Then $aa^{\dagger}f(x) = \frac{1}{2}\left(\hat{x} + \hbar\frac{d}{dx}\right) \times \left(\hat{x} - \hbar\frac{d}{dx}\right)f(x)$

and $a^{\dagger}af(x) = \frac{1}{2}\left(\hat{x} - \hbar\frac{d}{dx}\right) \times \left(\hat{x} + \hbar\frac{d}{dx}\right)f(x)$

The terms in $\hat{x}^2$ and $(d/dx)^2$ obviously drop out when the difference is taken and are ignored in what follows; thus

$$aa^{\dagger}f(x) = \frac{1}{2}\left(-\hat{x}\hbar\frac{d}{dx} + \hbar\frac{d}{dx}x\right)f(x)$$

$$a^{\dagger}af(x) = \frac{1}{2}\left(x\hbar\frac{d}{d}x - \hbar\frac{d}{dx}x\right)f(x)$$

These expressions are the negative of each other, therefore

$$(aa^{\dagger} - a^{\dagger}a)f(x) = \hbar\frac{d}{dx}\hat{x}f(x) - \hbar\hat{x}\frac{d}{dx}f(x)$$

$$= \hbar\left(\frac{d}{dx}\hat{x} - \hat{x}\frac{d}{dx}\right)f(x) = \hbar f(x)$$

Therefore, $(aa^{\dagger} - a^{\dagger}a) = \boxed{\hbar}$

Solutions to problems

Solutions to numerical problems

P8.1 A cavity approximates an ideal black body; hence the Planck distribution applies,

$$\rho = \frac{8\pi hc}{\lambda^5}\left(\frac{1}{e^{hc/\lambda kT} - 1}\right) [8.5].$$

Since the wavelength range is small (5 nm) we may write as a good approximation

$$\Delta E = \rho\Delta\lambda, \quad \lambda \approx 652.5\,\text{nm}.$$

$$\frac{hc}{\lambda k} = \frac{(6.626 \times 10^{-34}\,\text{J s}) \times (2.998 \times 10^{8}\,\text{m s}^{-1})}{(6.525 \times 10^{-7}\,\text{m}) \times (1.381 \times 10^{-23}\,\text{J K}^{-1})} = 2.205 \times 10^{4}\,\text{K}.$$

$$\frac{8\pi hc}{\lambda^5} = \frac{(8\pi) \times (6.626 \times 10^{-34}\,\text{J s}) \times (2.998 \times 10^{8}\,\text{m s}^{-1})}{(652.5 \times 10^{-9}\,\text{m})^5} = 4.221 \times 10^{7}\,\text{J m}^{-4}.$$

$$\Delta E = (4.221 \times 10^{7}\,\text{J m}^{-4}) \times \left(\frac{1}{e^{(2.205\times10^{4}\,\text{K})/T} - 1}\right) \times (5 \times 10^{-9}\,\text{m}).$$

(a) $T = 298\,\text{K}, \Delta E = \frac{0.211\,\text{J m}^{-3}}{e^{(2.205\times10^{4})/298} - 1} = \boxed{1.6 \times 10^{-33}\,\text{J m}^{-3}}.$

(b) $T = 3273\,\text{K}, \Delta E = \frac{0.211\,\text{J m}^{-3}}{e^{(2.205\times10^{4})/3273} - 1} = \boxed{2.5 \times 10^{-4}\,\text{J m}^{-3}}.$

COMMENT. The energy density in the cavity does not depend on the volume of the cavity, but the total energy in any given wavelength range does, as well as the total energy over all wavelength ranges.

Question. What is the total energy in this cavity within the range 650–655 nm at the stated temperatures?

P8.3

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

In terms of θ_E the Einstein equation [8.7] 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 8.1). The criterion for classical behavior is therefore that $\boxed{T \gg \theta_E}$.

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

(a) For $\nu = 4.65\times10^{13}$ Hz, $\theta_E = (4.798\times10^{-11})\times(4.65\times10^{13}\,\text{K}) = \boxed{2231\,\text{K}}$.

(b) For $\nu = 7.15\times10^{12}$ Hz, $\theta_E = (4.798\times10^{-11})\times(7.15\times10^{12}\,\text{K}) = \boxed{343\,\text{K}}$.

Hence

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

(b) $$\frac{C_V}{3R} = \left(\frac{343\,\text{K}}{298\text{K}}\right)^2 \times \left(\frac{e^{2231/(2\times298}}{e^{343/298}-1}\right)^2 = \boxed{0.897}.$$

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.

P8.5 The hydrogen atom wavefunctions are obtained from the solution of the Schrödinger equation in Chapter 10. Here we need only the wavefunction that is provided. It is the square of the wavefunction that is related to the probability (Section 8.4).

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

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 10 for part of the solution to this difficult question.)

P8.7 According to the uncertainty principle,

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

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

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

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 $\langle p^2 \rangle$.

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

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

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

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

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

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

We need to evaluate the derivatives:

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

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

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

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

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

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

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

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

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

which is the minimum product consistent with the uncertainty principle.

Solutions to theoretical problems

P8.9 $\quad \rho = \dfrac{8\pi hc}{\lambda^5}\left(\dfrac{1}{e^{hc/\lambda kT} - 1}\right)$ [8.5]

As λ increases, $hc/\lambda kT$ 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 [8.3].

P8.15 In each case form $\hat{\Omega}f$. If the result is ωf where ω is a constant, then f is an eigenfunction of the operat $\hat{\Omega}$ and ω is the eigenvalue [8.25b].

(a) $\dfrac{d}{dx}e^{ikx} = ik\,e^{ikx}$; $\boxed{\text{yes; eigenvalue} = ik}$.

(b) $\dfrac{d}{dx}\cos kx = -k\sin kx$; no.

(c) $\dfrac{d}{dx}k = 0$; $\boxed{\text{yes; eigenvalue} = 0}$.

(d) $\dfrac{d}{dx}kx = k = \dfrac{1}{x}kx$; no [$1/x$ is not a constant].

(e) $\dfrac{d}{dx}e^{-\alpha x^2} = -2\alpha x\,e^{-\alpha x^2}$; no [$-2\alpha x$ is not a constant].

P8.17 Follow the procedure of Problem 8.15.

(a) $\dfrac{d^2}{dx^2}e^{ikx} = -k^2 e^{ikx}$; yes; eigenvalue $= \boxed{-k^2}$.

(b) $\dfrac{d^2}{dx^2}\cos kx = -k^2\cos kx$; yes; eigenvalue $= \boxed{-k^2}$.

(c) $\dfrac{d^2}{dx^2}k = 0$; yes; eigenvalue $= \boxed{0}$.

(d) $\dfrac{d^2}{dx^2}kx = 0$; yes; eigenvalue $= \boxed{0}$.

(e) $\dfrac{d^2}{dx^2}e^{-\alpha x^2} = (-2\alpha + 4\alpha^2 x^2)e^{-\alpha x^2}$; no.

Hence, $\boxed{\text{(a, b, c, d) are eigenfunctions of } \dfrac{d^2}{dx^2}\text{; (b, d) are eigenfunctions of } \dfrac{d^2}{dx^2}\text{, but not of } \dfrac{d}{dx}}$.

P8.19 The kinetic energy operator, $\hat{T}$, is obtained from the operator analog of the classical equation

$$E_K = \frac{p^2}{2m},$$

that is,

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

$$\hat{p}_x = \frac{\hbar}{i}\frac{d}{dx}\ [8.26]; \quad \text{hence} \quad \hat{p}_x^2 = -\hbar^2\frac{d^2}{dx^2} \quad \text{and} \quad \hat{T} = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2}.$$

Then

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

$$= \frac{\dfrac{-\hbar^2}{2m}\int\psi^*\dfrac{d^2}{dx^2}(e^{ikx}\cos\chi + e^{-ikx}\sin\chi)\,d\tau}{\int\psi^*\psi\,d\tau}$$

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

(b) $$\frac{\mathrm{d}}{\mathrm{d}x}\hat{x}^2 f(x) = x^2 f'(x) + 2xf(x),$$

$$\hat{x}^2 \frac{\mathrm{d}}{\mathrm{d}x} f(x) = x^2 f'(x),$$

$$\left(\frac{\mathrm{d}}{\mathrm{d}x}\hat{x}^2 - \hat{x}^2 \frac{\mathrm{d}}{\mathrm{d}x}\right) f(x) = 2xf(x).$$

Thus, $\left(\frac{\mathrm{d}}{\mathrm{d}x}\hat{x}^2 - \hat{x}^2 \frac{\mathrm{d}}{\mathrm{d}x}\right) = \boxed{2x}$.

Solutions to problems

Solutions to numerical problems

P8.2 $$\lambda_{\max} T = \frac{c_2}{5} \text{ where } c_2 = \frac{hc}{k}$$

Therefore, $\lambda_{\max} T = hc/5k$ and, if we find the mean of the $\lambda_{\max} T$ values, we can obtain h from the equation $h = 5k/c\,(\lambda_{\max} T)_{\text{mean}}$. We draw up the following table.

$\theta/°\text{C}$	1000	1500	2000	2500	3000	3500
T/K	1273	1773	2273	2773	3273	3773
$\lambda_{\max}/\text{nm}$	2181	1600	1240	1035	878	763
$\lambda_{\max} T\ /\ (10^6\ \text{nm K})$	2.776	2.837	2.819	2.870	2.874	2.879

The mean is 2.84×10^6 nm K with a standard deviation of 0.04×10^6 nm K

and $$h = \frac{(5) \times (1.38066 \times 10^{-23}\ \text{J K}^{-1}) \times (2.84 \times 10^{-3}\ \text{m K})}{2.99792 \times 10^8\ \text{m s}^{-1}} = \boxed{6.54 \times 10^{-34}\ \text{J s}}$$

COMMENT. Planck's estimate of the constant h in his first paper of 1900 on black body radiation was 6.55×10^{-27} erg sec(1 erg $= 10^{-7}$ J) which is remarkably close to the current value of 6.626×10^{-34} J s and is essentially the same as the value obtained above. Also from his analysis of the experimental data he obtained values of k (the Boltzmann constant), N_A (the Avogadro constant), and e (the fundamental charge). His values of these constants remained the most accurate for almost 20 years.

P8.4 The full solution of the Schrödinger equation for the problem of a particle in a one-dimensional box is given in Chapter 9. Here we need only the wavefunction which is provided. It is the square of the wavefunction that is related to the probability. Here $\psi^2 = \frac{2}{L}\sin^2\frac{\pi x}{L}$ and the probability that the particle will be found between a and b is

$$P(a,b) = \int_a^b \psi^2 \mathrm{d}x \text{ [Section 8.4]}$$

$$= \frac{2}{L}\int_a^b \sin^2\frac{\pi x}{L}\mathrm{d}x = \left(\frac{x}{L} - \frac{1}{2\pi}\sin\frac{2\pi x}{L}\right)\Bigg|_a^b$$

$$= \frac{b-a}{L} - \frac{1}{2\pi}\left(\sin\frac{2\pi b}{L} - \sin\frac{2\pi a}{L}\right)$$

$L = 10.0\,\text{nm}$

(a) $$P(4.95, 5.05) = \frac{0.10}{10.0} - \frac{1}{2\pi}\left(\sin\frac{(2\pi)\times(5.05)}{10.0} - \sin\frac{(2\pi)\times(4.95)}{10.0}\right)$$
$$= 0.010 + 0.010 = \boxed{0.020}$$

(b) $$P(1.95, 2.05) = \frac{0.10}{10.0} - \frac{1}{2\pi}\left(\sin\frac{(2\pi)\times(2.05)}{10.0} - \sin\frac{(2\pi)\times(1.95)}{10.0}\right)$$
$$= 0.010 - 0.0031 = \boxed{0.007}$$

(c) $$P(9.90, 10.0) = \frac{0.10}{10.0} - \frac{1}{2\pi}\left(\sin\frac{(2\pi)\times(10.0)}{10.0} - \sin\frac{(2\pi)\times(9.90)}{10.0}\right)$$
$$= 0.010 - 0.009993 = \boxed{7\times10^{-6}}$$

(d) $P(5.0, 10.0) = \boxed{0.5}$ [by symmetry]

(e) $$P\left(\frac{1}{3}L, \frac{2}{3}L\right) = \frac{1}{3} - \frac{1}{2\pi}\left(\sin\frac{4\pi}{3} - \sin\frac{2\pi}{3}\right) = \boxed{0.61}$$

P8.6 The average position (angle) is given by:

$$\langle\phi\rangle = \int \psi^*\phi\psi\,\mathrm{d}\tau = \int_0^{2\pi} \frac{e^{im\phi}}{(2\pi)^{1/2}}\phi\frac{e^{-im\phi}}{(2\pi)^{1/2}}\,\mathrm{d}\phi = \frac{1}{2\pi}\int_0^{2\pi}\phi\,\mathrm{d}\phi = \frac{1}{2\pi}\frac{\phi^2}{2}\bigg|_0^{2\pi} = \boxed{\pi}.$$

Note: this result applies to all values of the quantum number m, for it drops out of the calculation.

P8.8 The expectation value of the commutator is:

$$\langle[\hat{x},\hat{p}]\rangle = \textstyle\int \psi^*[\hat{x},\hat{p}]\psi\,\mathrm{d}\tau.$$

First evaluate the commutator acting on the wavefunction. The commutator of the position and momentum operators is defined as

$$[\hat{x},\hat{p}] = \hat{x}\hat{p} - \hat{p}\hat{x} = x\times\frac{\hbar}{\mathrm{i}}\frac{\mathrm{d}}{\mathrm{d}x} - \frac{\hbar}{\mathrm{i}}\frac{\mathrm{d}}{\mathrm{d}x}x,$$

so the commutator acting on the wavefunction is

$$[\hat{x},\hat{p}]\psi = x\times\frac{\hbar}{\mathrm{i}}\frac{\mathrm{d}\psi}{\mathrm{d}x} - \frac{\hbar}{\mathrm{i}}\frac{\mathrm{d}}{\mathrm{d}x}(x\psi),$$

where $\psi = (2a)^{1/2}e^{-ax}$.

Evaluating this expression yields

$$[\hat{x},\hat{p}]\psi = \frac{x\hbar}{\mathrm{i}}(2a)^{1/2}a\,e^{-ax} - \frac{\hbar}{\mathrm{i}}[(2a)^{1/2}e^{-ax} + xa(2a)^{1/2}e^{-ax}],$$

$$[\hat{x},\hat{p}]\psi = \frac{\hbar(2a)^{1/2}e^{-ax}}{\mathrm{i}}(xa - 1 - xa) = \mathrm{i}\hbar(2a)^{1/2}e^{-ax},$$

P8.14 In each case form $N\psi$; integrate

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

set the integral equal to 1 and solve for N.

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

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

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

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

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

where we have used

$$\int_0^\infty x^n e^{-ax}\, dx = \frac{n!}{a^{n+1}} \text{ [Problem 8.13 and inside front cover]}$$

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

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

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

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

where we have used $\int_0^\pi \cos^n\theta \sin\theta\, d\theta = -\int_1^{-1} \cos^n\theta\, d\cos\theta = \int_{-1}^{1} x^n\, dx$ and the relations at the end of the solution to Problem 8.13.

(b) The functions will be orthogonal if the following integral, which uses the unnormalized functions, proves to equal zero.

$$\int \psi_1\psi_2 d\tau = \int \left\{\left(2 - \frac{r}{a_o}\right) e^{\frac{r}{2a_o}}\right\} \left\{r \sin\theta\ \cos\phi\ e^{\frac{r}{2a_o}}\right\} d\tau$$

$$= \int_0^\infty \left\{\left(2r - \frac{r^2}{a_o}\right) e^{\frac{r}{a_o}}\right\} dr \int_0^\pi \sin^2\theta\, d\theta \int_0^{2\pi} \cos\phi\, d\phi$$

The integral on the far right equals zero.

$$\int_0^{2\pi} \cos\phi \, d\phi = \sin\phi \Big|_0^{2\pi} = \sin(2\pi) - \sin(0) = 0 - 0 = 0$$

Consequently, the functions are orthogonal.

P8.16 Operate on each function with $\hat{\imath}$; if the function is regenerated multiplied by a constant, it is an eigenfunction of $\hat{\imath}$ and the constant is the eigenvalue.

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

$\hat{\imath}(x^3 - kx) = -x^3 + kx = -f$

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

(b) $f = \cos kx$

$\hat{\imath} \cos kx = \cos(-kx) = \cos kx = f$

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

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

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

Therefore, f is not an eigenfunction of $\hat{\imath}$.

P8.18 $\psi = (\cos\chi)e^{ikx} + (\sin\chi)\,e^{-ikx} = c_1 e^{ikx} + c_2\,e^{-ikx}$. The linear momentum operator is $\hat{p}_x = \dfrac{\hbar}{i}\dfrac{d}{dx}$ [8.26]

As demonstrated in the text (Example 8.6), e^{-ikx} is an eigenfunction of $\hat{p}_x$ with eigenvalue $+k\hbar$; likewise e^{-ikx} is an eigenfunction of $\hat{p}_x$ with eigenvalue $-k\hbar$. Therefore, by the principle of linear superposition (Section 8.5(d), *Justification* 8.4),

(a) $P = c_1^2 = \boxed{\cos^2\chi}$

(b) $P = c_2^2 = \boxed{\sin^2\chi}$

(c) $c_1^2 = 0.90 = \cos^2\chi$, so $\cos\chi = 0.95$

$c_2^2 = 0.10 = \sin^2\chi$, so $\sin\chi = \pm 0.32$; hence

$$\boxed{\psi = 0.95e^{ikx} \pm 0.32e^{-ikx}}$$

P8.20 $p_x = \dfrac{\hbar}{i}\dfrac{d}{dx}$ [8.26]

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

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

(a) $\psi = \mathrm{e}^{ikx}, \quad \dfrac{\mathrm{d}\psi}{\mathrm{d}x} = \mathrm{i}k\psi$

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

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

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

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

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

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

P8.22 $\psi = \left(\dfrac{1}{\pi a_0^3}\right)^{1/2} \mathrm{e}^{-r/a_0}$ [Example 8.4]

(a) $\langle V \rangle = \displaystyle\int \psi^* \hat{V} \psi \, \mathrm{d}\tau \left[\hat{V} = -\frac{e^2}{4\pi \varepsilon_0 r}, \text{ Section 10.1}\right]$

$$\langle V \rangle = \int \psi^* \left(\frac{-e^2}{4\pi \varepsilon_0} \cdot \frac{1}{r}\right) \psi \mathrm{d}\tau = \frac{1}{\pi a_0^3} \left(\frac{-e^2}{4\pi \varepsilon_0}\right) \int_0^{\infty} r\mathrm{e}^{-2r/a_0} \mathrm{d}r \times 4\pi$$

$$= \frac{1}{\pi a_0^3} \left(\frac{-e^2}{4\pi \varepsilon_0}\right) \times \left(\frac{a_0}{2}\right)^2 \times 4\pi = \boxed{\frac{-e^2}{4\pi \varepsilon_0 a_0}}$$

(b) For three-dimensional systems such as the hydrogen atom the kinetic energy operator is

$\hat{T} = -\dfrac{\hbar^2}{2m_e} \nabla^2$ [Table 8.1, $m_e \approx \mu$ for the hydrogen atom]

$\nabla^2 = \dfrac{\partial^2}{\partial r^2} + \dfrac{2}{r}\dfrac{\partial}{\partial r} + \dfrac{1}{r^2}\Lambda^2 = \left(\dfrac{1}{r}\right) \times \left(\dfrac{\partial^2}{\partial r^2}\right) r + \dfrac{1}{r^2}\Lambda^2$

$\Lambda^2 \psi = 0 \quad$ [ψ has no angular coordinates]

$$\nabla^2 \psi = \left(\frac{1}{\pi a_0^3}\right)^{1/2} \times \left(\frac{1}{r}\right) \times \left(\frac{\mathrm{d}^2}{\mathrm{d}r^2}\right) r\,\mathrm{e}^{-r/a_0}$$

$$= \left(\frac{1}{\pi a_0^3}\right)^{1/2} \times \left[-\left(\frac{2}{a_0 r}\right) + \frac{1}{a_0^2}\right] \mathrm{e}^{-r/a_0}$$