Name___________________________________ Student #____________________________

Quiz 4
CHEM 3PA3; Fall 2018

This quiz has 4 problems worth 25 points each.

1. Write the time-dependent Schrödinger equation.

We have studied two systems that are confined to the region $0 \le x \le a$. One is the particle-in-a-box, with Hamiltonian

$$\hat{H}_{\text{1d-box}} = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + \begin{Bmatrix} 0 & 0 < x < a \\ +\infty & \text{otherwise} \end{Bmatrix}$$

and the other (on an assignment) is the system with the Hamiltonian

$$\hat{H}_{\text{1d-box}} = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + \begin{Bmatrix} \left(ax - x^2\right)^{-1} & 0 < x < a \\ +\infty & \text{otherwise} \end{Bmatrix}$$

and the ground-state wavefunction

$$\Psi_{\text{quad}\Psi}(x) = A\left(x^2 - ax\right)$$

We will also consider the perturbed Hamiltonian,

$$\hat{H} = \hat{H}_{\text{1d-box}} + \lambda \hat{H}_{\text{quad}\Psi}$$

2. What is the normalization constant for $\Psi_{\text{quad}\Psi}(x)$?

3. Write an expression for the derivative $\left(\frac{\partial E}{\partial \lambda}\right)_{\lambda=1}$. Evaluate the integral (it is not hard).

Name____________________________________ Student #_____________________________

4. You can expand $\Psi_{\text{quad}\Psi}(x)$ exactly in terms of the eigenfunctions of the particle in a box,

$$\Psi_{\text{quad}\Psi}(x) = \sum_{n=0}^{\infty} c_n \Psi_{\text{1d-box};n}(x)$$

What are the values for c_n? You may find the following integrals useful,

$$\int x \sin(bx)\,dx = \frac{\sin(bx)}{b^2} - \frac{xcox(bx)}{b} + \text{constant}$$

$$\int x^2 \sin(bx)\,dx = -\left(\frac{x^2\cos(bx)}{b} + \frac{2x\cos\left(bx+\frac{1}{2}\pi\right)}{b^2} + \frac{2\cos(bx+\pi)}{b^3}\right) + \text{constant}$$

BONUS (10 points). The Integrated Hellmann-Feynman theorem says that given two Hamiltonians and their eigenfunctions/eigenvalues,

$$\hat{H}^{(1)}\Psi_k^{(1)}(x) = E_k^{(1)}\Psi_k^{(1)}(x)$$

$$\hat{H}^{(2)}\Psi_k^{(2)}(x) = E_k^{(2)}\Psi_k^{(2)}(x)$$

then

$$E_k^{(2)} - E_l^{(1)} = \frac{\int \left(\Psi_k^{(2)}(x)\right)^* \left(\hat{H}^{(2)} - \hat{H}^{(1)}\right)\Psi_l(x)\,dx}{\int \left(\Psi_k^{(2)}(x)\right)^* \Psi_l(x)\,dx}$$

Show that this is true.

Name________________________________ Student #__________________________

Quiz 4
CHEM 3PA3; Fall 2018

This quiz has 4 problems worth 25 points each.

1. Write the time-dependent Schrödinger equation.

$$\hat{H}(x,t)\Psi(x,t) = i\hbar\frac{\partial\Psi(x,t)}{\partial t}$$

We have studied two systems that are confined to the region $0 \le x \le a$. One is the particle-in-a-box, with Hamiltonian

$$\hat{H}_{\text{1d-box}} = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + \begin{cases} 0 & 0 < x < a \\ +\infty & \text{otherwise} \end{cases}$$

and the other (on an assignment) is the system with the Hamiltonian

$$\hat{H}_{\text{1d-box}} = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + \begin{cases} \frac{\hbar^2}{m}\left(ax - x^2\right)^{-1} & 0 < x < a \\ +\infty & \text{otherwise} \end{cases}$$

and the ground-state wavefunction

$$\Psi_{\text{quad}\Psi}(x) = A\left(x^2 - ax\right)$$

We will also consider the perturbed Hamiltonian,

$$\hat{H} = \hat{H}_{\text{1d-box}} + \lambda\hat{H}_{\text{quad}\Psi}$$

2. What is the normalization constant for $\Psi_{\text{quad}\Psi}(x)$?

We need to solve the equation,

$$1 = \int_0^a \Psi^*(x)\Psi(x)\,dx = \int_0^a \left(A\left(x^2 - ax\right)\right)^2 dx = A^2\int_0^a x^4 - 2ax^3 + a^2x^2 dx$$

$$1 = A^2\left[\frac{x^5}{5} - 2a\frac{x^4}{4} + a^2\frac{x^3}{3}\right]_0^a = A^2\left[\tfrac{1}{5}a^5 - \tfrac{1}{2}a^5 + \tfrac{1}{3}a^5\right] = \tfrac{6-15+10}{30}A^2a^5 = \tfrac{a^5}{30}A^2$$

$$A = \sqrt{\frac{30}{a^5}}$$

Name________________________________ Student #__________________________

3. Write an expression for the derivative $\left(\frac{\partial E}{\partial\lambda}\right)_{\lambda=1}$. Evaluate the integral (it is not hard).

This problem was unexpectedly tricky. I should have written instead $\hat{H}=(1-\lambda)\hat{H}_{\text{1d-box}}+\lambda\hat{H}_{\text{quad}\Psi}$ which would be easier. It is also easier to evaluate this at $\lambda=0$. As it is, we have

$$\left.\frac{\partial E}{\partial\lambda}\right|_{\lambda=\lambda_0}=\int_0^a\Psi(\lambda,x)\frac{\partial\hat{H}}{\partial\lambda}\Psi(\lambda,x)\,dx=\int_0^a\Psi(\lambda,x)\hat{H}_{\text{quad}}\Psi(\lambda,x)\,dx$$

(This is from the Hellmann-Feynman theorem.) In the case of interest we have:

$$\left.\frac{\partial E}{\partial\lambda}\right|_{\lambda=1}=\int_0^a\Psi(\lambda=1,x)\hat{H}_{\text{quad}}\Psi(\lambda=1,x)\,dx$$

Now we need to evaluate the wavefunction at $\lambda=1$. This is complicated by the fact that this is *not* the Hamiltonian we are used to evaluating. We have instead that

$$\begin{aligned}\hat{H}(\lambda=1)&=-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}+\frac{\hbar^2}{m\left(ax-x^2\right)}\\&=\frac{-\hbar^2}{m}\frac{d^2}{dx^2}+\frac{\hbar^2}{m\left(ax-x^2\right)}\\&=-\frac{\hbar^2}{m}\left(\frac{d^2}{dx^2}+\frac{1}{x^2-ax}\right)\end{aligned}$$

We can solve this differential equation but it is not trivial—it is not the same one we started with. So the best we can do in terms of an explicit expression is just the previous equation. If I had phrased this problem more intelligently, we would have had the definition $\hat{H}=(1-\lambda)\hat{H}_{\text{1d-box}}+\lambda\hat{H}_{\text{quad}\Psi}$ and the solution would have been

$$\begin{aligned}\left.\frac{\partial E}{\partial\lambda}\right|_{\lambda=1}&=\int_0^a\Psi(\lambda=1,x)\left(\hat{H}_{\text{quad}}-\hat{H}_{\text{1d-box}}\right)\Psi(\lambda=1,x)\,dx\\&=\int_0^a A\left(x^2-ax\right)\left(\tfrac{\hbar^2}{m}\left(ax-x^2\right)^{-1}\right)\left(A\left(x^2-ax\right)\right)dx\\&=-\frac{\hbar^2A^2}{m}\int_0^a\left(x^2-ax\right)dx=-\frac{\hbar^2A^2}{m}\left[\frac{x^3}{3}-\frac{ax^2}{2}\right]_0^a=-\frac{\hbar^2A^2}{m}\left(\tfrac{1}{3}a^3-\tfrac{1}{2}a^3\right)=\frac{\hbar^2a^3A^2}{6m}\\&=\frac{\hbar^2a^3}{6m}\left(\frac{15}{28a^5}\right)=\frac{5\hbar^2}{56a^2m}\end{aligned}$$

where I've used the normalization constant from the previous line.

Name________________________________ Student #__________________________

4. You can expand $\Psi_{\text{quad}\Psi}(x)$ exactly in terms of the eigenfunctions of the particle in a box,

$$\Psi_{\text{quad}\Psi}(x)=\sum_{n=0}^{\infty} c_n \Psi_{\text{1d-box};n}(x)$$

What are the values for c_n? You may find the following integrals useful,

$$\int x\sin(bx)\,dx=\frac{\sin(bx)}{b^2}-\frac{x\cos(bx)}{b}+\text{constant}$$

$$\int x^2\sin(bx)\,dx=-\left(\frac{x^2\cos(bx)}{b}+\frac{2x\cos\left(bx+\frac{1}{2}\pi\right)}{b^2}+\frac{2\cos(bx+\pi)}{b^3}\right)+\text{constant}$$

Cross-multiplying both sides of the equation in this problem by $\Psi^*_{\text{1d-box};m}(x)$, integrating, and using the orthonormality of the eigenfunctions gives the key expression (from class)

$$c_n=\int_0^a\sqrt{\frac{2}{a}}\sin\left(\frac{n\pi x}{a}\right)\left(A\left(x^2-ax\right)\right)dx=A\sqrt{\frac{2}{a}}\left(\int_0^a x^2\sin\left(\frac{n\pi x}{a}\right)dx-a\int_0^a x\sin\left(\frac{n\pi x}{a}\right)dx\right)$$

$$=A\sqrt{\frac{2}{a}}\left(\begin{array}{l}-\left(\dfrac{x^2\cos\left(\frac{n\pi x}{a}\right)}{\left(\frac{n\pi}{a}\right)}+\dfrac{2x\cos\left(\left(\frac{n\pi x}{a}\right)+\frac{1}{2}\pi\right)}{\left(\frac{n\pi}{a}\right)^2}+\dfrac{2\cos\left(\left(\frac{n\pi x}{a}\right)+\pi\right)}{\left(\frac{n\pi}{a}\right)^3}\right)\\ -a\left(\dfrac{\sin\left(\frac{n\pi x}{a}\right)}{\left(\frac{n\pi}{a}\right)^2}-\dfrac{x\cos\left(\frac{n\pi x}{a}\right)}{\left(\frac{n\pi}{a}\right)}\right)\end{array}\right)_0^a$$

$$=A\sqrt{\frac{2}{a}}\left(\begin{array}{l}-\left(\dfrac{a^2\cos(n\pi)}{\left(\frac{n\pi}{a}\right)}+\cancel{\dfrac{2a\cos\left(n\pi+\frac{1}{2}\pi\right)}{\left(\frac{n\pi}{a}\right)^2}}+\dfrac{2\cos\left((n+1)\pi\right)}{\left(\frac{n\pi}{a}\right)^3}\right)\\ -a\left(\cancel{\dfrac{\sin(n\pi)}{\left(\frac{n\pi}{a}\right)^2}}-\dfrac{a\cos(n\pi)}{\left(\frac{n\pi}{a}\right)}\right)+\dfrac{2\cos(\pi)}{\left(\frac{n\pi}{a}\right)^3}\end{array}\right)$$

$$=A\sqrt{\frac{2}{a}}\left(-\frac{a^3}{n\pi}(-1)^n+\frac{2a^3}{(n\pi)^3}(-1)^{n-1}+\frac{a^3}{n\pi}(-1)^n+\frac{2a^3}{(n\pi)^3}\right)$$

$$=\frac{A\sqrt{8a^5}}{(n\pi)^3}\left(1+(-1)^{n-1}\right)$$

Name________________________________ Student #____________________________

BONUS (10 points). The Integrated Hellmann-Feynman theorem says that given two Hamiltonians and their eigenfunctions/eigenvalues,

$$\hat{H}^{(1)}\Psi_k^{(1)}(x) = E_k^{(1)}\Psi_k^{(1)}(x)$$
$$\hat{H}^{(2)}\Psi_k^{(2)}(x) = E_k^{(2)}\Psi_k^{(2)}(x)$$

then

$$E_k^{(2)} - E_l^{(1)} = \frac{\int\left(\Psi_k^{(2)}(x)\right)^*\left(\hat{H}^{(2)} - \hat{H}^{(1)}\right)\Psi_l^{(1)}(x)\,dx}{\int\left(\Psi_k^{(2)}(x)\right)^*\Psi_l^{(1)}(x)\,dx}$$

Explain why this is true.

Start with the expression on the right-hand-side, use the facts that (1) the integral of a sum is the sum of the integrals, (2) the Hermitian property of the Hamiltonian and (3) the eigenvalue condition to obtain:

$$\begin{aligned}
\frac{\int\left(\Psi_k^{(2)}(x)\right)^*\left(\hat{H}^{(2)} - \hat{H}^{(1)}\right)\Psi_l^{(1)}(x)\,dx}{\int\left(\Psi_k^{(2)}(x)\right)^*\Psi_l^{(1)}(x)\,dx} &= \frac{\int\left(\Psi_k^{(2)}(x)\right)^*\hat{H}_2\Psi_l(x)\,dx - \int\left(\Psi_k^{(2)}(x)\right)^*\hat{H}_1\Psi_l^{(1)}(x)\,dx}{\int\left(\Psi_k^{(2)}(x)\right)^*\Psi_l^{(1)}(x)\,dx} \\
&= \frac{\int\left(\hat{H}_2\Psi_k^{(2)}(x)\right)^*\Psi_l(x)\,dx - \int\left(\Psi_k^{(2)}(x)\right)^*E_l^{(1)}\Psi_l^{(1)}(x)\,dx}{\int\left(\Psi_k^{(2)}(x)\right)^*\Psi_l^{(1)}(x)\,dx} \\
&= \frac{\int\left(E_k^{(2)}\Psi_k^{(2)}(x)\right)^*\Psi_l(x)\,dx - \int\left(\Psi_k^{(2)}(x)\right)^*E_l^{(1)}\Psi_l^{(1)}(x)\,dx}{\int\left(\Psi_k^{(2)}(x)\right)^*\Psi_l^{(1)}(x)\,dx} \\
&= \frac{E_k^{(2)}\int\left(\Psi_k^{(2)}(x)\right)^*\Psi_l(x)\,dx - E_l^{(1)}\int\left(\Psi_k^{(2)}(x)\right)^*\Psi_l^{(1)}(x)\,dx}{\int\left(\Psi_k^{(2)}(x)\right)^*\Psi_l^{(1)}(x)\,dx} \\
&= E_k^{(2)} - E_l^{(1)}
\end{aligned}$$