Theoretical 2007
1 (c) (iii)

The question wants the expectation value of the energy of $\Psi(x)$.

The Schrödinger equation is needed here: $\hat{H}\Psi(x) = E\Psi(x)$.

We calculated $\hat{H}\Psi(x)$ in part (ii):

$$\hat{H}\Psi(x) = E_2\psi_2(x) + 2E_3\psi_3(x)$$

$$= \frac{4h^2}{8mL^2}\psi_2(x) + 2\frac{9h^2}{8mL^2}\psi_3(x).$$

So $E\Psi(x) = E_2\psi_2(x) + 2E_3\psi_3(x)$.

Therefore $E = \dfrac{E_2\psi_2(x) + 2E_3\psi_3(x)}{\Psi(x)}$,

$$= \frac{E_2\psi_2(x) + 2E_3\psi_3(x)}{\psi_2(x) + 2\psi_3(x)}$$

$$= \frac{h^2}{8mL^2}\left(\frac{4\psi_2(x) + 18\psi_3(x)}{\psi_2(x) + 2\psi_3(x)}\right)$$

I can't simplify this any further as it is, so I'll substitute in the expressions for $\psi_2(x)$ and $\psi_3(x)$.

$$\psi_2(x) = \sqrt{\frac{2}{L}}\sin\left(\frac{2\pi}{L}x\right) \quad \text{and} \quad \psi_3(x) = \sqrt{\frac{2}{L}}\sin\left(\frac{3\pi}{L}x\right)$$

$$E = \frac{h^2}{8mL^2}\left(\frac{4\sqrt{\frac{2}{L}}\sin\left(\frac{2\pi}{L}x\right) + 18\sqrt{\frac{2}{L}}\sin\left(\frac{3\pi}{L}x\right)}{\sqrt{\frac{2}{L}}\sin\left(\frac{2\pi}{L}x\right) + 2\sqrt{\frac{2}{L}}\sin\left(\frac{3\pi}{L}x\right)}\right)$$

$$E = \frac{h^2}{8mL^2}\sqrt{\frac{2}{L}}\left(\frac{4\sin\left(\frac{2\pi}{L}x\right) + 18\sin\left(\frac{3\pi}{L}x\right)}{\sin\left(\frac{2\pi}{L}x\right) + 2\sin\left(\frac{3\pi}{L}x\right)}\right)$$

Therefore we resort to calculating the **expectation value** of the energy of $\Psi(x)$ – the question even asks for it!

The expectation value $\langle\hat{\Omega}\rangle$ of an operator $\hat{\Omega}$ is defined in *Atkins* (p. 316 of the 7th edn.) as $\langle\hat{\Omega}\rangle = \int \psi^* \hat{\Omega}\psi \ \mathrm{d}\tau$.

Dr Manby defines it (implicitly) as $\langle\hat{\Omega}\rangle = \int \psi\hat{\Omega}\psi \ \mathrm{d}\tau$ – I assume this is because we are always considering real wavefunctions and so $\psi^* = \psi$. In fact, his lecture notes give a formula for the expectation value of the energy of an approximate particle-in-a-box wavefunction, $\tilde{\psi}(x)$.

$$\tilde{E} = \int_0^L |\tilde{\psi}(x)|^2 \frac{\hat{H}\tilde{\psi}(x)}{\tilde{\psi}(x)} \ \mathrm{d}x = \int_0^L \tilde{\psi}(x)\hat{H}\tilde{\psi}(x) \ \mathrm{d}x$$

In this question, the equation becomes

$$\tilde{E} = \int_0^L \Psi(x)\hat{H}\Psi(x) \ \mathrm{d}x$$

$$= \int_0^L \{\psi_2(x) + 2\psi_3(x)\}\{E_2\psi_2(x) + 2E_3\psi_3(x)\} \ \mathrm{d}x$$

$$= \int_0^L E_2\psi_2^2 + 2(E_2 + E_3)\psi_2\psi_3 + 4E_3\psi_3^2 \ \mathrm{d}x$$

$$= E_2\int_0^L \psi_2^2 \ \mathrm{d}x + 2(E_2 + E_3)\int_0^L \psi_2\psi_3 \ \mathrm{d}x + 4E_3\int_0^L \psi_3^2 \ \mathrm{d}x$$

$$= E_2\int_0^L \psi_2^2 \ \mathrm{d}x + 2(E_2 + E_3)\int_0^L \psi_2\psi_3 \ \mathrm{d}x + 4E_3\int_0^L \psi_3^2 \ \mathrm{d}x$$

As we realised in part (i)

- $\psi_2(x)$ and $\psi_3(x)$ are already normalised, so $\int_0^L \psi_2^2(x) \ \mathrm{d}x = 1$ and $\int_0^L \psi_3^2(x) \ \mathrm{d}x = 1$

- $\psi_2(x)$ and $\psi_3(x)$ are different states and thus orthogonal: $\int_0^L \psi_2(x)\psi_3(x) \ \mathrm{d}x = 0$

This allows us to simplify our expression to

$$\tilde{E} = E_2\{1\} + 2(E_2 + E_3)\{0\} + 4E_3\{1\} = E_2 + 4E_3$$

Substituting in values for E_2 and E_3 gives a value for $\tilde{E}$:

$$E_2 = \frac{4h^2}{8mL^2} \text{ and } E_3 = \frac{9h^2}{8mL^2} \text{ and } \tilde{E} = E_2 + 4E_3$$

So $\tilde{E} = \frac{4h^2}{8mL^2}{}_2 + 4\frac{9h^2}{8mL^2}$

$$= (4 + 4 \times 9)\frac{h^2}{8mL^2}$$

$$= 40\frac{h^2}{8mL^2}$$

$$= \frac{5h^2}{mL^2}$$