Chapter 4

Light and Matter-Waves and/or Particles

Chapters 4 through 7, taken in sequence, aim to develop an elementary understanding of quantum chemistry: from its experimental and conceptual foundations (Chapter 4), to the one-electron atom (Chapter 5), to the many-electron atom (Chapter 6), and finally to the molecule (Chapter 7).

The present chapter builds to a point where the wave function and uncertainty principle emerge-heuristically, at least-as a way to reconcile the dualistic behavior of waves and particles. Electromagnetic waves undergo interference; so do electrons. "Pinging" atoms transfer energy and momentum; so do photons. A confined wave develops standing modes; so does the electron in hydrogen. The hope is to instill, above all, a respectfor the manifold difference between a deterministic macroworld and a statistical microworld.

The exercises have a further unashamedly practical goal: to help a reader become adept at handling some of the fundamental (yet mathematically simple) equations that underpin quantum mechanics.

1. *The relationship connecting the wavelength, frequency, and speed of a wave (especially as applied to electromagnetic radiation):* $\lambda \nu = c$

2. *The arithmetic of interference,*

   $$(\psi_A + \psi_B)^2 = \psi_A^2 + \psi_B^2 + 2\psi_A\psi_B$$

   and the double-slit diffraction equation as a corollary: $d \sin\theta = n\lambda$

3. *The Planck-Einstein formula:* $E = h\nu$

4. *The momentum of a photon:* $p = \dfrac{h}{\lambda}$

3. A wave crest appears only once per cycle. To observe 7200 crests at one point in space is therefore to observe 7200 completed cycles.

(a) Convert hours into seconds:

$$v = \frac{7200 \text{ cycles}}{\text{h}} \times \frac{1 \text{ h}}{60 \text{ min}} \times \frac{1 \text{ min}}{60 \text{ s}} = 2.0 \text{ cycles s}^{-1} = 2.0 \text{ Hz}$$

Two cycles, on the average, are completed every second; the *frequency* is 2.0 Hz.

(b) Period (T) is the reciprocal of frequency (v):

$$T = \frac{1}{v} = \frac{1}{2.0 \text{ s}^{-1}} = 0.50 \text{ s}$$

The time needed to complete *one* cycle (the period) is 0.50 s.

4. The 10 1 crests delineate 100 full cycles:

Cycle: |←1→|←2→| ··· |←100→|
Crest: 1 2 3 100 101

Since 100 cycles (not 101) are executed over a distance of 20 cm, the average wavelength is 0.20 cm, or 0.0020 m:

$$\lambda = \frac{20 \text{cm}}{100 \text{ cycles}} \times \frac{1 \text{m}}{100 \text{ cm}} = 0.0020 \text{ m} \quad \text{(per cycle)}$$

5. Given the speed (u) and wavelength (h),

$$u = 100 \text{ m s}^{-1}$$

$$\lambda = 2 \text{ m} \quad \text{(distance between troughs)}$$

we solve for the frequency (v) and period (T) of the wave:

$$\lambda\nu = u$$

$$\nu = \frac{u}{\lambda} = \frac{100 \text{ m s}^{-1}}{2 \text{ m}} = 50 \text{ s}^{-1}$$

$$T = \frac{1}{\nu} = \frac{1}{50 \text{ s}^{-1}} = 0.02 \text{ s}$$

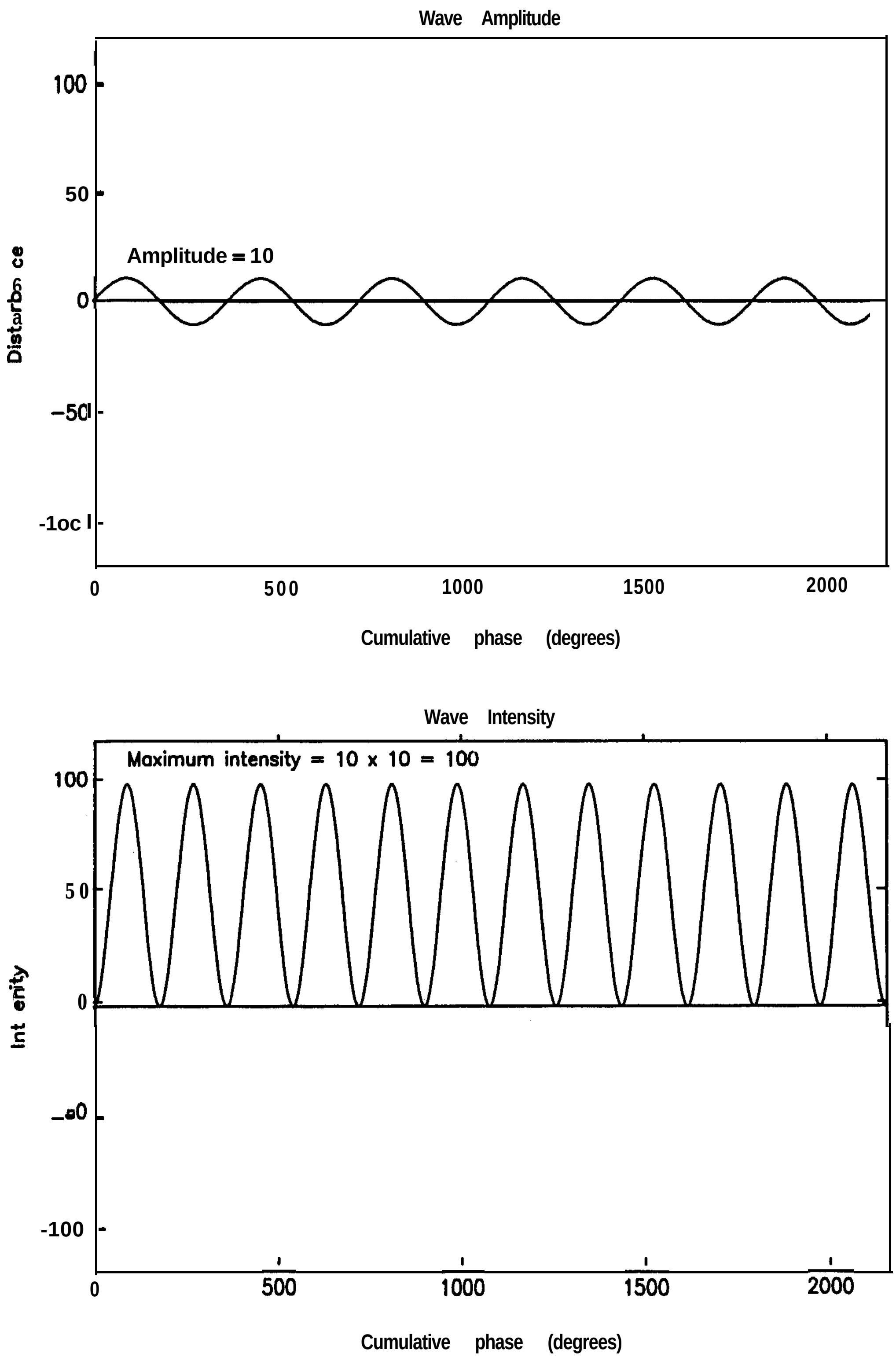


FIGURE 4.1 Wave patterns for Exercise 7. The upper panel shows the sinusoidal disturbance itself, oscillating positive and negative with an amplitude of 10 units. The intensity, depicted below, is everywhere positive and has a maximum value of 100 units (the square of the amplitude).

(a) See the graphs displayed in Figure 4.2 (next page). The wavelength off+ g remains the same as forfand g alone, but the combined amplitude doubles and the combined intensity quadruples:

$$\text{Amplitude: } A + A = 10 + 10 = 20$$

$$\text{Maximum intensity: } (A + A)^2 = 20^2 = 400$$

(b) With $A = 10$ for bothfand g, the combined intensity

$$I \propto 4A^2 \sin^2\theta = 400 \sin^2\theta$$

oscillates between a minimum of 0 (when $\sin^2\theta = 0$) and a maximum of $4A^2 = 400$ (when $\sin^2\theta = 1$):

$$0 \le I \le 400$$

(c) Energy is maximum at crest and trough.

(d) Energy is minimum (zero) where the disturbance is zero: midway between crest and trough.

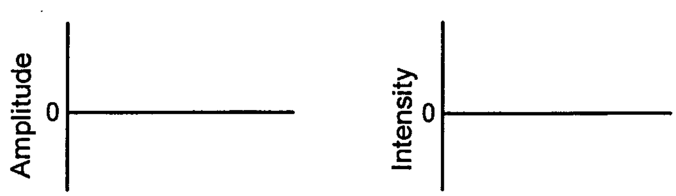
9. Destructive interference. Here we have two waves equal in amplitude and frequency, but differing in phase by π radians (180”):

$$f = A\sin\theta$$

$$g = A\sin(\theta + \pi) = -A\sin\theta$$

The oscillations are out of step by half a cycle: When f is at a crest, g is in a trough; when f is in a trough, g is at a crest. See Figure 4.3 on the second page following.

(a) The two waves, out of phase by 180°, annihilate each other. The combined amplitude and intensity are both zero-flat lines:



(b, c, d) Energy is zero everywhere.

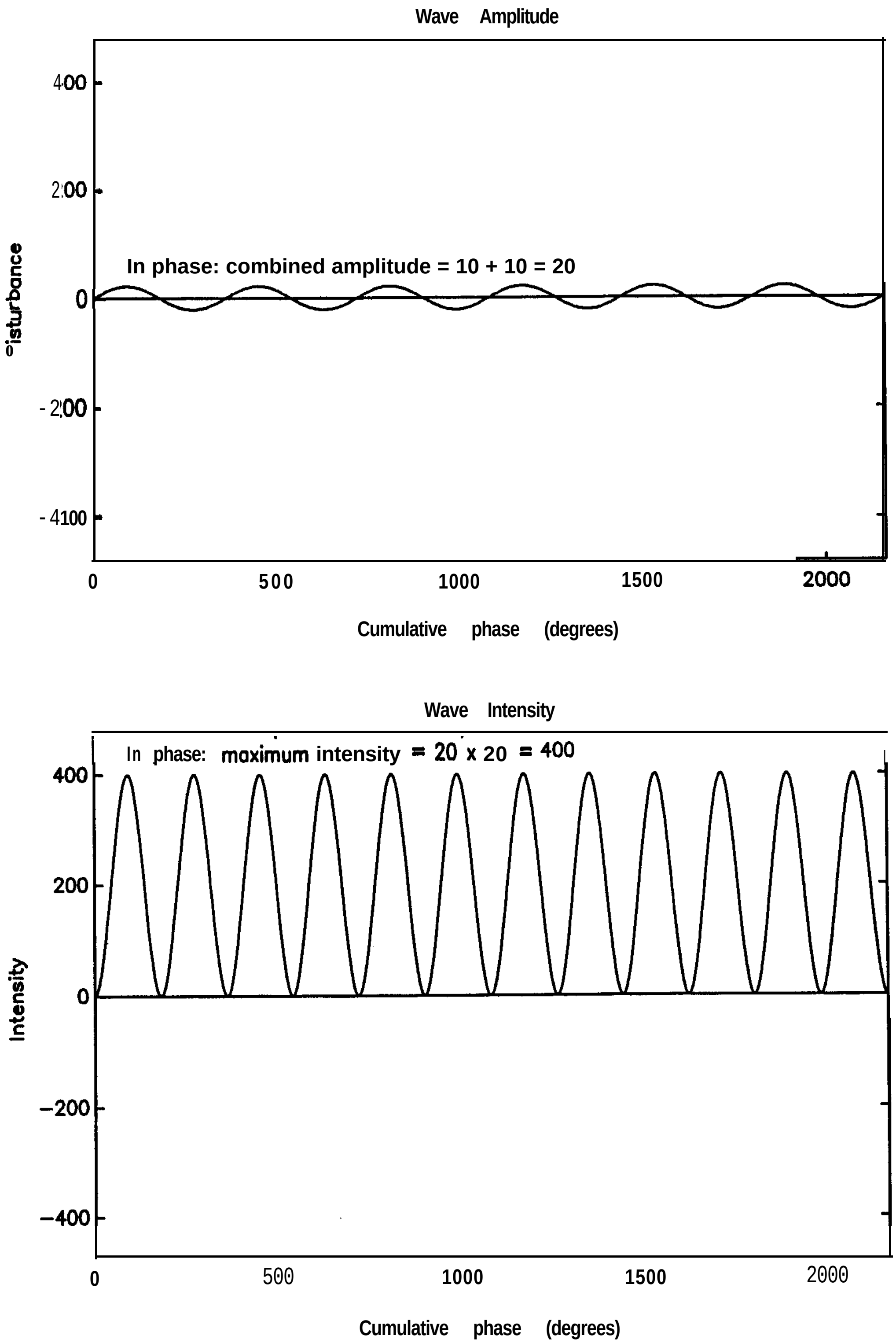


FIGURE 4.2 Wave patterns for Exercise 8. The combined amplitude of identical waves $f + g$ (upper panel) measures 20 units, twice the value found for the uncombined wave in Figure 4.1. The maximum intensity, the *square* of the amplitude, measures 400 units-four times the value obtained from the uncombined wave.

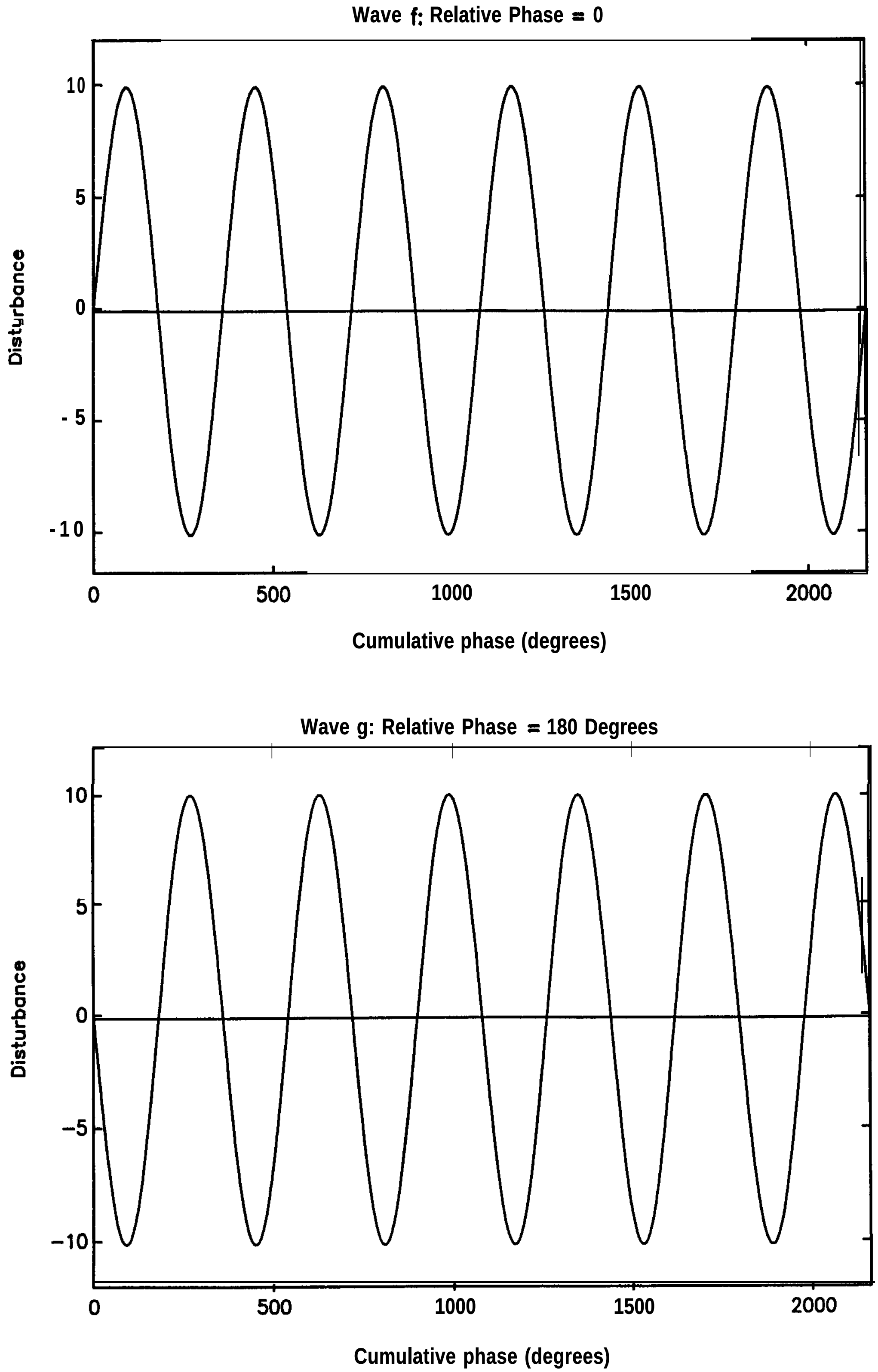


FIGURE 4.3 **Wave patterns for Exercise 9. Out of phase by one half-cycle (180°),** the two disturbances interfere destructively. Their combined amplitude and intensity are zero.

10. The waves will combine constructively, *in phase,* when their path lengths differ by some integral number of wavelengths:

$$d\sin\theta = n\lambda \qquad (n = 1, 2, \ldots)$$

For $n = 1$ (the first maximum) we find that the corresponding wavelength is 5.0×10^{-7} m, or 500 nm:

$$\lambda = d\sin\theta = (1.0 \times 10^{-6}\text{ m})(\sin 30^\circ)$$

$$= 5.0 \times 10^{-7}\text{ m} \times \frac{1\text{ nm}}{10^{-9}\text{ m}} = 5.0 \times 10^{2}\text{ nm}$$

See pages 113-115 of *PoC* and also Example 4-3 (beginning on page R4.8).

11. Use, as in the preceding exercise, the double-slit diffraction equation with $n = 1$:

$$d\sin\theta = n\lambda = \lambda \qquad (n = 1)$$

Specifying a wavelength of exactly 1 mm, for example, we see that a slit spacing of 2.9 mm will produce (within two significant figures) a diffraction maximum at 20°:

$$d = \frac{\lambda}{\sin\theta} = \frac{10^{-3}\text{ m}}{\sin 20^\circ} = 2.9 \times 10^{-3}\text{ m}$$

The remaining values follow directly:

	λ (m)	d (m)
(a)	10^{-3}	2.9×10^{-3}
(b)	10^{-6}	2.9×10^{-6}
(c)	10^{-9}	2.9×10^{-9}

Exercises 12 through 15 pertain to the classical picture of electromagnetic radiation.

12. We use the term *electromagnetic wave* to describe the influence produced by an oscillating electric and magnetic field. Propagating in vacuum at the speed of light,

$$c \approx 3.00 \times 10^{8}\text{ m s}^{-1}$$

the influence exerts a force on charged particles and electric currents. Wavelengths range from zero to infinity, in principle, with the corresponding frequencies determined reciprocally:

$$\lambda\nu = c$$

See pages 105-l 11, R4.2–R4.3, and Examples 4-1 and 4-2 in *PoC*.

13. In vacuum, electromagnetic waves propagate at the same speed regardless of frequency:

$$c = 2.99792458 \times 10^8 \text{ m s}^{-1}$$

The distance traveled in 1 .OOO s is therefore the same for each of the frequencies stated:

$$(2.99792458 \times 10^8 \text{ m s}^{-1})(1.000 \text{ s}) = 2.998 \times 10^8 \text{ m} \approx 3.00 \times 10^8 \text{ m}$$

QUESTION: Are there circumstances under which the speed of light will vary with frequency?

ANSWER: Yes, the phenomenon is very common. First, the value c is fixed only in vacuum. Everywhere else-in any material medium (plastic, glass, silicon, water, air, . . .)—electromagnetic waves travel at speeds ***slower*** than $2.99792458 \times 10^8 \text{ m s}^{-1}$, although the deviation in air is very slight. A parameter called the ***index of refraction (n)*** relates the speed in a material (u) to the speed in vacuum (c):

$$u = \frac{c}{n}$$

The index is different for different substances. Yellow-green light near 5500 A, for example, travels through air with $n = 1.0003$, but it travels through water with $n = 1.33$ and through glass with $n \approx 1.6$.

Second, even in the same material, the index of refraction varies with frequency and wavelength. We see this very effect, called ***dispersion,*** in the colors of the rainbow. Various wavelengths of visible light travel at different speeds through a glass prism, dispersing into bands of colors as the rays emerge at different points.

Remember, finally, that we often use the term "light" to mean electromagnetic radiation in general, not just the restricted portion of the spectrum known as ***visible*** light. Dispersion properties vary widely across the electromagnetic spectrum, and a material transparent to, say, X rays may well be opaque to ultraviolet or visible light.

QUESTION: Granted, electromagnetic radiation travels slower than c in a medium-but can it sometimes travel faster than c as well?

ANSWER: No. Classical electromagnetic theory fixes c as the maximum speed of transmission, attainable only in vacuum. Further, Einstein's theory of special relativity (see Chapter 2 1) shows that no signal of any kind may convey information faster than c.

QUESTION: The universe apparently imposes a large but finite speed limit: c = 3.00 x 10^8 m s^{-1}, the speed of light in vacuum. But now we know that light in a material (not vacuum) always propagates at some speed u *slower* than c. Is it possible for an object or signal to travel faster than u in a given material?

ANSWER: Yes, and the phenomenon can lead to interesting effects-sometimes even to an electromagnetic "shock wave" analogous to the sonic boom produced by a supersonic aircraft.

14. To calculate the wavelength, use the relationship

$$\lambda\nu = c$$

where c = 2.998 x 10^8 m s^{-1}. For example (with v = 7.67 x 10^{15} Hz):

$$\lambda = \frac{c}{v} = \frac{2.998 \times 10^8 \text{ m s}^{-1}}{7.67 \times 10^{15} \text{ s}^{-1}} = 3.91 \times 10^{-8} \text{ m}$$

Converting prefixed units as needed,

$$1 \text{ Hz} = 10^{-3} \text{ kHz} = 10^{-6} \text{ MHz} = 10^{-9} \text{ GHz} = 1 \text{ s}^{-1}$$

we then determine the full set of wavelengths:

	v (s^{-1} ≡ Hz)	λ (m)	COMMENT
(a)	7.67 x 10^{15}	3.91 x 10^{-8}	ultraviolet (≈ 400 A)
(b)	7.70 x 10^5	3.89 x 10^2	radio (770 kHz)
(c)	3.17 x 10^8	9.46 x 10^{-1}	radio (3 17 MHz)
(d)	1.03 x 10^9	2.91 x 10^{-1}	microwave (1.03 GHz)
(e)	5.00 x 10^{14}	6.00 x 10^{-7}	visible (600 nm, 6000 Å)
(f)	8.02 x 10^{13}	3.74 x 10^{-6}	infrared (≈ 4 μm)

Figure 4-4 and the text on pages 11 O-l 11 of *PoC* provide a rough breakdown of the electromagnetic spectrum according to wavelength and frequency.

15. Here we calculate the frequency v given the wavelength λ. Substitute

$$c = 2.998 \times 10^8 \text{ m s}^{-1}$$

into the equation

$$\lambda\nu = c$$

and solve for ν, making use of the following conversion factors:

$$1 \text{ m} = 10^3 \text{ mm} = 10^6 \text{ μm} = 10^9 \text{ nm} = 10^{10} \text{ Å}$$

One calculation of this type should suffice. Choose $\lambda = 0.761$ Å $= 7.6\ 1 \times 10^{-11}$ m:

$$\nu = \frac{c}{\lambda} = \frac{2.998 \times 10^8 \text{ m s}^{-1}}{7.61 \times 10^{-11} \text{ m}} = 3.94 \times 10^{18} \text{ s}^{-1}$$

Consult pages 110-l 11 in *PoC* to assign each wavelength to its portion of the electromagnetic spectrum:

	λ (m)	ν ($s^{-1} \equiv$ Hz)	COMMENT
(a)	7.61×10^{-11}	3.94×10^{18}	X ray (0.761 Å, borderline γ)
(b)	4.01×10^{-3}	7.48×10^{10}	microwave (4.01 mm, borderline ir)
(c)	1.15×10^{2}	2.61×10^{6}	radio (2.61 MHz)
(d)	5.617×10^{-7}	5.337×10^{14}	visible (5617 Å, 561.7 nm)
(e)	2.18×10^{-7}	1.38×10^{15}	ultraviolet (2180 Å, 218 nm)
(f)	1.06×10^{-6}	2.83×10^{14}	infrared (1.06 μm)

The shorter the wavelength, the higher the frequency.

Photons and the photoelectric effect are covered in Exercises 16 through 24. See Section 4-4, pages R4.3–R4.4, and Examples 4-4 and 4-5 in PoC.

16. Use the relationship

$$E = h\nu$$

between photon energy (E) and frequency (ν), substituting the value

$$h = 6.63 \times 10^{-34} \text{ J s}$$

for Planck's constant and converting all prefixed units of frequency into s^{-1}:

$$1 \text{ Hz} = 10^{-6} \text{ MHz} = 10^{-9} \text{ GHz} = 1 \text{ s}^{-1}$$

One sample calculation (for ν = 1 MHz) will illustrate the procedure:

$$E = h\nu = (6.63 \times 10^{-34} \text{ J s})\left(1 \text{ MHz} \times \frac{10^6 \text{ s}^{-1}}{\text{MHz}}\right) = 6.63 \times 10^{-28} \text{ J}$$

Full results follow:

	ν (Hz ≡ s^{-1})	E (J)	COMMENT
(a)	10^6	**6.63** x 10^{-28}	radio (1 MHz, 300 m)
(b)	10^8	**6.63** x 10^{-26}	radio (100 MHz, 3 m)
(c)	10^9	**6.63** x 10^{-25}	microwave (1 GHz, 0.3 m)
(d)	10^{12}	**6.63** x 10^{-22}	infrared (0.3 mm)
(e)	10^{15}	**6.63** x 10^{-19}	ultraviolet (3000 A)
(f)	10^{18}	**6.63** x 10^{-16}	X ray (3 A)

The higher the frequency, the higher the energy.

17. Combine the equation

$$\lambda\nu = c$$

with the Planck-Einstein relationship

$$E = h\nu$$

to obtain the dependence of photon energy on wavelength:

$$E = \frac{hc}{\lambda}$$

Thus for a wavelength of exactly 1 m, the corresponding energy has magnitude *hc:*

$$E = \frac{hc}{\lambda} = \frac{(6.626 \times 10^{-34}\ \text{J s})(2.998 \times 10^{8}\ \text{m s}^{-1})}{1\ \text{m}} = 1\ 986 \times 10^{-25}\ \text{J}$$

To express this benchmark energy in $kJ\ mol^{-1}$, as requested, we convert joules into kilojoules and multiply by Avogadro's number:

$$E = \frac{1.986 \times 10^{-25}\ \text{J}}{\text{photon}} \times \frac{1\ \text{kJ}}{1000\ \text{J}} \times \frac{6.022 \times 10^{23}\ \text{photons}}{\text{mole}} = 1.196 \times 10^{-4}\ \text{kJ mol}^{-1}$$

Three digits will be enough, however, for our present purposes, and so we shall take

$$E = 1.99 \times 10^{-25}\ \text{J per photon} = 1.20 \times 10^{-4}\ \text{kJ mol}^{-1}$$

as an approximate reference value. Energies for wavelengths other than 1 m scale in inverse proportion, provided that prefixed units of length are reexpressed in meters:

	λ (m)	*E* (J per photon)	*E* (kJ mol^{-1})	COMMENT
(a)	10^{0}	1.99×10^{-25}	1.20×10^{-4}	radio (1 m)
(b)	10^{-3}	1.99×10^{-22}	1.20×10^{-1}	infrared/microwave (1 mm)
(c)	10^{-6}	1.99×10^{-19}	1.20×10^{2}	infrared (1 μm)
(d)	10^{-9}	1.99×10^{-16}	1.20×10^{5}	X ray (1 nm)
(e)	10^{-12}	1.99×10^{-13}	1.20×10^{8}	γ ray (1 pm)
(f)	10^{-15}	1.99×10^{-10}	1.20×10^{11}	γ ray (1 fm)

The shorter the wavelength, the higher the energy.

18. A minor variation on the preceding exercise. We use the relationship

$$E = h\nu = \frac{hc}{\lambda}$$

to solve for frequency and wavelength:

$$\nu = \frac{E}{h} \qquad \lambda = \frac{hc}{E}$$

The calculation for $E = 10^{-26}$ J is typical:

$$\nu = \frac{E}{h} = \frac{10^{-26}\ \text{J}}{6.626 \times 10^{-34}\ \text{J s}} = 1.509 \times 10'\ \text{s}^{-1}$$

$$\lambda = \frac{hc}{E} = \frac{(6.626 \times 10^{-34}\ \text{J s})(2.998 \times 10^{8}\ \text{m s}^{-1})}{10^{-26}\ \text{J}} = 19\ 86\ \text{m}$$

The full set of values is tabulated below to three digits:

	E (J)	ν (Hz ≡ s^{-1})	λ (m)	COMMENT
(a)	10^{-26}	**1.51 x 10’**	1.99 x 10’	radio (≈20 m, 15 MHz)
(b)	10^{-25}	1.51×10^{8}	1.99×10^{0}	radio (≈2 m, 150 MHz)
(c)	10^{-21}	1.51×10^{12}	1.99×10^{-4}	infrared (≈0.2 mm)
(d)	10^{-20}	1.51×10^{13}	1.99×10^{-5}	infrared (≈20 pm)
(e)	10^{-19}	1.51×10^{14}	1.99×10^{-6}	infrared (≈2 μm)
(f)	10^{-16}	1.51 x 10”	1.99×10^{-9}	X ray (≈2 nm)

As energy goes up, so does the frequency. The wavelength, shorter at higher energies, decreases in inverse proportion.

19. Note the definition of electrical power implicit in the statement of the problem:

$$\text{Power} = \frac{\text{energy}}{\text{time}} \sim \frac{\text{J}}{\text{s}} \equiv \text{W (watt)}$$

(a) Given both power and time, we can calculate the total energy radiated:

$$\text{Energy} = \text{power x time}$$

To obtain a value in joules, we need only to convert the time from hours into seconds:

$$\text{Energy} = \frac{60.\ \text{J}}{\text{s}} \times \left(1\ \text{h} \times \frac{3600\ \text{s}}{\text{h}}\right) = 2.2 \times 10^5\ \text{J}$$

Wattage and time alone--irrespective of wavelength-specify the macroscopic energy.

(b) The total energy carried by N photons, E_N, is the sum of N quanta (each equal to hv):

$$E_N = Nh\nu = \frac{Nhc}{\lambda}$$

Inserting the wavelength λ (given as 5000 Å = 5.000 x 10^{-7} m) and the energy calculated above (2.16 x 10^5 J before round-off), we then solve for N:

$$N = \frac{\lambda E_N}{hc} = \frac{(5.000 \text{ x } 10^{-7}\ \text{m})(2.16 \text{ x } 10^5\ \text{J})}{(6.626 \text{ x } 10^{-34}\ \text{J s})(2.998 \text{ x } 10^8\ \text{m s}^{-1})} = 5.4 \text{ x } 10^{23} \text{ photons}$$

20. Carry over, from the preceding exercise, the expression we derived for the photon number N that gives rise to a total radiant energy E_N:

$$N = \frac{\lambda E_N}{hc}$$

Substituting unit values for λ and E_N, we first calculate a reference photon number

$$N = \frac{1}{hc} \quad (\lambda = 1\ \text{m},\ E_N = 1\ \text{J})$$

to be used throughout:

$$N = \frac{(1.00\ \text{m})(1.00\ \text{J})}{(6.626 \text{ x } 10^{-34}\ \text{J s})(2.998 \text{ x } 10^8\ \text{m s}^{-1})} = 5.03 \text{ x } 10^{24} \text{ photons} \quad (1\ \text{m},\ 1\ \text{J})$$

Values for all of the requested wavelengths scale in direct proportion:

		λ (m)	N
(a)	km	10^{3}	5.03×10^{27}
(b)	m	10^{0}	5.03×10^{24}
(c)	mm	10^{-3}	5.03×10^{21}
(d)	μm	10^{-6}	5.03×10^{18}
(e)	nm	10^{-9}	5.03×10^{15}
(f)	pm	10^{-12}	5.03×10^{12}
(g)	fm	10^{-15}	5.03×10^{9}

The shorter the wavelength, the more energetic is the photon. ***Fewer*** such photons are needed to produce a given total energy.

21. We use our workhorse equation

$$E = h\nu = \frac{hc}{\lambda}$$

once again, this time solving for the wavelength λ_0 that exactly matches the work function ($E_0 = 3.43 \times 10^{-19}$ J):

$$\lambda_0\ 10\frac{hc}{E_0} = \frac{(6.626 \times 10^{-34}\ \text{J s})(2.998 \times 10^{8}\ \text{m s}^{-1})}{343\text{x}\ 10^{-19}\ \text{J}} = 5.79 \text{ x} \qquad \text{m}$$

The threshold wavelength is 5.79×10^{-7} m (equivalently, 579 nm or 5790 A). Any photon with a longer wavelength will have an energy ***less*** than the required work function, 3.43×10^{-19} J.

22. Knowing the work function ($E_0 = 3.69 \times 10^{-19}$ J), we establish a maximum wavelength above which ***no*** photoelectron will be ejected:

$$\lambda_0 = \frac{hc}{E_0} = \frac{(6.626 \times 10^{-34}\ \text{J s})(2.998 \times 10^{8}\ \text{m s}^{-1})}{3.69 \times 10^{-19}\ \text{J}} = 5.38 \times 10^{-7}\ \text{m}\ \ (538\text{nm})$$

(a) A wavelength of 538 nm is just barely sufficient to overcome the work function. Each photon has an energy

$$E = h\nu = \frac{hc}{\lambda} = 3.69 \times 10^{-19}\ \text{J}$$

equal to E_0, as shown above for $\lambda = \lambda_0$.

Given the total energy E_N delivered by N photons,

$$E_N = Nh\nu = 3.69 \text{ x } 10^{-16} \text{ J}$$

we then calculate the number of quanta:

$$N = \frac{E_N}{h\nu} = \frac{3.69 \text{ x } 10^{-16} \text{ J}}{3.69 \times 10^{-19} \text{ J}} = 1.00 \times 10^3$$

(b) Wavelength = 500 nm. Here the individual photon energy

$$E = h\nu = \frac{hc}{\lambda} = \frac{(6.626 \times 10^{-34} \text{ J s})(2.998 \text{ x } 10^8 \text{ m s}^{-1})}{5.00 \text{ x } 10^{-7} \text{ m}} = 3.97 \text{ x } 10^{-19} \text{ J}$$

exceeds the work function ($E_0 = 3.69 \text{ x } 10^{-19}$ J), and therefore each photoelectron will emerge with a certain excess kinetic energy:

$$E_k = h\nu - E_0$$

The ***number*** of such photoelectrons, however, will be no greater than the number of incident photons that deliver the known total energy ($E_N = 3.97 \text{ x } 10^{-16}$ J):

$$N = \frac{E_N}{h\nu} = \frac{3.97 \times 10^{-16} \text{ J}}{3.97 \text{ x } 10^{-19} \text{ J}} = 1.00 \times 10^3$$

(c) Photons with a wavelength of 600 nm are insufficiently energetic, one by one, to expel a photoelectron from the metal. No photocurrent will be produced under any circumstances, even though the total energy ($E_N = 3.31 \text{ x } 10^{-14}$ J) is comparatively high.

23. Similar to Example 4-5. Ask, first, whether each individual photon can deliver enough energy to eject an electron:

$$E = h\nu = \frac{hc}{\lambda} = \frac{(6.6261 \times 10^{-34} \text{ J s})(2.9979 \times 10^8 \text{ m s}^{-1})}{4.390 \text{ x } 10^{-7} \text{ m}} = 4.5249 \times 10^{-19} \text{ J}$$

It can: The photon energy ($4.52 \text{ x } 10^{-19}$ J) is greater than the work function (given as $4.41 \text{ x } 10^{-19}$ J).

Note, in passing, that we have used the conversion

$$1 \text{ Å} = 10^{-10} \text{ m}$$

to reexpress λ in meters. Also, to minimize machine errors in this particular exercise, we quote ***h*** and c to five digits and (as usual) do not round off the intermediate results.

(a) Any difference between the photon energy $(E = hv)$ and the work function (E_0) is carried away by the photoelectron in the form of kinetic energy:

$$E_k = hv - E_0$$

$$= (4.5249 - 4.41) \times 10^{-19} \text{ J}$$

$$= 0.1149 \times 10^{-19} \text{ J}$$

$$= 1.1 \times 10^{-20} \text{ J} \quad \text{(2 sig fig)}$$

From the kinetic energy,

$$E_k = \frac{1}{2}mv^2$$

we then compute the magnitude of the velocity:

$$v = \sqrt{\frac{2E_k}{m}}$$

$$= \sqrt{\frac{2(1.149 \times 10^{-20} \text{ J})}{9.11 \times 10^{-31} \text{ kg}}} = \sqrt{\frac{2(1.149 \times 10^{-20} \text{ kg m}^2 \text{ s}^{-2})}{9.11 \times 10^{-31} \text{ kg}}}$$

$$= 1.59 \times 10^5 \text{ m s}^{-1}$$

$$= 1.6 \times 10^5 \text{ m s}^{-1} \quad \text{(2 sig fig)}$$

And also the momentum:

$$p = mv$$

$$= (9.11 \times 10^{-31} \text{ kg})(1.59 \times 10^5 \text{ m s}^{-1})$$

$$= 1.4 \times 10^{-25} \text{ kg m s}^{-1} \quad \text{(2 sig fig)}$$

(b) Each of N photons contributes

$$E = hv = 4.5249 \times 10^{-19} \text{ J}$$

to produce a total energy of 5.00 joules:

$$E_N = Nhv = 5.00 \text{ J}$$

The resulting value of N is good to three significant figures:

$$N = \frac{E_N}{h\nu} = \frac{5.00\text{ J}}{4.5249 \times 10^{-19}\text{ J}} = 1.10 \times 10^{19}$$

If each photon ejects a photoelectron (our implicit assumption), then illumination at this intensity will produce 1.10×10^{19} photoelectrons.

24. Here the energy of a single photon,

$$E = h\nu = (6.626 \times 10^{-34}\text{ J s})(6.63 \times 10^{13}\text{ s}^{-1}) = 4.39 \times 10^{-20}\text{ J}$$

is insufficient to overcome the stated work function:

$$E_0 = 4.41 \times 10^{-19}\text{ J}$$

No photocurrent will be produced.

Exercises in the next group deal with the de Broglie wavelength, illustrating its variability even among microscopic particles. Exercises 2.5 and 28 demonstrate, for example, that an electron has ***not just*** one *de Broglie wavelength, but rather it has as many de Broglie wavelengths as it has possible velocities. Exercises 26, 27, and 29 show that particles with different masses (electrons andprotons) will have the same de Broglie wavelength* ***if*** *they have the same momenta-but not* ***if they*** *have the same velocity Exercise 30, concluding the block, demonstrates that* λ_{deB} ***effectively*** *vanishes for macroscopic objects. See pages 133-136, page R4.4, and Example 4-6 in* PoC.

25. The de Broglie wavelength

$$\lambda_{deB} = \frac{h}{p} = \frac{h}{mv} \qquad (1)$$

is determined by the momentum of the particle:

$$p = mv$$

The momentum, in turn, is determined by the kinetic energy,

$$E_k = \frac{1}{2}mv^2 = \frac{p^2}{2m}$$

from which we derive an alternative expression for the magnitude ofp:

$$p = \sqrt{2mE_k} \qquad (2)$$

Combining equations (1) and (2), we then have a form

$$\lambda_{deB} = \frac{h}{p} = \frac{h}{\sqrt{2mE_k}} \qquad (3)$$

in which the kinetic energy is simply the difference between the photon energy ($E = h\nu = hc/\lambda$) and the work function:

$$E_k = E - E_0 = \frac{hc}{\lambda} - E_0 \qquad (4)$$

Note that λ (without subscript) denotes here the wavelength of the incident light, whereas the subscripted λ_{deB} in (3) denotes the de Broglie wavelength of the ejected photoelectron.

The units of λ_{deB}, finally, reduce properly to meters:

$$\lambda_{deB} = \frac{h}{\sqrt{2mE_k}} \sim \frac{\text{J s}}{\sqrt{\text{kg J}}} = \frac{\left(\text{kg m}^2\ \text{s}^{-2}\right)\text{s}}{\sqrt{\text{kg}\left(\text{kg m}^2\ \text{s}^{-2}\right)}} = \text{m}$$

(a) Arising from a wavelength of 3.0×10^{-7} m, the energy of the photon matches—but does not exceed—a work function of 6.6×10^{-19} J:

$$E = \frac{hc}{\lambda} = \frac{(6.626 \times 10^{-34}\ \text{J s})(2.998 \times 10^{8}\ \text{m s}^{-1})}{3.0 \times 10^{-7}\ \text{m}} = 6.6 \times 10^{-19}\ \text{J}$$

With little or no excess kinetic energy,

$$E_k = E - E_0 = (6.6 - 6.6) \times 10^{-19}\ \text{J} = 0$$

the photoelectron behaves as if its de Broglie wavelength were approaching infinity.

(b) Substitute the values

$$\lambda = 2.8 \times 10^{-7}\ \text{m}$$

$$E_0 = 6.6 \times 10^{-19}\ \text{J}$$

$$h = 6.626 \times 10^{-34}\ \text{J s}$$

$$c = 2.998 \times 10^{8}\ \text{m s}^{-1}$$

$$m = 9.11 \times 10^{-31}\ \text{kg}$$

into the expressions for E_k and λ_{deB} derived above:

$$E_k = \frac{hc}{\lambda} - E_0$$

$$\lambda_{deB} = \frac{h}{\sqrt{2mE_k}}$$

The value obtained for λ_{deB} is 2.2 x 10^{-9} m, approximately 2 nanometers.

(c) Recalculate λ_{deB} using the same method as in part (b), this time taking λ = 2.5 x 10^{-7} m for the wavelength of the photon. With more kinetic energy imparted to the photon, the value of λ_{deB} falls to approximately 1 nanometer:

$$\lambda_{deB} = 1.3 \times 10^{-9} \text{ m}$$

The de Broglie wavelength decreases as the velocity of the photoelectron increases.

26. Substitute

$$\lambda_{deB} = 1 \text{ Å} = 10^{-10} \text{ m}$$

into the defining relationship,

$$p = \frac{h}{\lambda_{deB}}$$

and solve for the momentum:

$$p = \frac{6.63 \times 10^{-34} \text{ J s}}{10^{-10} \text{ m}} = \frac{6.63 \times 10^{-34} (\text{kg m}^2 \text{ s}^{-2}) \text{ s}}{10^{-10} \text{ m}} = 6.63 \times 10^{-24} \text{ kg m s}^{-1}$$

The associated velocity follows directly:

$$p = mv$$

$$v = \frac{p}{m} = \frac{6.63 \times 10^{-24} \text{ kg m s}^{-1}}{9.11 \times 10^{-31} \text{ kg}} = 7.28 \times 10^6 \text{ m s}^{-1}$$

27. The de Broglie wavelength,

$$\lambda_{deB} = \frac{h}{P}$$

is identical for any two particles that happen to have the same momentum. Thus a proton with a wavelength of 1 Å,

$$\lambda_{deB} = 1 \text{ Å} = 10^{-10} \text{ m}$$

carries the same momentum as an electron with an equivalent 1-Å wavelength. Mass does not enter explicitly into the calculation:

$$p = \frac{h}{\lambda_{deB}}$$

$$= \frac{6.63 \times 10^{-34} \text{ J s}}{10^{-10} \text{ m}} = \frac{6.63 \times 10^{-34} (\text{kg m}^2 \text{ s}^{-2}) \text{ s}}{10^{-10} \text{ m}}$$

$$= 6.63 \times 10^{-24} \text{ kg m s}^{-1}$$

The velocity, however, derives from the relationship

$$p = mv$$

and scales in inverse proportion to the mass:

$$v = \frac{p}{m} = \frac{6.63 \times 10^{-24} \text{ kg m s}^{-1}}{1.67 \times 10^{-27} \text{ kg}} = 3.97 \times 10^{3} \text{ m s}^{-1}$$

The proton, more massive than the electron, moves more slowly for a given amount of momentum.

28. See Example l-6, beginning on page R1.14 of *PoC*, for the relationship between voltage and electrical work:

Work = voltage x charge transferred

The volt, with units of joules per coulomb, specifies the difference in potential energy between two points in an electric field:

$$1 \text{ V} = \frac{1 \text{ J}}{\text{C}}$$

An electron, with negative charge of magnitude e = 1.60 x 10^{-19} C, thus has a kinetic energy of 1.60 x 10^{-19} J after accelerating through a potential difference of 1 volt:

$$\frac{1 \text{ J}}{\text{C}} \times (1.60 \times 10^{-19} \text{ C}) = 1.60 \times 10^{-19} \text{ J}$$

When the potential difference is increased to 10^4 V, as here, the kinetic energy goes up by the same factor:

$$E_k = \frac{10^4 \text{ J}}{\text{C}} \times (1.60 \times 10^{-19} \text{ C})$$

$$= 1.60 \times 10^{-15} \text{ J}$$

$$= 1.60 \times 10^{-15} \text{ kg m}^2 \text{ s}^{-2}$$

Substituting both this value and the mass of an electron ($m = 9.11 \times 10^{-31}$ kg) into the expression for kinetic energy,

$$E_k = \frac{1}{2}mv^2$$

we solve for the terminal velocity (ignoring a small relativistic correction):

$$v = \sqrt{\frac{2E_k}{m}} = \sqrt{\frac{2(1.60 \times 10^{-15} \text{ kg m}^2 \text{ s}^{-2})}{9.11 \times 10^{-31} \text{ kg}}} = 5.93 \times 10^7 \text{ m s}^{-1}$$

The de Broglie wavelength, finally, is determined by the mass and velocity together:

$$\lambda_{\text{deB}} = \frac{h}{mv} = \frac{6.626 \times 10^{-34} (\text{kg m}^2 \text{ s}^{-2}) \text{ s}}{(9.11 \times 10^{-31} \text{ kg})(5.93 \times 10^7 \text{ m s}^{-1})} = 1.23 \times 10^{-11} \text{ m}$$

29. Since the charge on a proton,

$$e = 1.60 \times 10^{-19} \text{ C}$$

has the same magnitude as the charge on an electron, the proton attains the same kinetic energy calculated in the preceding example, Electrical energy is independent of mass:

$$E_k = \text{voltage} \times \text{charge transferred} = \text{electrical work}$$

$$= \frac{10^4 \text{ J}}{\text{C}} \times (1.60 \times 10^{-19} \text{ C})$$

$$= 1.60 \times 10^{-15} \text{ J}$$

$$= 1.60 \times 10^{-15} \text{ kg m}^2 \text{ s}^{-2}$$

With the larger mass, however, the proton accelerates to a smaller velocity but to a larger momentum-and consequently develops a smaller de Broglie wavelength.

The velocity (from $E_k = \frac{1}{2}mv^2$):

$$v = \sqrt{\frac{2E_k}{m}} = \sqrt{\frac{2\left(1.60 \times 10^{-15} \text{ kg m}^{-2} \text{ s}^{-2}\right)}{1.67 \times 10^{-27} \text{ kg}}} = 1.384 \times 10^6 \text{ m s}^{-1}$$

$= 1.38 \times 10^6 \text{ m s}^{-1}$ (3 sig fig)

The de Broglie wavelength:

$$\lambda_{deB} = \frac{h}{mv} = \frac{6.626 \times 10^{-34} (\text{kg m}^2 \text{ s}^{-2}) \text{ s}}{(1.67 \times 10^{-27} \text{ kg})(1.384 \times 10^6 \text{ m s}^{-1})} = 2.87 \times 10^{-13} \text{ m}$$

30. With objects so massive, the de Broglie wavelengths prove to be vanishingly small—far smaller than any atomic or nuclear scale.

(a) Substitute mass and velocity into the de Broglie relationship:

$$\lambda_{deB} = \frac{h}{mv} = \frac{6.63 \times 10^{-34} \left(\text{kg m}^2 \text{ s}^{-2}\right) \text{s}}{(70 \text{ kg})(10 \text{ m s}^{-1})} = 9.5 \times 10^{-37} \text{ m}$$

(b) Reexpress 10 g as 0.010 kg:

$$\lambda_{deB} = \frac{h}{mv} = \frac{6.63 \times 10^{-34} \text{ J s}}{(0.010 \text{ kg})(250 \text{ m s}^{-1})} = 2.7 \times 10^{-34} \text{ m}$$

(c) Convert grams into kilograms and miles per hour into meters per second:

$$200 \text{ g} \times \frac{1 \text{ kg}}{1000 \text{ g}} = 0.200 \text{ kg}$$

$$\frac{100 \text{ mi}}{\text{h}} \times \frac{5280 \text{ ft}}{\text{mi}} \times \frac{12 \text{ in}}{\text{ft}} \times \frac{2.54 \text{ cm}}{\text{in}} \times \frac{1 \text{ m}}{100 \text{ cm}} \times \frac{1 \text{ h}}{3600 \text{ s}} = 44.7 \text{ m s}^{-1}$$

The resulting de Broglie wavelength is 7.42×10^{-35} m:

$$\lambda_{deB} = \frac{h}{mv} = \frac{6.63 \times 10^{-34} \text{ J s}}{(0.200 \text{ kg})(44.7 \text{ m s}^{-1})} = 7.42 \times 10^{-35} \text{ m}$$

(d) The equivalence between mass (kilograms) and weight (pounds) in the earth's gravitational field is stated in Table C-4 of Appendix C (*PoC*, page A64):

$$0.453592 \text{ kg} \equiv 1 \text{ lb}$$

We convert pounds into kilograms and miles per hour into meters per second,

$$4000 \text{ lb} \times \frac{0.453592 \text{ kg}}{\text{lb}} = 1814 \text{ kg}$$

$$\frac{60 \text{ mi}}{\text{h}} \times \frac{5280 \text{ ft}}{\text{mi}} \times \frac{12 \text{ in}}{\text{ft}} \times \frac{2.54 \text{ cm}}{\text{in}} \times \frac{1 \text{ m}}{100 \text{ cm}} \times \frac{1 \text{ h}}{3600 \text{ s}} = 26.8 \text{ m s}^{-1}$$

from which we obtain the corresponding de Broglie wavelength:

$$\lambda_{\text{deB}} = \frac{h}{mv} = \frac{6.63 \times 10^{-34} \text{ J s}}{(1814 \text{ kg})(26.8 \text{ m s}^{-1})} = 1.4 \times 10^{-38} \text{ m}$$

The result is limited to two significant figures by the initial value of velocity.

The set concludes with an exploration of the Heisenberg uncertainty principle, similar in spirit to the treatment of the de Broglie wavelength just above. Issues considered include the basic operation and applicability of Heisenberg's equation, the difference between momentum and velocity, the effect of mass, and the apparent restoration of deterministic certainty in macroscopic systems. See pages 142-144, page R4.5, and Example 4-7 in PoC.

31. The uncertainty principle puts limits only on the *simultaneous* measurement of momentum and position:

$$\Delta p \Delta x > \approx h$$

We can measure either quantity (p or x) to theoretically arbitrary accuracy, albeit one at the expense of the other.

Thus to determine an electron's momentum with vanishing uncertainty ($\Delta p = 0$), we must do so under conditions where the uncertainty in position,

$$\Delta x > \frac{h}{\Delta p}$$

approaches infinity. To determine p with absolute certainty is to forfeit all knowledge of x, and—with perfect symmetry—to determine x with absolute certainty is to forfeit all knowledge of p. The two uncertainties *are relative*, not absolute; they stand in inverse proportion.

32. An electron confined to a small region in space manifests a large uncertainty in momentum. We know ***where*** the particle is, but we do not know what it is doing-its speed, direction, and momentum.

A poorly localized electron, by contrast, has a well-defined momentum within the limits of the Heisenberg uncertainty principle. The spreads in momentum and velocity decrease as the spatial interval becomes larger (Δx increases).

Since the positional uncertainty in our present system is already fixed ($\Delta x = |x_2 - x_1|$), the related uncertainty in momentum is bounded by the Heisenberg relationship. We continue to use the approximate form:

$$\Delta p \, \Delta x > h$$

$$\Delta p > \frac{h}{\Delta x}$$

The uncertainty in velocity is then determined straightforwardly from the definition of momentum:

$$\Delta p = m \Delta v > \frac{h}{\Delta x}$$

$$\Delta v > \frac{h}{m \Delta x}$$

Note further that the uncertainty in x,

$$\Delta x = |x_2 - x_1|$$

depends only on the ***difference*** between x_2 and x_1, not on any absolute position. Hence Δx is the same in parts (a), (b), and (c),

$$\Delta x = 1 \text{ mm} = 1 \times 10^{-3} \text{ m}$$

and we shall use this value for a rough sample calculation (rounded off to just one digit):

$$\Delta p > \frac{h}{\Delta x} = \frac{6.63 \times 10^{-34} \left(\text{kg m}^2 \text{ s}^{-2}\right) \text{s}}{1 \times 10^{-3} \text{ m}} \approx 7 \times 10^{-31} \text{ kg m s}^{-1}$$

$$\Delta v > \frac{h}{m \Delta x} = \frac{6.63 \times 10^{-34} \left(\text{kg m}^2 \text{ s}^{-2}\right) \text{s}}{(9.11 \times 10^{-31} \text{ kg})(1 \times 10^{-3} \text{ m})} \approx 0.7 \text{ m s}^{-1}$$

A complete set follows on the next page.

	Δx (m)	Δp (kg m s^{-1})	Δv (m s^{-1})
(a)	10^{-3}	$> 7 \times 10^{-31}$	$> 7 \times 10^{-1}$
(b)	10^{-3}	$> 7 \times 10^{-31}$	$> 7 \times 10^{-1}$
(c)	10^{-3}	$> 7 \times 10^{-31}$	$> 7 \times 10^{-1}$
(d)	10^{-6}	$> 7 \times 10^{-28}$	$> 7 \times 10^{2}$
(e)	10^{-9}	$> 7 \times 10^{-25}$	$> 7 \times 10^{5}$

33. Given a value for the kinetic energy,

$$E_k = \frac{1}{2}mv^2 = \frac{p^2}{2m}$$

$$= 1.6 \times 10^{-16} \text{ J}$$

$$= 1.6 \times 10^{-16} \text{ kg m}^2 \text{ s}^{-2}$$

we calculate the associated momentum and velocity.

Momentum:

$$p = \sqrt{2mE_k} = \sqrt{2(9.11 \times 10^{-31} \text{ kg})(1.6 \times 10^{-16} \text{ kg m}^2 \text{ s}^{-2})} = 1.7 \times 10^{-23} \text{ kg m s}^{-1}$$

Velocity:

$$p = mv$$

$$v = \frac{p}{m} = \frac{1.7 \times 10^{-23} \text{ kg m s}^{-1}}{9.11 \times 10^{-31} \text{ kg}} = 1.9 \times 10^7 \text{ m s}^{-1}$$

To estimate the minimum spreads in momentum, we then consult the corresponding uncertainties Δp already computed in the previous exercise-which remain fixed for a given spread in position, Δx:

	Δx (m)	$p \pm \Delta p$ (kg m s^{-1})	$v \pm \Delta v$ (m s^{-1})
(a)	10^{-3}	$(1.7 \times 10^{-23}) \pm (7 \times 10^{-31})$	$(1.9 \times 10^{7}) \pm (7 \times 10^{-1})$
(b)	10^{-6}	$(1.7 \times 10^{-23}) \pm (7 \times 10^{-28})$	$(1.9 \times 10^{7}) \pm (7 \times 10^{2})$
(c)	10^{-9}	$(1.7 \times 10^{-23}) \pm (7 \times 10^{-25})$	$(1.9 \times 10^{7}) \pm (7 \times 10^{5})$

Observe here that the indeterminacy in momentum,

$$\Delta p > \frac{h}{\Delta x}$$

is inversely proportional to Ax and thus becomes more important as the opening narrows. The percent uncertainties in momentum, for example, range from a mere

$$\frac{\Delta p}{p} \times 100\% \approx 0.000004\%$$

when Δx = 1 mm to a more substantial 4% when Ax = 1 nm.

34. Use the same method as in Exercises 32 and 33, this time substituting

$$m = 1.67 \times 10^{-27} \text{ kg}$$

for the mass of the particle.

Momentum:

$$p = \sqrt{2mE_k} = \sqrt{2\left(1.67 \times 10^{-27} \text{ kg})(1.6 \times 10^{-16} \text{ kg m}^2 \text{ s}^{-2}\right)} = 7.3 \times 10^{-22} \text{ kg m s}^{-1}$$

Velocity:

$$v = \frac{p}{m} = \frac{7.3 \times 10^{-22} \text{ kg m s}^{-1}}{1.67 \times 10^{-27} \text{ kg}} = 4.4 \times 10^5 \text{ m s}^{-1}$$

The values of Ap, dependent only on Ax, are the same for proton and electron. The proton's 1836-fold larger mass, however, shows up in its smaller values of Av:

	Δx (m)	$p \pm Ap$ (kg m s^{-1})	v ± Av (m s^{-1})
(a)	10^{-3}	$(7.3 \times 10^{-22}) \pm (7 \times 10^{-31})$	$(4.4 \times 10^5) \pm (4 \times 10^{-4})$
(b)	10^{-6}	$(7.3 \times 10^{-22}) \pm (7 \times 10^{-28})$	$(4.4 \times 10^5) \pm (4 \times 10^{-1})$
(c)	10^{-9}	$(7.3 \times 10^{-22}) \pm (7 \times 10^{-25})$	$(4.4 \times 10^5) \pm (4 \times 10^2)$

35. The method is the same as in the preceding three exercises. Results are tabulated at the top of the next page:

PARTICLE	MASS (kg)	Δx (m)	p ± Ap (kg m s^{-1})	v ± Av (m s^{-1})
(a) He	6.65 x 10^{-27}	10^{-3}	$(1.5 \times 10^{-21}) \pm (7 \times 10^{-31})$	$(2.2 \times 10^{5}) \pm (1 \times 10^{-4})$
		10”	$(1.5 \times 10^{-21}) \pm (7 \times 10^{-28})$	$(2.2 \times 10^{5}) \pm (1 \times 10^{-1})$
		10^{-9}	$(1.5 \times 10^{-21}) \pm (7 \times 10^{-25})$	$(2.2 \times 10^{5}) \pm (1 \times 10^{2})$
(b) N_2	4.65 x 10^{-26}	10^{-3}	$(3.9 \times 10^{-21}) \pm (7 \times 10^{-31})$	$(8.3 \times 10^{4}) \pm (1 \times 10^{-5})$
		10^{-6}	$(3.9 \times 10^{-21}) \pm (7 \times 10^{-28})$	$(8.3 \times 10^{4}) \pm (1 \times 10^{-2})$
		10^{-9}	$(3.9 \times 10^{-21}) \pm (7 \times 10^{-25})$	(8.3×10^{4}) ± (1 x 10’)
(c) $C_{12}H_{22}O_{11}$	5.68 x 10^{-25}	10^{-3}	$(1.3 \times 10^{-20}) \pm (7 \times 10^{-31})$	(2.4×10^{4}) ± (1 x 10”)
		10”	$(1.3 \times 10^{-20}) \pm (7 \times 10^{-28})$	$(2.4 \times 10^{4}) \pm (1 \times 10^{-3})$
		10^{-9}	$(1.3 \times 10^{-20}) \pm (7 \times 10^{-25})$	$(2.4 \times 10^{4}) \pm (1 \times 10^{0})$

36. The approximate uncertainty in velocity,

$$\Delta v > \text{k c} \frac{h}{m\Delta x} -$$

proves to be infinitesimally small for a macroscopic system. A large mass ensures that Av will be a tiny fraction of the velocity: $\Delta v/v << 1$.

(a) Converting grams into kilograms and microns into meters,

$$m=lOOgx \ \frac{1\text{ kg}}{1000\text{ g}} = 0.100\text{ kg}$$

$$\Delta x = 1\ \mu\text{m} \times \frac{1\text{ m}}{10^{6}\ \mu\text{m}} = 1 \times 10^{-6}\text{ m}$$

we obtain Av in meters per second:

$$\Delta v > \frac{h}{m\Delta x} = \frac{6.63 \times 10^{-34}\ (\text{kg m}^2\,\text{s}^{-2})\text{ s}}{(0.100\text{ kg})(1 \times 10^{-6}\text{ m})} = 7 \times 10^{-27}\text{ m s}^{-1}$$

(b) The percent indeterminacy in velocity is minuscule:

$$\frac{\Delta v}{v} \times 100\% = \frac{7 \times 10^{-27}\text{ m s}^{-1}}{30\text{ m s}^{-1}} \times 100\% = \left(2 \times 10^{-26}\right)\%$$

37. The description implies that Ap = 0. If so, then Ax must be infinite and we can say nothing about the position. The free electron is, so to speak, a "big" particle, completely delocalized. It might be anywhere. We don't know.

38. Near the nucleus, where the electron's indeterminacy in position is small, its indeterminacy in momentum is correspondingly large. See pages 150-l 5 1 in *PoC*.