# Chemistry 432
# Problem Set 2
# Spring 2018
# Solutions

1. By showing
$$f(x,t) = Ae^{i(kx-\omega t)}$$
satisfies the classical wave equation
$$\frac{\partial^2 f}{\partial x^2} = \frac{1}{v^2}\frac{\partial^2 f}{\partial t^2}.$$
determine a relation between $\omega, k$ and $v$.
**Answer**:
$$\frac{\partial f}{\partial x} = ikAe^{i(kx-\omega t)}$$
$$\frac{\partial^2 f}{\partial x^2} = -k^2Ae^{i(kx-\omega t)}$$
$$\frac{\partial f}{\partial t} = -i\omega Ae^{i(kx-\omega t)}$$
$$\frac{\partial^2 f}{\partial t^2} = -\omega^2Ae^{i(kx-\omega t)}$$
Then
$$\frac{\partial^2 f}{\partial x^2} = \frac{1}{v^2}\frac{\partial^2 f}{\partial t^2}$$
if
$$\frac{\omega}{k} = v$$

2. Consider the Schrödinger equation in time dependent form
$$i\hbar\frac{\partial \Psi}{\partial t} = \hat{H}\Psi$$
where
$$\hat{H} = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + V(x).$$

Show that if we write

$$\Psi(x,t) = \psi(x)e^{-iEt/\hbar}$$

we obtain

$$\hat{H}\psi = E\psi$$

where $E$ is the energy of the system.
**Answer**:

$$i\hbar\frac{\partial\Psi(x,t)}{\partial t} = i\hbar\psi(x)\frac{\partial}{\partial t}e^{-iEt/\hbar} = E\psi(x)e^{-iEt/\hbar}$$

$$\hat{H}\Psi(x,t) = e^{-iEt/\hbar}\hat{H}\psi(x)$$

Then

$$e^{-iEt/\hbar}\hat{H}\psi(x) = e^{-iEt/\hbar}E\psi(x)$$

or

$$\hat{H}\psi(x) = E\psi(x)$$

3. The *momentum operator* is defined by

$$\hat{p} = \frac{\hbar}{i}\frac{d}{dx}.$$

Determine which of the following functions are eigenfunctions of the momentum operator ($k$ is a constant):

(a) $\sin kx$
**Answer**:

$$\hat{p}\sin kx = \frac{\hbar}{i}\frac{d}{dx}\sin kx = \frac{\hbar}{i}k\cos kx \neq \text{const.}\sin kx$$

Not an eigenfunction

(b) $e^{ikx}$
**Answer**

$$\hat{p}e^{ikx} = \frac{\hbar}{i}\frac{d}{dx}e^{ikx} = \hbar k e^{ikx}$$

Eigenfunction

(c) $x^4$
**Answer**:

$$\hat{p}x^4 = \frac{\hbar}{i}\frac{d}{dx}x^4 = \frac{\hbar}{i}4x^3 \neq \text{const.}x^4$$

Not an eigenfunction

4. If 20 coins weigh 10 grams each, 30 coins weigh 4 grams each and 10 coins weigh 8 grams each, compute the average weight, $< w >$, of the 60 coins. Also compute $< w^2 >$ and $< w >^2$. If all the 60 coins weighed 5 grams each, find $< w >$, $< w^2 >$ and $< w >^2$.
**Answer**:

(a)

$$\langle w \rangle = \frac{20 \times 10 + 30 \times 4 + 10 \times 8}{60} \text{g} = 6.67\text{g}$$

$$\langle w^2 \rangle = \frac{20 \times 10^2 + 30 \times 4^2 + 10 \times 8^2}{60} \text{g}^2 = 52\text{g}^2$$

$$\langle w \rangle^2 = 44.5\text{g}^2$$

(b)

$$\langle w \rangle = 5\text{g}$$

$$\langle w^2 \rangle = \langle w \rangle^2 = 25\text{g}^2$$

5. The wavefunction for a quantum particle of mass $m$ confined to move in the domain $0 \leq x \leq L$ is given by

$$\psi(x) = N \sin(4\pi x/L)$$

where $N$ is the normalization factor.

(a) Normalize the wavefunction.
**Answer**:

$$N^2 \int_0^L \sin^2\left(\frac{4\pi x}{L}\right) dx = 1$$

$$y = \frac{4\pi x}{L} \qquad x = \frac{L}{4\pi} y \qquad dx = \frac{L}{4\pi} dy$$

$$\frac{LN^2}{4\pi} \int_0^{4\pi} \sin^2 y dy = N^2 \frac{L}{4\pi} \frac{4\pi}{2} = N^2 \frac{L}{2} = 1$$

$$N = \left(\frac{2}{L}\right)^{1/2}$$

$$\psi(x) = \left(\frac{2}{L}\right)^{1/2} \sin\left(\frac{4\pi x}{L}\right)$$

(b) Calculate the expectation value of $x$ for the particle.
**Answer**:

$$\langle x \rangle = \frac{2}{L} \int_0^L \sin\frac{4\pi x}{L} x \sin\frac{4\pi x}{L} dx$$

$$y = \frac{4\pi x}{L} \qquad x = \frac{L}{4\pi} y \qquad dx = \frac{L}{4\pi} dy$$

$$\langle x \rangle = \frac{2}{L} \left(\frac{L}{4\pi}\right)^2 \int_0^{4\pi} y \sin^2 y dy$$

$$= \frac{2L}{(4\pi)^2} \left[\frac{y^2}{4} - \frac{y \sin 2y}{4} - \frac{\cos 2y}{8}\right]_0^{4\pi}$$

$$= \frac{2L}{(4\pi)^2} \frac{(4\pi)^2}{4} = \frac{L}{2}$$

(c) Calculate the expectation value of $p$ for the particle.
**Answer**:

$$\langle p\rangle = \frac{2}{L}\int_0^L \sin\frac{4\pi x}{L}\frac{\hbar}{i}\frac{d}{dx}\sin\frac{4\pi x}{L}dx$$
$$= \frac{2h}{iL}\frac{4\pi}{L}\int_0^L \sin\frac{4\pi x}{L}\cos\frac{4\pi x}{L} = 0$$

(d) Calculate the expectation value of the kinetic energy of the particle.
**Answer**:

$$\langle T\rangle = \frac{2}{L}\int_0^L \sin\frac{4\pi x}{L}\left(-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\right)\sin\frac{4\pi x}{L}dx$$
$$\frac{d^2}{dx^2}\sin\frac{4\pi x}{L} = -\left(\frac{4\pi}{L}\right)^2\sin\frac{4\pi x}{L}$$
$$\langle T\rangle = \frac{2}{L}\frac{\hbar^2}{2m}\left(\frac{4\pi}{L}\right)^2\int_0^L \sin^2\frac{4\pi x}{L}dx$$
$$= \frac{2}{L}\frac{L}{2}\frac{16\hbar^2\pi^2}{2mL^2} = \frac{16\hbar^2\pi^2}{2mL^2}$$

(e) Calculate the probability of finding the particle in the region from $x = 0$ to $x = L/4$.
**Answer**:

$$P = \frac{2}{L}\int_0^{L/4}\sin^2\frac{4\pi x}{L}dx$$
$$= \frac{2}{L}\frac{L}{4\pi}\int_0^{\pi}\sin^2 y dy$$
$$= \frac{2}{L}\frac{L}{4\pi}\frac{\pi}{2} = \frac{1}{4}$$

6. The state of a one-dimensional quantum system is represented by the wavefunction

$$\psi(x) = N\sin(3\pi x)$$

for $0 < x < 1$ with $N$ being the normalization factor. Calculate the probability that a measurement of the position of the particle will give a result in the range $2/3 \le x < 1$.
**Answer**:

$$N^2\int_0^1 \sin^2 3\pi x\ dx = 1$$
$$y = 3\pi x \qquad dx = \frac{1}{3\pi}\ dy$$
$$\frac{N^2}{3\pi}\int_0^{3\pi}\sin^2 y\ dy = \frac{N^2}{3\pi}\left[\frac{y}{2} - \frac{1}{4}\sin 2y\right]_0^{3\pi} = \frac{N^2}{2} = 1$$

or

$$N = \sqrt{2}$$

$$P = 2\int_{2/3}^{1} \sin^2 3\pi x \, dx = \frac{2}{3\pi}\int_{2\pi}^{3\pi} \sin^2 y \, dy = \frac{2}{3\pi}\left[\frac{y}{2} - \frac{1}{4}\sin 2y\right]_{2\pi}^{3\pi}$$
$$= \frac{2}{3\pi}\frac{\pi}{2} = \frac{1}{3}.$$

7. The wavefunction for a one-dimensional particle of mass $m$ confined to move on the interval $0 \leq x \leq \pi$ is given by

$$\psi(x) = N\sin(7x)$$

where $N$ is the normalization constant. Normalize the wavefunction to calculate $N$, and then calculate the expectation value of the kinetic energy of the particle.
**Answer**:

$$N^2\int_0^{\pi} \sin^2 7x \, dx = 1$$

$$y = 7x \qquad dx = \frac{dy}{7}$$

$$\frac{N^2}{7}\int_0^{7\pi} \sin^2 y \, dy = \frac{N^2}{7}\left[\frac{y}{2} - \frac{1}{4}\sin 2y\right]_0^{7\pi} = \frac{N^2}{7}\frac{7\pi}{2} = N^2\frac{\pi}{2} = 1$$

$$N = \left(\frac{2}{\pi}\right)^{1/2} \qquad \text{and} \qquad \psi(x) = \left(\frac{2}{\pi}\right)^{1/2}\sin(7x)$$

$$\langle T\rangle = \frac{2}{\pi}\int_0^{\pi} \sin 7x\left(-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\right)\sin 7x \, dx$$
$$= \frac{49\hbar^2}{\pi m}\int_0^{\pi} \sin^2 7x \, dx$$
$$= \frac{49\hbar^2}{\pi m}\frac{\pi}{2} = \frac{49\hbar^2}{2m}$$

8. The wavefunction for a harmonic oscillator of mass $m$ and natural frequency $\omega$ is given by

$$\psi(x) = \exp(-m\omega x^2/2\hbar).$$

Normalize this wavefunction and evaluate $\langle x\rangle$. Note the domain of this problem is $-\infty < x < \infty$.
**Answer**:

$$N^2\int_{-\infty}^{\infty} \exp(-mwx^2/\hbar) \, dx = N^2\left(\frac{\pi\hbar}{m\omega}\right)^{1/2} = 1$$

$$N = \left(\frac{m\omega}{\pi\hbar}\right)^{1/4}$$

$$\langle x\rangle = \left(\frac{m\omega}{\pi\hbar}\right)^{1/2}\int_{-\infty}^{\infty} x\exp(-m\omega x^2/\hbar) \, dx = 0$$

9. The wavefunction for a quantum system on the domain $-\infty < x < \infty$ is given by $\psi(x) = Ne^{-ax^2}$, where $a$ is a constant and $N$ is the normalization constant. Normalize the wavefunction and calculate an expression for the expectation value of $x^2$; i.e. $\langle x^2 \rangle$.
**Answer**:

$$\int_{-\infty}^{\infty} |\psi|^2 dx = N^2 \int_{-\infty}^{\infty} e^{-2ax^2} dx$$

$$= N^2 \left(\frac{\pi}{2a}\right)^{1/2} = 1$$

$$N = \left(\frac{2a}{\pi}\right)^{1/4}$$

and

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

$$\langle x^2 \rangle = \int_{-\infty}^{\infty} \psi^*(x) x^2 \psi(x) dx$$

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

$$= \left(\frac{2a}{\pi}\right)^{1/2} \int_{-\infty}^{\infty} x^2 e^{-2ax^2} dx = \left(\frac{2a}{\pi}\right)^{1/2} \left(\frac{\pi^{1/2}}{2(2a)^{3/2}}\right) = \frac{1}{4a}$$

10. A particle of mass $m$ is confined to move in one dimension on the domain $0 \le x < \infty$, and its quantum state is associated with the wavefunction $\psi(x) = Nxe^{-ax}$ where $N$ is the normalization and $a$ is a constant having units of inverse length. Normalize the wavefunction and derive an expression for $\langle 1/x \rangle$ for the particle.
**Answer**

$$N^2 \int_0^{\infty} x^2 e^{-2ax} \, dx = N^2 \frac{2!}{(2a)^3} = \frac{N^2}{4a^3} = 1$$

$$N = 2a^{3/2}$$

$$\left\langle \frac{1}{x} \right\rangle = 4a^3 \int_0^{\infty} xe^{-ax} \frac{1}{x} \, xe^{-ax} \, dx$$

$$= 4a^3 \int_0^{\infty} xe^{-2ax} \, dx = 4a^3 \frac{1}{(2a)^2} = a$$

11. The ground-state wavefunction for a quantum particle of mass $m$ defined on the domain $0 \le x < \infty$ is given by $\psi(x) = Nx \, e^{-ax^2}$, where $a$ is a constant having units of inverse length squared and $N$ is the normalization constant. Derive an expression for $\langle x^{-2} \rangle$ for the particle.
**Answer**:

$$N^2 \int_0^{\infty} x^2 \, e^{-2ax^2} \, dx = N^2 \frac{1}{4} \frac{\sqrt{\pi}}{(2a)^{3/2}} = 1 \qquad N = \frac{2(2a)^{3/4}}{\pi^{1/4}}$$

$$\langle x^{-2}\rangle = \frac{4(2a)^{3/2}}{\sqrt{\pi}}\int_0^\infty e^{-2ax^2}\,dx$$
$$= \frac{4(2a)^{3/2}}{\sqrt{\pi}}\frac{1}{2}\frac{\sqrt{\pi}}{\sqrt{2a}} = 4a$$

12. The state of a one-dimensional quantum particle of mass $m$ on the interval $0 \leq x < \infty$ is represented by the wavefunction

$$\psi(x) = Nxe^{-ax}$$

where $N$ is the normalization constant and $a$ is a constant having units of inverse length. Normalize the wavefunction and use the normalized wavefunction to determine the expectation value of the linear momentum $p$ of the particle.
**Answer**:

$$\int_0^\infty |\psi(x)|^2 dx = N^2\int_0^\infty x^2e^{-2ax}dx = N^2\frac{2}{(2a)^3} = \frac{N^2}{4a^3} = 1$$
$$N = 2a^{3/2}$$
$$\langle p\rangle = \int_0^\infty \psi^*(x)\ \hat{p}\ \psi(x)\ dx = 4a^3\int_0^\infty xe^{-ax}\frac{\hbar}{i}\frac{d}{dx}xe^{-ax}\ dx$$
$$= 4a^3\frac{\hbar}{i}\int_0^\infty xe^{-ax}[e^{-ax} - axe^{-ax}]dx$$
$$= 4a^3\frac{\hbar}{i}[\int_0^\infty xe^{-2ax}dx - a\int_0^\infty x^2e^{-2ax}dx]$$
$$= 4a^3\frac{\hbar}{i}\left[\frac{1}{(2a)^2} - \frac{2a}{(2a)^3}\right] = 4a^3\frac{\hbar}{i}\left[\frac{1}{4a^2} - \frac{1}{4a^2}\right] = 0$$

13. A one-dimensional particle of mass $m$ occupies the interval $0 \leq x < \infty$ in a state defined by the wavefunction

$$\psi(x) = Nxe^{-ax}$$

where $N$ is the normalization constant and $a$ is a constant having units of inverse length. Normalize the wavefunction, and use the normalized wavefunction to calculate the expectation value of the kinetic energy $\langle T\rangle$ of the particle.
**Answer**:

$$N^2\int_0^\infty x^2e^{-2ax}dx = N^2\frac{2!}{(2a)^3} = \frac{N^2}{4a^3} = 1 \qquad N = 2a^{3/2}$$
$$\langle T\rangle = \int_0^\infty \psi^*(x)\left(-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\right)\psi(x)\ dx$$
$$= -\frac{\hbar^2}{2m}4a^3\int_0^\infty xe^{-ax}\frac{d^2}{dx^2}xe^{-ax}\ dx$$
$$\frac{d}{dx}\frac{d}{dx}xe^{-ax} = \frac{d}{dx}[e^{-ax} - axe^{-ax}] = -2ae^{-ax} + a^2xe^{-ax}$$

$$
\begin{aligned}
\langle T \rangle &= \frac{\hbar^2}{2m} 4a^3 [\int_0^\infty 2axe^{-2ax}\ dx - a^2 \int_0^\infty x^2 e^{-2ax}\ dx] \\
&= \frac{2\hbar^2 a^3}{m} \left[ \frac{1}{2a} - \frac{1}{4a} \right] = \frac{\hbar^2 a^2}{2m}
\end{aligned}
$$

14. The unnormalized wavefunction for a quantum particle on the domain $0 \leq x < \infty$ is given by

$$
\psi(x) = Nxe^{-ax^2}
$$

where $N$ is the normalization and $a$ is a constant having units of the square of the inverse length. Calculate the expectation value of $x^2$ for the particle.
**Answer**:

$$
N^2 \int_0^\infty x^2\ e^{-2ax^2}\ dx = N^2 \frac{1}{4} \frac{\pi^{1/2}}{(2a)^{3/2}} = 1 \qquad N = 2 \left[ \frac{(2a)^{3/2}}{\pi^{1/2}} \right]^{1/2}
$$

$$
\langle x^2 \rangle = 4 \left[ \frac{(2a)^{3/2}}{\pi^{1/2}} \right] \int_0^\infty x\ e^{-ax^2}\ x^2 x\ e^{-ax^2}\ dx
$$

$$
= 4 \left[ \frac{(2a)^{3/2}}{\pi^{1/2}} \right] \int_0^\infty x^4 e^{-2ax^2}\ dx = 4 \left[ \frac{(2a)^{3/2}}{\pi^{1/2}} \right] \frac{3\pi^{1/2}}{8(2a)^{5/2}} = \frac{3}{4a}
$$