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Quiz 9
CHEM 3PA3; Fall 2018

This quiz has 5 problems worth 20 points each.

1. **Write the electronic and nuclear Schrödinger Equations for the Hydrogen molecule within the Born-Oppenheimer approximation. Do not use atomic units. (That is, write out the dependence on fundamental constants.)**

The next 4 problems go together:

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

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

2. **The energy eigenvalues of the harmonic oscillator are $E_n = \hbar\left(n+\tfrac{1}{2}\right)\sqrt{\kappa/m}$ with $n = 0,1,2,\ldots$. For the CN molecule, we have $m = 1.07\cdot 10^{-26}\,\text{kg}$, $\kappa = 1630\,\tfrac{\text{N}}{\text{m}} = 1630\,\tfrac{\text{kg}}{\text{s}^2}$. 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 $h = 6.626\cdot 10^{-34}\,\tfrac{\text{kg}\cdot\text{m}^2}{\text{s}}$ and $c = 2.998\cdot 10^{8}\,\tfrac{\text{m}}{\text{s}}$.**

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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,

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

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

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

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

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

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.

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Bonus: (10 points) You can expand $\Psi_{\text{quad}\Psi}(x)$ exactly in terms of the eigenfunctions of the particle in a box,

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

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

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

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

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

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electronic Schrodinger Eq.

$$\left(\begin{array}{l} -\tfrac{\hbar^2}{2m_e}\nabla^2_{\mathbf{r}_1} - -\tfrac{\hbar^2}{2m_e}\nabla^2_{\mathbf{r}_2} + \dfrac{e^2}{4\pi\varepsilon_0|\mathbf{r}_1-\mathbf{r}_2|} + \dfrac{e^2}{4\pi\varepsilon_0|\mathbf{R}_1-\mathbf{R}_2|} \\ -\dfrac{e^2}{4\pi\varepsilon_0|\mathbf{r}_1-\mathbf{R}_1|} - \dfrac{e^2}{4\pi\varepsilon_0|\mathbf{r}_1-\mathbf{R}_2|} - \dfrac{e^2}{4\pi\varepsilon_0|\mathbf{r}_2-\mathbf{R}_1|} - \dfrac{e^2}{4\pi\varepsilon_0|\mathbf{r}_2-\mathbf{R}_2|} \end{array}\right)\psi_{el}(\mathbf{r}_1,\mathbf{r}_2|\mathbf{R}_1,\mathbf{R}_2) = U(\mathbf{R}_1,\mathbf{R}_2)\psi_{el}(\mathbf{r}_1,\mathbf{r}_2|\mathbf{R}_1,\mathbf{R}_2)$$

nuclear Schrodinger Eq.

$$\left(-\tfrac{\hbar^2}{2M_H}\nabla^2_{\mathbf{R}_1} - \tfrac{\hbar^2}{2M_H}\nabla^2_{\mathbf{R}_2} + U(\mathbf{R}_1,\mathbf{R}_2)\right)\chi_{nuc}(\mathbf{R}_1,\mathbf{R}_2) = E_{\text{total}}\chi_{nuc}(\mathbf{R}_1,\mathbf{R}_2)$$

The next 4 problems go together:
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

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

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., $(n=0)\to(n=1)$ in this system? Recall that $h = 6.626\cdot10^{-34}\,\frac{\text{kg}\cdot\text{m}^2}{\text{s}}$ and $c = 2.998\cdot10^{8}\,\frac{\text{m}}{\text{s}}$.**

The excitation energy is

$$E_1 - E_0 = \hbar\left(1+\tfrac{1}{2}\right)\sqrt{\kappa/m} - \hbar\left(0+\tfrac{1}{2}\right)\sqrt{\kappa/m} = \hbar\sqrt{\kappa/m} = \hbar\cdot\sqrt{\left(1630\,\tfrac{\text{kg}}{\text{s}^2}\right)/\left(1.07\cdot10^{-26}\,\text{kg}\right)}$$

$$\hbar\omega = \hbar\cdot\sqrt{\left(1630\,\tfrac{\text{kg}}{\text{s}^2}\right)/\left(1.07\cdot10^{-26}\,\text{kg}\right)}$$

$$\omega = 3.903\cdot10^{14}\ \text{s}^{-1}$$

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

$$c = \lambda\nu$$

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

$$k = \frac{2\pi}{\lambda} = \frac{2\pi\nu}{c} = \frac{\omega}{c} = \frac{3.903\cdot10^{14}\text{s}^{-1}}{2.998\cdot10^{8}\,\frac{\text{m}}{\text{s}}} = 1.301\cdot10^{6}\text{m}^{-1} = 1.301\cdot10^{4}\text{cm}^{-1}$$

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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,

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

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

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

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

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

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

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

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)

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

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

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

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

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

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