Quantum Mechanics and Spectroscopy
CHEM 3PA3
Assignment 1 Answers

1. Indicate if the following statements are true (T) or false (F).

   (a) Doubling the wavelength of the radiation doubles its frequency. F

   $$\begin{aligned} &c = \lambda_1\nu_1 = \lambda_2\nu_2 \\ &\lambda_2 = 2\lambda_1 \\ &\lambda_2\nu_2 = 2\lambda_1\nu_2 = \lambda_1\nu_1 \\ &\nu_2 = \frac{\lambda_1\nu_1}{2\lambda_1} = \frac{\nu_1}{2} \end{aligned}$$

   (b) Doubling the frequency of the radiation halves its traveling speed. F
   The speed of radiation does not depend on frequency.

   (c) The wavefunction of the particle in a box must be a real function. F

2. Calculate the expectation value of position ($\hat{x} = x$) for the particle in a box. Remember that $\Psi_n(x) = \sqrt{\frac{2}{a}} \sin\frac{n\pi x}{a}$. Draw the probability distribution $|\Psi_n(x)|^2$ for $n = 1$ and $n = 2$. Does the expectation value depend on n? What can you conclude from the expectation value and the probability distribution for $n = 2$? $a/2$; no; although the probability of finding the particle at $x = a/2$ for n_2 is 0, the average is still the middle of the box.

$$\begin{aligned} \int_0^a \Psi^\star(x)\hat{x}\Psi(x)dx &= \int_0^a \left[\frac{2}{a}\sin\left(\frac{n\pi x}{a}\right)\right](x)\left[\frac{2}{a}\sin\left(\frac{n\pi x}{a}\right)\right]dx \\ &= \frac{2}{a}\int_0^a x\sin^2\left(\frac{n\pi x}{a}\right)dx \\ &= \frac{2}{a}\int_0^a x\left[\frac{1}{2}\left(1-\cos\left(\frac{2n\pi x}{a}\right)\right)\right]dx \\ &= \frac{2}{a}\left[\int_0^a \frac{x}{2}dx - \int_0^a\left[\frac{x}{2}\cos\left(\frac{2n\pi x}{a}\right)\right)\right]dx \\ &= \frac{1}{a}\left[\frac{x^2}{2}\Big|_0^a - \left[\left(\frac{a}{2n\pi}\right)\left(x\sin\left(\frac{2n\pi x}{a}\right)\right)\Big|_0^a - \int_0^a \sin\left(\frac{2n\pi x}{a}\right)dx\right]\right] \\ &= \frac{1}{a}\left[\frac{a^2}{2} - \left(\frac{a}{2n\pi}\right)\left(0 - \cos\left(\frac{2n\pi x}{a}\right)\Big|_0^a\right)\right] \\ &= \frac{a}{2} - 0 \end{aligned}$$

3. Is the position operator linear? yes

$$\begin{aligned} &\hat{x}(\Psi_1(x) + \Psi_2(x)) = x(\Psi_1(x) + \Psi_2(x)) = x\Psi_1(x) + x\Psi_2(x) \\ &\hat{x}(c\Psi(x)) = x(c\Psi(x)) = c(x\Psi(x)) \end{aligned}$$

4. Is the position operator hermitian? yes

$$\begin{aligned}
\int \Psi_1^\star(x)\hat{x}\Psi_2(x)dx &= \int \Psi_1^\star(x)x\Psi_2(x)dx \\
&= \int \Psi_1^\star(x)x\Psi_2(x)dx \\
&= \int \Psi_1^\star(x)x^\star\Psi_2(x)dx \\
&= \int \Psi_2(x)(x^\star\Psi_1^\star(x))dx \\
&= \int \Psi_2(x)(x\Psi_1(x))^\star dx
\end{aligned}$$

5. The radioactive isotope Co-60 is used in nuclear medicine to treat certain types of cancer. Calculate the wavelength and frequency of the emitted radiation if the energy is of 1.29×10^{11} J/mol. (Notice the units of energy) 9.27×10^{-13} m

$$E_{mol} = 1.29 \times 10^{11} \text{ J/mol}$$

$$E_{photon} = \frac{1.29 \times 10^{11} \text{ J/mol}}{6.022 \times 10^{23} \text{ photon/mol}} = 2.14 \times 10^{-13} \text{ J}$$

$$\lambda = \frac{hc}{E_{photon}} = \frac{(6.626 \times 10^{-34} \text{ J}\cdot\text{s})(2.998 \times 10^{8} \text{ m/s})}{2.14 \times 10^{-13} \text{ J}} = 9.27 \times 10^{-13} \text{ m}$$

6. Consider the butadiene molecule, $CH_2{=}CHCH{=}CH_2$ as system of particles in a box of 7.0 $\AA$ of length.

   (a) Write the electron configuration. $(n{=}1)^2(n{=}2)^2$

   (b) Calculate the lowest excitation energy. 6.1×10^{-19} J

$$\Delta E = E_{ES} - E_{GS} = \frac{(6.626 \times 10^{-34} \text{ J}\cdot s)^2(3^2 - 2^2)}{8 \times (9.11 \times 10^{-31} \text{ kg})(7.0 \times 10^{-10} \text{ m})^2} = 6.1 \times 10^{-19} \text{ J}$$

   (c) What is the wavelength of the photon that corresponds to this transition? 3.2×10^{-7} m

$$\lambda = \frac{hc}{\Delta E} = \frac{(6.626 \times 10^{-34} \text{ J}\cdot s)(2.998 \times 10^{8} \text{ m/s})}{6.1 \times 10^{-19} \text{ J}} = 3.2 \times 10^{-7} \text{ m}$$

   (d) Evaluate the De Broglie wavelength for the electron in the highest energy level of the ground state. 7.0×10^{-10} m

$$E_{n=2} = \frac{h^2n^2}{8ma^2} = \frac{p^2}{2m}$$

$$p = \sqrt{\frac{2mh^2n^2}{8ma^2}} = \sqrt{\frac{h^2n^2}{2^2a^2}} = \frac{hn}{2a}$$

$$\lambda = \frac{h}{p} = \frac{h(2a)}{hn} = \frac{2a}{n} = \frac{2a}{2} = a = 7.0 \times 10^{-10} \text{ m}$$