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Quiz 3
CHEM 3PA3; Fall 2018

This quiz has 5 problems worth 20 points each.

The Hamiltonian for the quantum harmonic oscillator is

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

You are told that its ground-state wavefunction and energy are is

$$\Psi_0(x) = \left(\frac{\sqrt{\kappa m}}{\pi\hbar}\right)^{1/4} \exp\left(-\frac{\sqrt{\kappa m}x^2}{2\hbar}\right) \qquad E_0 = \frac{\hbar}{2}\sqrt{\frac{\kappa}{m}}$$

1. **What is the expectation value of the kinetic energy in the ground state of the harmonic oscillator?**

2. **The energy eigenvalues of the harmonic oscillator are** $E_n = \hbar\left(n+\frac{1}{2}\right)\sqrt{\kappa/m}$ **with** $n = 0,1,2,\ldots$**. For the CN molecule, we have** $m = 1.07\cdot10^{-26}\,\text{kg}$**,** $\kappa = 1630\,\frac{\text{N}}{\text{m}} = 1630\,\frac{\text{kg}}{\text{s}^2}$**. For vibrations, usually the absorption/emissions are reported in wavenumbers. What is the wavenumber corresponding to the lowest-energy excitation from the ground state (i.e.,** $(n=0)\rightarrow(n=1)$ **in this system? Recall that** $h = 6.626\cdot10^{-34}\,\frac{\text{kg}\cdot\text{m}^2}{\text{s}}$ **and** $c = 2.998\cdot10^{8}\,\frac{\text{m}}{\text{s}}$**.**

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You are given a system with the potential energy,

$$V(x,y) = \tfrac{1}{2}\kappa x^2 + V_{\text{box}}^a(y)$$

$$V_{\text{box}}^a(y) = \begin{cases} 0 & 0 \le y \le a \\ +\infty & \text{otherwise} \end{cases}$$

3. Write the expression for the zero-point energy of this system.

4. What is the ground-state wavefunction for one electron in this system.

The harmonic oscillator is sometimes a poor model for a system. To improve the model, additional terms are sometimes added. In particular, sometimes a quartic term is added,

$$\hat{H} = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + \frac{1}{2}\kappa x^2 + \delta x^4 \qquad 0 < \delta \ll \kappa$$

It is assumed that the quartic term is very small. The following integrals might be helpful,

$$\int_{-\infty}^{\infty} e^{-ax^2} dx = \sqrt{\frac{\pi}{a}}$$

$$\int_{-\infty}^{\infty} x^{2n} e^{-ax^2} dx = \frac{1\times 3\times 5\times\cdots\times(2n-3)\times(2n-1)}{(2a)^n}\sqrt{\frac{\pi}{a}} \qquad n = 1, 2, \ldots$$

$$\int_{0}^{\infty} x^{2n+1} e^{-ax^2} dx = \frac{n!}{2a^{n+1}} \qquad n = 1, 2, \ldots$$

5. Use first-order perturbation theory to find an expression for the energy of the system when $\delta = \frac{1}{100}\kappa$ using first-order perturbation theory.

Bonus (5 pt) Suppose that $\hat{C}$ is a linear Hermitian operator and that $\Psi_1(x)$ and $\Psi_2(x)$ are both eigenfunctions of $\hat{C}$, but that the eigenvalues associated with $\Psi_1(x)$ and $\Psi_2(x)$ are different. Show that $\Psi_1(x)$ and $\Psi_2(x)$ *<u>must</u>* be orthogonal to each other.

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You are told that its ground-state wavefunction and energy are is

$$\Psi_0(x) = \left(\frac{\sqrt{\kappa m}}{\pi\hbar}\right)^{1/4} \exp\left(-\frac{\sqrt{\kappa m}x^2}{2\hbar}\right)$$

$$E_0 = \frac{\hbar}{2}\sqrt{\frac{\kappa}{m}}$$

1. What is the expectation value of the kinetic energy in the ground state of the harmonic oscillator?

Using the Hellmann-Feynman theorem,

$$\frac{\partial E_0}{\partial \hbar} = \int_{-\infty}^{\infty} \Psi_0^*(x)\frac{\partial \hat{H}}{\partial \hbar}\Psi_0(x)\,dx$$

Substituting in the expressions from the problem statement,

$$\frac{\partial E_0}{\partial \hbar} = \frac{1}{2}\sqrt{\frac{\kappa}{m}} = \int_{-\infty}^{\infty} \Psi_0^*(x)\frac{\partial \hat{H}}{\partial \hbar}\Psi_0(x)\,dx = \int_{-\infty}^{\infty} \Psi_0^*(x)\left(-\frac{\hbar}{m}\frac{d^2}{dx^2}\right)\Psi_0(x)\,dx$$

$$\frac{1}{2}\sqrt{\frac{\kappa}{m}} = \int_{-\infty}^{\infty} \Psi_0^*(x)\left(-\frac{\hbar}{m}\frac{d^2}{dx^2}\right)\Psi_0(x)\,dx$$

Finally, multiply both sides by $\frac{1}{2}\hbar$ to obtain

$$\frac{\hbar}{4}\sqrt{\frac{\kappa}{m}} = \int_{-\infty}^{\infty} \Psi_0^*(x)\left(-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\right)\Psi_0(x)\,dx = \int_{-\infty}^{\infty} \Psi_0^*(x)\hat{T}\Psi_0(x)\,dx = \langle \hat{T} \rangle$$

2. The energy eigenvalues of the harmonic oscillator are $E_n = \hbar\left(n+\frac{1}{2}\right)\sqrt{\kappa/m}$ with $n = 0,1,2,\ldots$. For the CN molecule, we have $m = 1.07\cdot 10^{-26}\,\text{kg}$, $\kappa = 1630\,\frac{\text{N}}{\text{m}} = 1630\,\frac{\text{kg}}{\text{s}^2}$. For vibrations, usually the absorption/emissions are reported in wavenumbers. What is the wavenumber corresponding to the lowest-energy excitation from the ground state (i.e., $(n=0)\to(n=1)$ in this system? Recall that $h = 6.626\cdot 10^{-34}\,\frac{\text{kg}\cdot\text{m}^2}{\text{s}}$ and $c = 2.998\cdot 10^{8}\,\frac{\text{m}}{\text{s}}$.

The excitation energy is

$$E_1 - E_0 = \hbar\left(1+\tfrac{1}{2}\right)\sqrt{\kappa/m} - \hbar\left(0+\tfrac{1}{2}\right)\sqrt{\kappa/m} = \hbar\sqrt{\kappa/m} = \hbar\cdot\sqrt{\left(1630\,\tfrac{\text{kg}}{\text{s}^2}\right)\Big/\left(1.07\cdot 10^{-26}\,\text{kg}\right)}$$

$$\hbar\omega = \hbar\cdot\sqrt{\left(1630\,\tfrac{\text{kg}}{\text{s}^2}\right)\Big/\left(1.07\cdot 10^{-26}\,\text{kg}\right)}$$

$$\omega = 3.903\cdot 10^{14}\ \text{s}^{-1}$$

In the second line I used $E = \hbar\omega$. I also have

$$c = \lambda\nu$$

$$\frac{1}{\lambda} = \frac{\nu}{c}$$

$$k = \frac{2\pi}{\lambda} = \frac{2\pi\nu}{c} = \frac{\omega}{c} = \frac{3.903\cdot 10^{14}\,\text{s}^{-1}}{2.998\cdot 10^{8}\,\frac{\text{m}}{\text{s}}} = 1.301\cdot 10^{6}\,\text{m}^{-1} = 1.301\cdot 10^{4}\,\text{cm}^{-1}$$

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$$V_{\text{box}}^{a}(y) = \begin{cases} 0 & 0 \le y \le a \\ +\infty & \text{otherwise} \end{cases}$$

3. Write the expression for the zero-point energy of this system.

$$E = \frac{\hbar}{2}\sqrt{\frac{\kappa}{m}} + \frac{h^2}{8ma^2}$$

4. What is the ground-state wavefunction for one electron in this system.

$$\Psi(x,y) = \left[\left(\frac{\sqrt{\kappa m}}{\pi\hbar}\right)^{1/4}\exp\left(-\frac{\sqrt{\kappa m}x^2}{2\hbar}\right)\right]\left[\sqrt{\frac{2}{a}}\sin\left(\frac{\pi y}{a}\right)\right]$$

The harmonic oscillator is sometimes a poor model for a system. To improve the model, additional terms are sometimes added. In particular, sometimes a quartic term is added,

$$\hat{H} = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + \frac{1}{2}\kappa x^2 + \delta x^4 \qquad 0 < \delta \ll \kappa$$

It is assumed that the quartic term is very small. The following integrals might be helpful,

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$$\int_{0}^{\infty} x^{2n+1} e^{-ax^2}\,dx = \frac{n!}{2a^{n+1}} \qquad n = 1, 2, \ldots$$

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5. Use first-order perturbation theory to find an expression for the energy of the system when $\delta = \frac{1}{100}\kappa$ using first-order perturbation theory.

The change in energy due to the parameter δ can be determined from the integral,

$$\left.\frac{\partial E}{\partial \delta}\right|_{\delta=0} = \int_{-\infty}^{\infty} \Psi_0^*(x)\left[\frac{\partial \hat{H}}{\partial \delta}\right]_{\delta=0} \Psi_0(x)\,dx$$

$$= \int_{-\infty}^{\infty}\left(\frac{\sqrt{\kappa m}}{\pi\hbar}\right)^{1/4}\exp\left(-\frac{\sqrt{\kappa m}x^2}{2\hbar}\right)x^4\left(\frac{\sqrt{\kappa m}}{\pi\hbar}\right)^{1/4}\exp\left(-\frac{\sqrt{\kappa m}x^2}{2\hbar}\right)dx$$

$$= \sqrt{\frac{\sqrt{\kappa m}}{\pi\hbar}}\int_{-\infty}^{\infty} x^4 \exp\left(-\frac{\sqrt{\kappa m}x^2}{\hbar}\right)dx$$

$$= \sqrt{\frac{\sqrt{\kappa m}}{\pi\hbar}}\cdot\left(\frac{3}{\left(2\frac{\sqrt{\kappa m}}{\hbar}\right)^2}\right)\sqrt{\frac{\pi}{\frac{\sqrt{\kappa m}}{\hbar}}} = \left(\frac{(\kappa m)^{\frac{1}{4}}}{\pi^{\frac{1}{2}}\hbar^{\frac{1}{2}}}\right)\left(\frac{3\hbar^2}{4(\kappa m)}\right)\left(\frac{\pi^{\frac{1}{2}}\hbar^{\frac{1}{2}}}{(\kappa m)^{\frac{1}{4}}}\right)$$

$$= \frac{3\hbar^2}{4\kappa m}$$

Then, using the Taylor series,

$$E\left(\delta = \tfrac{1}{100}\kappa\right) = E(\delta = 0) + \left(\tfrac{1}{100}\kappa\right)\cdot\left.\frac{\partial E}{\partial \delta}\right|_{\delta=0}$$

$$= \frac{\hbar}{2}\sqrt{\frac{\kappa}{m}} + \frac{\kappa}{100}\cdot\frac{3\hbar^2}{4\kappa m}$$

$$= \frac{\hbar}{2}\sqrt{\frac{\kappa}{m}} + \frac{3\hbar^2}{400m}$$

Bonus (5 pt) Suppose that $\hat{C}$ is a linear Hermitian operator and that $\Psi_1(x)$ and $\Psi_2(x)$ are both eigenfunctions of $\hat{C}$, but that the eigenvalues associated with $\Psi_1(x)$ and $\Psi_2(x)$ are different. Show that $\Psi_1(x)$ and $\Psi_2(x)$ <u>*must*</u> be orthogonal to each other.

The eigenvalue relations are

$$\hat{C}\Psi_1(x) = \gamma_1\Psi_1(x)$$
$$\hat{C}\Psi_2(x) = \gamma_2\Psi_2(x)$$

Then writing the expectation value for $\hat{C}$ and using the Hermitian property of the operator and the eigenvalue equations, we have, Name_________________________________ Student #___________________________

$$\int \Psi_1^*(x)\hat{C}\Psi_2(x)\,dx = \int \left(\hat{C}\Psi_1(x)\right)^* \Psi_2(x)\,dx$$

$$\int \Psi_1^*(x)\gamma_2\Psi_2(x)\,dx = \int \left(\gamma_1\Psi_1(x)\right)^* \Psi_2(x)\,dx$$

$$\gamma_2\int \Psi_1^*(x)\Psi_2(x)\,dx = \gamma_1\int \Psi_1^*(x)\Psi_2(x)\,dx$$

$$0 = (\gamma_2 - \gamma_1)\cdot\int \Psi_1^*(x)\Psi_2(x)\,dx$$

The last equations implies that either $(\gamma_2 - \gamma_1) = 0$ or $\int \Psi_1^*(x)\Psi_2(x)\,dx = 0$. The first is not true because the eigenvalues for the wavefunctions are different (by assumption). Therefore it must be that the wavefunction are orthogonal,

$$\int \Psi_1^*(x)\Psi_2(x)\,dx = 0.$$