CML 100: 2017-2018
Quantum Tutorial 1

1. **In algebra it can be easily shown that $(P + Q)(P - Q) = P^2 - Q^2$. What is the value of $(P + Q)(P - Q)$ if P and Q are operators? Under what conditions will this result be equal to $P^2 - Q^2$.**

$$(P+Q)(P-Q) = P^2 + QP - PQ - Q^2$$

If $QP - PQ = 0$, i.e. P and Q commute, then $(P+Q)(P-Q) = P^2 - Q^2$

2. **Find $[z^3, \frac{d}{dz}]$ and $[\frac{d^2}{dx^2}, ax^2 + bx + c]$.**

First put an arbitrary function f

$$\left[z^3, \frac{d}{dz}\right] f = z^3 \frac{d}{dz} f - \frac{d}{dz}(z^3 f) = z^3 \frac{df}{dz} - z^3 \frac{df}{dz} - f(3z^2) = 3z^2 f$$

In the end remove the arbitrary function to get the result $3z^2$

$$\left[\frac{d^2}{dx^2}, ax^2 + bx + c\right] f = \frac{d^2}{dx^2}(ax^2 f + bxf + cf) - (ax^2 + bx + c)\frac{d^2 f}{dx^2}$$

$$= \frac{d}{dx}(2axf) + ax^2 \frac{d^2 f}{dx^2} + \frac{d}{dx}(bf) + bx\frac{d^2 f}{dx^2} + 0.f + c\frac{d^2 f}{dx^2} - (ax^2 + bx + c)\frac{d^2 f}{dx^2}$$

$$= 2af + 2ax\frac{df}{dx} + 0.f + b\frac{df}{dx} = 2af + (2ax + b)\frac{df}{dx}$$

Now remove f to get, $2a + (2ax + b)\frac{d}{dx}$

3. **Which of the following functions cannot be solutions of the Schrödinger equation for all values of x? Why not? (a) $Asec(x)$; (b) $Atan(x)$; (c) $Aexp(x^2)$; (d) $Aexp(-x^2)$.**

For functions to be solutions, they must be "well behaved".
$A \sec x$ approaches ∞ as $x \to 90°$ - not acceptable
$A \tan x$ approaches ∞ as $x \to 90°$ - not acceptable
$A \exp x^2$ approaches ∞ as $x \to \pm\infty$ and therefore is not normalizable – not acceptable
$A \exp -x^2$ is a smooth, single-valued function, approaches 0 at large values of x. It is normalizable – acceptable.

4. **Write down the Hamiltonian for the following systems: (a) a particle of mass m in a cubical box of side a; (b) a particle of mass m in a spherical box of radius a; (c) a particle of mass m moving on the x-axis subjected to a force directed towards the origin, of magnitude proportional to the distance from the origin; (d) an electron moving in the presence of a nuclear charge $+Ze$; (e) two electrons moving in the presence of a fixed nucleus of charge $+Ze$.**

(a) a particle of mass m in a cubical box of side a:

$$\hat{H} = -\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right) + V(x, y, z)$$

(b) a particle of mass m in a spherical box of radius a:

$$\hat{H} = -\frac{\hbar^2}{2ma^2}\left[\frac{\partial^2}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) - \hat{l}^2\right] + V(x,y,z)$$

Where,

$$\hat{l}^2 = -\frac{1}{\sin^2\theta}\left[\sin\theta\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{\partial^2}{\partial\phi^2}\right]$$

(c) a particle of mass m moving on the x-axis subjected to a force directed towards the origin, of magnitude proportional to the distance from the origin

$$\hat{H} = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + \frac{1}{2}kx^2$$

(d) an electron moving in the presence of a nuclear charge $+Ze$

$$\hat{H} = -\frac{\hbar^2}{2mr^2}\left[\frac{\partial^2}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) - \hat{l}^2\right] - \frac{Ze^2}{4\pi\varepsilon_0 r}$$

$$\hat{l}^2 = -\frac{1}{\sin^2\theta}\left[\sin\theta\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{\partial^2}{\partial\phi^2}\right]$$

Or,

$$\hat{H} = -\frac{\hbar^2}{2m}\nabla^2 - \frac{Ze^2}{4\pi\varepsilon_0 r}$$

(e) two electrons moving in the presence of a fixed nucleus of charge $+Ze$

$$\hat{H} = -\frac{\hbar^2}{2m}\nabla_1^2 - \frac{\hbar^2}{2m}\nabla_2^2 - \frac{Ze^2}{4\pi\varepsilon_0 r_1} - \frac{Ze^2}{4\pi\varepsilon_0 r_2} + \frac{e^2}{4\pi\varepsilon_0 r_{12}}$$

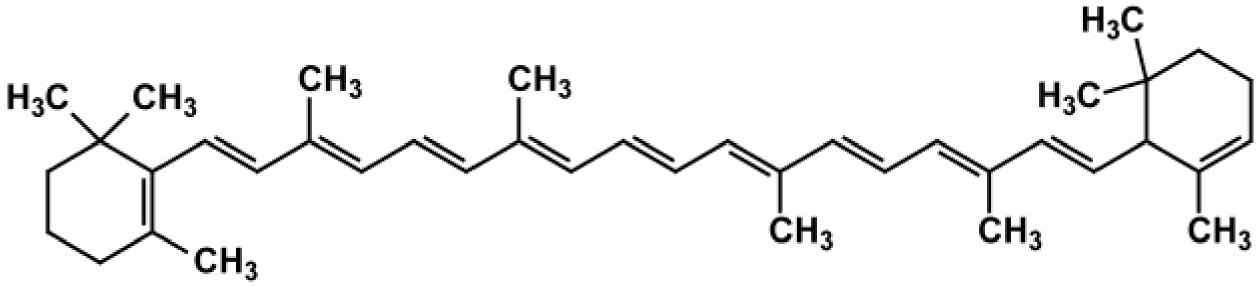
5. (a) Evaluate the probability of locating a particle in the middle third of 1-D box. (b) Find the probability that a particle in a box $\boldsymbol{L}$ wide can be found between $\boldsymbol{x = 0}$ and $\boldsymbol{x = L/n}$ when it is in the nth state.

$$(a)\quad \int_{\frac{L}{3}}^{\frac{2L}{3}} \frac{2}{L}\sin^2\frac{n\pi x}{L}\,dx = \frac{1}{L}\int_{\frac{L}{3}}^{\frac{2L}{3}}\left(1-\cos\frac{2n\pi x}{L}\right)dx = \frac{1}{L}\left[x - \frac{L}{2n\pi}\sin\frac{2n\pi x}{L}\right]_{L/3}^{2L/3}$$

$$= \frac{1}{3} - \frac{L}{2n\pi}\left\{\sin\frac{4n\pi}{3} - \sin\frac{2n\pi}{3}\right\}$$

$$(b)\quad \int_0^{\frac{L}{n}} \frac{2}{L}\sin^2\frac{n\pi x}{L}\,dx = \frac{1}{L}\left[x - \frac{L}{2n\pi}\sin\frac{2n\pi x}{L}\right]_0^{L/n} = \frac{1}{L}\left[\frac{L}{n} - \frac{L}{2n\pi}\sin 2\pi\right] = \frac{1}{n}$$

6. **Describe the color of carrots using the particle in a box model. (Hint: Consider the π electrons to be confined to a box whose length is the length of the molecule. Use 1.54 Å as a C−C and 1.35 Å as a C=C bond length.)**



10 conjugated double bonds, 9 single bonds in between, 2 end carbons.

Total $L = 1.54 \times 9 + 1.35 \times 10 + 1.54 = 28.9$ Å

$$\bar{\nu} = \frac{\Delta E}{hc} = \frac{h}{8mL^2c}(11^2 - 10^2) = \frac{6.6 \times 10^{-34}}{8 \times 9.1 \times 10^{-31} \times (2.89 \times 10^{-9})^2 \times 3 \times 10^8}(21)$$
$$= 13.1 \times 10^{-7}\text{m}^{-1}$$

$$\lambda = \frac{1}{\bar{\nu}} = 1310 \text{ nm}$$

This is in the infra-red. The model is very crude and does not predict the color of carrots to be red, but gives an estimate that is not too far off.

7. **Many proteins contain metal porphyrin molecules. These molecules are approximated as square planar and contain 26 π electrons. If the edge of the molecule is ~1000 pm, then what is the predicted lowest energy absorption of the porphyrin molecule?**

This is an example of particle in a 2D box. We need to use the equation

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

Fill up 26 electrons in the levels, (1,1), {(1,2),(2,1)}, (2,2), {(1,3),(3,1)}, {(2,3),(3,2)}, {(1,4),(4,1)},(3,3), {(4,2),(2,4)}

Transition is from (4,2) to next level i.e. (4,3)

$$\Delta E = \{(4^2 + 3^2) - (4^2 + 2^2)\}\frac{h^2}{8ml^2} = \frac{5 \times (6.6 \times 10^{-34})^2}{8 \times 9.1 \times 10^{-31} \times (1 \times 10^{-9})^2}$$
$$= 2.99 \times 10^{-19} Joules\ mol^{-1} = \frac{2.99 \times 10^{14}}{1.6 \times 10^{-19}} = 1.87\ eV\ molecule^{-1}$$

8. **The possible values obtained from a measurement of a discrete variable, x, are 1, 2, 3, and 4. (a) If the respective probabilities are 1/4, 1/4, 1/4, and 1/4, calculate the expectation values of x and x^2. (b) If the respective probabilities are 1/12, 5/12, 5/12, and 1/12, calculate the expectation values of x and x^2.**

$$< x > = \sum_i p_i x_i \quad and < x^2 > = \sum_i p_i x_i^2$$

$$< x > = 1 \times \frac{1}{4} + 2 \times \frac{1}{4} + 3 \times \frac{1}{4} \times 4 \times \frac{1}{4} = \frac{5}{2}$$
$$< x^2 > = \ 1^2 \times \frac{1}{4} + 2^2 \times \frac{1}{4} + 3^2 \times \frac{1}{4} \times 4^2 \times \frac{1}{4} = \frac{15}{2}$$
$$< x > = 1 \times \frac{1}{12} + 2 \times \frac{5}{12} + 3 \times \frac{5}{12} \times 4 \times \frac{1}{12} = \frac{5}{2}$$
$$< x^2 > = \ 1^2 \times \frac{1}{12} + 2^2 \times \frac{5}{12} + 3^2 \times \frac{5}{12} \times 4^2 \times \frac{1}{12} = \frac{82}{12}$$

9. Why can the electron not be at the nucleus? Using the uncertainty principle, find the value of the Bohr radius for electron in a H-atom in the ground state.

Momentum can be from 0 to max. value, position can also be from 0 to max. value.

$$\Delta p = p, \Delta x = r$$
$$\frac{\mathrm{e}^2}{4\pi\varepsilon_0 r^2} = \frac{mv^2}{r} = \frac{p^2}{mr} \ or \ p = \sqrt{\frac{me^2}{4\pi\varepsilon_0}}$$
$$\Delta p. \Delta x \sim \hbar => \ \sqrt{\frac{me^2}{4\pi\varepsilon_0 r}} \ .r \sim \hbar \ or \ r = \frac{4\pi\varepsilon_0\hbar^2}{me^2} \sim 0.5 \text{ Å}$$

10. The wave function of the first excited state of a harmonic oscillator is $Ax \exp -ax^2$. By substituting in the Schrödinger equation determine a. Determine A from the normalization condition.

$$-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}(Ax \exp -ax^2) + \frac{1}{2}kx^2(Ax \exp -ax^2) = \frac{3}{2}\hbar\omega(Ax \exp -ax^2)$$
$$=> \ -\frac{\hbar^2}{2m}\left\{\frac{d}{dx}\left(A\ e^{-ax^2} - 2Aax^2e^{-ax^2}\right)\right\} + \frac{1}{2}kx^2\left(Axe^{-ax^2}\right) = \frac{3}{2}\hbar\omega\left(Axe^{-ax^2}\right)$$
$$=> -\frac{\hbar^2}{2m}\left\{-2Aaxe^{-ax^2} - 4Aaxe^{-ax^2} + 4Aa^2x^3e^{-ax^2}\right\} + \frac{1}{2}kx^2\left(Axe^{-ax^2}\right)$$
$$= \frac{3}{2}\hbar\omega\left(Axe^{-ax^2}\right)$$
$$=> \ -\frac{\hbar^2}{2m}\{-6a + 4a^2x^2\}\psi_1 + \frac{1}{2}kx^2\psi_1 = \frac{3}{2}\hbar\omega\psi_1$$
$$6a = \frac{3}{2}\frac{2m\omega}{\hbar}, a = \frac{m\omega}{2\hbar}$$

Normalization,

$$\int_{-\infty}^{\infty} A^2x^2e^{-2ax^2}dx = 2\int_{0}^{\infty} A^2x^2e^{-2ax^2}dx$$
$$Standard\ integral, \qquad \int_{0}^{\infty} x^2e^{-\alpha x^2}dx = \frac{1}{4\alpha}\sqrt{\frac{\pi}{\alpha}}$$

$$2\int_0^{\infty} A^2 x^2 e^{-2ax^2}\,dx = 2A^2\left(\frac{1}{8a}\right)\sqrt{\frac{\pi}{2a}} = 1$$

$$A = \sqrt{4a}\left(\frac{2a}{\pi}\right)^{1/4}$$

11. **Verify the recursion relation $H_{n+1}(z) - 2zH_n(z) + 2nH_{n-1}(z) = 0$ using the first four Hermite polynomials.**
    Hermite polynomials

$$H_0(y) = 1, H_1(y) = 2y, H_2(y) = 4y^2 - 2, H_3(y) = 8y^3 - 12y$$

12. **In the vibrational motion of HI, the iodine atom remains stationary because of its large mass. Assume that the hydrogen atom undergoes harmonic motion and that the force constant is 317 N m^{-1}, what is the vibrational frequency ν_0? What is the zero point energy if H is replaced by D? Assume that there is no change in the force constant.**

$$\nu_0 = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}}$$

Iodine is 127 heavier than H. We can use mass of H instead of the reduced mass.

$$\nu_0 = \frac{1}{2\pi}\sqrt{\frac{317}{1.67\times 10^{-27}}} = 6.93\times 10^{13}\ \text{Hz}$$

$$ZPE = \frac{1}{2}h\nu_0 = 4.574\times 10^{-20}\ J\ mol^{-1} = 0.285\ eV\ molecule^{-1}$$

Replacing H by D, divide the ZPE by $\sqrt{2}$ to get 0.201 $eV\ molecule^{-1}$