MATHCHAPTER B

Probability and Statistics

PROBLEMS AND SOLUTIONS

B–1. Consider a particle to be constrained to lie along a one-dimensional segment 0 to a. We will learn in the next chapter that the probability that the particle is found to lie between x and $x + dx$ is given by

$$p(x)dx = \frac{2}{a}\sin^2\frac{n\pi x}{a}dx$$

where $n = 1, 2, 3, \ldots$. First show that $p(x)$ is normalized. Now calculate the average position of the particle along the line segment. The integrals that you need are (*The CRC Handbook of Chemistry and Physics* or *The CRC Standard Mathematical Tables*, CRC Press)

$$\int \sin^2\alpha x dx = \frac{x}{2} - \frac{\sin 2\alpha x}{4\alpha}$$

and

$$\int x\sin^2\alpha x dx = \frac{x^2}{4} - \frac{x\sin 2\alpha x}{4\alpha} - \frac{\cos 2\alpha x}{8\alpha^2}$$

If $p(x)$ is normalized, then $\int_0^a p(x)dx = 1$.

$$\begin{aligned}\int_0^a p(x)dx &= \int_0^a \frac{2}{a}\sin^2\frac{n\pi x}{a}dx \\ &= \left[\frac{2}{a}\left(\frac{x}{2} - \frac{\sin 2n\pi a^{-1}x}{4n\pi a^{-1}}\right)\right]_0^a \\ &= \frac{2}{a}\left[\frac{a}{2} - \frac{\sin 2n\pi}{4n\pi a^{-1}} - 0 + \frac{\sin 0}{4n\pi a^{-1}}\right] \\ &= \frac{2}{a}\left(\frac{a}{2}\right) = 1\end{aligned}$$

Thus, $p(x)$ is normalized. To find the average position of the particle along the line segment, use Equation B.12:

$$\begin{aligned}\langle x\rangle &= \int_0^a xp(x)dx = \int_0^a x\frac{2}{a}\sin^2\frac{n\pi x}{a}dx \\ &= \frac{2}{a}\left[\frac{x^2}{4} - \frac{x\sin 2n\pi a^{-1}x}{4n\pi a^{-1}} - \frac{\cos 2n\pi a^{-1}x}{8n^2\pi^2a^{-2}}\right]_0^a \\ &= \frac{2}{a}\left[\frac{a^2}{4} - \frac{a\sin 2n\pi}{4n\pi a^{-1}} - \frac{\cos 2n\pi}{8n^2\pi^2a^{-2}} + \frac{\cos 0}{8n^2\pi^2a^{-2}}\right] \\ &= \frac{2}{a}\left[\frac{a^2}{4} - \frac{1}{8n^2\pi^2a^{-2}} + \frac{1}{8n^2\pi^2a^{-2}}\right] = \frac{2}{a}\left(\frac{a^2}{4}\right) \\ &= \frac{a}{2}\end{aligned}$$

B–2. Calculate the variance associated with the probability distribution given in Problem B–1. The necessary integral is (*CRC tables*)

$$\int x^2 \sin^2 \alpha x dx = \frac{x^3}{6} - \left(\frac{x^2}{4\alpha} - \frac{1}{8\alpha^3}\right)\sin 2\alpha x - \frac{x\cos 2\alpha x}{4\alpha^2}$$

Use Equation B.13:

$$\begin{aligned}
\langle x^2\rangle &= \int_0^a x^2 p(x)dx = \frac{2}{a}\int_0^a x^2 \sin^2\frac{n\pi x}{a}dx \\
&= \frac{2}{a}\left[\frac{x^3}{6} - \left(\frac{x^2}{4n\pi a^{-1}} - \frac{1}{8n^3\pi^3 a^{-3}}\right)\sin 2n\pi a^{-1}x - \frac{x\cos 2n\pi a^{-1}x}{4n^2\pi^2 a^{-2}}\right]_0^a \\
&= \frac{2}{a}\left[\frac{a^3}{6} - \left(\frac{a^2}{4n\pi a^{-1}} - \frac{1}{8n^3\pi^3 a^{-3}}\right)\sin 2n\pi - \frac{a\cos 2n\pi}{4n^2\pi^2 a^{-2}} - 0\right] \\
&= \frac{2}{a}\left(\frac{a^3}{6} - \frac{a^3}{4n^2\pi^2}\right) \\
&= \frac{a^2}{3} - \frac{a^2}{2n^2\pi^2}
\end{aligned}$$

The variance σ^2 is given by

$$\sigma^2 = \langle x^2\rangle - \langle x\rangle^2 \qquad \text{(B.8)}$$

Using the result of Problem B–1 and the above result for $\langle x^2\rangle$ gives

$$\begin{aligned}
\sigma^2 &= \frac{a^2}{3} - \frac{a^2}{2n^2\pi^2} - \frac{a^2}{4} \\
&= \frac{a^2}{12} - \frac{a^2}{2n^2\pi^2}
\end{aligned}$$

B–3. Using the probability distribution given in Problem B–1, calculate the probability that the particle will be found between 0 and $a/2$. The necessary integral is given in Problem B–1.

The probability that the particle will lie within the region 0 to $a/2$ is given by $\int_0^{a/2} p(x)dx$ (Equation B.10).

$$\begin{aligned}
\int_0^{a/2} p(x)dx &= \int_0^{a/2} \frac{2}{a}\sin^2\frac{n\pi x}{a}dx \\
&= \frac{2}{a}\int_0^{a/2} \sin^2\frac{n\pi x}{a}dx \\
&= \frac{2}{a}\left[\frac{x}{2} - \frac{\sin 2n\pi a^{-1}x}{4n\pi a^{-1}}\right]_0^{a/2} \\
&= \frac{2}{a}\left[\frac{a}{4} - \frac{\sin 2n\pi}{8n\pi a^{-1}} + \frac{\sin 0}{4n\pi a^{-1}}\right] \\
&= \frac{2}{a}\left(\frac{a}{4}\right) = \frac{1}{2}
\end{aligned}$$

The probability of the particle being found in exactly half the box is 0.5.

B–4. Prove explicitly that

$$\int_{-\infty}^{\infty} e^{-\alpha x^2}dx = 2\int_0^{\infty} e^{-\alpha x^2}dx$$

by breaking the integral from $-\infty$ to ∞ into one from $-\infty$ to 0 and another from 0 to ∞. Now let $z = -x$ in the first integral and $z = x$ in the second to prove the above relation.

$$\int_{-\infty}^{\infty} e^{-\alpha x^2}dx = \int_{-\infty}^{0} e^{-\alpha x^2}dx + \int_0^{\infty} e^{-\alpha x^2}dx$$

We can let $z = -x$ in the first integral and $z = x$ in the second and write

$$\begin{aligned}
\int_{-\infty}^{\infty} e^{-\alpha x^2}dx &= -\int_{\infty}^{0} e^{-\alpha z^2}dz + \int_0^{\infty} e^{-\alpha x^2}dx \\
&= \int_0^{\infty} e^{-\alpha z^2}dz + \int_0^{\infty} e^{-\alpha z^2}dz \\
&= 2\int_0^{\infty} e^{-\alpha z^2}dz = 2\int_0^{\infty} e^{-\alpha x^2}dx
\end{aligned}$$

B–5. By using the procedure in Problem B–4, show explicitly that

$$\int_{-\infty}^{\infty} xe^{-\alpha x^2}dx = 0$$

$$\int_{-\infty}^{\infty} xe^{-\alpha x^2}dx = \int_{-\infty}^{0} xe^{-\alpha x^2}dx + \int_0^{\infty} xe^{-\alpha x^2}dx$$

We can let $x = -z$ in the first integral to get

$$\begin{aligned}
\int_{-\infty}^{\infty} xe^{-\alpha x^2}dx &= \int_{\infty}^{0} ze^{-\alpha z^2}dz + \int_0^{\infty} xe^{-\alpha x^2}dx \\
&= -\int_0^{\infty} ze^{-\alpha z^2}dz + \int_0^{\infty} xe^{-\alpha x^2}dx \\
&= -\int_0^{\infty} xe^{-\alpha x^2}dx + \int_0^{\infty} xe^{-\alpha x^2}dx \\
&= 0
\end{aligned}$$

B–6. We will learn in Chapter 25 that the molecules in a gas travel at various speeds, and that the probability that a molecule has a speed between v and $v + dv$ is given by

$$p(v)dv = 4\pi\left(\frac{m}{2\pi k_B T}\right)^{3/2} v^2 e^{-mv^2/2k_B T}dv \qquad 0 \le v < \infty$$

where m is the mass of the particle, k_B is the Boltzmann constant (the molar gas constant R divided by the Avogadro constant), and T is the Kelvin temperature. The probability distribution of molecular speeds is called the Maxwell-Boltzmann distribution. First show that $p(v)$ is normalized, and then determine the average speed as a function of temperature. The necessary integrals are (*CRC tables*)

$$\int_0^{\infty} x^{2n}e^{-\alpha x^2}dx = \frac{1\cdot 3\cdot 5\cdots(2n-1)}{2^{n+1}\alpha^n}\left(\frac{\pi}{\alpha}\right)^{1/2} \qquad n \ge 1$$

and

$$\int_0^\infty x^{2n+1}e^{-ax^2}dx = \frac{n!}{2\alpha^{n+1}}$$

where $n!$ is n factorial, or $n! = n(n-1)(n-2)\cdots(1)$.

First, we demonstrate that $p(v)$ is normalized by showing that $\int_0^\infty p(v)dv = 1$:

$$\begin{aligned}\int_0^\infty p(v)dv &= 4\pi\left(\frac{m}{2\pi k_B T}\right)^{3/2}\int_0^\infty v^2 e^{-mv^2/2k_B T}dv \\ &= 4\pi\left(\frac{m}{2\pi k_B T}\right)^{3/2}\frac{2k_B T}{4m}\left(\frac{2\pi k_B T}{m}\right)^{1/2} \\ &= \pi^{3/2}\left(\frac{m}{2\pi k_B T}\right)^{3/2}\left(\frac{2k_B T}{m}\right)^{3/2} \\ &= 1\end{aligned}$$

Using Equation B.12, we write

$$\begin{aligned}\langle v\rangle &= 4\pi\left(\frac{m}{2\pi k_B T}\right)^{3/2}\int_0^\infty v^3 e^{-mv^2/2k_B T}dv \\ &= 4\pi\left(\frac{m}{2\pi k_B T}\right)^{3/2}\left[2\left(\frac{m}{2k_B T}\right)^2\right]^{-1} \\ &= 2\pi\left(\frac{m}{2\pi k_B T}\right)^{3/2}\left(\frac{2k_B T}{m}\right)^2 \\ &= \left(\frac{8k_B T}{\pi m}\right)^{1/2}\end{aligned}$$

B–7. Use the Maxwell-Boltzmann distribution in Problem B–6 to determine the average kinetic energy of a gas-phase molecule as a function of temperature. The necessary integral is given in Problem B–6.

Kinetic energy, KE, is defined as $\text{KE} = \frac{1}{2}mv^2$, so $\langle\text{KE}\rangle = \frac{1}{2}m\langle v^2\rangle$. Using Equation B.13, we write

$$\begin{aligned}\langle v^2\rangle &= 4\pi\left(\frac{m}{2\pi k_B T}\right)^{3/2}\int_0^\infty v^4 e^{-mv^2/2k_B T}dv \\ &= 4\pi\left(\frac{m}{2\pi k_B T}\right)^{3/2}\frac{3}{8}\left(\frac{2k_B T}{m}\right)^2\left(\frac{2\pi k_B T}{m}\right)^{1/2} \\ &= \frac{3k_B T}{m}\end{aligned}$$

And so $E = \frac{1}{2}m\langle v^2\rangle = \frac{3}{2}k_B T$.

CHAPTER 3

The Schrödinger Equation and a Particle in a Box

PROBLEMS AND SOLUTIONS

3–1. Evaluate $g = \hat{A}f$, where $\hat{A}$ and f are given below:

	$\hat{A}$	f
(a)	SQRT	x^4
(b)	$\frac{d^3}{dx^3} + x^3$	e^{-ax}
(c)	$\int_0^1 dx$	$x^3 - 2x + 3$
(d)	$\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$	$x^3y^2z^4$

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a. $\text{SQRT}(x^4) = \pm x^2$

b. $\frac{d^3e^{-ax}}{dx^3} + x^3e^{-ax} = -a^3e^{-ax} + x^3e^{-ax} = e^{-ax}(x^3 - a^3)$

c. $\int_0^1 (x^3 - 2x + 3)\,dx = \frac{x^4}{4} - x^2 + 3x\Big|_0^1 = \frac{9}{4}$

d. $\frac{\partial^2(x^3y^2z^4)}{\partial x^2} + \frac{\partial^2(x^3y^2z^4)}{\partial y^2} + \frac{\partial^2(x^3y^2z^4)}{\partial z^2} = 6xy^2z^4 + 2x^3z^4 + 12x^3y^2z^2$

3–2. Determine whether the following operators are linear or nonlinear:

a. $\hat{A}f(x) = \text{SQR}f(x)$ [square $f(x)$]

b. $\hat{A}f(x) = f^*(x)$ [form the complex conjugate of $f(x)$]

c. $\hat{A}f(x) = 0$ [multiply $f(x)$ by zero]

d. $\hat{A}f(x) = [f(x)]^{-1}$ [take the reciprocal of $f(x)$]

e. $\hat{A}f(x) = f(0)$ [evaluate $f(x)$ at $x = 0$]

f. $\hat{A}f(x) = \ln f(x)$ [take the logarithm of $f(x)$]
