Chem 542 Problem Set 8

1. Let's look back at question 1c from problem set 6, where you proved:

$$\sum_{n=1}^{\infty} \psi_n^*(x')\psi_n(x'') = \delta(x'' - x')$$

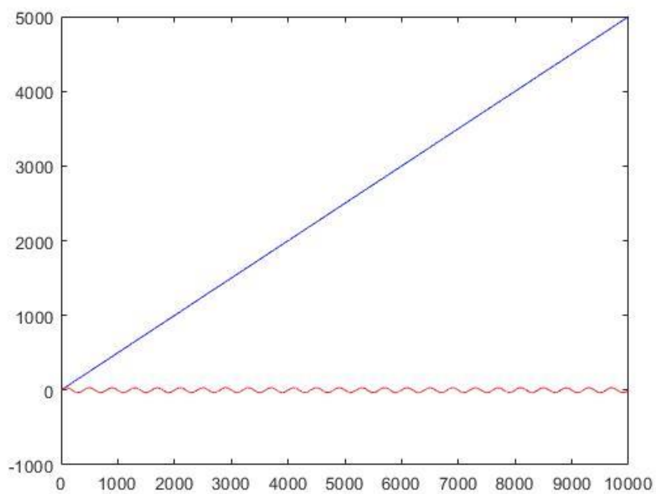
What does this really mean? To figure this out, let's use a MATLAB script to evaluate the summation using particle in a box wavefunctions:

$$\psi_n^*(x) = \psi_n(x) = \sqrt{\frac{2}{L}} \cdot cos\left(\frac{n\pi x}{L}\right)$$

where n is the order of the eigenfunction (n=1 for the ground state, etc.). For this problem, please graph the sum as a function of the upper limit of n from 1→10^5 states. You will need to show two sets of data, one for a sum where $x' = x''$ and another for $x' \neq x''$. For example, in the answer key I used: L=2 nm, $x' = x'' = 1$ nm for one set of conditions which was compared to a sum using: L=2 nm, $x' = 1$ nm, $x'' = 1.01$ nm. As usual, please send your code along with a graph.

Answer: Here is my MATLAB script and graph. Overall the result seems valid:

```
sumtot1=0;
sumtot2=0;
for n=1:10000
    sumtot1=sumtot1+sqrt(2/2)*cos(n*pi*1.0/2)*cos(n*pi*1.0/2);
    result(n)=sumtot1;
    sumtot2=sumtot2+sqrt(2/2)*cos(n*pi*1/2)*cos(n*pi*1.01/2);
    result2(n)=sumtot2;
end;
plot(result,'b'); hold on; plot(result2,'r');
```



2. The formula for a Gaussian wavepacket in the real space representation is:

$$\langle x|\psi\rangle = \frac{1}{\sqrt{d\sqrt{\pi}}} e^{\left(ikx - \frac{x^2}{2d^2}\right)}$$

For this problem, please:

a. Transform the above into the momentum representation, i.e. $\langle p|\psi\rangle$, using Mathematica, and,

b. Check that the result is normalized, and,

c. Then use it to calculate $\langle \hat{p}^2\rangle$. ***Hint:*** In the momentum frame, $\hat{p}$ is not $\hat{p} = \frac{\hbar}{i}\frac{\partial}{\partial x}$! What do you think the operator is? ***Double hint:*** its way easier than you think!

d. Based on the result from pt. c, please comment on how does greater localization of the real space wavefunction (smaller d) affect the kinetic energy.

Answer: You need to use Mathematica:

```
In[•]:= f[x] = 1 / Pi^(1 / 4) / Sqrt[d] * Exp[ⅈ * k * x - x * x / 2 / d / d]
```

Out[•]= $\frac{e^{i k x - \frac{x^2}{2 d^2}}}{\sqrt{d}\, \pi^{1/4}}$

```
In[•]:= Integrate[1 / Sqrt[2 * Pi * hbar] * Exp[-ⅈ * p * x / hbar] * f[x],
  {x, -Infinity, Infinity}, Assumptions → {hbar > 0, d > 0, k > 0}]
```

Out[•]= $\frac{d\, e^{-\frac{d^2 (-\text{hbar}\, k + p)^2}{2\, \text{hbar}^2}}}{\sqrt{d\, \text{hbar}}\, \pi^{1/4}}$

Unfortunately this requires some simplification; Mathematica isn't perfect:

$$\langle p|\psi\rangle = \frac{\sqrt{d}}{\sqrt{\hbar\sqrt{\pi}}} e^{-\frac{d^2}{2\hbar^2}(p-\hbar k)^2}$$

b. This can be done in a straightforward manner with Mathematica:

In[•]:=
```
f2[p] = Integrate[1 / Sqrt[2 * Pi * hbar] * Exp[-ⅈ * p * x / hbar] * f[x],
  {x, -Infinity, Infinity}, Assumptions → {hbar > 0, d > 0, k > 0}]
```

Out[•]= $\frac{d\, e^{-\frac{d^2 (-\text{hbar}\, k+p)^2}{2\, \text{hbar}^2}}}{\sqrt{d\, \text{hbar}}\, \pi^{1/4}}$

In[•]:=
```
Integrate[Conjugate[f2[p]] * f2[p], {p, -Infinity, Infinity},
 Assumptions → {hbar > 0, k > 0, d > 0}]
```

Out[•]= 1

c. Now the trick here is to note that the momentum operator in p space is:

Thus you are trying to solve:

$$\langle \hat{p}^2 \rangle = \int_{-\infty}^{\infty} \langle \psi | p \rangle p^2 \langle p | \psi \rangle \partial p$$

Again using Mathematica:

In[•]:=
```
Integrate[Conjugate[f2[p]] * p * p * f2[p], {p, -Infinity, Infinity},
 Assumptions → {hbar > 0, k > 0, d > 0}]
```

Out[•]= $\frac{1}{2}\, \text{hbar}^2 \left(\frac{1}{d^2} + 2\, k^2\right)$

Thus $\langle \hat{p}^2 \rangle = \frac{1}{2} \hbar^2 \left(\frac{1}{d^2} + 2k^2\right)$

d. Now here we see that greater localization results in greater kinetic energy due to the $\frac{1}{d^2}$ term in the result from part c.

3. A Poisson Bracket $\{F, G\}$ is defined in classical mechanics as:

$$\{F, G\} = \frac{\partial F}{\partial q}\frac{\partial G}{\partial p} - \frac{\partial F}{\partial p}\frac{\partial G}{\partial q}$$

where q are coordinates (i.e. $q = x, y, z$) and p is momentum. Let's do some derivations.

a. For a function of coordinates and momenta $F(q, p)$, where are functions of time, i.e. $q(t)$ and $p(t)$, please express: $\frac{\partial F(q(t), p(t))}{\partial t}$ of in terms of $\frac{\partial p}{\partial t}$ and $\frac{\partial q}{\partial t}$. ***Hint:*** Use the chain rule!

b. Now insert the classical relations: $\frac{\partial q}{\partial t} = \frac{\partial H}{\partial p}$ and: $\frac{\partial p}{\partial t} = -\frac{\partial H}{\partial q}$ where H is the Hamiltonian and express the final result as a Poisson bracket.

c. Now let's apply the Poisson bracket to calculate the motion of a spring, for which $V(q) = \frac{1}{2}k_f \cdot q(t)^2$ (note: it is traditional to use "x" as the coordinate for the spring problem, but to be consistent we will just use q in place of x). The Hamiltonian of such a system is:

$$H = \frac{p(t)^2}{2m} + \frac{1}{2}k_f \cdot q(t)^2$$

Can you show that you can solve the Poisson brackets:

$$\frac{\partial q(t)}{\partial t} = \{q(t), H\} \text{ and } \frac{\partial p(t)}{\partial t} = \{p(t), H\}$$

to show that $\frac{\partial q(t)}{\partial t} = \frac{p(t)}{m}$ and $\frac{\partial p(t)}{\partial t} = -k_f q(t)$? ***Hint:*** $\frac{\partial q}{\partial q} = \frac{\partial p}{\partial p} = 1$ and $\frac{\partial q}{\partial p} = \frac{\partial p}{\partial q} = 0$.

d. The above relationship appears to be unsolvable for $q(t)$ since it is related to $p(t)$, which itself is related back to $q(t)$! This can be resolved, however, by taking the double derivative of the coordinate: $\frac{\partial q(t)^2}{\partial t^2}$ and then using the mechanics of 2nd order differential equations to solve for $q(t)$.

Hint: Let's use an online ODE (ordinary differential equation) solver for this one, such as Symbolab's. It accepts inputs such as: $q'' = -c \cdot q$ and then solves for $q(t)$.

e. It turns out that you need to know that, at t=0 the mass was at q=0. Can you now solve for $q(t)$ without any un-defined constants from the ODE solver?

Answer. a. $\frac{\partial F(q(t),p(t))}{\partial t} = \frac{\partial F}{\partial q}\frac{\partial q}{\partial t} + \frac{\partial F}{\partial p}\frac{\partial p}{\partial t}$.

b. $\frac{\partial F(q(t),p(t))}{\partial t} = \frac{\partial F}{\partial q}\frac{\partial H}{\partial p} - \frac{\partial F}{\partial p}\frac{\partial H}{\partial q} = \{F, H\}$

c. Using the definition of the Poisson bracket:

$$\frac{\partial q(t)}{\partial t} = \{q, H\} = \frac{\partial q}{\partial q}\frac{\partial H}{\partial p} - \frac{\partial q}{\partial p}\frac{\partial H}{\partial q} = \frac{\partial H}{\partial p} = \frac{\partial}{\partial p}\left\{\frac{p^2}{2m} + \frac{1}{2}k_f q^2\right\} = \frac{p}{m}$$

since $\frac{\partial q}{\partial p} = 0$ and likewise:

$$\frac{\partial p(t)}{\partial t} = \{p, H\} = \frac{\partial p}{\partial q}\frac{\partial H}{\partial p} - \frac{\partial p}{\partial p}\frac{\partial H}{\partial q} = -\frac{\partial H}{\partial q} = -\frac{\partial}{\partial q}\left\{\frac{p^2}{2m} + \frac{1}{2}k_f q^2\right\} = -k_f q$$

d. $\frac{\partial q(t)^2}{\partial t^2} = \frac{\partial}{\partial t}\frac{\partial q(t)}{\partial t} = \frac{\partial}{\partial t}\frac{p(t)}{m} = \frac{1}{m}\frac{\partial p(t)}{\partial t} = \frac{-k_f}{m}q(t)$.

Here, we can apply standard differential equation theory to solve using the Symbolab site. I used an input of: $q'' = -c \cdot q$ to get an output of:

$$q(t) = c_1 \cdot cos(\sqrt{c} \cdot t) + c_2 \cdot sin(\sqrt{c} \cdot t)$$

Inserting our problem specific information $\left(c = \frac{k_f}{m}\right)$ yields:

$$q(t) = c_1 \cdot cos\left(\sqrt{\frac{k_f}{m}} \cdot t\right) + c_2 \cdot sin\left(\sqrt{\frac{k_f}{m}} \cdot t\right)$$

e. Last, since we know that at $q(t = 0) = 0$, we can solve for the above as:

$$0 = c_1 \cdot cos(0) + c_2 \cdot sin(0)$$

which makes $c_1 = 0$ and $c_2 = 1$; thus

$$q(t) = sin\left(\sqrt{\frac{k_f}{m}} \cdot t\right)$$

4. a. For the ground state particle in a box wavefunction: $\psi(x) = \sqrt{\frac{2}{L}} \cdot cos\left(\frac{\pi x}{L}\right)$, what is the expectation value $\langle \hat{x} \rangle$? I actually wouldn't care if you just remembered the answer and wrote it down.

b. For the time-dependent particle in a box wavefunction:

$$\psi(x,t) = e^{-i\hat{H}t/\hbar}\,\psi(x) = e^{-i\frac{\hbar\pi^2}{2mL^2}}\sqrt{\frac{2}{L}} \cdot cos\left(\frac{\pi x}{L}\right)$$

please calculate $\langle \hat{x}(t) \rangle = \langle \psi(x,t) | \hat{x} | \psi(x,t) \rangle$ ***without using Mathematica***.
Hint: this question is actually stupid-simple and barely needs any derivation. This is because, once you start working on the answer, you will find that you will get the same answer as part a. Please prove why that is the case.

c. Based on your result for pt. b., what do you expect will happen for any expectation value $\langle \hat{\Omega}(t) \rangle$ when applied to the time-evolving eigenstate of the Hamiltonian?

Answer: a. I don't mind if you just wrote L/2. However, if you set it up you will find:

$$\langle \hat{x} \rangle = \int_0^L \psi(x)^* \cdot x \cdot \psi(x) \cdot \partial x = \int_0^L \frac{2}{L} cos^2\left(\frac{\pi x}{L}\right) \cdot \partial x = \frac{L}{2}$$

which is best done with Mathematica:

In[ ]:=
```
Integrate[2 / L * x * Cos[Pi * x / L] ^2, {x, 0, L}, Assumptions → L > 0]
```
Out[ ]= $\frac{L}{2}$

b. You don't need Mathematica to realize that the time dependence gets canceled out, yielding the same result as for the time-independent equation:

$$\langle\hat{x}(t)\rangle = \int_{-\infty}^{\infty} \psi(x,t)^* \cdot x \cdot \psi(x,t) \cdot \partial x$$

You should already be able to see that you will cancel out the time dependent function due to the complex conjugate:

$$\psi(x,t)^* \cdot x \cdot \psi(x,t) = e^{i\frac{\hbar\pi^2}{2mL^2}} \sqrt{\frac{2}{L}} \cdot cos\left(\frac{\pi x}{L}\right) \cdot x \cdot e^{-i\frac{\hbar\pi^2}{2mL^2}} \sqrt{\frac{2}{L}} \cdot cos\left(\frac{\pi x}{L}\right) = \frac{2}{L} cos^2\left(\frac{\pi x}{L}\right)$$

Integration of this will still yield L/2.

c. The expectation values never change with time when applied to the eigenstate of a Hamiltonian.

Mathematica Examples

Proof that for the Gaussian wavepacket:

$$\langle x|\psi\rangle = \frac{1}{\sqrt{d\sqrt{\pi}}} e^{\left(ikx-\frac{x^2}{2d^2}\right)}$$

Satisfies the minimum uncertainty principle:

$$\langle(\Delta\hat{x})^2\rangle\langle(\Delta\hat{p})^2\rangle = \frac{1}{4}\hbar^2$$

Define the function:

In[∘]:=
```
f[x] = 1 / Pi^(1 / 4) / Sqrt[d] * Exp[ⅈ * k * x - x * x / 2 / d / d]
```

Out[∘]= $\frac{e^{i k x-\frac{x^2}{2 d^2}}}{\sqrt{d}\,\pi^{1/4}}$

Double check normalization:

In[∘]:=
```
Integrate[Conjugate[f[x]] * f[x], {x, -Infinity, Infinity},
 Assumptions → {hbar > 0, k > 0, d > 0}]
```

Out[∘]= 1

Calculate $\langle(\Delta\hat{x})^2\rangle = \langle\hat{x}^2\rangle - \langle\hat{x}\rangle^2$:

$\langle\hat{x}\rangle$:

In[∘]:=
```
Integrate[Conjugate[f[x]] * x * f[x], {x, -Infinity, Infinity},
 Assumptions → {hbar > 0, k > 0, d > 0}]
```

Out[∘]= 0

$\langle\hat{x}^2\rangle$:

In[∘]:=
```
Integrate[Conjugate[f[x]] * x * x * f[x], {x, -Infinity, Infinity},
 Assumptions → {hbar > 0, k > 0, d > 0}]
```

Out[∘]= $\frac{d^2}{2}$

Hence $\langle(\Delta\hat{x})^2\rangle = \langle\hat{x}^2\rangle - \langle\hat{x}\rangle^2 = \frac{d^2}{2}$

Calculate $\langle(\Delta\hat{p})^2\rangle = \langle\hat{p}^2\rangle - \langle\hat{p}\rangle^2$:

$\langle\hat{p}\rangle$:

In[ ]:=
```
Integrate[hbar / ⅈ * Conjugate[f[x]] * D[f[x], x],
  {x, -Infinity, Infinity}, Assumptions → {hbar > 0, k > 0, d > 0}]
```

Out[ ]= hbar k

$\langle \hat{p}^2 \rangle$:

In[ ]:=
```
Integrate[-hbar * hbar * Conjugate[f[x]] * D[D[f[x], x], x],
  {x, -Infinity, Infinity}, Assumptions → {hbar > 0, k > 0, d > 0}]
```

Out[ ]= $\frac{1}{2}\, \text{hbar}^2 \left(\frac{1}{d^2} + 2\, k^2\right)$

Hence $\langle (\Delta \hat{p})^2 \rangle = \langle \hat{p}^2 \rangle - \langle \hat{p} \rangle^2 = \frac{1}{2}\frac{\hbar^2}{d^2} + \hbar^2 k^2 - \hbar^2 k^2 = \frac{1}{2}\frac{\hbar^2}{d^2}$

As a result:

$$\langle (\Delta \hat{x})^2 \rangle \langle (\Delta \hat{p})^2 \rangle = \frac{d^2}{2} \cdot \frac{1}{2}\frac{\hbar^2}{d^2} = \frac{1}{4}\hbar^2$$