Homework 5 Key

1. Average value of operator $\hat{p_x^{2022}}$ over PIB of length a.

   $\langle p_x^{2022} \rangle = \int_0^a \psi^* \hat{p_x^{2022}} \psi dx$

   $= \int_0^a \sqrt{\frac{2}{a}} \sin(\frac{\pi n x}{a})(-i\hbar)^{2022} \frac{\partial^{2022}}{\partial x^{2022}} \sqrt{\frac{2}{a}} \sin(\frac{\pi n x}{a}) dx$

   $= -\hbar^{2022} \frac{2}{a} \int_0^a \sin(\frac{\pi n x}{a}) \frac{\partial^{2022}}{\partial x^{2022}} \sin(\frac{\pi n x}{a}) dx$

   The pattern for sin(x) derivatives is 1st cos(x) 2nd -sin(x) 3rd -cos(x) 4th sin(x) and repeat. The 2022nd derivative fits the 2nd derivative pattern.

   $= (\frac{2}{a})(\frac{\pi \hbar n}{a})^{2022} \int_0^a \sin^2(\frac{\pi n x}{a})$

   $= (\frac{\pi \hbar n}{a})^{2022}$

   (a) Optional. Find $\langle e^{\hat{p_x}} \rangle$ if $e^{\hat{p_x}} = \hat{I} + \sum_{k=1} \frac{\hat{p_x^k}}{k!}$ over PIB of length a.

   $\langle e^{\hat{p_x}} \rangle = \int_0^a \psi^* (\hat{I} + \sum_{k=1} \frac{\hat{p_x^k}}{k!})$

   $\langle e^{\hat{p_x}} \rangle = \int_0^a \psi^* (1 + \sum_{k=1} \frac{(-i\hbar)^k \frac{\partial^k}{\partial x^k}}{k!})$

   The pattern for sin(x) derivatives is 1st cos(x) 2nd -sin(x) 3rd -cos(x) 4th sin(x) and repeat. When it is an odd derivative, the integral = 0 because odd times even function is odd function. So only even terms are accounted. $(-i)^2 = -1$ with 2nd derivative $-sin(x)$ gets positive results. $(-i)^4 = 1$ with 4th derivative $sin(x)$ gets positive results. All evens terms have positive numbers.

   $= 1 + 0 + \frac{(\pi \hbar n)^2}{2!} + 0 + \frac{(\pi \hbar n)^4}{4!} + 0 + \frac{(\pi \hbar n)^6}{6!} + ...$

   models the taylor expansion of $\cosh(\frac{\pi \hbar n}{a}), 1 + \frac{x^2}{2!} + \frac{x^4}{4!} + ...$

2. Find expectation value for energy for each case.

   Recall that time-independent Schrodinger equation is $\hat{H}\psi = E\psi$

   $-\frac{\hbar^2}{2m} \frac{d^2\psi(x)}{dx^2} + V(x)\psi(x) = E\psi(x)$

   For region II x between 0 and a, the potential energy is 0, so the equation becomes:

   $-\frac{\hbar^2}{2m} \frac{d^2\psi(x)}{dx^2} = E\psi(x)$, therefore $\hat{H} = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2}$. Hence, to find expectation value, $\langle E\rangle = \frac{\int_0^a \psi^* \hat{H}\psi dx}{\int_0^a \psi^* \psi dx}$.

(a) $\langle E\rangle = \frac{\int_0^a \psi^* \hat{H}\psi dx}{\int_0^a \psi^* \psi dx}$

numerator

$= -\frac{\hbar^2}{2m}\int_0^a (\frac{30}{a-1})^{1/2}\frac{x}{a}(1-\frac{x}{a})\frac{d^2}{dx^2}(\frac{30}{a-1})^{1/2}\frac{x}{a}(1-\frac{x}{a})dx$

$= -\frac{\hbar^2}{2m}(\frac{30}{a-1})(-\frac{2}{a^2})(\frac{1}{a})\int_0^a x - \frac{x^2}{a}dx$

$= -\frac{\hbar^2}{2m}(\frac{30}{a-1})(-\frac{2}{a^2})(\frac{1}{a})\left[\frac{x^2}{2} - \frac{x^3}{3a}\right]_0^a$

$= -\frac{\hbar^2}{2m}(\frac{30}{a-1})(-\frac{2}{a^2})(\frac{1}{a})\frac{a^2}{6}$;

$= \frac{5\hbar^2}{(a-1)am}$; and $\hbar = \frac{h}{2\pi}$

$= \frac{5h^2}{4\pi^2 am(a-1)}$

denominator

$\int_0^a \psi^*\psi dx = \frac{a}{a-1}$

divide and get $\frac{5h^2}{4\pi^2 a^2 m}$

(b) $\langle E\rangle = \frac{\int_0^a \psi^* \hat{H}\psi dx}{\int_0^a \psi^* \psi dx}$

$= -\frac{\hbar^2}{2m}\int_0^a (\frac{2}{a+1})^{1/2}\sin(\frac{4\pi x}{a})\frac{d^2}{dx^2}(\frac{2}{a+1})^{1/2}\sin(\frac{4\pi x}{a})dx$

$= -\frac{\hbar^2}{2m}(\frac{2}{a+1})\int_0^a \sin(\frac{4\pi x}{a})\frac{d^2}{dx^2}\sin(\frac{4\pi x}{a})dx$

$= -\frac{\hbar^2}{2m}(\frac{2}{a+1})(-\frac{4\pi}{a})^2\int_0^a \sin^2(\frac{4\pi x}{a})dx$

$= \frac{\hbar^2}{2m}(\frac{2}{a+1})(\frac{16\pi^2}{a^2})(\frac{1}{2}a)$; using trig identity and integrate

$= \frac{2h^2}{ma(a+1)}$; simplify and $\hbar = \frac{h}{2\pi}$

denominator

$\int_0^a \psi^*\psi dx = \frac{a}{a+1}$

divide and get $\frac{2h^2}{a^2 m}$

(c) $\langle E\rangle = \frac{n^2h^2}{8ma^2}$ and it was shown in detail in process in 2b where n = energy level within the sin term.

$\psi = (\frac{2}{a})^{1/2}\Big(0.7\sin(\frac{3\pi x}{a})\Big) + (\frac{2}{a})^{1/2}\Big(0.6\sin(\frac{5\pi x}{a})\Big)$

$\langle E\rangle = 0.7\frac{9h^2}{8ma^2} + 0.6\frac{25h^2}{8ma^2}$

Now you have a linear combination of observing energy levels, n=3 and n=5. So you want the probability of observing two states to be equal to one because $\sum |c_k|^2 = 1$

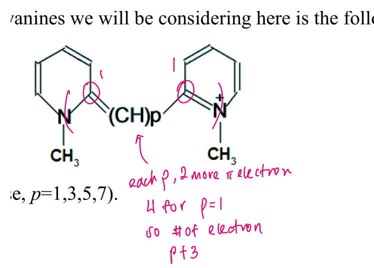
$0.7^2 x + 0.6^2 x = 1 \; x = \frac{100}{85}$

$0.7^2 x \frac{9h^2}{8ma^2} + 0.6^2 x \frac{25h^2}{8ma^2}$

$\frac{49}{85}\frac{9h^2}{8ma^2} + \frac{36}{85}\frac{25h^2}{8ma^2}$

3. π system

   (a) of π electron = p + 3



   Click for review on counting pi electrons

   (b) The energy level of a 1D PIB is described as $E = \frac{n^2h^2}{8ma^2}$.

   To find the energy absorbed from going from HOMO to LUMO:

   $\Delta E = E_{LUMO} - E_{HOMO}$

   $\Delta E = (n^2_{LUMO} - n^2_{HOMO})\frac{h^2}{8m_eL^2}$

   Two electrons occupy one orbital and we want to find energy associated with exciting one electron so $n = (\frac{N}{2}+1)^2 - (\frac{N}{2})^2$. Simplify that and you get $n = N + 1$

   $\Delta E = (N+1)\frac{h^2}{8m_eL^2}$

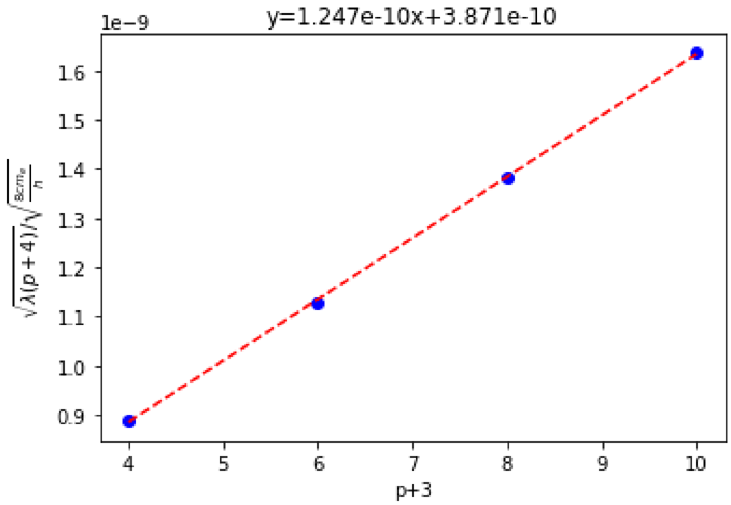
   $\Delta E = (p+3+1)\frac{h^2}{8m_eL^2}$; plugging in our equation from 3a

   $\frac{c}{\lambda} = (p+4)\frac{h}{8m_eL^2}$

   $\lambda = \frac{8cm_eL^2}{(p+4)h}$

   $\sqrt{\lambda(p+4)} = \sqrt{\frac{8cm_e}{h}}\left[(p+3)l + a\right]$

   $\frac{\sqrt{\lambda(p+4)}}{\sqrt{\frac{8cm_e}{h}}} = (p+3)l + a$; you can see the $y = mx + b$ format



$l = 0.1247$ nm $a = 0.3871$ nm