# Chem 542 Exam 1

1) Here is an interesting fact about Dirac delta functions- they are eigenfunctions of the position operator $\hat{x}$. Can you show that $\delta(x-a)$ is the eigenfunction of $\hat{x}$ with an eigenvalue of a? **Hint:** This question is stupid simple- I just want to make sure you know what an eigenfunction is. Just look at the cheat sheet!

Answer: There is an identity in the cheat sheet: $f(x)\delta(x-a) = f(a)\delta(x-a)$

$$\hat{x}\delta(x-a) = a\delta(x-a)$$

You should note that this is of the proper form $\hat{\Omega}\Phi = \omega\Phi$

2) Shown here is the %transmission through a positive double delta potential; one is at x=0 and the other at x=L. The one on the left is for a trap of L = 1 nm while the right hand one has L = 2 nm. The reason that there is 100% transmission is due to the formation of particle in a box wavefunctions between the traps. Each T=100% resonance can be associated with a higher quantum number box state.
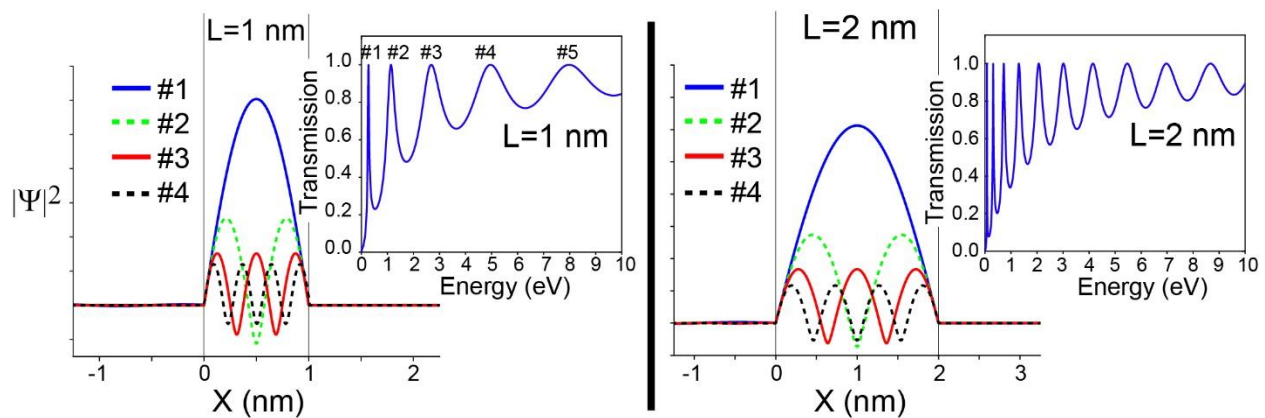
a. Shown here are the energies of the T=100% resonances for both the L= 1 nm and L = 2 nm trap potentials. Can you explain why the L = 2 nm trap resonances are at energies that are ~1/4 as much as for L=1 nm?

b. The quadratic fits to the data are shown by the lines though the datapoints ($\sim fit \propto resonance\ \#^2$). Can you state why the energies for resonances are separated quadratically in energy?
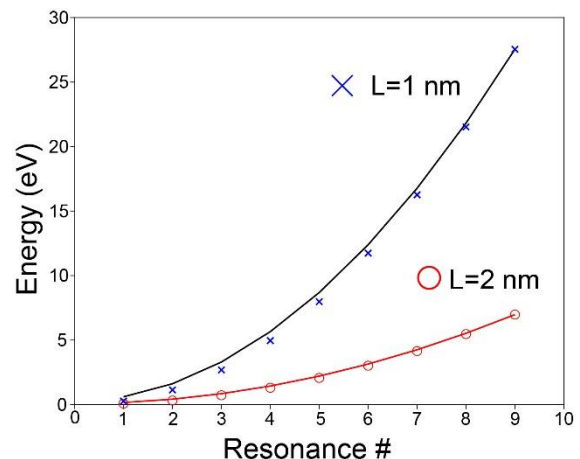
Answer: This is all a manifestation of particle in a box energy. **a.** The particle in a box energy is proportional to $1/L^2$. **b.** The particle in a box energy is proportional to quantum number squared, i.e. n^2.

3) Let's say that we need to change a Hamiltonian from a set of x and y coordinates to spin up α and down β, where: $x^2 = \alpha + \beta$ and $y^2 = \alpha - i \cdot \beta$

For this problem, please show that $\frac{\partial}{\partial x} = 2\sqrt{\alpha + \beta} \left(\frac{\partial}{\partial \alpha} + \frac{\partial}{\partial \beta} \right)$; no need to do $\frac{\partial}{\partial y}$ since its so similar.

Answer: The proper form is:

$$\frac{\partial}{\partial x} = \frac{\partial \alpha}{\partial x} \frac{\partial}{\partial \alpha} + \frac{\partial \beta}{\partial x} \frac{\partial}{\partial \beta}$$

Next, we just do the two derivatives:

$$\frac{\partial \alpha}{\partial x} = \frac{\partial (x^2 - \beta)}{\partial x} = 2x = 2\sqrt{\alpha + \beta}$$

Likewise $\frac{\partial \beta}{\partial x} = 2\sqrt{\alpha + \beta}$. Therefore the answer is

$$\frac{\partial}{\partial x} = 2\sqrt{\alpha + \beta} \left(\frac{\partial}{\partial \alpha} + \frac{\partial}{\partial \beta} \right)$$

4) a. In your current homework on the He atom's atomic structure, why is it ok to convert the Coulomb integral of r_2 from $0 \to \infty$ (on the left) into two separate ones shown on the right, the first from $0 \to r_1$ and the second from $r_1 \to \infty$?

$$\frac{e^2}{4\pi\epsilon_0} \int_{r_1=0}^{r_1=\infty} \int_{r_2=0}^{r_2=\infty} \sim \frac{1}{r_>} \partial r_2 \partial r_1 = \frac{e^2}{4\pi\epsilon_0} \int_{r_1=0}^{r_1=\infty} \int_{r_2=0}^{r_2=r_1} \sim \frac{1}{r_>} \partial r_2 \partial r_1 + \frac{e^2}{4\pi\epsilon_0} \int_{r_1=0}^{r_1=\infty} \int_{r_2=r_1}^{r_2=\infty} \sim \frac{1}{r_>} \partial r_2 \partial r_1$$

b. Now why can I assign $r_>$ to r_1 in the first term? Hint, $r_>$ represents either r_1 or r_2 depending on which is greater than the other.

Answer: a. Integrals are areas, and areas add.

**b.** Since r_2 is always less than r_1 according to the limits of integration.

5) Some theory research groups develop new basis functions for multielectron atoms using sums of Gaussian functions (at least three) with different weighing coefficients (C_n) and distance dependences (a_n) as:

$$\psi(r) = C_1 \cdot e^{-r^2/a_1} + C_2 \cdot e^{-r^2/a_2} + C_3 \cdot e^{-r^2/a_3}$$

Why are they doing so? And how would you know what makes a good set of C_n and a_n?

Answer: The fact that the atom has multiple electrons means that we don't every know the correct function, and any guess we make won't be correct. As such, the energy of the wavefunction will always be too high, so a good set of C_n and a_n will minimize the calculated energy.

6) The following Hamiltonian was derived to describe my cat Zoe. There are two variables, x and θ.
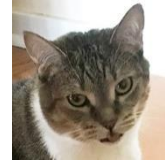
$$\widehat{H}(x,\theta) = \hbar \frac{\partial}{\partial x} - \frac{\omega}{x} \cdot \frac{\partial}{\partial \theta}$$

a. The expression doesn't seem separable due to the 2nd term that has both x and θ in it, but actually I think it is separable. Can you study it and see if: $\psi_{cat}(x,\theta) = \psi(x)\psi(\theta)$?

b. What variable controls the energy (is it x or θ)?

c. If $\frac{\partial \psi(\theta)}{\partial \theta} = 0$, can you show that $\psi(x) = e^{\frac{E}{\hbar}x}$ is a reasonable x eigenfunction?

Answer: a. First act on the right and divide by the left:

$$\frac{1}{\psi_{cat}} \widehat{H}\psi_{cat} = \frac{1}{\psi_{cat}} E\psi_{cat} = E$$

Let's work on $\frac{1}{\psi_{cat}} \widehat{H}\psi_{cat}$:

$$\frac{1}{\psi(x)\psi(\theta)} \left(\hbar \frac{\partial}{\partial x} - \frac{\omega}{x} \cdot \frac{\partial}{\partial \theta} \right) \psi(x)\psi(\theta) = \frac{\hbar}{\psi(x)} \frac{\partial \psi(x)}{\partial x} - \frac{\omega}{x \cdot \psi(\theta)} \frac{\partial \psi(\theta)}{\partial \theta}$$

To show separability multiply everything by x, and you have it:

$$\hbar \left(\frac{x}{\psi(x)} \right) \frac{\partial \psi(x)}{\partial x} - \frac{\omega}{\psi(\theta)} \cdot \frac{\partial \psi(\theta)}{\partial \theta} = x \cdot E$$

b. If you do a bit more algebra its perhaps easier to see how there are two "mini" Schrodinger equations, with the energy belonging to the x one:

$$\hbar \left(\frac{x}{\psi(x)} \right) \frac{\partial \psi(x)}{\partial x} - x \cdot E = \frac{\omega}{\psi(\theta)} \cdot \frac{\partial \psi(\theta)}{\partial \theta}$$

c. If $\frac{\partial \psi(\theta)}{\partial \theta} = 0$ then $\left(\frac{\hbar}{\psi(x)} \right) \frac{\partial \psi(x)}{\partial x} = E$. So if we insert: $\psi(x) = e^{\frac{E}{\hbar}x}$ then:

$$\hbar \left(\frac{1}{e^{-\frac{E}{\hbar}x}} \right) \frac{\partial e^{\frac{E}{\hbar}x}}{\partial x} = \frac{E}{\hbar} \cdot \hbar \left(\frac{e^{-\frac{E}{\hbar}x}}{e^{-\frac{E}{\hbar}x}} \right) = E$$

which satisfies the separated diffi-eq.

Equations

Constants: $h = 6.626 \times 10^{-34} \text{kg} \cdot \text{m}^2 \cdot \text{s}^{-1}$ $\hbar = \frac{h}{2\pi} = 1.055 \times 10^{-34} \text{kg} \cdot \text{m}^2 \cdot \text{s}^{-1}$

$c = 3 \times 10^8$ m/s $k_B = 1.38 \times 10^{-23}$ J/K   electron mass: $9.11 \times 10^{-31} \text{kg}$

proton mass: $1.67 \times 10^{-27} \text{kg}$

Imaginary identities: $|\psi|^2 = \psi^*\psi$ $\sqrt{-1} = i$ $i^2 = -1$ $\sin(k \cdot x) = \frac{e^{ik \cdot x} - e^{-ik \cdot x}}{2i}$

$\cos(k \cdot x) = \frac{e^{ik \cdot x} + e^{-ik \cdot x}}{2}$ $e^{i\pi \cdot 0} = 1$ $e^{i\pi/2} = I$ $e^{i\pi} = -1$ $e^{i\pi \cdot (3/2)} = -i$

$e^{i\pi \cdot 2} = 1$ $\left(e^{i\pi}\right)^* = e^{-i\pi}$ $\sin(a \cdot x)^* = \sin(a \cdot x)$

Calc IDs: 2D: $\partial\tau = \partial r\, \partial\phi$ **3D:** $\partial\tau = r^2 \sin(\theta) \cdot \partial r \cdot \partial\phi \cdot \partial\theta$ $\int_0^\pi \int_0^{2\pi} \int_0^\infty r^2 \sin(\theta) \cdot \partial r \cdot \partial\phi \cdot \partial\theta$

$\frac{\partial}{\partial x} e^{a \cdot x} = a \cdot e^{a \cdot x}$ $\frac{\partial}{\partial x} x^a = a \cdot x^{a-1}$ $\frac{\partial}{\partial\theta} \cos(\theta) = -\sin(\theta)$ $\frac{\partial}{\partial\theta} \sin(\theta) = \cos(\theta)$

$\frac{\partial}{\partial\theta}[\sin(\theta)\cos(\theta)] = 1 - 2\sin^2(\theta)$ $\frac{\partial}{\partial\theta}\sin^2(\theta) = 2\sin(\theta)\cos(\theta)$ $\frac{\partial}{\partial\theta}\cos^2(\theta) = -2\sin(\theta)\cos(\theta)$

Chain Rule: $\frac{\partial}{\partial x} = \frac{\partial y}{\partial x}\frac{\partial}{\partial y}$ **Product Rule:** $\frac{\partial(uv)}{\partial x} = u\frac{\partial v}{\partial x} + v\frac{\partial u}{\partial x}$

Delta function: $f(x)\delta(x - a) = f(a)\delta(x - a)$

General Equations: momentum: m·v   Energy: $h\nu = hc/\lambda$ de Broglie wavelength: $\lambda = \frac{h}{p}$

$\widehat{\Omega}\psi = \omega\psi$ $|\psi|^2 = \psi^*\psi$ Free wave (flat V): $\psi = A \cdot e^{ik_x \cdot x} + B \cdot e^{-ik_x \cdot x}$

Separability: $\frac{1}{\psi(r,\theta,\phi)}\widehat{\Omega}\psi(r,\theta,\phi) = \{r\ terms\} + \{\theta\ terms\} + \{\phi\ terms\} = 0$

Operators: Hamiltonian: $\frac{-\hbar^2}{2m}\nabla^2 + \widehat{V}$ position: $\hat{x} = x$ momentum: $\hat{p}_x = \frac{\hbar}{i}\frac{\partial}{\partial x}$

kinetic energy: $\frac{\hat{p}_x^2}{2m} = \frac{-\hbar^2}{2m}\frac{\partial^2}{\partial x^2}$ Hamiltonian: $\frac{-\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + V(x)$ Free wave: $\psi = A \cdot e^{ikx} + B \cdot e^{-ikx}$

Expectation value: $\langle\widehat{\Omega}\rangle = \int_{\text{all limits}} \psi^* \cdot \widehat{\Omega} \cdot \psi \cdot \partial x = \omega$

Orthonormality: $\int_{\text{all limits}} \psi_i^* \cdot \psi_j \cdot \partial\tau = 0$ if i≠j $\int_{\text{all limits}} \psi_i^* \cdot \psi_j \cdot \partial\tau = 1$ if i=j

Particle in a box wavefunction: $\psi = \sqrt{\frac{2}{L}}\sin\left(\frac{n\pi x}{L}\right)$, n (quantum number) = 1,2,3,…

Particle in a box energy: $\frac{h^2 n^2}{8mL^2}$, n=quantum number, m=mass, *L is length of the box*.