

SOLUTIONS

PROBLEM SET 2

CHM 3411, Dr. Chatfield

1. P7B.4 The normalized wavefunction is $\psi = \left(\frac{2}{L}\right)^{1/2} \sin\left(\frac{\pi x}{L}\right)$ and the probability that the particle will be found between a and b is:

$$\begin{aligned} P(a,b) &= \int_a^b \psi^2 dx \\ &= \frac{2}{L} \int_a^b \sin^2 \frac{\pi x}{L} dx = \frac{2}{L} \left(\frac{x}{2} - \frac{L}{4\pi} \sin \frac{2\pi x}{L} \right) \Big|_a^b \quad [\text{standard integral}] \\ &= \left(\frac{x}{L} - \frac{1}{2\pi} \sin \frac{2\pi x}{L} \right) \Big|_a^b \\ &= \frac{b-a}{L} - \frac{1}{2\pi} \left(\sin \frac{2\pi b}{L} - \sin \frac{2\pi a}{L} \right) \end{aligned}$$

Calculations with the above expression may be compared to the small-range approximation that uses the mid-range value $m = (a + b)/2$:

$$P(a,b) \approx |\psi(m)|^2 \times (b-a) = \frac{2}{L} \times \left(\sin \left(\frac{\pi \times m}{L} \right) \right)^2 \times (b-a)$$

$$L = 10.0 \text{ nm}$$

$$\text{(a)} \quad P(4.95, 5.05) = \frac{0.10}{10.0} - \frac{1}{2\pi} \left(\sin \frac{(2\pi) \times (5.05)}{10.0} - \sin \frac{(2\pi) \times (4.95)}{10.0} \right) = \boxed{0.020}$$

$$\text{Small range approximation: } \frac{2}{10} \times \left(\sin \left(\frac{\pi \times 5.00}{10} \right) \right)^2 \times (5.05 - 4.95) = 0.020$$

$$\text{(b)} \quad P(1.95, 2.05) = \frac{0.10}{10.0} - \frac{1}{2\pi} \left(\sin \frac{(2\pi) \times (2.05)}{10.0} - \sin \frac{(2\pi) \times (1.95)}{10.0} \right) = \boxed{6.91 \times 10^{-3}}$$

$$\text{Small range approximation: } \frac{2}{10} \times \left(\sin \left(\frac{\pi \times 2.00}{10} \right) \right)^2 \times (2.05 - 1.95) = 6.91 \times 10^{-3}$$

$$\text{(c)} \quad P(9.90, 10.0) = \frac{0.10}{10.0} - \frac{1}{2\pi} \left(\sin \frac{(2\pi) \times (10.0)}{10.0} - \sin \frac{(2\pi) \times (9.90)}{10.0} \right) = \boxed{6.58 \times 10^{-6}}$$

$$\text{Small range approximation: } \frac{2}{10} \times \left(\sin \left(\frac{\pi \times 9.95}{10} \right) \right)^2 \times (10.00 - 9.90) = 4.93 \times 10^{-6}$$

$$\text{(d)} \quad P(5.0, 10.0) = \boxed{0.5} \quad [\text{because the wavefunction is symmetrical around } x = L/2]$$

$$\text{(e)} \quad P\left(\frac{1}{3}L, \frac{2}{3}L\right) = \frac{1}{3} - \frac{1}{2\pi} \left(\sin \frac{4\pi}{3} - \sin \frac{2\pi}{3} \right) = \boxed{0.609}$$

$$\text{Small range approximation: } \frac{2}{10} \times \left(\sin \left(\frac{\pi}{2} \right) \right)^2 \times \left(\frac{2}{3} - \frac{1}{3} \right) \times 10 = 0.6667$$

Note in the above that the “small range approximation” is appropriate when the probability density does not change much over the range considered [not the case in (e)]. If you are not sure, calculate the integral explicitly – that always works.

2. P7B.1 (i, ii, iii)

$$i. \quad 1 = \int \psi^* \psi dx = \int_0^L N^2 \sin^2 \left(\frac{n\pi x}{L} \right) dx = N^2 \int_0^L \sin^2 \left(\frac{n\pi x}{L} \right) dx$$

$$[\text{Look up: } \int \sin^2 ax dx = \frac{1}{2} x - \frac{\sin 2ax}{4a} + c]$$

$$= N^2 \left[\frac{1}{2} x - \frac{\sin \left(\frac{2n\pi x}{L} \right)}{4n\pi/L} \right]_0^L \quad \left\langle \text{using } a = \frac{n\pi}{L} \right.$$

$$= N^2 \left[\left(\frac{L}{2} - 0 \right) - (0 - 0) \right] = N^2 \frac{L}{2}$$

$\sin(2n\pi) = 0$ for $n = 0, 1, 2, \dots$

$$N = \left(\frac{2}{L} \right)^{1/2} \quad \boxed{\psi = \left(\frac{2}{L} \right)^{1/2} \sin \left(\frac{n\pi x}{L} \right)}$$

$$ii. \quad 1 = \int_{-L}^L N^2 c^2 dx \quad (c = \text{the constant})$$

$$= N^2 c^2 [x]_{-L}^L = 2L N^2 c^2$$

$$N = (\sqrt{2L} c)^{-1} \quad \boxed{\psi = \frac{1}{c\sqrt{2L}} \quad c = \frac{1}{\sqrt{2L}}}$$

$$iii. \quad 1 = N^2 \int_0^{2\pi} \int_0^\pi \int_0^\infty e^{-2r/a} r^2 \sin \theta dr d\theta d\phi$$

$$= N^2 \underbrace{\left(\int_0^{2\pi} d\phi \right)}_{2\pi} \underbrace{\left(\int_0^\pi \sin \theta d\theta \right)}_2 \underbrace{\left(\int_0^\infty r^2 e^{-2r/a} dr \right)}_{n=2, "a" = \frac{2}{a} \Rightarrow \int = \frac{2!}{(2/a)^3} = \frac{10^3}{4}}$$

$$[\text{Look up: } \int_0^\infty x^n e^{-ax} dx = \frac{n!}{a^{n+1}}]$$

$$N = \left(\frac{1}{\pi a^3} \right)^{1/2} \quad \boxed{\psi = \left(\frac{1}{\pi a^3} \right)^{1/2} e^{-r/a}}$$

3. P7C.4

7C.4 Operate on each function f with \hat{i} (the inversion operator, which has the effect of making the replacement $x \rightarrow -x$). If the result of the operation is f multiplied by a constant, f is an eigenfunction of \hat{i} and the constant is the eigenvalue [7C.2a, b, and c].

(a) $f = x^3 - kx$

$$\hat{i}(x^3 - kx) = -x^3 + kx = -f$$

Yes, f is an eigenfunction with eigenvalue .

(b) $f = \cos kx$

$$\hat{i} \cos kx = \cos(-kx) = \cos kx = f$$

Yes, f is an eigenfunction with eigenvalue .

(c) $f = x^2 + 3x - 1$

$$\hat{i}(x^2 + 3x - 1) = x^2 - 3x - 1 \neq \text{constant} \times f$$

No, f is not an eigenfunction of \hat{i} .

4. P7C.2 (a, b, c only)

7C.2 The quantum mechanical operators are constructed by first writing the classical expression for the observable and then making operator substitutions for position and momentum. The operators for the x components of position and momentum are

$$\hat{x} = x \times \quad \text{and} \quad \hat{p}_x = \frac{\hbar}{i} \frac{d}{dx} \quad [7C.3]$$

The operator for p_x^2 is

$$\begin{aligned} \hat{p}_x^2 &= \hat{p}_x \hat{p}_x = \left(\frac{\hbar}{i} \frac{d}{dx} \right) \left(\frac{\hbar}{i} \frac{d}{dx} \right) \\ &= -\hbar^2 \frac{d^2}{dx^2} \quad \text{for one-dimensional systems} \\ &= -\hbar^2 \left(\frac{\partial^2}{\partial x^2} \right)_{y,z} \quad \text{for three-dimensional systems} \end{aligned}$$

(a) Kinetic energy in one dimension

$$\hat{E}_k = \frac{1}{2m} \hat{p}_x^2 = \boxed{-\frac{\hbar^2}{2m} \frac{d^2}{dx^2}}$$

Kinetic energy in three dimensions

$$\begin{aligned} \hat{E}_k &= \frac{1}{2m} (\hat{p}_x^2 + \hat{p}_y^2 + \hat{p}_z^2) = -\frac{\hbar^2}{2m} \left(\left(\frac{\partial^2}{\partial x^2} \right)_{y,z} + \left(\frac{\partial^2}{\partial y^2} \right)_{x,z} + \left(\frac{\partial^2}{\partial z^2} \right)_{x,y} \right) \\ &= \boxed{-\frac{\hbar^2}{2m} \nabla^2} \quad \text{where } \nabla^2 = \left(\frac{\partial^2}{\partial x^2} \right)_{y,z} + \left(\frac{\partial^2}{\partial y^2} \right)_{x,z} + \left(\frac{\partial^2}{\partial z^2} \right)_{x,y} = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \end{aligned}$$

(b) The inverse separation, $1/x$

$$\frac{\hat{1}}{x} = \boxed{\frac{1}{x} \times}$$

The inverse separation in three dimensions is determined by the vector magnitude of the position vector $\vec{r} = x\vec{i} + y\vec{j} + z\vec{k}$:

$$\frac{\hat{1}}{r} = \boxed{\frac{1}{\{x^2 + y^2 + z^2\}^{1/2}}}$$

(c) The electric dipole moment for J point charges Q_J at the positions x_J is $\boxed{\sum_J Q_J x_J}$. Similarly, the electric

dipole moment operator for J point charges Q_J at the vector positions \vec{r}_J is

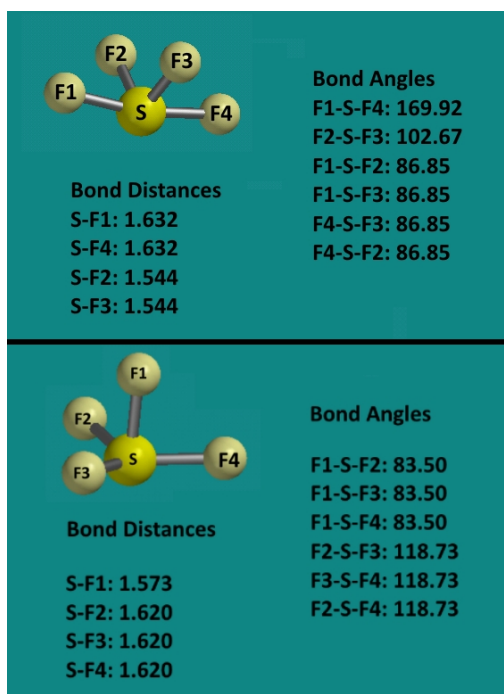
$$\hat{\mu}_x \vec{i} + \hat{\mu}_y \vec{j} + \hat{\mu}_z \vec{k} = \sum_J Q_J x_J \vec{i} + \sum_J Q_J y_J \vec{j} + \sum_J Q_J z_J \vec{k}$$

The magnitude of the electric dipole moment, μ , is

$$\mu = \left\{ \mu_x^2 + \mu_y^2 + \mu_z^2 \right\}^{1/2} = \left\{ \left(\sum_J Q_J x_J \right)^2 + \left(\sum_J Q_J y_J \right)^2 + \left(\sum_J Q_J z_J \right)^2 \right\}^{1/2}$$

5. Both structures are energy minima, as stable geometries were obtained for both upon geometry optimization. Both structures maintained the initial symmetry during the optimization, although bond distances and angles were adjusted. However, the see-saw conformation is favored by 143.9 kJ/mol (the Spartan energies are in Hartrees, and the conversion is 1 Hartree = 2625.5 kJ/mol), and so at room temperature the population of the trigonal bipyramidal conformation is 6.16×10^{-26} %, and thus would not be detected. The Boltzmann equation was used to determine the relative population of a species:

$\frac{N_2}{N_1} = e^{-\Delta E/RT}$ where R is the gas constant, 8.314 J/mol K, T is temperature in Kelvin, assumed to be room temperature (298 K), ΔE is the difference between the energies of the two species, and N_1 and N_2 are the populations of the two species.



Addendum to Problem 5 solution:

In class, we said that the fraction of molecules in a higher-energy minimum geometry is:

$$\frac{n_2}{n_1 + n_2} = \frac{e^{\Delta E/RT}}{1 + e^{\Delta E/RT}}$$

This looks a little different from what is calculated above. But it really is just two related things. The equation immediately above gives the fraction of molecules in state n_2 . The equation on the previous page gives the ratio of the number of molecules in state n_2 to those in state n_1 . Sorry for inconsistency, but I think you get the message. By the way, the ΔE should always be positive. It is the energy of the higher-energy conformer minus the energy of the lower-energy conformer.