Problem 1 (9 points). Are the following wave functions orthogonal to each other? Support your answer by carrying out the appropriate integration.

(A) Wave functions of the harmonic oscillator corresponding to the states with $n = 1$ and $n = 2$.

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

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

Because $\Psi_{n=1}(x)$ is an odd function of x while $\Psi_{n=2}(x)$ is an even function of x, the integrand is an odd function of x, and therefore the integral from -∞ to 0 and the integral from 0 to +∞ have the same value but different sign, and cancel each other.

(B) Wave functions of the harmonic oscillator corresponding to the states with $n = 1$ and $n = 3$.

$$\int_{-\infty}^{\infty} \Psi_{n=1}^{*} \cdot \Psi_{n=3} dx \rightarrow \int_{-\infty}^{\infty} x \cdot x\left(2\alpha x^2 - 3\right) \cdot e^{-\alpha x^2} dx = \int_{-\infty}^{0} x^2 \left(2\alpha x^2 - 3\right) \cdot e^{-\alpha x^2} dx + \int_{0}^{\infty} x^2 \left(2\alpha x^2 - 3\right) \cdot e^{-\alpha x^2} dx =$$

$$= 2\int_{0}^{\infty} x^2 \left(2\alpha x^2 - 3\right) \cdot e^{-\alpha x^2} dx = 2\left(2\alpha \int_{0}^{\infty} x^4 \cdot e^{-\alpha x^2} dx - 3\int_{0}^{\infty} x^2 \cdot e^{-\alpha x^2} dx \right) = (\text{use table integrals}) =$$

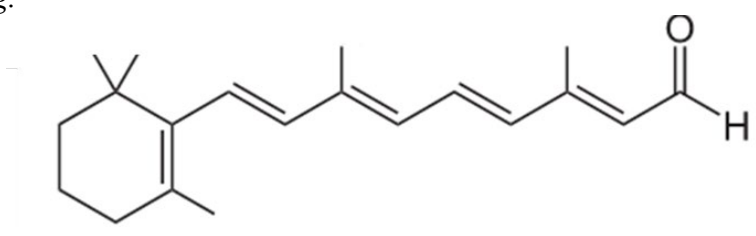
$$= 2\left(2\alpha \sqrt{\frac{\pi}{\alpha}} \frac{3}{8\alpha^2} - 3\sqrt{\frac{\pi}{\alpha}} \frac{1}{4\alpha} \right) = 2\sqrt{\frac{\pi}{\alpha}} \left(\frac{3}{4\alpha} - \frac{3}{4\alpha} \right) = 0$$

(C) Wave functions of a particle on a ring corresponding to the states with $m_l = 3$ and $m_l = -3$.

$$\int_{0}^{2\pi} \Psi_{m_l=3}^{*} \cdot \Psi_{m_l=-3} \, d\varphi = \frac{1}{2\pi} \int_{0}^{2\pi} \left(e^{i3\varphi}\right)^{*} \cdot e^{-i3\varphi} d\varphi = \frac{1}{2\pi} \int_{0}^{2\pi} e^{-i3\varphi} \cdot e^{-i3\varphi} d\varphi = \frac{1}{2\pi} \int_{0}^{2\pi} e^{-i6\varphi} d\varphi =$$

$$= -\frac{1}{2\pi} \frac{1}{6i} e^{-i6\varphi} \Big|_{0}^{2\pi} = \frac{i}{12\pi} \left(e^{-i12\pi} - e^{0} \right) = \frac{i}{12\pi} \left(1 - 1 \right) = 0$$

Problem 2 (4 points). Consider electrons in the π-network in the retinal as particles in a 1-D box. For simplicity you can ignore carbons in the ring. Recall that each double-bonded carbon atom donates one electron to the π-network. The C=C bond length is 1.34 Å, the C–C bond length is 1.54 Å (1 Å = 10^{-10} m). What is the longest wavelength of light required to induce a transition from the ground state to one of the excited states of these electrons? *Briefly explain your reasoning.*



If we ignore the ring carbons, the remaining carbons form a box of length $a = 4 \times 1.34$ Å + 4×1.54 Å = 15.8 Å = 11.52×10^{-10} m (four C-C and four C=C bonds). The total number of donated

π-electrons = 8: with no more than two electrons per level, they will completely occupy 4 lowest energy levels (n=1 to 4). This will be the ground state of the system, and the transition to the first excited state(s) will involve a change in the quantum number n from 4 to 5. The corresponding quantum of energy is the smallest of all possible transition-associated quanta in this system, and therefore it corresponds to the longest wavelength of light:

$\Delta E_{4\to5} = E_{n=5} - E_{n=4} = \frac{9h^2}{8m_e a^2}$. Using the energy conservation law and Einstein's equation for photon's energy: $\Delta E_{4\to5} = h\nu_{4\to5}$ we get the corresponding wavelength: $\lambda_{4\to5} = \frac{c}{\nu_{4\to5}} = \frac{8m_e a^2 c}{9h} =$ 4.86 ×10^{-7} m = 486 nm, which corresponds to blue light range.

If you included also the C-C bond to the ring carbon as part of the box, this would give a = 4 ×1.34 Å + 5 × 1.54 Å = 13.06 Å = 13.06 ×10^{-10} m, while the number of electrons remains the same. This gives $\lambda_{4\to5}$ = = 6.247 ×10^{-7} m = 625 nm (this corresponds to red light near the edge between orange and red).

Problem 3 (12 points). Consider a hydrogen fluoride molecule absorbed on a flat surface. Assume that there is no coupling between the translational, vibrational, and rotational states, i.e. these motions are independent of each other. Here are some relevant characteristics of the molecule: the equilibrium bond length is 0.9168 Å (1Å=10^{-10} m), the force constant is 966 N·m^{-1} (1 N=1 kg·m·s^{-2}).

(A) Assume that vibrational states of the HF molecule can be described by the harmonic oscillator model. Calculate the quantum of energy that is absorbed when the molecule undergoes a transition from the ground state to the first excited vibrational state.

By the energy conservation law, the quantum of energy equals the energy difference between the two vibrational states: $\Delta E_{vib} = E_{n=1} - E_{n=0} = h\nu = \hbar\sqrt{\frac{k}{\mu}}$. Substituting the reduced mass of HF, μ = 1*19/20 amu = 1.577 10^{-27} kg (1 amu = 1.66 ×10^{-27} kg), and the force constant, we get ΔE_{vib}=8.25×10^{-20} J.

(B) What is the smallest quantum of energy that can be emitted by the HF molecule when it undergoes a transition from one rotational state to another? Assume that molecular rotations can be described by the particle on a ring model.

Because the energy of a particle on a ring is proportional to m_l^2, the smallest distance between any two energy levels is that between the ground state (m_l=0) and the first excited state (m_l=1), Therefore, the smallest emitted quantum of energy corresponds to a transition from m_l=1 to m_l =0:

$\Delta E_{rot} = E_1 - E_0 = \frac{\hbar^2}{2I}\left(1^2 - 0\right) = \frac{\hbar^2}{2\mu r^2}$. Substituting the reduced mass of HF, and the bond length into this equation, we obtain: ΔE_{rot}=4.2×10^{-22} J.

Note that the quantum of energy associated with rotations is ~200 times smaller (!) than that associated with vibrations.

(C) How will your answers to questions A and B change if the hydrogen is substituted by deuteron? Support your answers by calculations. Assume that the equilibrium bond length and the force constant remain the same.

The reduced mass of $^2H^{19}F$ is approximately 2 times greater than for $^1H^{19}F$: 2*19/21 amu = 3.0 10^{-27} kg. Note that $\Delta E_{vib} \propto \mu^{-½}$ while $\Delta E_{rot} \propto \mu^{-1}$, so both energies will be reduced. The quantum of energy associated with the vibrational transition will be approximately √2 smaller: 5.98×10^{-20} J. The quantum of energy associated with the rotational transition will be approximately 2 times smaller: 2.2×10^{-22} J.

(D) When approximating the actual potential energy of inter-atomic interaction using the harmonic potential, we assumed that the amplitudes of bond vibrations are small compared to the equilibrium bond length. *Does this assumption hold for HF molecule?* To answer this question, estimate the vibrational amplitude of the HF 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 $\Delta x = \sqrt{\langle x^2 \rangle} = \sqrt{\frac{\hbar}{2\sqrt{k\mu}}}$. Substituting all the relevant parameters into this equation, we get $\Delta x \approx 6.54\times10^{-12}$ m. This value is ~ 7% of the equilibrium bond length, therefore, the assumption of a small amplitude of bond length fluctuations is entirely valid.

(Note that you can calculate $<x^2>$ 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 (as discussed in the textbook), i.e. $<V>=<E>/2 = h\nu/4$).