spectral lines

The Electron State Hypothesis (Idea 1.12) fits with experimental facts about how a single atom interacts with light. Suppose that we inject energy into a few isolated atoms by filling a chamber with low-pressure neon gas and passing electricity through it. The electrons in each atom can then get knocked from their ground state to one of higher energy. For an atom to revert to its ground state, it must lose a sharply defined amount of energy (the difference between the two discrete levels). According to the Light Hypothesis, that energy can appear as a single photon, which must therefore also have a sharply defined frequency. Thus, if we sort the emerging photons by frequency (or by wavelength), then we expect their distribution to display sharp “spectral lines” (Figure 1.8). Those lines are characteristic of the type of atoms we placed in the chamber.

Another way to promote the electrons to an excited state is to shine light onto the gas. If an incoming photon has just the right energy to promote the electrons in an atom to an allowed state of higher energy, then the photon may be absorbed. Later, an identical photon may be reemitted, bringing the atom back to its ground state. But the new photon may not be traveling in the same direction as the original one; that is, the net effect of the absorption/emission process may be to “scatter” the incoming light.

This system also displays a crucial difference between ejection and rearrangement of electrons: Rather than just a threshold for excitation, as in the photoelectric effect, triggering a transition between two electron states requires a well-defined energy, and hence a specific wavelength of light. That is, a photon may be either “too red” (that is, not energetic enough) or “too blue” (too energetic) to participate in this process; in those cases, it will pass by the atom without interacting.

Section 1.6.2’ (page 56) discusses some finer points about the Electron State Hypothesis.

Figure 1.8: [Experimental data.] Observed emission spectrum of neon gas. An ordinary neon light bulb emits light with a spectrum showing multiple sharp peaks.
Chapter 1: What Is Light?

1.6.3 Molecules: fluorescence

Molecules, too, can absorb and emit light, but with some features not found in single atoms. This section will describe a particular form of the combined process of absorption followed by reemission of light by a molecule, called fluorescence.

A molecule differs from an isolated atom because it can rearrange the relative positions of its atomic nuclei. For example, a molecule of carbon dioxide has three nuclei. The nuclei are usually drawn as lying on a straight line, but they can move slightly, flexing the molecule. Similarly, the three nuclei of a water molecule normally lie in a bent configuration, but again the angle of that bend can change slightly, as can the distances between nuclei. The relative positions of the nuclei are a set of vectors that we can collectively call \( y \) (the “configuration” of the molecule). We can think of each configuration as a point in a complicated “configuration space” of allowed \( y \) values. Then a molecular transformation corresponds to a trip in configuration space from the starting to the ending conformation. There will be many possible routes to take on that trip, because \( y \) is a many-component quantity, but for our purposes we can restrict attention to just the one route that follows the easiest flexing motion of the molecule. Thus, we will regard \( y \) as a single variable (the “reaction coordinate”), describing where the molecule is currently sitting along that route.

Each allowed state of the electrons depends on the positions of the nuclei. Hence, the total energy of the molecule in each such state, including mutual repulsion of the nuclei, also depends on \( y \). For example, the energy of the ground state is the function we called \( U_0(y) \) in Section 1.6.1 (depicted as the lower curve in Figure 1.9). The molecule spends most of its life near the configuration \( \bar{y}_0 \) that minimizes this function.

When molecules are not isolated, for example, when they are dissolved in water (or

Figure 1.9: Schematic energy diagram. Physical model for fluorescence. 1: The positions of the nuclei in a molecule fluctuate near \( \bar{y}_0 \), the minimum of the energy function \( U_0(y) \) appropriate for electrons in their ground state. 2: Absorption of a photon promotes the electrons to an excited state. The differing lengths of the dashed and dotted lines indicate that the required photon energy depends on the momentary value of the nuclear position coordinate \( y \). 3: The nuclei respond by moving toward the minimum of the new, excited-state energy function \( U_\star(y) \). 4: Then the nuclei fluctuate about the new minimum \( \bar{y}_\star \). 5: Eventually a new photon is emitted (right), sending the electrons back to their ground state. The lengths of the dashed and dotted lines again indicate that there is variation in the precise energy of the emitted photon. 6: The nuclear positions then readjust back to the neighborhood of \( \bar{y}_0 \). The typical difference in length between the ascending and descending arrows represents the Stokes shift of this fluorescent molecule (fluorophore).
1.6 Fluorescence and Photoisomerization

Figure 1.10: [Experimental data.] Excitation and emission spectra. (a) Excitation spectra for five popular fluorophores. The curves have been separately rescaled; each is proportional to the probability that an incoming photon will excite a fluorophore, as a function of that photon’s vacuum wavelength. The abbreviation a.u. refers to “arbitrary units”; see Appendix B. (b) Emission spectra for the same fluorophores. This time, the vertical axis represents the probability density function for emission of photons of various wavelengths by the excited fluorophore. The spectra are much broader than those of single atoms (compare Figure 1.8). Also, the peak of each molecule’s emission spectrum is Stokes-shifted toward red, relative to its peak wavelength for excitation (arrow; see Idea 1.13). [Data courtesy Yuval Garini.]

in the complex environment of a living cell), they constantly bump one another, due to their thermal motion. Each such collision imparts relative motion to a molecule’s nuclei—that is, it changes $y$. Thus, the nuclei are likely to be close to, but not exactly in, the configuration $y_0$: $y$ fluctuates about $y_0$. The curved, double-headed arrow in step 1 of Figure 1.9 represents this incessant flexing and stretching motion.

Once the molecule has been excited, its new electron state creates a different effective potential energy function for the nuclei (upper curve labeled $U_\star(y)$ in Figure 1.9). The amount of energy needed to change the electron state is represented by the distance between a point on the ground-state energy curve and the corresponding point on the excited-state curve. Because $y$ was fluctuating prior to the transition, this “excitation energy” is variable. Thus, the energy required for excitation is not as sharply defined as it is for a single atom: We say that the molecule’s excitation spectrum is “broadened,” compared with the narrow spectral lines of a single atom (compare Figures 1.8 and 1.10a). The range of wavelengths at which the excitation spectrum is nonnegligible is called the molecule’s excitation band. Similarly, after a molecule has been excited, it also gives off light in a broadened distribution (its
emission spectrum; see Figure 1.10b) as it transitions back to the ground state. These ideas lead to an important insight about fluorescence. The minimal-energy configuration for the excited-state potential energy function, called $y^*$, in Figure 1.9, may be different from the one appropriate to the ground state ($y_0$). After the transition, the nuclei therefore begin to move from the neighborhood of $y_0$ toward $y^*$, typically shedding their excess potential energy by colliding with the surrounding water molecules and heating them slightly. Figure 1.9 represents this process by the step labeled 3. Thus, the energy released when the excited molecule reverts to its ground state is somewhat less than the energy required to enter the excited state, because the downhill “sliding” step 3 reduces the energy available for the reversion.

In short,

$$\text{The emitted light from molecular fluorescence has a broad spectrum, which peaks at a longer wavelength than the light required to excite that fluorescence. In contrast, light emitted from an isolated excited atom has a sharply defined wavelength and is unshifted.}$$ (1.13)

A molecule, or group within a molecule, with this behavior is called a fluorophore. The difference between the excitation and reemission peak wavelengths is a characteristic of the fluorophore, called its Stokes shift (Figure 1.10). The Stokes shift may be familiar to you from the visible glow that many fabrics and brightly colored inks give off when lit by a “black light” (ultraviolet light source).

The excitation and emission spectra are signatures that can be used to identify which fluorophore we are seeing. Analysis of some phenomenon (here fluorescence) in terms of some spectrum (here those of the incoming and outgoing light) is generically called spectroscopy. Chapter 2 will discuss how the Stokes shift, a spectroscopic feature of fluorescence, led to a revolution in microscopy.

Good fluorophores are distinguished from generic molecules by having excited states that have a high probability of releasing their energy by photon emission, and that persist long enough (typically a nanosecond or so) for the nuclei to arrive at $y^*$ before reverting to the ground state.

A fluorophore is a distinct concept from a “chromophore,” which is a molecule or group that absorbs light preferentially in a particular wavelength band but does not reemit a Stokes shifted photon. That is, a chromophore creates color by selectively absorbing light; light that is not absorbed is transmitted or scattered without changing its wavelength.

Some other light-emission phenomena are closely related to fluorescence. If the energy source is a chemical reaction, not an incoming photon, the process is called “chemiluminescence” (as seen in chemical glow-wand toys). In the special case where the source is the metabolism of a living cell, we use the more specific term “bioluminescence” (as seen in the glow of fireflies, jellyfish, and even some bacteria; see Figure 1.11).

Section 1.6.3’ (page 57) discusses why the electronic transitions are represented

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25 Another common situation is that an excited molecule loses energy by some process not involving a photon, typically in a collision with some other molecule. The excited molecule does not fluoresce, but if its excitation spectrum has a peak in the visible range it may be useful as a paint pigment, because it preferentially removes light in that band.

26 Another, similar energy loss mechanism is also depicted in step 6 of Figure 1.9: When the electron configuration reverts to its ground state, the nuclei are initially not at the minimum of $U_0(y)$. Thus, $y$ must again slide down to $y_0$, dissipating even more energy as heat.

27 The term pigment can refer to a chromophore, or a large molecule containing a chromophore. The less specific word dye is often used to mean either chromophore or fluorophore.
by vertical lines in Figure 1.9, and makes more precise the meaning of energy functions like $U(y)$.

### 1.6.4 Molecules: photoisomerization

The ground-state potential energy for the nuclei in a molecule may have more than one local minimum, separated by an energy barrier (Figure 1.12). If the nuclei are arranged in a way corresponding to one of the local minima, then a small deformation will generate a restoring force pushing them back. Larger deformations, however, can “pop” the molecule over to the other stable state. If the barrier between the states is much larger than the typical thermal energy, then collisions will only rarely suffice to excite such transitions; we then say that the molecule has multiple geometric isomers, or conformations. Once in the alternate conformation, the molecule stays there until we push on it again.

Figure 1.12 outlines a way in which light can change the conformation of a molecule, a process called photoisomerization. Extending the ideas of Section 1.6.3, we can think of the variable $y$ in the figure as giving the position along the critical path. This is the “easiest” path in configuration space joining two conformations of the molecule, that is, the path for which the highest value of $U_0$ attained along the way is minimal.

**Your Turn 1B**

Compute the energy of a visible photon (choose any wavelength in the visible range). Next, compute the typical energy of thermal motion at room temperature (Section 0.6, page 17). Then compare those two numbers and make a comment on photoisomerization.

As before, the excited-state energy curve $U_*(y)$ generally has a different minimum-energy conformation $y_*$ from the original. If the excited-state equilibrium conformation

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Section 0.6 (page 17) introduced the energy of thermal motion.

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Figure 1.12: [Schematic energy diagram.] **Physical model for photoisomerization.** The first steps are analogous to those in Figure 1.9. Now, however, the ground-state energy function has two local minima, at \( \tilde{y}_{\text{trans}} \) and \( \tilde{y}_{\text{cis}} \). Promoting the molecule to its excited electron state sometimes enables it to fall back to a different conformation from the one in which it began (\( 5' \rightarrow 6' \)), bypassing the ground-state energy barrier between the two conformations. Depending on the momentary configuration at the time of emission, however, the molecule may instead return to its initial conformation (\( 5 \rightarrow 6 \)). Steps 5 and 5’ may or may not involve photon emission; for example, energy may instead be lost via collision.

lies between the alternate isomeric form and the original one, as in Figure 1.12, then the molecule may end up in the alternate conformation upon reversion to its electronic ground state. Thus, even if isomerization is extremely unlikely to happen spontaneously via thermal agitation, it may nevertheless happen readily in the presence of light of suitable wavelength.

Although the ideas just outlined are general, they have special significance in the context of biomolecules, whose detailed conformation profoundly affects their function. In its new conformation, the molecule may engage in different molecular recognition events than the original:

\[ \text{Light can isomerize some molecules from biologically inactive to active conformations, or vice versa.} \tag{1.14} \]

Chapter 10 will apply this insight to understanding the first events in human vision.

A simpler example concerns **phototherapy**. Section 1.3.4 mentioned that prematurely born infants sometimes have an excess of *trans*-bilirubin in the blood, which their immature livers cannot clear effectively. Shining blue light on their skin can isomerize this molecule to a water-soluble form called *cis*-bilirubin, minimizing the toxic effects of the *trans* form without the need for any drug or other invasive procedure.

Photoisomerization can also have a dark side! A normally fluorescent molecule can pop into a nonfluorescent conformation, destroying its fluorescence either temporarily (**blinking**) or permanently (**photobleaching**).\(^{29}\)

Section 1.6 has shown how fluorescence and photoisomerization, two processes important throughout biophysics, are qualitatively understandable based on the Light

\(^{29}\)You’ll study blinking further in Problem 7.6.
Hypothesis and Electron State Hypothesis.

Section 1.6.4 (page 58) discusses a fine point about conformational change relevant for the very fast transitions that occur in visual pigments.

1.7 TRANSPARENT MEDIA ARE UNCHANGED BY THE PASSAGE OF LIGHT, BUT SLOW IT DOWN

The ejection of an electron from its atomic home is a major change. The promotion of an electron to a new state is less violent, but still a discrete event (Section 1.6). Even milder forms of interaction are possible as well. An electron can absorb a photon, then immediately reemit it without lingering in any definite new state. Most phenomena involving reflection or scattering of light by matter work in this way, for example, the reflection of light from white paper. In other materials, the electrons are more likely to absorb a photon, then transfer the energy to the general thermal motion of all the atoms in a sample, heating it. Here an everyday example is the heating of black pavement in bright sunshine.

More subtly, some materials are transparent, at least to some kinds of light. For example, glass is transparent to visible light. When a stream of photons travels through such a medium, their frequencies do not change; however, the interactions with its electrons do have the net effect of slowing the light down. We write the net speed for light of frequency $\nu$ as $c/n$, where $n$ is called the medium’s index of refraction, a dimensionless number larger than 1. More precisely, the index can depend on frequency, so the relation can better be written as $c/n(\nu)$. We can measure the speed of light in each medium, and for each frequency determine $n$ from these measurements. For example, visible light travels in water at roughly 3/4 its vacuum speed: $n_w(\nu) \approx 1.33–1.34$ over this frequency range. A change in speed implies a change in Equation 1.1, which now says that the wavelength in the medium is

$$\lambda_{\text{medium}} = \frac{c}{n(\nu)} \frac{1}{\nu} \quad \text{wavelength in transparent medium} \tag{1.15}$$

Air is another common transparent medium. But the density of air is much smaller than that of water or glass, so its index of refraction is very close to 1; for most optical phenomena, we may treat air as essentially the same as vacuum.

As mentioned in Section 1.3.1, it is customary to describe monochromatic light by the wavelength that light of the same frequency would have had, were it propagating in vacuum. This “vacuum wavelength” is still given as a function of frequency by $\lambda = c/\nu$, even though the true wavelength is given by Equation 1.15.

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30 Section 12.3.3 (page 396) will discuss the origin of this slowdown.

31 Chapter 4 will discuss how this phenomenon can give rise to rainbows when light passes through a prism (or through droplets of water suspended in the air after a rainstorm).

32 In a sentence that defines notation, like this one, the underlined initial “w” in the word “water” is a hint about the meaning of the notation: The subscript on the symbol $n_w$ refers to water.
Chapter 1 What Is Light?

THE BIG PICTURE

This chapter has presented some surprising phenomena involving light, and proposed that “light consists of photons.” At the moment, that phrase is little more than a slogan, involving a word whose definition so far is “not exactly analogous to a water wave, nor to a stream of sand grains flying through space.” This chapter has mostly pointed out phenomena that require a non-wave interpretation. Chapters 2 and 3 will show some more biophysical phenomena that are consistent with the minimal portrait of photons described here. Chapter 4 will then develop the physics of photons in greater detail, developing a physical model that embraces both particle and wave aspects. Chapter 9 will examine the question of whether the lumpy character of light is actually relevant to human vision.

There is a third aspect of light that you probably studied in first-year physics, namely its connection to electricity and magnetism. This book will not emphasize that aspect, because a detailed understanding is rarely essential for biophysics. A bigger theoretical framework, called field quantization, incorporates all three aspects of light. The more limited framework we will use in this book, however, shows some lessons more simply than the elaborate complete theory, including many that are relevant to living systems and the instruments used to study them.

KEY FORMULAS

- ** Photons:** Light consists of lumps called photons. A photon can be thought of as carrying energy $E_{\text{photon}}$, whose value determines where it falls in the light spectrum. In some situations, monochromatic light behaves analogously to a wave with frequency $\nu = E_{\text{photon}} / 2\pi \hbar$, where the reduced Planck constant $\hbar \approx 1.05 \times 10^{-34} \text{Js}$. In vacuum or air, the wavelength $\lambda$ equals $c/\nu$, where $c \approx 3.0 \times 10^8 \text{m/s}$ is the speed of light.

- **Electric potential energy versus electric potential:** The potential energy $U$ of a charge $q$ in a region with electric potential $\Phi$ is equal to $q\Phi$.

- **Photoelectric effect:** Light can eject electrons from the surface of a piece of metal in vacuum. The minimum potential energy barrier needed to stop the photocurrent (the stopping energy) is

$$U_{\text{stop}}(\nu) = 2\pi \hbar \nu - W,$$

[1.7, page 34]

The intercept, $-W$, depends only on the kind of metal. The stopping energy can be reexpressed in terms of an electric potential, by using the relation in the preceding point.

- **Poisson process:** A random process generates sequences of numbers (“blip times”). A Poisson process has the properties that any infinitesimal time slot from $t$ to $t + \Delta t$ has probability $\beta \Delta t$ of containing a blip, and the number in one such slot is statistically independent of the number in any other (nonoverlapping) slot, where $\beta$ is a positive number called the mean rate. The waiting times for this process have an Exponential distribution, with expectation $\beta^{-1}$.

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33 Chapter 13 will introduce field quantization.
34 Photons also carry momentum, but its magnitude is tied to the energy by $p = E/c$ (Section 1.3.3’b, page 51). There is also a property called “polarization,” which is discussed in Chapter 13.
The probability of getting $\ell$ blips in a finite time interval of duration $T_1$ follows a Poisson distribution with expectation $\mu = \beta T_1$. 

- **Molecular energy:** The total energy of the electrons in some state of an atom or molecule equals their potential energy in each others' fields (and those of the atomic nuclei), plus other contributions such as their kinetic energy. Section 1.6 introduced a viewpoint in which all forms of electron energy in a molecule were considered as effectively a contribution to the potential energy function for the atomic nuclei. When combined with the mutual electric repulsion energy of the nuclei, we called this function $U_\alpha(y)$; it depends on electron state $\alpha$ as well as on nuclear positions, collectively denoted $y$. 

- **Transparent medium:** In a medium like water, the speed of light is reduced to $c/n$, where $n$ is the index of refraction, a dimensionless factor greater than 1. The wavelength formula is then $\lambda = c/(n\nu)$, but we continue to characterize light by its vacuum wavelength $c/\nu$ (or by its frequency $\nu$). 

**FURTHER READING**

*Semipopular:*  
Feynman, 1985; Feynman, 1967; Breslin & Montwill, 2013. (See also Media 2.)  

*Intermediate:*  

*Technical:*  
Bioluminescence: Branchini et al., 2015; Haddock et al., 2010.  
Single-molecule fluorescence methods: Hinterdorfer & van Oijen, 2009, chapt. 1, 2; Roy et al., 2008; Selvin & Ha, 2008.  
Blinking of fluorophores: Stefani et al., 2009.  
Chapter 1 What Is Light?

1.3.1 Quantum randomness is distinct from classical chaos

1. Some classical dynamical systems can give effectively unpredictable results, a situation called deterministic chaos. Such a system’s behavior may be “random” in the practical sense that many attempted repetitions of an experiment, with initial conditions set up identically (within the limits of the apparatus precision), can lead to final results with no discernible, relevant structure. Indeed, probability ideas are often helpful when modeling such systems; for example, Section 0.1 (page 1) used weather as an illustration of an effectively random system.

However, it’s more correct to say that a chaotic dynamical system has a characteristic time scale beyond which we cannot make accurate predictions. If we measure the initial conditions with some level of accuracy, then we can predict the system’s state into the future for times less than this “Lyapunov time.” In contrast, quantum randomness is intrinsic and cannot be suppressed, or predicted, even over short times.

2. The main text argued somewhat loosely that the steady flow of a continuous fluid will not give rise to random blips (Figure 1.3). In fact, a dripping faucet can behave chaotically, seeming to invalidate this argument. However, there is no obvious way to implement this idea with energy transport by waves.

3. Quantum physics does not say that “everything is uncertain.” For example, if we prepare an initial state of an isolated system with definite energy, then that energy will remain definite (and unchanging) throughout its future development. Quantum physics does say that there are states in which the measured values of certain observable quantities are not predictable, and that such states are not only possible, but even unavoidable in some situations.

1.3.3 The reality of photons

Einstein was aware that the evidence for his model that was available in 1905 was not fully convincing. In fact, much later, it was found that the main features of the photoelectric effect can also be explained in a “semiclassical” model, in which light itself is not quantized (reviewed in Mandel & Wolf, 1995, chapt. 9).

An experiment by P. Grangier and coauthors finally provided compelling evidence for Einstein’s intuition (Grangier et al., 1986). The experimenters prepared single-photon states by waiting for a single excited calcium atom to drop to its ground state. The resulting light was directed through a beam splitter. Detectors on each branch of the beam were then found never to respond simultaneously. In contrast, if light were a classical wave we could readily divert bits of it to two different detectors, where it would (at least sometimes) trigger simultaneous events in each branch. For more details, see Pearson & Jackson, 2010, and Greenstein & Zajonc, 2006, chapt. 2.

Actually, exotic materials do exist that can split a single photon into two, via an effect called spontaneous parametric down-conversion (SPDC).35 The resulting two photons can then simultaneously arrive at, and excite, two detectors. But ordinary

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35Section 9.4.3 (page 305) gives an application of SPDC to biology.
partial reflection does not produce this effect. Moreover, unlike in the classical model, the two emerging photons have frequencies different from the incoming one: By energy conservation and the Einstein relation, their frequencies must sum to the original photon’s value. Finally, SPDC crystals typically split only one out of a million incident photons, leaving the rest unaffected.

1.3.3′b Light also carries momentum

Einstein proposed that light be regarded as consisting of lumps. We have seen that, in some ways, that description is reasonable:

- Light can travel through empty space at a huge but finite speed.
- Light interacts in a highly localized way with matter.
- Any projectile carries momentum as well as energy, and indeed, J. C. Maxwell’s older theory of electromagnetic radiation already said something about this.

About that last point, Maxwell’s classical wave theory quantitatively predicted that a beam of light transports momentum per time per area equal to its energy per time per area divided by c. This momentum transport gives rise to a “radiation pressure” effect; it had been experimentally observed prior to Einstein’s work.36

But the notion of light as a “particle” had many unappealing aspects as well, including

- a. Unlike sand grains or electrons, light in vacuum always travels at a single universal speed.
- b. Nevertheless, the energy of a photon is variable, not the constant $\frac{1}{2}m_{\text{photon}}c^2$, as Newtonian particle mechanics might lead us to believe.
- c. Newton’s formulas for energy, $E = \frac{1}{2}mv^2$, and momentum, $p = mv$, imply $E = vp/2$, which disagrees the electrodynamically result given above by a factor of 2.

Einstein was able to see through these paradoxes because at the same time as his light-quantum work, he was also creating the theory of relativity. He proposed that the Newtonian formulas were approximate, valid only in the realm of objects moving with speeds much slower than c, and that more generally they should be replaced by

$$p = \frac{mv}{\sqrt{1 - (v/c)^2}} \quad \text{and} \quad E = \frac{mc^2}{\sqrt{1 - (v/c)^2}}. \tag{1.16}$$

For a particle that moves with $v \ll c$, the first formula reduces to Newton’s $mv$, while the second reduces to a constant plus Newton’s $\frac{1}{2}mv^2$. For velocities approaching that of light, both formulas seem to be divergent. Einstein realized, however, that there was an intriguing loophole: If the mass $m$ is sent to zero while $v$ approaches $c$, then $E$ and $p$ can both exist, with the relation

$$p_{\text{photon}} = E_{\text{photon}}/c, \tag{1.17}$$

in agreement with the electrodynamical result and hence addressing point c above. Indeed, a massless particle has no choice but to move at speed $c$. Otherwise, its energy and momentum would both vanish. That observation addresses point a above. Finally, we can take the limit in a way that gives $E$ any value we like, addressing point b.

36Chapter 13 gives a route to this result. P. Debye later used the concept to explain why comet tails always point away from the Sun.
For other kinds of particles, eliminating $v$ from Equations 1.16 gives

$$E = \sqrt{m^2c^4 + p^2c^2}. \quad (1.18)$$

Experiments on the collisions of individual x-ray photons with electrons confirmed that momentum is conserved if we take the photon’s and electron’s momenta to be connected to energy via Equations 1.17 and 1.18, respectively.

The photon hypothesis, combined with momentum conservation, thus imply that, when a macroscopic object either absorbs or emits a lump of light, it must also change its momentum. If photons are absorbed or scattered at some mean rate, then the object will receive momentum at that mean rate times $E_{\text{photon}}/c$; in other words, it will experience a force. The biophysical relevance of these remarks comes when we seek ways to apply precisely controlled forces to single molecules (for example, a motor protein). A small, transparent object that bends a beam of light can be attached to the molecule in question by using an antibody linker. Typically this object is a micrometer-scale sphere of plastic, which acts as a lens. Deflecting the photons in a beam of light changes their momentum, because momentum is a vector. That change of photon momentum implies a compensating change in the plastic sphere; the resulting force (rate of momentum transfer) can be adjusted to the piconewton range. This optical tweezers apparatus has proven to be versatile, enabling delicate measurements on single biomolecules (Nelson, 2014, chapt. 6; van Mameren et al., 2011).

### 1.3.3′c The thermal radiation spectrum

A key motivation for the Light Hypothesis was the outstanding mystery in 1905 of the spectrum of light from a hot object (or more precisely, the light filling a cavity inside such an object).\(^{37}\) This spectrum had recently been measured experimentally, as a function of frequency and the object’s temperature, but by 1905 its high-frequency limiting behavior still defied theoretical explanation. Besides its fundamental importance, such thermal radiation also appears in the living world: Light from the Sun, with which we see, has a spectrum of roughly this form.

The experimental result can be expressed by stating the energy density $d\nu$ (energy per volume) in a cavity, carried by photons with frequencies in a certain range, $d\nu$. Max Planck found that the experimental data could be fit to a function of this form:

$$d\nu = \frac{16\pi^2 \hbar^3}{c^3} \left( e^{2\pi\hbar\nu/(k_B T)} - 1 \right)^{-1} d\nu. \quad (1.19)$$

Here $k_B T$ denotes the product of the absolute temperature times the Boltzmann constant.\(^{38}\) Planck’s formula cannot be understood in terms of classical electrodynamics combined with classical statistical physics; we will now see how it emerges as a consequence of Einstein’s photon hypothesis.

We begin by focusing attention only on photons located in one region of space $d^3r$, with momenta only in a range $d^3p$. (Other photons not in these ranges are statistically independent of these ones, and make additive contributions to the mean energy density.) We need one crucial idea not yet known to Einstein in 1905, which is that all photons with a particular momentum, in a particular location in space, are indistinguishable.\(^{39}\) That is, a state is completely specified as soon as we give the numbers of photons present in each such range $d^3r d^3p$.

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\(^{37}\) Section B.4 gives more details about thermal radiation. Some authors call it “blackbody radiation.”

\(^{38}\) Section 0.6 (page 17) introduced this constant.

\(^{39}\) Einstein only arrived at this idea in 1924, starting from a suggestion by S. Bose. To see how
Photons can be emitted or absorbed by atoms in the walls of the surrounding chamber. The energy $E$ of those photons is a random variable; we want its expectation. We cannot make direct use of the classical result in Section 0.6 (page 17), because giving each of the infinitely many photon states the same energy would give the vacuum an unphysical, infinite energy content (and specific heat). However, a related statement from classical physics does make sense and continues to hold in the quantum world:

At absolute temperature $T$, a system can occupy any of its allowed states. The probability of occupying a state of energy $E$ depends on temperature as $e^{-E/k_B T}$ times a normalization constant.

Thus, the expectation we seek is the sum of terms corresponding to states with $n = 0, 1, \ldots$ photons present. Each state has energy $E_n = (2\pi\hbar\nu)/n$, where Equations 1.17 and 1.6 (page 34) give the frequency as $\nu = \|p\|c/(2\pi\hbar)$. Each state has occupation probability given by the Boltzmann factor (Idea 1.20) divided by an overall constant (independent of $n$) for normalization:

$$\langle E \rangle_{r,p} = \frac{E_0 e^{-E_0/k_B T} + E_1 e^{-E_1/k_B T} + \ldots}{e^{-E_0/k_B T} + e^{-E_1/k_B T} + \ldots}.$$ 

The denominator of this expression can be evaluated by using the geometric series formula (page 18). To evaluate the numerator, we can write it as a derivative:

$$\sum_{n=0}^{\infty} nE_1 e^{-nE_1/k_B T} = -\frac{d}{d\beta} \sum_{n=0}^{\infty} e^{-n\beta E_1} \bigg|_{\beta=1/(k_B T)} = -\frac{d}{d\beta} (1 - e^{-\beta E_1})^{-1} \bigg|_{\beta=1/(k_B T)}.$$

To arrive at the total energy density, we integrate this expression over $d^3r d^3p/(2\pi\hbar)^3$ (the $\hbar$ factors are needed to give a dimensionless quantity). Doing the integral over position yields a factor of the cavity’s volume. Doing the integral over the directions of $p$ gives a factor of $4\pi$. There is another factor of 2 because photons have two possible polarizations. Dividing by the volume to obtain energy density yields an expression that agrees with Planck’s empirical formula for the experimentally observed thermal energy spectrum, Equation 1.19.

**1.3.3’d The role of frequency**

The main text regarded “frequency” as an arbitrary label to distinguish various kinds of light (Section 1.3.1, page 27). This attitude may leave doubts about the falsifiable content of the Einstein relation (Equation 1.6, page 34). Is $\nu$ nothing more than an abbreviation for $E_{\text{photon}}/(2\pi\hbar)$? But Section 1.3.3 hinted (and Chapter 4 will show) that $\nu$ can be regarded as the frequency that, in the classical model of light, would reproduce the interference behavior actually observed with a given source. With this definition, both sides of the Einstein relation are independently defined, so it does makes falsifiable predictions.


This statement is part of the Light Hypothesis part 1, Idea 1.11 (page 37).

Section 13.5.1 (page 403) will discuss polarization in detail.
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Moreover, in some situations, photon frequency can be measured more directly. For example, the radio band of the light spectrum involves frequencies much lower than that of visible light, so a lab instrument can simply count wave crests in a particular time window to get the frequency. The energy per photon is correspondingly small, but nevertheless certain nuclear spin transitions have energy splittings in this range, which indeed are found to be induced only by radiation with the frequency predicted by the Einstein relation. This observation (“nuclear magnetic resonance” or NMR) forms the basis for magnetic resonance imaging, which has become both an indispensable medical tool and a method to determine molecular structure.

1.4′ Corrections to Poisson emission and detection

The main text pointed out that, when a light source of uniform intensity illuminates a detector, individual photon detection events follow a random process. The data shown were consistent with a Poisson process, and indeed this is usually an excellent approximation. For example, the distribution of photon counts in a fixed time interval follows Poisson statistics exactly for continuous-wave laser light. An incandescent source, such as the Sun, has a characteristic time scale called its “coherence time.” When we count detector blips over a time window that is much longer than the source’s coherence time, then again the counts are Poisson distributed.

Moreover, photon counts in different time windows separated by an interval $\tau$ are mutually uncorrelated for laser light, and also for sunlight when $\tau$ exceeds the coherence time. (For a discussion see Loudon, 2000, chapt. 6.) Matters are different, however, for more exotic light sources, for example, emission by a single fluorophore or cathode-ray tube.

The distribution of photon detection events depends on the detector as well as on the source. Many detectors have a significant “dead time” after registering a blip, during which they are insensitive to other photons, cutting off the distribution of observed waiting times. Some detector types can give artifacts such as random multiplicative factors, afterpulsing, and so on.

1.5′a Gamma rays

Even before the invention of ultrasensitive electronic detectors for visible light, it was well known that some radioactive substances give off rays that behave like light (“gamma rays”), and that generate discrete blips in radiation detectors. Like the blips from a photomultiplier tube or avalanche photodiode, gamma-ray blips were also found to arrive in a Poisson process; they’re easier to detect individually than visible photons because each carries much more energy.

In positron emission tomography (PET) scanning, a radioactive element is bound into a sugar molecule (typically fluoro-deoxy-glucose, made with the radioactive isotope fluorine-18), which accumulates in tissue wherever metabolism is intense. This
particular kind of radioactivity involves the nucleus emitting a “positron” (the anti-matter counterpart of an electron). Before traveling very far, that positron finds an ordinary electron and they annihilate each other, giving off two photons in the gamma part of the spectrum. The two gamma photons emerge back-to-back, by conservation of momentum. By detecting them both, the PET scan can therefore determine a line along which the original fluorine-18 nucleus was located. After enough such photon pairs have been detected, it becomes possible to infer a three-dimensional map of metabolic activity in the organ being studied, for example, a living patient’s brain.

1.5.1'b More about the Light Hypothesis

1. The Light Hypothesis in the main text only attributes one property to a photon: its energy (or equivalently its frequency or vacuum wavelength). Section 1.3.3'b (page 51) also mentioned momentum, but said that it was determined once we state the photon’s energy and direction of motion. In fact, however, one additional distinction can be made between photons of a given energy and direction: They can have either of two polarizations. We will neglect this aspect of light until Chapter 13, because our eyes do not seem to detect polarization. Light from special sources, like lasers, can have additional characteristics, for example, the degree of coherence among the photons, which lie beyond the scope of this book.

2. The Light Hypothesis states that photons interact with electrons. Photons also interact in the same way with any charged particle, for example, a proton or the positron mentioned in (a) above. For many purposes, however, we can neglect interactions with protons because their effects are suppressed by the proton’s high mass.

3. The Light Hypothesis refers to photon absorption as involving a single electron. In fact, a free (isolated) electron cannot absorb a photon without reemission, because there is no way for that process to conserve energy and momentum. However, an atom or molecule can absorb photons. The atom or molecule recoils to conserve momentum, but is so much more massive than the electron that its recoil absorbs very little energy; thus, it is still a good approximation to say the photon “transfers all its energy” to the electron.

4. Even a free electron can absorb a photon, exist briefly in a state with energy and momentum values that are not normally allowed, then reemit a new photon with a different frequency from the initial one (“Compton scattering”). The difference in incoming and outgoing photon energies shows up in net kinetic energy lost or gained by the electron.

1.5.3’ Mechanism of DNA photodamage

Ultraviolet photons damage the DNA molecules of living organisms in various ways.

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42Section 13.6.4 (page 409) will return to the creation and destruction of electrons and positrons.
43By a linear change of basis, we can equivalently speak of two “spin angular momentum” states for a photon. Electrons, too, are indistinguishable, apart from having two polarization states (“electron spin”).
44Some other animals can detect polarization; see Section 13.7.2.
In one common photodamage event (caused by shorter-wavelength UV light), two adjacent thymine bases bond covalently with each other, instead of forming hydrogen bonds to their partners on the other chain of the double helix (a “thymine dimer,” Figure 1.7). But UV light below the threshold for such direct DNA damage can nevertheless induce “indirect damage,” by exciting another molecule that in turn generates an excited state of an oxygen molecule (a free radical); the oxygen in turn can damage DNA.

1.6.1’ Dense media

1. In dense media, such as water solution, we must extend the definition of the reaction coordinate \( y \) to include also the state of the surrounding water molecules. For example, those molecules can align, setting up a local electric field, which in turn can interact with the molecule of interest via the molecule’s dipole moment.

2. The total energy functions \( U(y) \) in diagrams like Figure 1.9 should also be interpreted as free energy functions, to acknowledge the effect of entropy changes in the surroundings that accompany rearrangement in the one molecule under study.\(^{45}\)

3. Finally, the main text simplified by neglecting the kinetic energy of nuclear motion. In dense media, this sometimes makes sense (friction from surrounding molecules dominates inertial effects). However, for an isolated molecule in vacuum, and sometimes even in solution, the “vibrational spectrum” is significant and must be taken into account; see Section 1.6.3’b.

1.6.2’a More about atoms and light

Section 1.6.2 claimed that, for an atom to revert spontaneously to its ground state, it must lose a sharply defined amount of energy, the difference between the two discrete energy levels. Two finer points must be mentioned.

1. The difference in energy levels may be slightly different from the energy of the emitted photon, because of the uncertainty relation for energy: Extremely short-lived states will have significant uncertainty, and therefore an intrinsic width to their emission spectrum. But for the long-lived states relevant for fluorescence, this source of spectral width is negligible compared to the broadening mechanism discussed in the main text.

2. In principle, the energy difference between levels could be shared between two or more photons of longer wavelength. Such processes are usually much less probable than single-photon emission, but nevertheless they lie at the heart of two-photon microscopy (Section 2.7, page 79) and spontaneous parametric down-conversion (Section 1.3.3’a, page 50).

\(^{45}\)Free energy is discussed, for example, in Dill & Bromberg, 2010, and Nelson, 2014, chapt. 6.
Figure 1.13: [Experimental data with fit.]
Gamma-ray absorption spectrum of iron-57. Error bars reflect the standard deviation of count data (Section 0.5.3, page 16). See also Problem 1.5. The curve shows a constant minus a Cauchy distribution. [Data from Ruby & Bolef, 1960 (Dataset 3).]

1.6.2 A Cauchy distribution in physics
Section 1.6.2 pointed out that the probability for an atom to absorb a photon depends on the photon’s wavelength, and exhibits a peak at some optimal value. Similarly, the photons emitted by an atom as it transitions from an excited to the ground state will have a range of wavelengths, with a probability density function called the emission spectrum. Several real-world complications alter the apparent shape of atomic emission and absorption lines, but analogous spectra can be accurately obtained for some nuclear transitions. Figure 1.13 shows the intensity of gamma-ray light passing through (not absorbed by) a sample of iron-57. A monochromatic emitter was set in motion relative to the sample; the resulting Doppler shift effectively swept it through a narrow range of wavelengths. The solid curve shows a fit to a Cauchy distribution (Equation 0.40, page 13).

1.6.3 Born-Oppenheimer approximation
The main text subdivided a molecule into two sets of variables, describing electrons and nuclei respectively, and proposed that

- The nuclei set up an electrostatic potential energy landscape for the electrons, whose energy levels are then quantized as if the nuclei were fixed in space.
- The electronic energy levels, in turn, create an effective potential energy landscape for the slower motion of the nuclei.

The validity of this “Born–Oppenheimer approximation” (subdividing the system and solving one sector at a time) rests on the fact that an electron has much lower mass than any nucleus, and hence moves much more rapidly. The formal justification can be found in books on molecular quantum mechanics (for example, Atkins & Friedman, 2011; Atkins & de Paula, 2011). In the context of photophysics, this approximation amounts to saying that absorption of a photon instantaneously promotes the electrons to an excited state, and that during this event we may neglect nuclear motions (the “Franck-Condon principle”). Thus, the transitions in Figures 1.9 and 1.12 are shown as vertical lines; horizontal displacement in the figure corresponds to nuclear motion.
1.6.3'b Classical approximation for nuclear motion

The main text described electrons in atoms and molecules as being subject to the Electron State Hypothesis (Idea 1.12, page 40), yet seemed to treat nuclei as classical objects, for example, “sliding with friction” on an effective potential energy landscape (arrows labeled 3, 6, and 6' in Figures 1.9 and 1.12).

In fact, nuclei are subject to the same quantum physics as electrons; for example, their motions give rise to quantized energy levels in an isolated molecule, which can be measured by methods such as Raman spectroscopy. However, in a crowded environment such as water solution, a fluorophore is not isolated. Its constant interaction with neighboring molecules washes out fine structure in its energy levels and destroys its quantum-mechanical coherence on a characteristic time scale shorter than the one for fluorescence.\(^\text{46}\) In such situations, we may treat the fluorophore’s nuclear motion as effectively classical, which helps clarify key features of fluorescence such as the Stokes shift. This approximation breaks down for some ultrafast processes, apparently including those involved in photosynthesis and the photoisomerization of the visual pigment retinal.\(^\text{47}\) We will continue, however, to treat it as a useful approximate guide.

1.6.3'c Debye relaxation

The main text mentioned one complication connected with fluorescence in solution: a “friction” effect that drains away energy from a molecule if its configuration is not close to the one minimizing the effective potential energy function. The origin of this friction was imagined as literal collisions with surrounding water molecules. A more realistic picture also acknowledges the electrostatic coupling between the dipole moment of the excited molecule and those of the highly polar water molecules in its neighborhood (Section 1.6.1'). The loss of energy from a molecule’s internal degrees of freedom into the surroundings by this interaction is called “Debye relaxation.”

1.6.4' Fast conformational changes

The mechanism envisioned in Figure 1.12 for photoisomerization is in some cases an oversimplification. Particularly for molecules with very fast conformation changes, the excited- and ground-state energy curves can approach very close to each other near \(\gamma\). The corresponding electron energy states can then mix quantum-mechanically, giving a very rapid, nonradiative route to the electronic ground state (Bialek, 2012, chapt. 2).

\(^{46}\)Chapter 14 will discuss the role of decoherence in FRET.

\(^{47}\)Section 10.4.1 will introduce the photoisomerization of retinal. For its ultrafast dynamics, see Section 1.6.4’ below and Bialek, 2012.
PROBLEMS

1.1 **Thump**
Newton imagined light as a stream of tiny material particles obeying the same sort of laws as ordinary matter. Benjamin Franklin objected to this model; in 1752 he wrote in a letter “Must not the smallest particle conceivable, have with such a motion, a force exceeding that of a [cannonball]?” Suppose that a tiny particle, weighing just a picogram, could be brought up to the speed of light. Evaluate the Newtonian kinetic energy formula, \( \frac{1}{2}mv^2 \), for this particle, and comment on Franklin’s assertion. Then compare your result to Equation 1.6, with frequency appropriate to visible light.

1.2 **Count distribution**
Prove Equation 1.9.

1.3 **Photon shot noise**
The audio file Media 1 represents a time series, the output of a light detector at very low illumination level, recorded for five seconds. Dataset 1 gives the same information numerically; it contains the arrival times of each individual photon blip.

a. Obtain Dataset 1. (See page xx for how to obtain the datasets.) The first column gives the arrival times of 290 blips, in units of 50\( \text{ns} \). Convert the times to seconds.

b. Convert to a list giving waiting times (time intervals between successive events).

c. Make a convenient choice of time bins and make a histogram of waiting times. Then draw another graph showing the probabilities for each of your bins. Make a third graph showing an estimate of the probability density function. Does your answer resemble one of the families of explicit PDFs in this book’s Prologue? If so, add a second curve to your graph showing a member of that family that appears to match well.

d. Find the sample mean of the waiting times. Convert your list to a string of zeros and ones, where \( s_i = 0 \) if waiting time \( #i \) is smaller than the sample mean, and \( s_i = 1 \) if it’s larger.

e. Find the probability distribution \( P(s_i) \), which is just two numbers because \( s_i \) takes only two values. Find the joint probability distribution \( P_{\text{joint}}(s_i, s_{i+1}) \) of neighboring pairs, which consists of four numbers. Comment on whether the successive waiting times appear to be statistically independent.

f. What else might you want to check to see if successive wait times are independent?

g. Go back to the original list of arrival times. Divide the 5-second total recording time into bins of width 0.1\( \text{s} \). Find how many events happened in each bin. Do a simple calculation to see if this time series might have come from a Poisson process, and comment.

h. Repeat (g) with bins of width 0.05\( \text{s} \) and comment on how the sample mean and variance change.

i. The dataset has 290 blips in five seconds, or a mean rate of 58\( \text{s}^{-1} \). Re-express your answers to (g, h) as follows: From the counts in one bin, you can make an estimate of the average rate of events in that bin. Which bin size, 0.1 or 0.05\( \text{s} \), gives a smaller spread of values around the “true” value, and why?

1.4 **Extreme sensitivity**
If you haven’t done Problem 0.7 (touch sensitivity of skin), do it before this problem.

a. A source creates monochromatic light with vacuum wavelength 550\( \text{nm} \). How much
energy does one photon of this light transfer to an electron when it is absorbed?
b. Chapter 9 will present evidence that your eyes can detect a flash of the light
described in (a) consisting of only 100 photons. Assuming that this claim is true,
how much more sensitive must your eyes be than your skin?

1.5 \[ T_2 \] Spectral line shape

Obtain Dataset 3. Find a Cauchy distribution that gives a good fit to these data (see
Section 1.6.2'b, page 57).