Week 2: The wave function, Particle in a box

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- Q5.5 Explain how it is possible to create a three-dimensional electron conductor that has a continuous energy spectrum in two dimensions and a discrete energy spectrum in the third.

Example exercises calculated by me

- P4.19 Show that the eigenfunctions of a 3D particle in a box with lengths along the x, y, and z directions of a, b, and c, respectively, are

$$\psi_{n_x,n_y,n_z}(x,y,z) = N \sin\left(\frac{n_x \pi x}{a}\right) \sin\left(\frac{n_y \pi y}{b}\right) \sin\left(\frac{n_z \pi z}{c}\right)$$

  Obtain an expression for E_{n_x,n_y,n_z} in terms of n_x, n_y, n_z, and a, b, and c.

- P4.35 Is the superposition wave function

$$\psi(x) = \sqrt{2/a}[\sin(n\pi x/a) + \sin(m\pi x/a)]$$

  an eigenfunction of the total energy operator for the particle in the box?

One more example

P5.5 For the π-network of β-carotene modeled with the particle in the box approach, the position-dependent probability density of finding 1 of the 22 electrons is given by

$$P_n(x) = |\psi_n(x)|^2 = \frac{2}{a}\sin^2\left(\frac{n\pi x}{a}\right)$$

The quantum number n in this equation is determined by the energy level of the nth electron. Would you also expect the total probability density defined by $P_{\text{total}}(x) = \sum_n |\psi_n(x)|^2$ to be strongly position dependent? The sum is over all the electrons in the π-network. Calculate the total probability density $P_{\text{total}}(x) = \sum_n |\psi_n(x)|^2$ using the box length $a = 2.90\ \mathrm{nm}$ and plot your results as a function of x. Does $P_{\text{total}}(x)$ have the same value near the ends and at the middle of the molecule?
What value would you expect for $P_{\text{total}}(x)$ if the electrons were uniformly distributed over the molecule? How does this value compare with your previous result?

Exercises 1

- P4.2 Show that the energy eigenvalues for the free particle, $E = \hbar^2 k^2/2m$, are consistent with the classical result $E = (1/2)mv^2$.
- P5.1 Calculate the energy levels of the π-network in butadiene, $\mathrm{C_4H_6}$, using the particle in the box model. To calculate the box length, assume that the molecule is linear and use the values 135 and 154 pm for $\mathrm{C = C}$ and $\mathrm{C - C}$ bonds. What is the wavelength of light required to induce a transition from the ground state to the first excited state? How does this compare with the experimentally observed value of 290 nm ? What does the comparison suggest to you about estimating the length of the π-network by adding bond lengths for this molecule?

Exercises 2

- P4.30 (This exercise is wrong as it is formulated in the book) Suppose that the wave function for a system can be written as

$$\psi(x) = \frac{\sqrt{2}}{4}\phi_1(x) + \frac{1}{\sqrt{2}}\phi_2(x) + \frac{2+\sqrt{2}i}{4}\phi_3(x)$$

  and that $\phi_1(x), \phi_2(x)$, and $\phi_3(x)$ are orthonormal eigenfunctions of the operator $\hat{H}$ with eigenvalues $E_1, 2E_1$, and $4E_1$, respectively.
  - Verify that $\psi(x)$ is normalized.
  - What are the possible values that you could obtain in measuring the energy $\hat{H}$ on identically prepared systems?
  - What is the probability of measuring each of these eigenvalues?
  - What is the average value of $\langle \hat{H} \rangle$ that you would obtain from a large number of measurements?
- Exercise P5.1 for a challenge!