"Applicability of the particle-in-the-box (PIB) model to conjugated systems of π-orbitals"

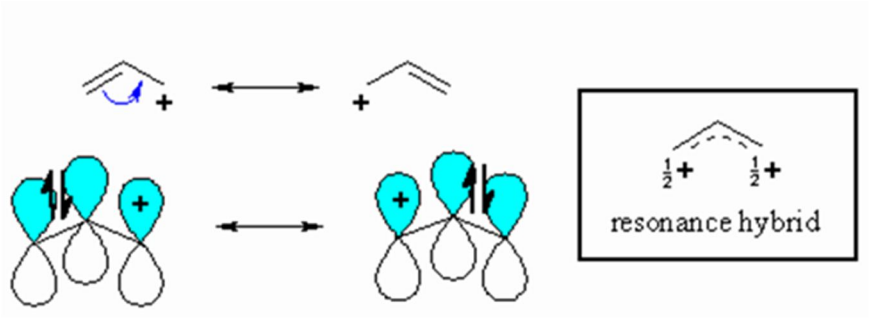
Let's recall the PIB model, where the electron is confined to a 1-dimensional box of length L. The possible states of the electron are described by wavefunctions ($n = 1, 2, 3, \ldots..$).

$$\Psi_n(x) = \sqrt{\frac{2}{L}}\sin(\frac{n\pi}{L}x)$$

with respective energies:

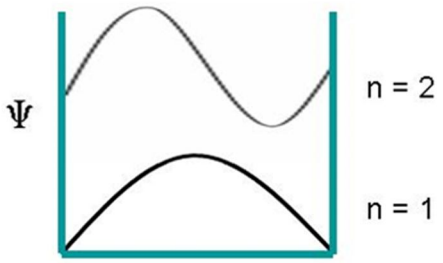
$$E_n = \frac{n^2h^2}{8mL^2}$$

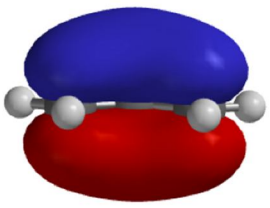
How does this picture apply to conjugated bond systems? Consider the simple allylic carbocation $C_3H_5^+$ below.



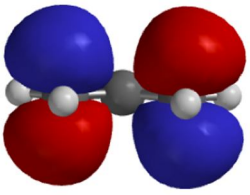
Here, every carbon is sp2-hybridized and the resonance structure means that electrons in π-orbitals are spread out across the entire molecule. In this case, electrons "feel" a potential very much like the PIB potential, low-energy in the "box" defined by the extent of the molecule, but high energy outside this "box".

Pairs of π-orbital electrons fill up these states (a spin-up/spin-down pair for each orbital). For $C_3H_5^+$ there are only two electrons, so only the "n=1" state is occupied (the highest-occupied molecular orbital, HOMO). The "n=2" state is the lowest unoccupied molecular orbital (LUMO).



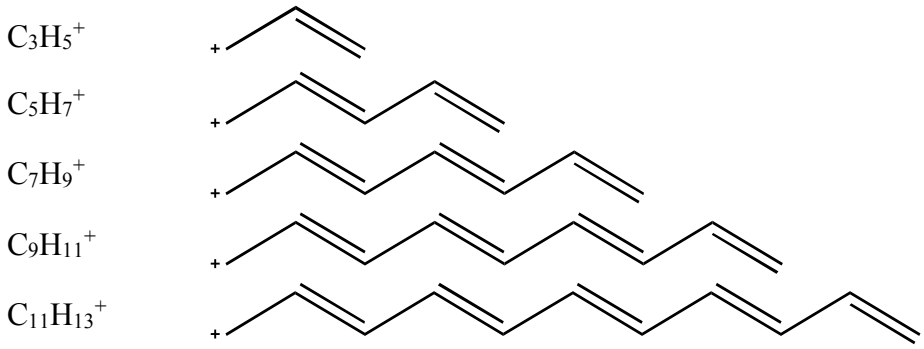


HOMO, *n*=1



LUMO, *n=2*

Consider the following series of allylic carbocations:



For longer allylic chains, there are more electrons in π-orbitals, and there are more occupied "PIB states" for higher values of n.

Another prediction of the PIB model is how the energy gap ΔE between the HOMO and LUMO levels varies with the "box" length L. Notice that when there are k carbons in the molecule, the quantum number of the HOMO is always $n = (k\text{-}1)/2$. So, the HOMO/LUMO gap for $C_kH_{k+2}^+$ should be

$$\Delta E = \frac{h^2}{8mL^2}\left[(n+1)^2 - n^2\right] = \frac{h^2}{8mL^2}(2n+1) = \frac{h^2}{8mL^2}k$$

If we also measure the "box" length L in terms of the number of carbon atoms, then $L = k$, and the energy gap should be inversely proportional to the number of carbons,

$$\Delta E \propto \frac{1}{k}$$

Let's explore how well PIB applies to the above systems (at least according to calculations that we can perform in Spartan).

For each of these molecules, do the following:

1. **Build the molecule, and optimize its geometry**
    a. Setup > Calculations….
    b. Calculate Equilibrium Geometry for the Ground State, using Hartree-Fock with a modest basis set (6-31G*). Set total charge to "Cation" with 0 unpaired electrons, and Print Orbitals/Energies.
    c. The calculation should take a minute or two, but keep mind the larger molecules will take longer to calculate.

2. **Inspect the calculated orbitals.**
    a. Click on the Orbital Energies icon. Click on an energy level in the spectrum on the left, and Spartan will display the molecular orbital corresponding to it.
    b. You should be able to use the up and down arrows to move up and down the spectrum. Visual inspection of the shape of the orbitals will allow you to easily identify the "n=1" PIB state, for instance. Ignore the lowest-energy states, which will consist of electrons in σ-bonds.

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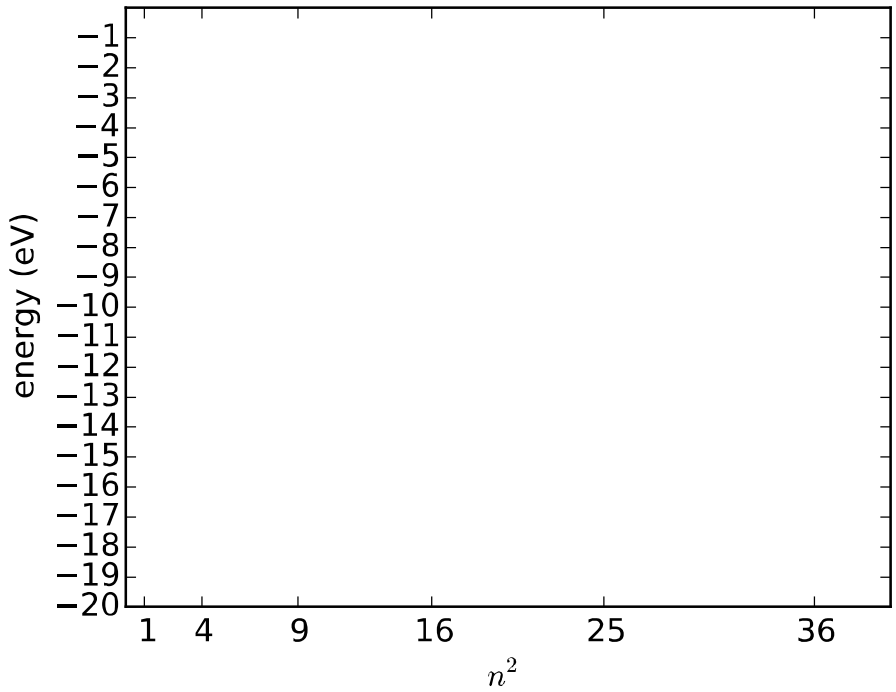
Enter the energies (in units eV) of all the PIB-like orbitals, up to the LUMO, in the Data **Table.1** below.

Data Table.1

"n"	$C_3H_5^+$	$C_5H_7^+$	$C_7H_9^+$	$C_9H_{11}^+$	$C_{11}H_{13}^+$
6					LUMO
5				LUMO	HOMO
4			LUMO	HOMO	
3		LUMO	HOMO		
2	LUMO	HOMO			
1	HOMO				

Part A.

1. The PIB model predicts that the energy E_n is proportion to n^2. Pick one of the columns in Data Table above (for $C_5H_7^+$ or larger), and plot the data points on the axes below to see if this is true.



2. You won't get a perfectly straight line, but something like it. Can you think of any reason why PIB might not do a great job for certain energy levels?
   Answer:

Part B.

Compute the HOMO/LUMO energy gaps for each k using the number you calculated in the Data Table, entering your result in the table below. Then plot the results on the axes given to see if ΔE is proportional to $1/k$.

k	$(E_{LUMO} - E_{HOMO})$ for $C_kH_{k+2}^+$ (eV)
3	
5	
7	
9	
11