Quantum Mechanics and Spectroscopy
CHEM 3PA3
Tutorial 1

1. What is the de Broglie wavelenght for a baseball (0.14 kg) travelling at 40 m/s?

$$\lambda = \frac{h}{p} = \frac{h}{mv} = \frac{6.626 \times 10^{-34}\,\mathrm{J \cdot s}}{(0.14\,\mathrm{kg})(40\,\mathrm{m/s})} = 1.2 \times 10^{-34}\,\mathrm{m}$$

   Note that the wavelength is so small that it is insignificant compared to the size of the baseball.

2. Given a photon with wave number $k = 10^7 m$,

   - what is the wavelength of the photon?

   $$\lambda = \frac{2\pi}{k} = 6.283 \times 10^{-7}\,\mathrm{m} = 628.3\,\mathrm{nm}$$

   - what is the momentum of the photon?

   $$p = \frac{h}{\lambda} = \frac{6.626 \times 10^{-34}\,\mathrm{J \cdot s}}{6.283 \times 10^{-7}\,\mathrm{m}} = 1.055 \times 10^{-27}\,\mathrm{kg \cdot m/s}$$

   - what is the energy of the photon?
     The photon travels at the speed of light, so $v = c = 2.998 \times 10^8$ m/s.

   $$E = h\nu = \frac{hc}{\lambda} = pc = (1.055 \times 10^{-27}\,\mathrm{kg \cdot m/s})(2.998 \times 10^8\,\mathrm{m/s} = 3.162 \times 10^{-19}\,\mathrm{kg \cdot m^2/s^2}$$

   - what is the relativistic mass of the photon (photons do not have actual mass)?

   $$m = \frac{p}{c} = \frac{1.055 \times 10^{-27}\,\mathrm{kg \cdot m/s}}{2.998 \times 10^8\,\mathrm{m/s}} = 3.52 \times 10^{-36}\,\mathrm{m}$$

3. Calculate the expected 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 expectated 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.

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

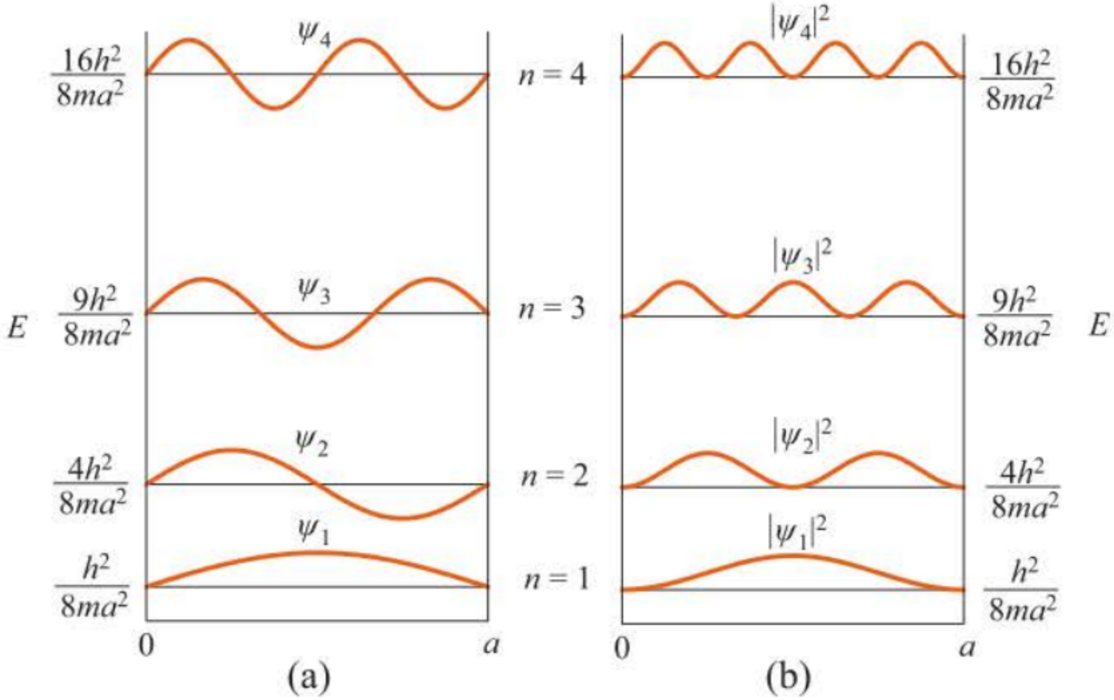

Figure 1: The energy levels, wave functions (a), and probability densities (b) for the particle in a box. Figure taken from Quantum Chemistry by Donald A. McQuarrrie.

4. Consider a particle in a two-dimensional box, where the potential energy is given by

$$V(x,y) = \begin{cases} 0 & \text{if } 0 < x < a \text{ and } 0 < y < b \\ \infty & \text{otherwise} \end{cases}$$

The Schrödinger equation only the kinetic energy terms,

$$-\frac{\hbar^2}{2m}\left(\frac{\partial^2\Psi}{\partial x^2}+\frac{\partial^2\Psi}{\partial y^2}\right)=E\Psi. \tag{1}$$

The wavefunction can be written as $\Psi(x,y) = f(x)g(y)$, and substituting in the Schrödinger equation,

$$-\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2}\left[f(x)g(y)\right]+\frac{\partial^2}{\partial y^2}\left[f(x)g(y)\right]\right)=Ef(x)g(y). \tag{2}$$

Terms that are not affected by the derivative can be factored out:

$$-\frac{\hbar^2}{2m}\left(g(y)\frac{\partial^2 f(x)}{\partial x^2}+f(x)\frac{\partial^2 g(y)}{\partial y^2}\right)=Ef(x)g(y), \tag{3}$$

and dividing by $f(x)g(y)$,

$$-\frac{\hbar^2}{2m}\left(\frac{1}{f(x)}\frac{\partial^2 f(x)}{\partial x^2}+\frac{1}{g(y)}\frac{\partial^2 g(y)}{\partial y^2}\right)=E, \tag{4}$$

Note that the x and y term are independent of each other, so we can separate the total energy into E_x and E_y,

$$\begin{aligned}E_x &= -\frac{\hbar^2}{2m}\frac{1}{f(x)}\frac{\partial^2 f(x)}{\partial x^2}\\ E_y &= -\frac{\hbar^2}{2m}\frac{1}{g(y)}\frac{\partial^2 g(y)}{\partial y^2}\end{aligned} \tag{5}$$

Both equations represent the particle in a one dimensional box. The solution for the energy and wavefunction is given by:

$$\begin{aligned}E_x &= \frac{n_x^2h^2}{8ma^2} \qquad n_x = 1,2,\ldots\\ E_y &= \frac{n_y^2h^2}{8mb^2} \qquad n_y = 1,2,\ldots\\ f(x) &= \left(\frac{2}{a}\right)^{1/2}\sin\left(\frac{n_x\pi x}{a}\right)\\ g(y) &= \left(\frac{2}{b}\right)^{1/2}\sin\left(\frac{n_y\pi x}{b}\right)\end{aligned} \tag{6}$$

The total energy is then the sum of the x and y contribution and the wavefunction is the multiplication of them,

$$\begin{aligned}E &= \frac{h^2}{8m}\left(\frac{n_x^2}{a^2}+\frac{n_y^2}{b^2}\right)\\ \Psi(x,y) &= \left(\frac{4}{ab}\right)^{1/2}\sin\left(\frac{n_x\pi x}{a}\right)\sin\left(\frac{n_y\pi y}{b}\right)\end{aligned} \tag{7}$$

- What is the probability of finding the electron in the ground state inside of the box given by $0 \leq x \leq a/2$ and $0 \leq y \leq b/2$?

$$\begin{aligned}
\rho(x,y) &= \int_0^{a/2} dx \int_0^{b/2} dy \Psi^\star(x,y)\Psi(x,y) \\
&= \left(\frac{4}{ab}\right) \int_0^{a/2} dx \sin^2\left(\frac{n_x \pi x}{a}\right) \int_0^{b/2} dy \sin^2\left(\frac{n_y \pi y}{b}\right) \\
&= \left(\frac{1}{ab}\right) \int_0^{a/2} dx \left(1 - \cos\left(\frac{2n_x \pi x}{a}\right)\right) \int_0^{b/2} dy \left(1 - \cos\left(\frac{2n_y \pi y}{b}\right)\right) \\
&= \left(\frac{1}{ab}\right) \left(x - \frac{a}{2n_x\pi}\sin\left(\frac{2n_x \pi x}{a}\right)\right)\Bigg|_0^{a/2} \left(y - \frac{b}{2n_y\pi}\sin\left(\frac{2n_y \pi y}{b}\right)\right)\Bigg|_0^{a/2} \\
&= \frac{1}{4}
\end{aligned}$$

- What is the degeneracy of the first excited state for a square box ($a = b$)?

For a square box, energy is given by

$$E = \frac{h^2}{8ma^2}\left(n_x^2 + n_y^2\right)$$

If we make a table for the possible values of n_x and n_y, we get that the set $(1,1)$ gives the lowest energy (ground state) and $(1,2)$ and $(2,1)$ give the same energy for the first exited state.

n_x	n_y	E = ($\# \times \frac{h^2}{8ma^2}$)
1	1	2
1	2	5
2	1	5