**Problem 1 (4 points).** Consider electrons in the π-network in decapentaene ($C_{10}H_{12}$, see the structure drawing below) as particles in a 1-D box. Recall that each carbon atom donates one electron to the π-network. The C=C bond length is 1.35 Å, the C–C bond length is 1.54 Å (1Å = 10^{-10} m). What is the longest wavelength of light required to induce a transition from the ground state of these electrons to one of the excited states of these electrons?
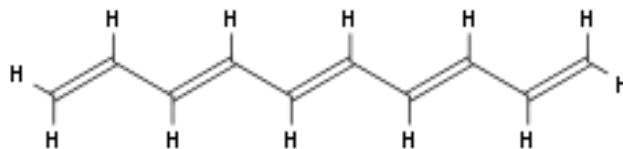
The box length can be estimated as a = 5 ×1.35 Å + 4 × 1.54 Å = 12.91 Å =12.91 ×10^{-10} m. The total number of donated π-electrons = 10: with no more than two electrons per energy level (according to Pauli exclusion principle), they will completely occupy 5 lowest energy levels (n =1 to 5). This will be the ground state of the system. Because the wavelength of emitted/absorbed light $\lambda = \dfrac{c}{v} = \dfrac{c}{\Delta E/h}$ is inversely proportional to ΔE, the longest wavelength corresponds to the smallest quantum of energy. Since the energy of particle in a box increases as n^2, the smallest quantum of energy will involve the transition to the first excited state(s). This will involve a change in the quantum number n from 5 to 6. The corresponding quantum of energy is:

$$\Delta E_{5\rightarrow6} = E_{n=6} - E_{n=5} = \frac{h^2}{8m_e a^2}(6^2 - 5^2) = \frac{11h^2}{8m_e a^2}.$$ Using the energy conservation law and Einstein's equation for photon's energy: $\Delta E_{5\rightarrow6} = h v_{5\rightarrow6}$ we get the corresponding wavelength:

$$\lambda_{5\rightarrow6} = \frac{c}{v_{5\rightarrow6}} = \frac{8m_e a^2 c}{11h} = 4.99 \times10^{-7} \text{ m} = 499 \text{ nm (this corresponds to green light near the edge}$$
between green and blue).

Problem 2 (4 points). Are the wave functions listed below orthogonal to each other? Support your answer by performing the appropriate integration over the corresponding interval. *Show your calculation.*

(A) wave functions of a particle in a 1D box corresponding to the states with $n=2$ and $n=4$.
Yes they are. Here is my calculation:

$$\int_0^a \Psi_{n=4} \cdot \Psi_{n=2}\, dx = \frac{2}{a}\int_0^a \sin(\frac{4\pi x}{a}) \cdot \sin(\frac{2\pi x}{a})\, dx = \frac{1}{a}\int_0^a \left[\cos(\frac{2\pi x}{a}) - \cos(\frac{6\pi x}{a})\right] dx =$$

$$= \frac{1}{a}\left[\frac{a}{2\pi}\sin(\frac{2\pi x}{a})\Big|_0^a - \frac{a}{6\pi}\sin(\frac{6\pi x}{a})\Big|_0^a\right] = \frac{1}{a}(0-0-0+0) = 0$$

Here I simplified the integrand using the trigonometric identity

$$\sin A \cdot \sin B = \frac{1}{2}\left[\cos(A-B) - \cos(A+B)\right]$$

(B) wave functions of the harmonic oscillator corresponding to the states with $n = 0$ and $n = 2$; interval: $-\infty < x < \infty$

Yes they are. Here is my calculation:

$$\int_{-\infty}^{\infty} \Psi_{n=0}^* \cdot \Psi_{n=2} dx \rightarrow \int_{-\infty}^{\infty} \left(2\alpha x^2 - 1\right) \cdot e^{-\alpha x^2} dx = \int_{-\infty}^{0}\left(2\alpha x^2 - 1\right)\cdot e^{-\alpha x^2} dx + \int_{0}^{\infty}\left(2\alpha x^2 - 1\right)\cdot e^{-\alpha x^2} dx =$$

$$= 2\int_{0}^{\infty}\left(2\alpha x^2 - 1\right)\cdot e^{-\alpha x^2} dx = \text{(use table integrals)} = 2\left(2\alpha\sqrt{\frac{\pi}{\alpha}}\frac{1}{4\alpha} - \sqrt{\frac{\pi}{\alpha}}\frac{1}{2}\right) = 2\sqrt{\frac{\pi}{\alpha}}\left(\frac{1}{2} - \frac{1}{2}\right) = 0$$

Problem 3 (4 points). Is it possible to know with arbitrary precision both the angular coordinate ϕ and the angular momentum l_z of a particle moving on a ring? Support your answer by evaluating the corresponding commutator. Show your calculation. Based on your results, formulate a mathematical equation representing the uncertainty principle for these two observables.

Evaluate the commutator of the corresponding QM operators:

$$\left[\hat{\phi}, \hat{l}_z\right]\Psi = \left[\hat{\phi}, -i\hbar\frac{d}{d\phi}\right]\Psi = -i\hbar\left(\phi\frac{d}{d\phi}\Psi - \frac{d}{d\phi}\phi\Psi\right) = -i\hbar\left(\phi\frac{d}{d\phi}\Psi - \Psi - \phi\frac{d}{d\phi}\Psi\right) = i\hbar\Psi \ . \ \text{Thus}$$

$$\left[\hat{\phi}, \hat{l}_z\right] = i\hbar \ . \ \text{Because the commutator is not zero, we conclude that the corresponding two}$$
physical observables (the angular momentum l_z and the angular coordinate ϕ of the particle) cannot be known simultaneously with arbitrary precision.

By full analogy of this commutator with that of $\hat{x}$ and $\hat{p}$, and the analogy between x and ϕ and between p and l_z, we can formulate the uncertainty principle for ϕ and l_z as $\Delta\phi \times \Delta l_z \geq \dfrac{\hbar}{2}$. The

same result can be obtained rigorously by plugging in $\left[\hat{\phi}, \hat{l}_z\right] = i\hbar$ into the equation that relates the uncertainties of observables A and B to the commutator of the corresponding operators

$$\Delta A \times \Delta B \geq \frac{1}{2}\left|\left\langle\left[\hat{A}, \hat{B}\right]\right\rangle\right| \ \text{where in this case} \ \left\langle\left[\hat{A}, \hat{B}\right]\right\rangle = \left\langle\left[\hat{\phi}, \hat{l}_z\right]\right\rangle = \left\langle i\hbar\right\rangle = i\hbar \ .$$

Problem 4 (8 points). Consider vibrations of an oxygen molecule. Here are some relevant characteristics of the molecule: the equilibrium bond length is 1.208 Å (1Å=10^{-10} m), the force constant is 1177 N·m^{-1} (1 N=1 kg·m·s^{-2}).

(A) Assume that vibrational states of the oxygen molecule can be described by the harmonic oscillator model. Calculate the quantum of energy required for a transition between vibrational states with quantum numbers n and $n+1$ of the oxygen molecule.

By the energy conservation law, the quantum of energy equals the energy difference between the

two vibrational states: $\Delta E = E_{n+1} - E_n = h\nu = \hbar\sqrt{\dfrac{k}{\mu}}$. Substituting the reduced mass of O_2, $\mu = 8$

amu = 1.328×10^{-26} kg (1 amu = 1.66×10^{-27} kg), and the force constant, we get ΔE=3.14×10^{-20} J.

(B) When approximating the actual potential energy of the inter-atomic interaction by the harmonic potential (parabola), $V = \frac{1}{2}kx^2$, we assumed that the amplitudes of bond vibrations are small compared to the equilibrium bond length. *Does this assumption hold for molecular oxygen?* To answer this question, estimate the vibrational amplitude of the oxygen molecule in the ground state by calculating $\Delta x = \sqrt{\langle x^2 \rangle}$, and compare your result with the equilibrium bond length.

Because of the symmetry of the harmonic potential,

$$< x^2 >= \int_{-\infty}^{\infty} \Psi_0^* x^2 \Psi_0 dx = \sqrt{\frac{\alpha}{\pi}} \int_{-\infty}^{\infty} x^2 \cdot e^{-\alpha x^2} dx = 2\sqrt{\frac{\alpha}{\pi}} \int_0^{\infty} x^2 \cdot e^{-\alpha x^2} dx = \frac{1}{2\alpha} = \frac{\hbar}{2\sqrt{k\mu}}.$$ Then the

vibrational amplitude can be estimated as $\Delta x = \sqrt{\langle x^2 \rangle} = \sqrt{\dfrac{\hbar}{2\sqrt{k\mu}}}$. Substituting all the relevant

parameters into this equation, we get $\Delta x \approx 3.65 \times 10^{-12}$ m. This value is only 3% of the equilibrium bond length in O_2, therefore, **the assumption of a relatively small amplitude of bond length variations is valid**.

(Note that you can evaluate $<x^2>$ without integration if you realize that it is directly related to the average potential energy, $<V> = k<x^2>/2$, and recall the equipartitioning of the kinetic and potential energies of harmonic oscillator (we showed this in class), i.e. $<V>=<E>/2 = h\nu/4$).

The following table integrals might or might not turn useful:

$$\int_0^{\infty} e^{-ax^2} x^{2m} \, dx = \sqrt{\frac{\pi}{a}} \frac{1\cdot 3\cdot 5\cdot ... \cdot (2m-1)}{2^{m+1} a^m}, \text{ (for } m \geq 1); \qquad \int_0^{\infty} e^{-ax^2} \, dx = \frac{1}{2}\sqrt{\frac{\pi}{a}}; \qquad \int_0^{\infty} x^m e^{-ax} dx = \frac{m!}{a^{m+1}}$$