

Chem 30324, Spring 2025, Homework 5

Due February 28, 2025


Real-world particle-in-a-box.

A one-dimensional particle-in-a-box is a simple but plausible model for the π electrons of a conjugated alkene, like butadiene (C_4H_6 , shown here). Suppose all the C–C bonds in a polyene are 1.4 Å long and the polyenes are perfectly linear.

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1. Plot out the normalized $n = 2$ particle-in-a-box wavefunction for an electron in butadiene and the normalized $n = 2$ probability distribution. Indicate on the plots the most probable location(s) of the electron, the average location of the electron, and the positions of any nodes.
2. Butadiene has 4 π electrons, and we will learn later that in its lowest energy state, two of these are in the $n = 1$ and two in the $n = 2$ levels. Compare the wavelength of light (in nm) necessary to promote ("excite") one electron from either of these levels to the empty $n = 3$ level.
3. The probability of an electron jumping between two energy states by emitting or absorbing light is proportional to the square of the "transition dipole," given by the integral $|\langle \psi_{\text{final}} | \hat{x} | \psi_{\text{initial}} \rangle|^2$. Contrast the relative probabilities of an electron jumping from $n = 1$ to $n = 3$ and from $n = 2$ to $n = 3$ levels. Can you propose any general rules about "allowed" and "forbidden" jumps?

4. Consider the reaction of two ethylene molecules to form butadiene:

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5. As a very simple estimate, you could take the energy of each molecule as the sum of the energies of its π electrons, allowing only two electrons per energy level. Again taking each C—C bond as 1.4 Å long and treating the π electrons as particles in a box, calculate the total energy of an ethylene and a butadiene molecule within this model (in kJ/mol), and from these calculate the net reaction energy. Compare your results to the experimental reaction enthalpy. How well did the model do?

6. This particle-in-a-box model has many flaws, not the least of which is that the ends of the polyene "box" are not infinitely high potential walls. In a somewhat better model the π electrons would travel in a finite-depth potential well. State two things that would change from the infinite depth to the finite depth model.

Really large box with a particle.

A gas molecule rattling around in a bottle can be described as a particle in a 3-dimensional box. Consider ethylene gas in a cubic "bottle" 1 dm on a side.

7. What is the particle-in-a-box "zero point energy" of one of these ethylene molecules, in kJ/mol? Is this energy of chemical significance?

8. According to the kinetic theory of gases, the average kinetic energy of an ethylene molecule in any one direction is $\frac{1}{2}k_B T$. What is the approximate value of $\frac{1}{2}k_B T$ of a gas molecule in this box and with this kinetic energy at 298 K?

9. Suppose you can measure the average kinetic energy in a direction within 1 ppm. Estimate the number of $\frac{1}{2}k_B T$ within 1 ppm of $\frac{1}{2}k_B T$ at 298 K (this is called a "density

of states"). Do you have any hope of determining the exact value of n_x for a particular molecule?

Quantum mechanics of vibrating NO.

The diatomic nitric oxide (NO) is an unusual and important molecule. It has an odd number of electrons, which is a rarity for stable molecule. It acts as a signaling molecule in the body, helping to regulate blood pressure, is a primary pollutant from combustion, and is a key constituent of smog. It exists in several isotopic forms, but the most common, $^{14}\text{N} = ^{16}\text{O}$, has a bond length of 1.15077 Å and vibrational force constant of 1594.8 N/m.

10. Compute the **reduced mass** μ (amu), **harmonic vibrational frequency** (cm^{-1}), and **zero point vibrational energy** (kJ/mol) of $^{14}\text{N} = ^{16}\text{O}$. Recall $1/\mu = 1/M_{\text{N}} + 1/M_{\text{O}}$.

11. Calculate the classical minimum and maximum values of the $^{14}\text{N} = ^{16}\text{O}$ bond length for a molecule in the ground vibrational state. Hint: Calculate the classical limits on x , the value of x at which the kinetic energy is 0 and thus the total energy equals the potential energy.

12. The normalized ground vibrational wavefunction of $\text{N}=\text{O}$ can be written

$$\Psi_{\text{vib}}(x) = \left(\frac{1}{\alpha \sqrt{\pi}} \right)^{1/2} e^{-x^2/2\alpha^2}, \quad x = R - R_{\text{eq}}, \quad \alpha = \left(\frac{\hbar^2}{\mu k} \right)^{1/4}$$

where $x = R - R_{\text{eq}}$. Plot the normalized probability of x vs x . Indicate on your plot the classical limits on x . Do the probabilities vanish beyond those classical limits? What do we call this behavior?

13. The *general selection rule* for whether light can excite a vibration of a molecule is that the dipole moment of the molecule must change as it vibrates. Based on this criterion, do

you expect NO to exhibit an absorption vibrational spectrum?

14. The *specific selection rule* for whether light can excite a vibration of a molecule is that $\Delta v = \pm 1$. At ambient temperature, what initial and final vibrational states would contribute most significantly to an NO vibrational spectrum? Justify your answer. (*Hint:* What does the Boltzmann distribution say about the probability to be in each ν state?)

15. Based on your answers to questions 13 and 14, what do you expect the vibrational spectrum of an $^{14}\text{N}^{16}\text{O}$ molecule to look like? If it has a spectrum, in what region of the spectrum does it absorb (e.g., ultraviolet, x-ray, ...)?

Two-dimensional harmonic oscillator

Imagine an H atom embedded in a two-dimensional sheet of MoS₂. The H atom vibrates like a two-dimensional harmonic oscillator with mass 1 amu and force constants k_x and k_y in the two directions.

16. Write down the Schrödinger equation for the vibrating H atom. Remember to include any boundary conditions on the solutions.

17. The Schrödinger equation is *separable*, so the wavefunctions are products of one-dimensional wavefunctions and the eigenenergies are sums of corresponding one-dimensional energies. Derive an expression for the H atom vibrational energy states, assuming $k_x = k_y/4 = k$.

18. A spectroscopic experiment reveals that the spacing between the first and second energy levels is 0.05 eV. What is k , in N/m?

19. What are the *energies* and *degeneracies* of the four lowest-energy vibrational levels of the H atom?