Solution Set 3. Particle in the Box type problems.

1 MS-2.11. The wavefunction is oscillatory in both space and time. We can determine the spatial period \( L \) (the wavelength) by examining the smallest non-zero \( L \) such that \( y(x + L, t) = y(x, t) \). Similarly the (smallest) time period \( T \) is obtained from \( y(x, t + T) = y(x, t) \) and the frequency is determined as \( \nu = 1/T \). By translating over a single period (in either space or time) the argument of the sine just shifts by \( 2\pi \), hence

\[
\frac{2\pi}{\lambda} (x + Vt) - \frac{2\pi}{\lambda} (x - Vt) = 2\pi \to \frac{Vt}{\lambda} = 1, \text{ or the wavelength } L = \lambda
\]

\[
\frac{2\pi}{\lambda} (x - V(t + T)) - \frac{2\pi}{\lambda} (x - Vt) = 2\pi \to -\frac{VT}{\lambda} = 1 \text{ or (taking } T \text{ as positive)}
\]

\( 1/T = \nu = V/\lambda \)

To see that it represents a wavefunction traveling to the right, sketch the wave for time \( t \) and examine what happens if \( t \to t + \Delta t \) (positive increment). We see that the function value (or the argument of the sine) stays the same if we increment \( x \) by a positive amount \( \Delta x = \Delta t / \nu \), or \( \nu = \Delta x / \Delta t \).

2. MS-B.6: Integrate and show \( \int_0^\infty p(v)dv = 1, \int_0^\infty \nu p(v)dv = \sqrt{8k_B T / \pi m} \) using the integral formulas given.

3. MS 3-3: \( \frac{d^2}{dx^2} \cos(\omega x) = -\omega^2 \cos(\omega x) \to \nu = \omega^2 \), similarly to find the eigenvalues \( i\omega, \alpha^2 + 2\alpha + 3, 6 \).

4 MS 3-5: a. \( \frac{d^2}{dx^2} \frac{d^2}{dx^2} f(x) = \frac{d^4}{dx^4} f(x) \); Since this is true for any function \( f(x) \), we can write for the operator \( \left( \frac{d^2}{dx^2} \right)^2 = \frac{d^4}{dx^4} \). This is the same for all cases in the problem below, and I will not explicitly state this.

\[
(d_x^2 + x)(d_x^2 + x)f(x) = (\frac{d^4}{dx^4} - 2x \frac{d^3}{dx^3} + x^2 \frac{d^2}{dx^2} + x^2 f(x))
\]

b. \( f(x) = (\frac{d^2}{dx^2} + 2x \frac{d}{dx} + x^2 + 1) f(x) \)

c. \( \frac{d^4}{dx^4} f(x) - 2x \frac{d^3}{dx^3} + x^2 \frac{d^2}{dx^2} - 2x \frac{d}{dx} + x^2 f(x) \)

\( = \frac{d^4}{dx^4} f(x) - 4 \frac{d^3}{dx^3} + x^3 f(x) + 2x \frac{d^2}{dx^2} + 4x \frac{d}{dx} + 2x^2 f(x) \)

\( = \frac{d^4}{dx^4} f(x) - 4 \frac{d^3}{dx^3} + (4x^2 - 2) \frac{d^2}{dx^2} - 8x \frac{d}{dx} + f(x) = \frac{d^4}{dx^4} f(x) - 4 \frac{d^3}{dx^3} + (4x^2 - 2) \frac{d^2}{dx^2} + 1) f(x) \)
5 MS 3.16.
\[ \int_0^a \sin(n \pi x / a) \sin(m \pi x / a) \, dx = \frac{1}{2} \int_0^a \cos((n - m) \pi x / a) \, dx + \frac{1}{2} \int_0^a \cos((n + m) \pi x / a) \, dx \]
Since the integral of the cosine is a sine and the sine vanishes in the endpoints if \((n - m)\) and \((n + m)\) are integers (they are constructed that way through the boundary conditions) all of the integrals vanish except the first integral if \(n = m\). This suffices to prove the orthogonality of the functions if \(n \neq m\).

6. Not considered this week. See next week’s problem set.

7. Hexatriene makes a one-dimensional box of length 8.64 Å, with energy levels
\[ E_n = \frac{\hbar^2 n^2}{8ma^2} = \frac{8.07 \times 10^{-20} \text{ } n^2 J}{0.50 \text{ } eV} \approx 0.50 n^2 \text{ eV} \]
So the first 4 levels are at 0.50, 2.0, 4.50 and 8.0 eV. There are six electrons in the \(\pi\) system, so the HOMO lies at 4.50 and the LUMO at 8.0 eV. The excitation energy is 3.5 eV = 5.63 \times 10^{-19} J. This corresponds to \(\lambda = hc / E = 353 \text{ nm}\).

8. The particle on the ring. The general solution is \(\Psi(\varphi) = Ae^{i\lambda\varphi} + Be^{-i\lambda\varphi}\) with energy \(E = -\frac{\hbar^2 \lambda^2}{2I}\), where \(I = mR^2\) is the moment of inertia. The wavefunction should be periodic (single-valued) over \(2\pi\), from which we get the boundary condition \(\Psi(\varphi + 2\pi) = \Psi(\varphi)\) or \(Ae^{i\lambda(\varphi+2\pi)} + Be^{-i\lambda(\varphi+2\pi)} = Ae^{i\lambda\varphi} + Be^{-i\lambda\varphi}\). This relation is satisfied if \(e^{i2\pi} = 1 \rightarrow \lambda = in\), \(n = 0, \pm1, \pm2, \pm3, E_n = \frac{\hbar^2 n^2}{2I} = \frac{\hbar^2 n^2}{2mR^2}\), independent of the values of \(A\) and \(B\). Again the energy is quantized because of the boundary conditions. The general solution is \(\Psi(\varphi) = Ae^{i\varphi} + Be^{-i\varphi} = C\sin(n\varphi) + D\cos(n\varphi)\). These are solutions of the problem, in principle for all values \(A\) and \(B\). For \(n = 0\) (energy 0 !) there is only one (normalized) solution \(\Psi(\varphi) = 1/(\sqrt{2\pi})\), for every other positive integer value of \(n\) we get two independent solutions, that can be written in various ways. It is convenient to use real eigenfunctions, and the normalized functions then take the form
\[ \frac{1}{\sqrt{\pi}} \sin(n\varphi), \frac{1}{\sqrt{\pi}} \cos(n\varphi) \]. There is hence 1 energy level \(E=0\), and 2 levels (wavefunctions) for every energy energy \(E_n = \frac{\hbar^2 n^2}{2I} = \frac{\hbar^2 n^2}{2mR^2}, n=1,2,3,...\) (degeneracy 2).