Probability

CHEM 361B: Introduction to Physical Chemistry

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Lecture 5

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Learning Objective: Develop mathematical tools in the context of describing probabilities

References:

- McQuarrie §B

A Little Stats

You are given this information:

No. of people	Age
1	14
1	15
3	16
2	22
2	24
5	25

1. What is the probability of being 15?
2. What is the most probable age?
3. What is the average age?
4. What is the average of the squares of the ages?
5. What is the standard deviation of the ages?

We will spend this lecture defining how to answer these questions.

Some Definitions

Consider an experiment (like flipping a coin) with n possible outcomes, each with probability p_j, where $j = 1, 2, \ldots, n$. If the experiment is repeated an infinite number of times then

$$p_j = \lim_{N \to \infty} \frac{N_j}{N} \quad j = 1, 2, \ldots, n$$

where N_j is the number of times the event j occurs, and N is the total number of repetitions of the experiment.

Some Definitions (cont.)

Because $0 \leq N_j \leq N$, p_j must satisfy the condition

$$0 \leq p_j \leq 1$$

When $p_j = 1$, the event j will occur with 100% certainty and when $p_j = 0$ then the event j is impossible. In addition, because

$$\sum_{j=1}^{n} N_j = N$$

We have the normalisation condition

$$\sum_{j=1}^{n} p_j = 1$$

which means that the probability that some event occurs is a certainty.

Calculating the Expectation Value

The average value, also known as the expectation value is defined as

$$\langle x \rangle = \sum_{j=1}^{n} x_j p(x_j)$$

where $p(x_j)$ is the probability of realising the event x_j.

For the birthday example, the average age is:

$$\begin{aligned}\langle age \rangle = 14(1/14) + 15(1/14) + 16(3/14) \\ + 22(2/14) + 24(2/14) + 25(5/14) = 21\end{aligned}$$

Calculating the Second Moment

The average of the squares of a set of events or the second moment is defined as

$$\langle x^2 \rangle = \sum_{j=1}^{n} x_j^2 p(x_j)$$

where $p(x_j)$ is the probability of realising the event x_j.

For the birthday example, the second moment of the age is:

$$\begin{aligned}\langle age^2 \rangle = {} & 14^2(1/14) + 15^2(1/14) + 16^2(3/14) \\ & + 22^2(2/14) + 24^2(2/14) + 25^2(5/14) = 459.6\end{aligned}$$

Calculating The Standard Deviation

To determine the standard deviation or 'spread' of some data set around the average it is logical to find out how far each value is from the average

$$\delta x_j = x_j - \langle x \rangle$$

but the average or expectation value of this would be zero. To solve this we take the square before averaging (instead of absolute values)

$$\sigma_x^2 = \langle (\delta x_j)^2 \rangle = \sum_{j=1}^{n} (x_j - \langle x \rangle)^2 p(x_j) = \langle x^2 \rangle - \langle x \rangle^2$$

This is called the variance of the distribution. The standard deviation is the square root of the variance:

$$\sigma_x = \sqrt{\langle x^2 \rangle - \langle x \rangle^2}$$

For Continuous Distributions

Flipping a coin, or the birthday example are discrete distributions (only certain values of x_j are allowed). In this course we will look at continuous distributions (all values between two numbers, say a and b are allowed and have a probability associated with them). This means:

$$Prob(x, x + dx) = p(x)\ dx$$

so the total probability of a set of events between a and b is:

$$Prob(a \leq x \leq b) = \int_a^b p(x)\ dx$$

For Continuous Distrubutions (cont.)

Therefore, the normalisation condition is

$$\int_{-\infty}^{\infty} p(x)\ dx = 1$$

and

$$\begin{aligned} \langle x \rangle &= \int_{-\infty}^{\infty} x p(x)\ dx \\ \langle x^2 \rangle &= \int_{-\infty}^{\infty} x^2 p(x)\ dx \\ \sigma_x^2 &= \int_{-\infty}^{\infty} (x - \langle x \rangle)^2 p(x)\ dx \end{aligned}$$

Continuous Distribution Example

Perhaps the simplest continuous distribution is the so-called uniform distribution, where

$$p(x) = \begin{cases} A & 1 \leq x \leq 2 \\ 0 & \text{otherwise} \end{cases}$$

Determine A, $\langle x \rangle$, $\langle x^2 \rangle$, σ_x^2 and σ_x for this distribution.

Summary

- Quantum mechanics is a probabilistic model where objects are represented as waves and events occur with some likelihood.
- We will employ the normalisation condition, the $\langle x \rangle$, and σ_x to find physical, measurable quantities from quantum mechanical systems.