Part 2: Structure

11 Quantum theory: introduction and principles

Solutions to exercises

Discussion questions

E11.1(b) A successful theory of black-body radiation must be able to explain the energy density distribution of the radiation as a function of wavelength, in particular, the observed drop to zero as $\lambda \to 0$. Classical theory predicts the opposite. However, if we assume, as did Planck, that the energy of the oscillators that constitute electromagnetic radiation are quantized according to the relation $E = nh\nu = nhc/\lambda$, we see that at short wavelengths the energy of the oscillators is very large. This energy is too large for the walls to supply it, so the short-wavelength oscillators remain unexcited. The effect of quantization is to reduce the contribution to the total energy emitted by the black-body from the high-energy short-wavelength oscillators, for they cannot be sufficiently excited with the energy available.

E11.2(b) In quantum mechanics all dynamical properties of a physical system have associated with them a corresponding operator. The system itself is described by a wavefunction. The observable properties of the system can be obtained in one of two ways from the wavefunction depending upon whether or not the wavefunction is an eigenfunction of the operator.

When the function representing the state of the system is an eigenfunction of the operator Ω, we solve the eigenvalue equation (eqn 11.30)

$$\Omega\Psi = \omega\Psi$$

in order to obtain the observable values, ω, of the dynamical properties.

When the function is not an eigenfunction of Ω, we can only find the average or expectation value of dynamical properties by performing the integration shown in eqn 11.39

$$\langle\Omega\rangle = \int \Psi^*\Omega\Psi \, d\tau.$$

E11.3(b) No answer.

Numerical exercises

E11.4(b) The power is equal to the excitance M times the emitting area

$$\begin{aligned} P &= MA = \sigma T^4(2\pi rl) \\ &= (5.67 \times 10^{-8}\,\mathrm{W\,m^{-2}\,K^{-4}}) \times (3300\,\mathrm{K})^4 \times (2\pi) \times (0.12 \times 10^{-3}\,\mathrm{m}) \times (5.0 \times 10^{-2}\,\mathrm{m}) \\ &= \boxed{2.5 \times 10^2\,\mathrm{W}} \end{aligned}$$

Comment. This could be a 250 W incandescent light bulb.

E11.5(b) Wien's displacement law is

$$T\lambda_{\max} = c_2/5 \quad \text{so} \quad \lambda_{\max} = \frac{c_2}{5T} = \frac{1.44 \times 10^{-2}\,\mathrm{m\,K}}{5(2500\,\mathrm{K})} = 1.15 \times 10^{-6}\,\mathrm{m} = \boxed{1.15\,\mu\mathrm{m}}$$

E11.6(b) The de Broglie relation is

$$\lambda = \frac{h}{p} = \frac{h}{mv} \quad \text{so} \quad v = \frac{h}{m\lambda} = \frac{6.626 \times 10^{-34}\,\mathrm{J\,s}}{(1.675 \times 10^{-27}\,\mathrm{kg}) \times (3.0 \times 10^{-2}\,\mathrm{m})}$$

$$v = \boxed{1.3 \times 10^{-5}\,\mathrm{m\,s^{-1}}}$$

E11.7(b) The de Broglie relation is

$$\lambda = \frac{h}{p} = \frac{h}{mv} \quad \text{so} \quad v = \frac{h}{m\lambda} = \frac{6.626 \times 10^{-34}\,\text{J s}}{(9.11 \times 10^{-31}\,\text{kg}) \times (0.45 \times 10^{-9}\,\text{m})}$$

$$v = \boxed{1.6 \times 10^{6}\,\text{m s}^{-1}}$$

E11.8(b) The momentum of a photon is

$$p = \frac{h}{\lambda} = \frac{6.626 \times 10^{-34}\,\text{J s}}{350 \times 10^{-9}\,\text{m}} = \boxed{1.89 \times 10^{-27}\,\text{kg m s}^{-1}}$$

The momentum of a particle is

$$p = mv \quad \text{so} \quad v = \frac{p}{m} = \frac{1.89 \times 10^{-27}\,\text{kg m s}^{-1}}{2(1.0078 \times 10^{-3}\,\text{kg mol}^{-1}/6.022 \times 10^{23}\,\text{mol}^{-1})}$$

$$v = \boxed{0.565\,\text{m s}^{-1}}$$

E11.9(b) The energy of the photon is equal to the ionization energy plus the kinetic energy of the ejected electron

$$E_{\text{photon}} = E_{\text{ionize}} + E_{\text{electron}} \quad \text{so} \quad \frac{hc}{\lambda} = E_{\text{ionize}} + \tfrac{1}{2}mv^2$$

$$\text{and } \lambda = \frac{hc}{E_{\text{ionize}} + \frac{1}{2}mv^2} = \frac{(6.626 \times 10^{-34}\,\text{J s}) \times (2.998 \times 10^{8}\,\text{m s}^{-1})}{5.12 \times 10^{-18}\,\text{J} + \frac{1}{2}(9.11 \times 10^{-31}\,\text{kg}) \times (345 \times 10^{3}\,\text{m s}^{-1})^2}$$

$$= 3.48 \times 10^{-8}\,\text{m} = \boxed{38.4\,\text{nm}}$$

E11.10(b) The uncertainty principle is

$$\Delta p \Delta x \geq \tfrac{1}{2}\hbar$$

so the minimum uncertainty in position is

$$\Delta x = \frac{\hbar}{2\Delta p} = \frac{\hbar}{2m\Delta v} = \frac{1.0546 \times 10^{-34}\,\text{J s}}{2(9.11 \times 10^{-31}\,\text{kg}) \times (0.000\,010) \times (995 \times 10^{3}\,\text{m s}^{-1})}$$

$$= \boxed{5.8 \times 10^{-6}\,\text{m}}$$

E11.11(b) $E = h\nu = \dfrac{hc}{\lambda}$; $\quad E(\text{per mole}) = N_A E = \dfrac{N_A hc}{\lambda}$

$$hc = (6.62608 \times 10^{-34}\,\text{J s}) \times (2.99792 \times 10^{8}\,\text{m s}^{-1}) = 1.986 \times 10^{-25}\,\text{J m}$$

$$N_A hc = (6.02214 \times 10^{23}\,\text{mol}^{-1}) \times (1.986 \times 10^{-25}\,\text{J m}) = 0.1196\,\text{J m mol}^{-1}$$

Thus, $E = \dfrac{1.986 \times 10^{-25}\,\text{J m}}{\lambda}$; $E(\text{per mole}) = \dfrac{0.1196\,\text{J m mol}^{-1}}{\lambda}$

We can therefore draw up the following table

λ	E/J	$E/(\mathrm{kJ\,mol^{-1}})$
(a) 200 nm	9.93×10^{-19}	598
(b) 150 pm	1.32×10^{-15}	7.98×10^{5}
(c) 1.00 cm	1.99×10^{-23}	0.012

E11.12(b) Assuming that the ^{4}He atom is free and stationary, if a photon is absorbed, the atom acquires its momentum p, achieving a speed v such that $p = mv$.

$$v = \frac{p}{m} \qquad m = 4.00 \times 1.6605 \times 10^{-27}\,\mathrm{kg} = 6.64\bar{2} \times 10^{-27}\,\mathrm{kg}$$

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

(a) $$p = \frac{6.626 \times 10^{-34}\,\mathrm{J\,s}}{200 \times 10^{-9}\,\mathrm{m}} = 3.31\bar{3} \times 10^{-27}\,\mathrm{kg\,m\,s^{-1}}$$

$$v = \frac{p}{m} = \frac{3.31\bar{3} \times 10^{-27}\,\mathrm{kg\,m\,s^{-1}}}{6.642 \times 10^{-27}\,\mathrm{kg}} = \boxed{0.499\,\mathrm{m\,s^{-1}}}$$

(b) $$p = \frac{6.626 \times 10^{-34}\,\mathrm{J\,s}}{150 \times 10^{-12}\,\mathrm{m}} = 4.41\bar{7} \times 10^{-24}\,\mathrm{kg\,m\,s^{-1}}$$

$$v = \frac{p}{m} = \frac{4.41\bar{7} \times 10^{-24}\,\mathrm{kg\,m\,s^{-1}}}{6.642 \times 10^{-27}\,\mathrm{kg}} = \boxed{665\,\mathrm{m\,s^{-1}}}$$

(c) $$p = \frac{6.626 \times 10^{-34}\,\mathrm{J\,s}}{1.00 \times 10^{-2}\,\mathrm{m}} = 6.626 \times 10^{-32}\,\mathrm{kg\,m\,s^{-1}}$$

$$v = \frac{p}{m} = \frac{6.626 \times 10^{-32}\,\mathrm{kg\,m\,s^{-1}}}{6.642 \times 10^{-27}\,\mathrm{kg}} = \boxed{9.98 \times 10^{-6}\,\mathrm{m\,s^{-1}}}$$

E11.13(b) Each emitted photon increases the momentum of the rocket by h/λ. The final momentum of the rocket will be Nh/λ, where N is the number of photons emitted, so the final speed will be $\dfrac{Nh}{\lambda m_{\mathrm{rocket}}}$.
The rate of photon emission is the power (rate of energy emission) divided by the energy per photon (hc/λ), so

$$N = \frac{tP\lambda}{hc} \quad \text{and} \quad v = \left(\frac{tP\lambda}{hc}\right) \times \left(\frac{h}{\lambda m_{\mathrm{rocket}}}\right) = \frac{tP}{cm_{\mathrm{rocket}}}$$

$$v = \frac{(10.0\,\mathrm{yr}) \times (365\,\mathrm{day\,yr^{-1}}) \times (24\,\mathrm{h\,day^{-1}}) \times (3600\,\mathrm{s\,h^{-1}}) \times (1.50 \times 10^{3}\,\mathrm{W})}{(2.998 \times 10^{8}\,\mathrm{m\,s^{-1}}) \times (10.0\,\mathrm{kg})}$$

$$= \boxed{158\,\mathrm{m\,s^{-1}}}$$

E11.14(b) Rate of photon emission is rate of energy emission (power) divided by energy per photon (hc/λ)

(a) $$\text{rate} = \frac{P\lambda}{hc} = \frac{(0.10\,\mathrm{W}) \times (700 \times 10^{-9}\,\mathrm{m})}{(6.626 \times 10^{-34}\,\mathrm{J\,s}) \times (2.998 \times 10^{8}\,\mathrm{m\,s^{-1}})} = \boxed{3.52 \times 10^{17}\,\mathrm{s^{-1}}}$$

(b) $$\text{rate} = \frac{(1.0\,\mathrm{W}) \times (700 \times 10^{-9}\,\mathrm{m})}{(6.626 \times 10^{-34}\,\mathrm{J\,s}) \times (2.998 \times 10^{8}\,\mathrm{m\,s^{-1}})} = \boxed{3.52 \times 10^{18}\,\mathrm{s^{-1}}}$$

E11.15(b) Wien's displacement law is

$$T\lambda_{\max} = c_2/5 \quad \text{so} \quad T = \frac{c_2}{5\lambda_{\max}} = \frac{1.44 \times 10^{-2}\,\mathrm{m\,K}}{5(1600 \times 10^{-9}\,\mathrm{m})} = \boxed{1800\,\mathrm{K}}$$

E11.16(b) Conservation of energy requires

$$E_{\text{photon}} = \Phi + E_K = h\nu = hc/\lambda \quad \text{so} \quad E_K = hc/\lambda - \Phi$$

and $E_K = \frac{1}{2}m_e v^2$ so $v = \left(\dfrac{2E_K}{m_e}\right)^{1/2}$

(a) $$E_K = \frac{(6.626 \times 10^{-34}\,\text{J s}) \times (2.998 \times 10^8\,\text{m s}^{-1})}{650 \times 10^{-9}\,\text{m}} - (2.09\,\text{eV}) \times (1.60 \times 10^{-19}\,\text{J eV}^{-1})$$

But this expression is negative, which is unphysical. There is no kinetic energy or velocity because the photon does not have enough energy to dislodge the electron.

(b) $$E_K = \frac{(6.626 \times 10^{-34}\,\text{J s}) \times (2.998 \times 10^8\,\text{m s}^{-1})}{195 \times 10^{-9}\,\text{m}} - (2.09\,\text{eV}) \times (1.60 \times 10^{-19}\,\text{J eV}^{-1})$$

$$= \boxed{6.84 \times 10^{-19}\,\text{J}}$$

and $$v = \left(\frac{2(3.20 \times 10^{-19}\,\text{J})}{9.11 \times 10^{-31}\,\text{kg}}\right)^{1/2} = \boxed{1.23 \times 10^6\,\text{m s}^{-1}}$$

E11.17(b) $E = h\nu = h/\tau$, so

(a) $E = 6.626 \times 10^{-34}\,\text{J s}/2.50 \times 10^{-15}\,\text{s} = \boxed{2.65 \times 10^{-19}\,\text{J} = 160\,\text{kJ mol}^{-1}}$

(b) $E = 6.626 \times 10^{-34}\,\text{J s}/2.21 \times 10^{-15}\,\text{s} = \boxed{3.00 \times 10^{-19}\,\text{J} = 181\,\text{kJ mol}^{-1}}$

(c) $E = 6.626 \times 10^{-34}\,\text{J s}/1.0 \times 10^{-3}\,\text{s} = \boxed{6.62 \times 10^{-31}\,\text{J} = 4.0 \times 10^{-10}\,\text{kJ mol}^{-1}}$

E11.18(b) The de Broglie wavelength is

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

The momentum is related to the kinetic energy by

$$E_K = \frac{p^2}{2m} \quad \text{so} \quad p = (2mE_K)^{1/2}$$

The kinetic energy of an electron accelerated through 1 V is $1\,\text{eV} = 1.60 \times 10^{-19}\,\text{J}$, so

$$\lambda = \frac{h}{(2mE_K)^{1/2}}$$

(a) $$\lambda = \frac{6.626\times10^{-34}\,\mathrm{J\,s}}{(2(9.11\times10^{-31}\,\mathrm{kg})\times(100\,\mathrm{eV})\times(1.60\times10^{-19}\,\mathrm{J\,eV^{-1}}))^{1/2}} = \boxed{1.23\times10^{-10}\,\mathrm{m}}$$

(b) $$\lambda = \frac{6.626\times10^{-34}\,\mathrm{J\,s}}{(2(9.11\times10^{-31}\,\mathrm{kg})\times(1.0\times10^{3}\,\mathrm{eV})\times(1.60\times10^{-19}\,\mathrm{J\,eV^{-1}}))^{1/2}} = \boxed{3.9\times10^{-11}\,\mathrm{m}}$$

(c) $$\lambda = \frac{6.626\times10^{-34}\,\mathrm{J\,s}}{(2(9.11\times10^{-31}\,\mathrm{kg})\times(100\times10^{3}\,\mathrm{eV})\times(1.60\times10^{-19}\,\mathrm{J\,eV^{-1}}))^{1/2}} = \boxed{3.88\times10^{-12}\,\mathrm{m}}$$

E11.19(b) The minimum uncertainty in position is $\boxed{100\,\mathrm{pm}}$. Therefore, since $\Delta x\Delta p \geq \frac{1}{2}\hbar$

$$\Delta p \geq \frac{\hbar}{2\Delta x} = \frac{1.0546\times10^{-34}\,\mathrm{J\,s}}{2(100\times10^{-12}\,\mathrm{m})} = 5.3\times10^{-25}\,\mathrm{kg\,m\,s^{-1}}$$

$$\Delta v = \frac{\Delta p}{m} = \frac{5.3\times10^{-25}\,\mathrm{kg\,m\,s^{-1}}}{9.11\times10^{-31}\,\mathrm{kg}} = \boxed{5.8\times10^{-5}\,\mathrm{m\,s^{-1}}}$$

E11.20(b) Conservation of energy requires

$$E_{\mathrm{photon}} = E_{\mathrm{binding}} + \tfrac{1}{2}m_e v^2 = h\nu = hc/\lambda \quad \text{so} \quad E_{\mathrm{binding}} = hc/\lambda - \tfrac{1}{2}m_e v^2$$

and $$E_{\mathrm{binding}} = \frac{(6.626\times10^{-34}\,\mathrm{J\,s})\times(2.998\times10^{8}\,\mathrm{m\,s^{-1}})}{121\times10^{-12}\,\mathrm{m}} - \tfrac{1}{2}(9.11\times10^{-31}\,\mathrm{kg})\times(5.69\times10^{7}\,\mathrm{m\,s^{-1}})^2 = \boxed{1.67\times10^{-16}\,\mathrm{J}}$$

Comment. This calculation uses the non-relativistic kinetic energy, which is only about 3 per cent less than the accurate (relativistic) value of 1.52×10^{-15} J. In this exercise, however, E_{binding} is a small difference of two larger numbers, so a small error in the kinetic energy results in a larger error in E_{binding}: the accurate value is $E_{\mathrm{binding}} = 1.26\times10^{-16}$ J.

Solutions to problems

Solutions to numerical problems

P11.3 $$\theta_E = \frac{h\nu}{k}, \qquad [\theta_E] = \frac{\mathrm{J\,s}\times\mathrm{s^{-1}}}{\mathrm{J\,K^{-1}}} = \mathrm{K}$$

In terms of θ_E the Einstein equation [11.9] for the heat capacity of solids is

$$C_V = 3R\left(\frac{\theta_E}{T}\right)^2\times\left(\frac{e^{\theta_E/2T}}{e^{\theta_E/T}-1}\right)^2, \quad \text{classical value} = 3R$$

It reverts to the classical value when $T \gg \theta_E$ or when $\frac{h\nu}{kT} \ll 1$ as demonstrated in the text (Section 11.1). The criterion for classical behaviour is therefore that $\boxed{T \gg \theta_E}$.

$$\theta_E = \frac{h\nu}{k} = \frac{(6.626\times10^{-34}\,\mathrm{J\,Hz^{-1}})\times\nu}{1.381\times10^{-23}\,\mathrm{J\,K^{-1}}} = 4.798\times10^{-11}\,(\nu/\mathrm{Hz})\mathrm{K}$$

(a) For $\nu = 4.65 \times 10^{13}$ Hz, $\theta_E = (4.798 \times 10^{-11}) \times (4.65 \times 10^{13}\,K) = \boxed{2231\,K}$

(b) For $\nu = 7.15 \times 10^{12}$ Hz, $\theta_E = (4.798 \times 10^{-11}) \times (7.15 \times 10^{12}\,K) = \boxed{343\,K}$

Hence

(a) $$\frac{C_V}{3R} = \left(\frac{2231\,K}{298\,K}\right)^2 \times \left(\frac{e^{2231/(2\times298)}}{e^{2231/298} - 1}\right)^2 = \boxed{0.031}$$

(b) $$\frac{C_V}{3R} = \left(\frac{343\,K}{298\,K}\right)^2 \times \left(\frac{e^{343/(2\times298)}}{e^{343/298} - 1}\right)^2 = \boxed{0.897}$$

Comment. For many metals the classical value is approached at room temperature; consequently, the failure of classical theory became apparent only after methods for achieving temperatures well below 25°C were developed in the latter part of the nineteenth century.

P11.5 The hydrogen atom wavefunctions are obtained from the solution of the Schrödinger equation in Chapter 13. Here we need only the wavefunction which is provided. It is the square of the wavefunction that is related to the probability (Section 11.4).

$$\psi^2 = \frac{1}{\pi a_0^3} e^{-2r/a_0}, \qquad \delta\tau = \frac{4}{3}\pi r_0^3, \quad r_0 = 1.0\,\text{pm}$$

If we assume that the volume $\delta\tau$ is so small that ψ does not vary within it, the probability is given by

$$\psi^2\delta\tau = \frac{4r_0^3}{3a_0^3} e^{-2r/a_0} = \frac{4}{3} \times \left(\frac{1.0}{53}\right)^3 e^{-2r/a_0}$$

(a) $r = 0:$ $$\psi^2\delta\tau = \frac{4}{3}\left(\frac{1.0}{53}\right)^3 = \boxed{9.0 \times 10^{-6}}$$

(b) $r = a_0:$ $$\psi^2\delta\tau = \frac{4}{3}\left(\frac{1.0}{53}\right)^3 e^{-2} = \boxed{1.2 \times 10^{-6}}$$

Question. If there is a nonzero probability that the electron can be found at $r = 0$ how does it avoid destruction at the nucleus? (*Hint.* See Chapter 13 for part of the solution to this difficult question.)

P11.7 According to the uncertainty principle,

$$\Delta p \Delta q \geq \tfrac{1}{2}\hbar,$$

where Δq and Δp are root-mean-square deviations:

$$\Delta q = (\langle x^2 \rangle - \langle x \rangle^2)^{1/2} \quad \text{and} \quad \Delta p = (\langle p^2 \rangle - \langle p \rangle^2)^{1/2}.$$

To verify whether the relationship holds for the particle in a state whose wavefunction is

$$\Psi = (2a/\pi)^{1/4} e^{-ax^2},$$

We need the quantum-mechanical averages $\langle x \rangle$, $\langle x^2 \rangle$, $\langle p \rangle$, and $\langle p^2 \rangle$.

$$\langle x \rangle = \int \Psi^* x^2 \Psi \, d\tau = \int_{\infty-}^{\infty} \left(\frac{2a}{\pi}\right)^{1/4} e^{-ax^2} x \left(\frac{2a}{\pi}\right)^{1/4} e^{-ax^2} dx,$$

$$\langle x\rangle = \left(\frac{2a}{\pi}\right)^{1/2}\int_{-\infty}^{\infty} x\mathrm{e}^{-2ax^2}\mathrm{d}x = 0;$$

$$\langle x^2\rangle = \int_{-\infty}^{\infty}\left(\frac{2a}{\pi}\right)^{1/4}\mathrm{e}^{-ax^2}x^2\left(\frac{2a}{\pi}\right)^{1/4}\mathrm{e}^{-ax^2}\mathrm{d}x = \left(\frac{2a}{\pi}\right)^{1/2}\int_{\infty-}^{\infty} x^2\mathrm{e}^{-2ax^2}\mathrm{d}x,$$

$$\langle x^2\rangle = \left(\frac{2a}{\pi}\right)^{1/2}\frac{\pi^{1/2}}{2(2a)^{3/2}} = \frac{1}{4a};$$

so $\Delta q = \dfrac{1}{2a^{1/2}}$.

$$\langle p\rangle = \int_{-\infty}^{\infty}\Psi^*\left(\frac{\hbar}{\mathrm{i}}\frac{\mathrm{d}\Psi}{\mathrm{d}x}\right)\mathrm{d}x \quad\text{and}\quad \langle p^2\rangle = \int_{-\infty}^{\infty}\Psi^*\left(-\hbar^2\frac{\mathrm{d}^2\Psi}{\mathrm{d}x^2}\right)\mathrm{d}x.$$

We need to evaluate the derivatives:

$$\frac{\mathrm{d}\Psi}{\mathrm{d}x} = \left(\frac{2a}{\pi}\right)^{1/4}(-2ax)\mathrm{e}^{-ax^2}$$

and $$\frac{\mathrm{d}^2\Psi}{\mathrm{d}x^2} = \left(\frac{2a}{\pi}\right)^{1/4}[(-2ax)^2\mathrm{e}^{-ax^2} + (-2a)\mathrm{e}^{-ax^2}] = \left(\frac{2a}{\pi}\right)^{1/4}(4a^2x^2 - 2a)\mathrm{e}^{-ax^2}.$$

So $$\langle p\rangle = \int_{-\infty}^{\infty}\left(\frac{2a}{\pi}\right)^{1/4}\mathrm{e}^{-ax^2}\left(\frac{\hbar}{\mathrm{i}}\right)\left(\frac{2a}{\pi}\right)^{1/4}(-2ax)\mathrm{e}^{-ax^2}\,\mathrm{d}x$$

$$= -\frac{2\hbar}{\mathrm{i}}\left(\frac{2a}{\pi}\right)^{1/2}\int_{-\infty}^{\infty} x\mathrm{e}^{-2ax^2}\mathrm{d}x = 0;$$

$$\langle p^2\rangle = \int_{-\infty}^{\infty}\left(\frac{2a}{\pi}\right)^{1/4}\mathrm{e}^{-ax^2}(-\hbar^2)\left(\frac{2a}{\pi}\right)^{1/4}(4a^2x^2 - 2a)\mathrm{e}^{-ax^2}\mathrm{d}x,$$

$$\langle p^2\rangle = (-2a\hbar^2)\left(\frac{2a}{\pi}\right)^{1/2}\int_{-\infty}^{\infty}(2ax^2 - 1)\mathrm{e}^{-2ax^2}\mathrm{d}x,$$

$$\langle p^2\rangle = (-2a\hbar^2)\left(\frac{2a}{\pi}\right)^{1/2}\left(2a\frac{\pi^{1/2}}{2(2a)^{3/2}} - \frac{\pi^{1/2}}{(2a)^{1/2}}\right) = a\hbar^2;$$

and $\Delta p = a^{1/2}\hbar$.

Finally, $\Delta q\,\Delta p = \dfrac{1}{2a^{1/2}} \times a^{1/2}\hbar = 1/2\hbar$,

which is the minimum product consistent with the uncertainty principle.

Solutions to theoretical problems

P11.9 We look for the value of λ at which ρ is a maximum, using (as appropriate) the short-wavelength (high-frequency) approximation

$$\rho = \frac{8\pi hc}{\lambda^5}\left(\frac{1}{e^{hc/\lambda kT}-1}\right) \quad [11.5]$$

$$\frac{d\rho}{d\lambda} = -\frac{5}{\lambda}\rho + \frac{hc}{\lambda^2 kT}\left(\frac{e^{hc/\lambda kT}}{e^{hc/\lambda kT}-1}\right)\rho = 0 \quad \text{at } \lambda = \lambda_{max}$$

Then, $-5 + \dfrac{hc}{\lambda kT} \times \dfrac{e^{hc/\lambda kT}}{e^{hc/\lambda kT}-1} = 0$

Hence, $5 - 5e^{hc/\lambda kT} + \dfrac{hc}{\lambda kT}e^{hc/\lambda kT} = 0$

If $\dfrac{hc}{\lambda kT} \gg 1$ [short wavelengths, high frequencies], this expression simplifies. We neglect the initial 5, cancel the two exponents, and obtain

$$hc = 5\lambda kT \quad \text{for} \quad \lambda = \lambda_{max} \quad \text{and} \quad \frac{hc}{\lambda kT} \gg 1$$

or $\boxed{\lambda_{max}T = \dfrac{hc}{5k} = 2.88\ \text{mm K}}$, in accord with observation.

Comment. Most experimental studies of black-body radiation have been done over a wavelength range of a factor of 10 to 100 of the wavelength of visible light and over a temperature range of 300 K to 10 000 K.

Question. Does the short-wavelength approximation apply over all of these ranges? Would it apply to the cosmic background radiation of the universe at 2.7 K where $\lambda_{max} \approx 0.2$ cm?

P11.10

$$\rho = \frac{8\pi hc}{\lambda^5}\left(\frac{1}{e^{hc/\lambda kT}-1}\right) \quad [11.5]$$

As λ increases, $\dfrac{hc}{\lambda kT}$ decreases, and at very long wavelength $hc/\lambda kT \ll 1$. Hence we can expand the exponential in a power series. Let $x = hc/\lambda kT$, then

$$e^x = 1 + x + \frac{1}{2!}x^2 + \frac{1}{3!}x^3 + \cdots$$

$$\rho = \frac{8\pi hc}{\lambda^5}\left[\frac{1}{1 + x + \frac{1}{2!}x^2 + \frac{1}{3!}x^3 + \cdots - 1}\right]$$

$$\lim_{\lambda\to\infty}\rho = \frac{8\pi hc}{\lambda^5}\left[\frac{1}{1+x-1}\right] = \frac{8\pi hc}{\lambda^5}\left(\frac{1}{hc/\lambda kT}\right)$$

$$= \frac{8\pi kT}{\lambda^4}$$

This is the Rayleigh–Jeans law [11.3].

P11.12 $\rho = \dfrac{8\pi hc}{\lambda^5} \times \dfrac{1}{e^{hc/\lambda kT} - 1}$ [11.5]

$$\begin{aligned}\frac{\partial\rho}{\partial\lambda} &= -\frac{40\pi hc}{\lambda^6} \times \left(\frac{1}{e^{hc/\lambda kT} - 1}\right) - \left(\frac{8\pi hc}{\lambda^5}\right) \times \frac{e^{hc/\lambda kT} \times \left(-\frac{hc}{\lambda^2 kT}\right)}{\left(e^{hc/\lambda kT} - 1\right)^2} \\ &= \frac{8\pi hc}{\lambda^5} \times \left(\frac{1}{e^{hc/\lambda kT} - 1}\right) \times \left[-\frac{5}{\lambda} + \frac{hc}{\lambda^2 kT}\frac{e^{hc/\lambda kT}}{e^{hc/\lambda kT} - 1}\right] \\ &= \left(-\frac{5}{\lambda}\right) \times \rho\left[1 - \frac{hc}{5\lambda kT}\frac{1}{1 - e^{-hc/\lambda kT}}\right]\end{aligned}$$

$$\frac{\partial\rho}{\partial\lambda} = 0 \quad \text{when } \lambda = \lambda_{\max} \quad \text{and}$$

$$\frac{hc}{5\lambda_{\max}kT}\left[\frac{1}{1 - e^{-hc/\lambda_{\max}kT}}\right] = 1$$

$$\frac{5\lambda_{\max}kT}{hc}\left(1 - e^{-hc/\lambda_{\max}kT}\right) = 1$$

Let $x = \dfrac{hc}{\lambda_{\max}kT}$; then $\dfrac{5}{x}\left(1 - e^{-x}\right) = 1$ or $\dfrac{5}{x} = \dfrac{1}{1 - e^{-x}}$

The solution of this equation is $x = 4.965$.

Then $h = \dfrac{4.965\lambda_{\max}kT}{c}$ (1)

However

$M = \sigma T^4 = \left(\dfrac{2\pi^5 k^4}{15c^2h^3}\right)T^4$ (2)

Substituting (1) into (2) yields

$$\begin{aligned}M &\approx \left(\frac{2\pi^5 k^4}{15c^2}\right) \times \left(\frac{c}{4.965\lambda_{\max}kT}\right)^3 T^4 \\ &\approx \frac{2\pi^5 ckT}{1835.9\lambda_{\max}^3} \\ k &\approx \frac{1835.9\lambda_{\max}^3 M}{2\pi^5 cT} \\ &\approx \frac{1835.9(1.451 \times 10^{-6}\,\text{m})^3 \times (904.48 \times 10^3\,\text{W})}{2\pi^5(2.998 \times 10^8\,\text{m s}^{-1}) \times (2000\,\text{K}) \times (1.000\,\text{m}^2)}\end{aligned}$$

$\boxed{k \approx 1.382 \times 10^{-23}\,\text{J K}^{-1}}$ (3)

Substituting (3) into (1)

$$h \approx \frac{5(1.451 \times 10^{-6}\,\mathrm{m}) \times (1.382 \times 10^{-23}\,\mathrm{J\,K^{-1}}) \times (2000\,\mathrm{K})}{2.998 \times 10^{8}\,\mathrm{m\,s^{-1}}}$$

$$\boxed{h \approx 6.69 \times 10^{-34}\,\mathrm{J\,s}}$$

Comment. These calculated values are very close to the currently accepted values for these constants.

P11.14 In each case form $N\psi$; integrate

$$\int (N\psi)^*(N\psi)\,\mathrm{d}\tau$$

set the integral equal to 1 and solve for N.

(a)
$$\psi = N\left(2 - \frac{r}{a_0}\right)\mathrm{e}^{-r/2a_0}$$

$$\psi^2 = N^2\left(2 - \frac{r}{a_0}\right)^2 \mathrm{e}^{-r/a_0}$$

$$\int \psi^2\,\mathrm{d}\tau = N^2 \int_0^\infty \left(4r^2 - \frac{4r^3}{a_0} + \frac{r^4}{a_0^2}\right)\mathrm{e}^{-r/a_0}\,\mathrm{d}r \int_0^\pi \sin\theta\,\mathrm{d}\theta \int_0^{2\pi}\mathrm{d}\phi$$

$$= N^2\left(4 \times 2a_0^3 - 4 \times \frac{6a_0^4}{a_0} + \frac{24a_0^5}{a_0^2}\right) \times (2) \times (2\pi) = 32\pi a_0^3 N^2;$$

hence $\boxed{N = \left(\frac{1}{32\pi a_0^3}\right)^{1/2}}$

where we have used

$$\int_0^\infty x^n \mathrm{e}^{-ax}\,\mathrm{d}x = \frac{n!}{a^{n+1}} \text{ [Problem 11.13]}$$

(b)
$$\psi = Nr\sin\theta\cos\phi\,\mathrm{e}^{-r/(2a_0)}$$

$$\int \psi^2\,\mathrm{d}\tau = N^2 \int_0^\infty r^4 \mathrm{e}^{-r/a_0}\,\mathrm{d}r \int_0^\pi \sin^2\theta\sin\theta\,\mathrm{d}\theta \int_0^{2\pi}\cos^2\phi\,\mathrm{d}\phi$$

$$= N^2 4! a_0^5 \int_{-1}^{1}(1 - \cos^2\theta)\,\mathrm{d}\cos\theta \times \pi$$

$$= N^2 4! a_0^5\left(2 - \frac{2}{3}\right)\pi = 32\pi a_0^5 N_0^2; \quad \text{hence} \quad \boxed{N = \left(\frac{1}{32\pi a_0^5}\right)^{1/2}}$$

where we have used $\int_0^\pi \cos^n\theta\sin\theta\,\mathrm{d}\theta = -\int_1^{-1}\cos^n\theta\,\mathrm{d}\cos\theta = \int_{-1}^{1} x^n\,\mathrm{d}x$

and the relations at the end of the solution to Problem 11.8. [See *Student's solutions manual*.]

P11.16 Operate on each function with i; if the function is regenerated multiplied by a constant, it is an eigenfunction of i and the constant is the eigenvalue.

(a) $f = x^3 - kx$

$i(x^3 - kx) = -x^3 + kx = -f$

Therefore, f is an eigenfunction with eigenvalue, $\boxed{-1}$

(b) $f = \cos kx$

$i \cos kx = \cos(-kx) = \cos kx = f$

Therefore, f is an eigenfunction with eigenvalue, $\boxed{+1}$

(c) $f = x^2 + 3x - 1$

$i(x^2 + 3x - 1) = x^2 - 3x - 1 \neq \text{constant} \times f$

Therefore, f is not an eigenfunction of i.

P11.19 The kinetic energy operator, $\hat{T}$, is obtained from the operator analogue of the classical equation

$$E_{\mathrm{K}} = \frac{p^2}{2m}$$

that is,

$$\hat{T} = \frac{(\hat{p})^2}{2m}$$

$$\hat{p}_x = \frac{\hbar}{\mathrm{i}}\frac{\mathrm{d}}{\mathrm{d}x}\ [11.32]; \quad \text{hence} \quad \hat{p}_x^2 = -\hbar^2\frac{\mathrm{d}^2}{\mathrm{d}x^2} \quad \text{and} \quad \hat{T} = -\frac{\hbar^2}{2m}\frac{\mathrm{d}^2}{\mathrm{d}x^2}$$

Then

$$\langle T\rangle = N^2\int \psi^*\left(\frac{\hat{p}_x^2}{2m}\right)\psi\,\mathrm{d}\tau = \frac{\int \psi^*\left(\frac{\hat{p}^2}{2m}\right)\psi\,\mathrm{d}\tau}{\int \psi^*\psi\,\mathrm{d}\tau} \quad \left[N^2 = \frac{1}{\int \psi^*\psi\,\mathrm{d}\tau}\right]$$

$$= \frac{\frac{-\hbar^2}{2m}\int \psi^*\frac{\mathrm{d}^2}{\mathrm{d}x^2}(\mathrm{e}^{\mathrm{i}kx}\cos\chi + \mathrm{e}^{-\mathrm{i}kx}\sin\chi)\,\mathrm{d}\tau}{\int \psi^*\psi\,\mathrm{d}\tau}$$

$$= \frac{\frac{-\hbar^2}{2m}\int \psi^*(-k^2)\times(\mathrm{e}^{\mathrm{i}kx}\cos\chi + \mathrm{e}^{-\mathrm{i}kx}\sin\chi)\,\mathrm{d}\tau}{\int \psi^*\psi\,\mathrm{d}\tau} = \frac{\hbar^2k^2\int \psi^*\psi\,\mathrm{d}\tau}{2m\int \psi^*\psi\,\mathrm{d}\tau} = \boxed{\frac{\hbar^2k^2}{2m}}$$

P11.20

$$p_x = \frac{\hbar}{\mathrm{i}}\frac{\mathrm{d}}{\mathrm{d}x}\ [11.32]$$

$$\langle p_x\rangle = N^2\int \psi^*\hat{p}_x\psi\,\mathrm{d}x; \quad N^2 = \frac{1}{\int \psi^*\psi\,\mathrm{d}\tau}$$

$$= \frac{\int \psi^*\hat{p}_x\psi\,\mathrm{d}x}{\int \psi^*\psi\,\mathrm{d}x} = \frac{\frac{\hbar}{\mathrm{i}}\int \psi^*\left(\frac{\mathrm{d}\psi}{\mathrm{d}x}\right)\mathrm{d}x}{\int \psi^*\psi\,\mathrm{d}x}$$

(a) $\psi = \mathrm{e}^{\mathrm{i}kx}, \qquad \frac{\mathrm{d}\psi}{\mathrm{d}x} = \mathrm{i}k\psi$

Hence,

$$\langle p_x\rangle = \frac{\frac{\hbar}{\mathrm{i}}\times \mathrm{i}k\int \psi^*\psi\,\mathrm{d}x}{\int \psi^*\psi\,\mathrm{d}x} = \boxed{k\hbar}$$

(b) $\psi = \cos kx, \qquad \dfrac{d\psi}{dx} = -k \sin kx$

$$\int_{-\infty}^{\infty} \psi^* \frac{d\psi}{dx}\, dx = -k \int_{-\infty}^{\infty} \cos kx \sin kx\, dx = 0$$

Therefore, $\langle p_x \rangle = \boxed{0}$

(c) $\psi = e^{-\alpha x^2}, \quad \dfrac{d\psi}{dx} = -2\alpha x e^{-\alpha x^2}$

$$\int_{-\infty}^{\infty} \psi^* \frac{d\psi}{dx}\, dx = -2\alpha \int_{-\infty}^{\infty} x e^{-2\alpha x^2}\, dx = 0 \quad \text{[by symmetry, since } x \text{ is an odd function]}$$

Therefore, $\langle p_x \rangle = \boxed{0}$

P11.23 No solution.

Solution to applications

P11.27 **(a)** Consider any infinitesimal volume element $dx\ dy\ dz$ within the hemisphere (Figure 11.1) that has a radius equal to the distance traveled by light in the time dt ($c\,dt$). The objective is to find the total radiation flux perpendicular to the hemisphere face at its center. Imagine an infinitesimal area A at that point. Let r be the distance from $dx\ dy\ dz$ to A and imagine the infinitesimal area A' perpendicular to $\vec{r}$. E is the total isotropic energy density in $dx\ dy\ dz$. $E\ dx\,dy\,dz$ is the energy emitted in dt. $A'/4\pi r^2$ is the fraction of this radiation that passes through A'. The radiation flux that originates from $dx\ dy\ dz$ and passes through A' in dt is given by:

$$J_{A'} = \frac{\left(\frac{\cancel{A'}}{4\pi r^2}\right) E\ dx\ dy\ dz}{\cancel{A'}\, dt} = \frac{E\ dx\ dy\ dz}{4\pi r^2\, dt}$$

The contribution of $J_{A'}$ to the radiation flux through A, J_A, is given by the expression $J_{A'} \times (\cancel{A} \cos\theta)/\cancel{A} = J_{A'} \cos\theta$. The integration of this expression over the whole hemisphere gives an

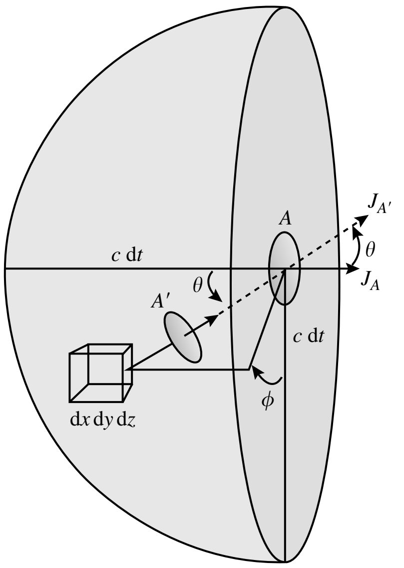

Figure 11.1

expression for J_A. Spherical coordinates facilitate to integration: $\mathrm{d}x\,\mathrm{d}y\,\mathrm{d}z = r^2 \sin\theta\,\mathrm{d}\theta\,\mathrm{d}\phi\,\mathrm{d}r = -r^2\mathrm{d}(\cos\theta)\,\mathrm{d}\phi\,\mathrm{d}r$ where $0 \le \theta \le 2\pi$ and $0 \le \theta \le \pi/2$.

$$\begin{aligned}
J_A &= \int_{\text{hemisphere}} \cos(\theta) \left\{ \frac{E\,\mathrm{d}x\,\mathrm{d}y\,\mathrm{d}z}{4\pi r^2\,\mathrm{d}t} \right\} \\
&= \int_{\text{hemisphere}} \cos(\theta) \left\{ \frac{E}{4\pi \cancel{r^2}\mathrm{d}t} \right\} \{-\cancel{r^2}\mathrm{d}(\cos\theta)\,\mathrm{d}\phi\,\mathrm{d}r\} \\
&= -\left(\frac{E}{4\pi\,\mathrm{d}t}\right) \int_{\cos(0)}^{\cos(\pi/2)} \cos(\theta)\,\mathrm{d}(\cos\theta) \int_0^{2\pi} \mathrm{d}\phi \int_0^{c\,dt} \mathrm{d}r \\
&= -\left(\frac{E}{\cancel{4\pi\mathrm{d}t}}\right) \left[\int_1^0 w\,\mathrm{d}w \right] (2\cancel{\pi})\,(c\cancel{\mathrm{d}t}) \\
J_A &= -\frac{cE}{4}\left(\frac{-1}{\cancel{2}}\right)(\cancel{2}) \text{ \{Subscript “A” has been a bookkeeping device. It may be dropped.\}}
\end{aligned}$$

$$\boxed{J = \frac{cE}{4}} \quad \text{or} \quad \boxed{\mathrm{d}J = \frac{c}{4}\,\mathrm{d}E}$$

$$\mathrm{d}E = \frac{8\pi hc\,\mathrm{d}\lambda}{\lambda^5(\mathrm{e}^{hc/\lambda RT} - 1)} \quad \text{[eqn 11.5]}$$

By eqn 16.1 $\tilde{\nu} = 1/\lambda$. Taking differentials to be positive, $\mathrm{d}\tilde{\nu} = \mathrm{d}\lambda/\lambda^2$ or $\mathrm{d}\lambda = \lambda^2\,\mathrm{d}\tilde{\nu} = \mathrm{d}\tilde{\nu}/\tilde{\nu}^2$. The substitution of $\tilde{\nu}$ for λ gives:

$$\mathrm{d}E = \frac{8\pi hc\tilde{\nu}^3}{\mathrm{e}^{hc\tilde{\nu}/kT} - 1}\,\mathrm{d}\tilde{\nu}$$

Thus, $\mathrm{d}J = \mathrm{f}(\tilde{\nu})\,\mathrm{d}\tilde{\nu}$ where $\boxed{\mathrm{f}(\tilde{\nu}) = \dfrac{2\pi hc^2\tilde{\nu}^3}{\mathrm{e}^{hc\tilde{\nu}/kT} - 1}}$

The value of the Stefan–Boltzmann constant σ is defined by the low $n = \int_0^\infty \mathrm{d}J(\tilde{\nu}) = \sigma T^4$. n is called the total exitance. Let $x = hc\tilde{\nu}/kT$ (or $\tilde{\nu} = kTx/hc$), substitute the above equation for $\mathrm{d}J(\tilde{\nu})$ into the Stefan–Boltzmann low, and integrate.

$$\begin{aligned}
n &= \int_o^\infty \frac{2\pi hc^2\tilde{\nu}^3\mathrm{d}\tilde{\nu}}{\mathrm{e}^{hc\tilde{\nu}/kT} - 1} = \frac{2\pi k^4T^4}{h^3c^2}\int_0^\infty \frac{x^3\mathrm{d}x}{e^x - 1} \\
&= \left(\frac{2\pi k^4T^4}{h^3c^2}\right)\left(\frac{\pi^4}{15}\right) = \left(\frac{2\pi^5k^4}{15\,h^3c^2}\right)T^4
\end{aligned}$$

Thus, $\boxed{\sigma = \dfrac{2\pi^5k^4}{15h^3c^2} = 5.6704 \times 10^{-8}\ \mathrm{W\,m^{-2}\,K^{-4}}}$

The function $f(\tilde{\nu})$ gives radiation density in units that are compatible with those often used in discussions of infrared radiation which lies between about 33 $\mathrm{cm^{-1}}$ and 12 800 $\mathrm{cm^{-1}}$ (Fig. 11.2).

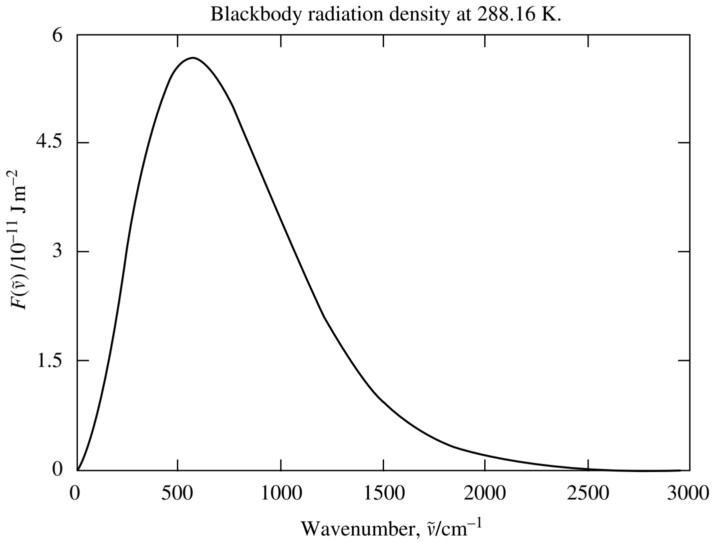

Figure 11.2

By graphing $f(\tilde{\nu})$ at the observed average temperature of the Earth's surface (288.16 K) we easily see that the Earth's black-body emissions are in the infrared with a maximum at about 600 cm^{-1}.

(b) Let R represent the radius of the Earth. Assuming an average balance between the Earth's absorption of solar radiation and Earth's emission of black-body radiation into space gives:

Solar energy absorbed = black-body energy lost

$\pi R^2(1 - \text{albedo})(\text{solar energy flux}) = (4\pi R^2)(\sigma T^4)$

Solving for T gives:

$$T = \left[\frac{(1 - \text{albedo})(\text{solar energy flux})}{4\sigma}\right]^{1/4}$$

$$= \left[\frac{(1 - 0.29)(0.1353\ \text{W cm}^{-2})}{4(5.67 \times 10^{-12}\ \text{W cm}^{-2}\ \text{K}^{-4}}\right]^{1/4} = \boxed{255\ \text{K}}$$

This is an estimate of what the Earth's temperature would be in the absence of the greenhouse effect.