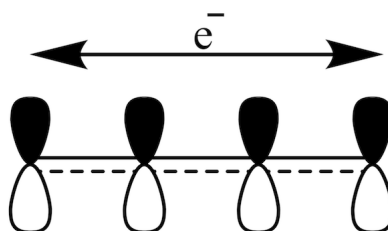


# Chem 30324, Spring 2018, Homework 5

Due February 27, 2018

## Real-world particle-in-a-box. ¶

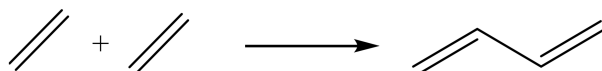
A one-dimensional particle-in-a-box is a simple but plausible model for the  $\pi$  electrons of a conjugated alkene, like butadiene ( $\text{C}_4\text{H}_6$ , shown here). Suppose all the C–C bonds in a polyene are 1.4 Å long and the polyenes are perfectly linear.



1. Plot out the energies of the  $n = 1 - 6$  particle-in-a-box states for ethylene (2 carbon chain), butadiene (4 carbon chain), hexatriene (6 carbon chain), octatetraene (8 carbon chain), and decapentaene (10 carbon chain). What happens to the spacing between energy levels as the molecule gets longer? As  $n$  gets larger?
2. 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.
3. Butadiene has 4  $\pi$  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 excite one electron from either of these levels to the empty  $n = 3$  level.

4. We'll learn later that 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  $|\langle \psi_{\text{initial}} | e\hat{x} | \psi_{\text{final}} \rangle|^2$  ( $e$  is the electron charge). 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?

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



As a very simple estimate, you could take the energy of each molecule as the sum of the energies of its  $\pi$  electrons, allowing only two electrons per energy level. Again taking each C—C bond as 1.4 Å long and treating the  $\pi$  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  $\pi$  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 m 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, what is the average kinetic energy of an ethylene molecule at 298 K? What is the approximate value of

$n = \sqrt{n_x^2 + n_y^2 + n_z^2}$  of a gas molecule molecule with this energy at 298 K?

**9. What is the energy difference between the  $n$  and  $n + 1$  levels (in kJ/mol)? Is it possible to determine the exact value of  $n$  for a particular molecule?**

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