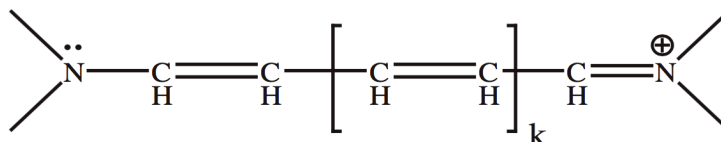


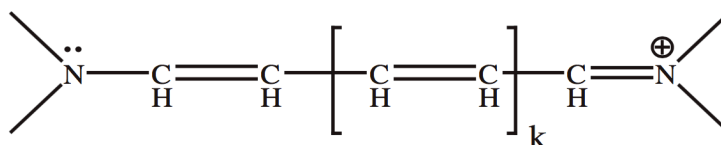
I. Considering the molecule given below



where $k = 0, 1, 2, 3, 4, \dots$ and a total of $m = 2k + 5$ atoms in the conjugated chain including the nitrogen atoms, whereas the hydrogen atoms are excluded, because they are not part of the conjugated network of bonds. Treat this molecular system as linear molecule. Answer the following questions by the application of quantum mechanical particle in a box (PIB) model.

1. How many electron pairs participate in the π -system of the molecule (when $k=0$)?
2. Is the number of π -electrons equals to the quantum number of the ground state HOMO? Provide your rationale.
3. Identify n_{HOMO} and HOMO – LUMO gap with increase of k . Show that ΔE is inversely proportional to length (L) of the molecule. Provide a schematic diagram (a graph) for this inverse relation between ΔE and L .
4. Would there be a value of k for which the molecule loses its HOMO-LUMO gap (aka the band gap)? Would that be metallic?
5. Can a metallic state be achieved for larger values of k ? Provide your rationale.
6. Do you see a transition from molecule to a crystal for larger values of k ? How would you justify that?

Explanation: The PIB model is frequently used for rationalizing the electronic spectra of linear chain π -conjugated molecules. In the application of this model, one uses the PIB eigenstates (energy levels) to describe the spacing of the π orbitals of conjugated molecules; for example, one would consider symmetric cyanine molecule (these are also the popular dyes), which is shown below.



where $k = 0, 1, 2, 3, \dots$ and a total of $m = 2k + 5$ atoms in the conjugated chain including the nitrogen atoms, whereas the hydrogen atoms are excluded, because they are not part of the conjugated network of bonds.

Usually in the experiments of UV-Vis spectroscopy, the longest wavelength absorption resulting from a transition from the electronic ground state to the first excited state can be observed.

The wavelength of light absorbed by the molecule as it transitions into the excited state is related to the energy difference ΔE between the excited state and the ground state by Planck's equation

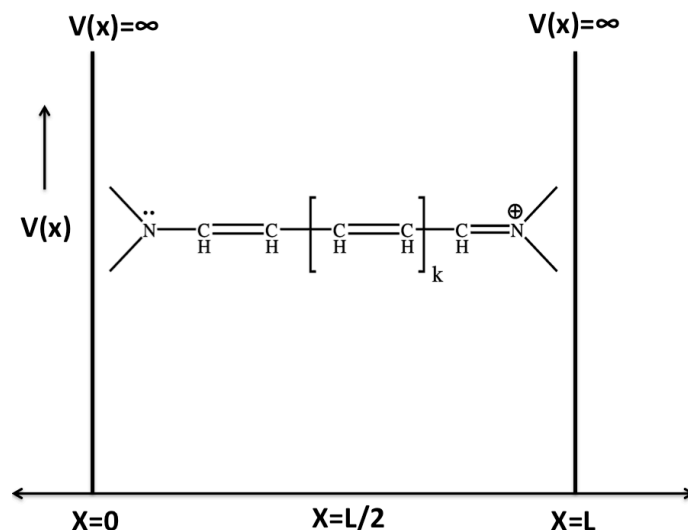
$$E^{\text{photon}} = h\nu = \hbar\omega = hc \frac{1}{\lambda} = hc\tilde{\nu}$$

\hbar is equal to $h/(2\pi)$

The first electronic excited state is assigned to a transition from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO).

Important: Most of the times, for π -conjugated molecules, the HOMO is a π orbital, and the LUMO is also a π orbital and often labeled π^* (antibonding) to indicate that it is not occupied in the ground state. For π -conjugated chains, the π -type orbitals are the ones representing the frontier molecular orbitals (FMO), the HOMO, LUMO, and the few levels above and below these MOs.

The energies of the π orbitals are then identified with the energy levels of the PIB, the linear extension of the conjugated π chain corresponds to the x -axis of the PIB model (the box length L), and the box boundaries roughly correspond to the terminal groups of the molecule (see the given structure of the molecule).

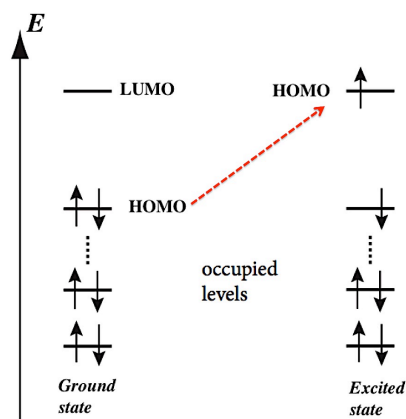


The number of electron pairs participates in the π system is equal to the quantum number of the ground state HOMO. It is important to know that for the cyanine molecule given in the question, there are $n_{\text{HOMO}} = k + 3$ electron pairs. This values of n_{HOMO} increases as the box length increases with k .

The excitation energy is then approximated by the equation given below: Note that $n_{\text{LUMO}} = n_{\text{HOMO}} + 1$

$$\Delta E = E_{n_{\text{LUMO}}} - E_{n_{\text{HOMO}}}$$

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



Schematic energy level diagram indicating ground and first excited state

Assume that all C–C bond lengths are equal roughly equal to 144 pm.

Assume that the length of –CH=CH– unit is 250 pm (*a*). And, assume a length of 570 pm (*b*) for =CH– with NR₂ end members added together. That would lead to a generic expression as

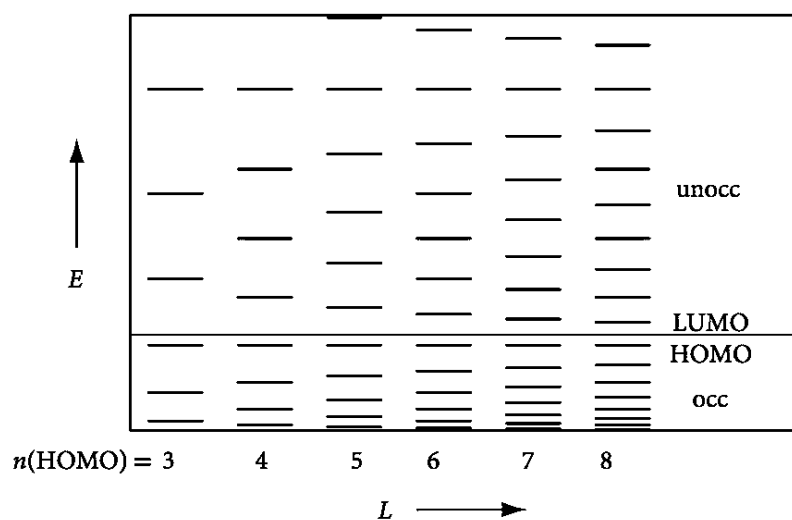
$$L = a(k+1)+b \text{ pm}$$

From the expression above, one can see that ΔE is inversely proportional to length (*L*) of the molecule. In other words wavelength (λ) increases with the molecular length. In turn, in other words, the HOMO-LUMO gap decreases with increase of the length of the molecule.

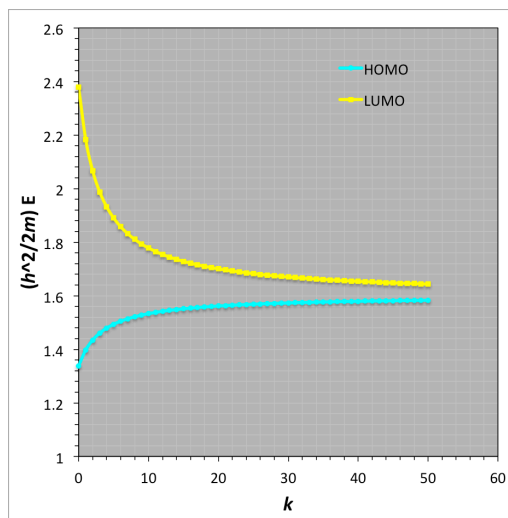
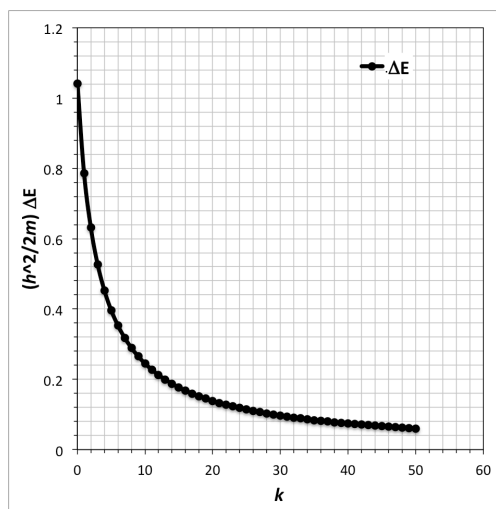
For example: See the Table below:

<i>k</i>	<i>n</i> _{HOMO}	$\approx \lambda$
0	3	300
1	4	400
2	5	500
3	6	600

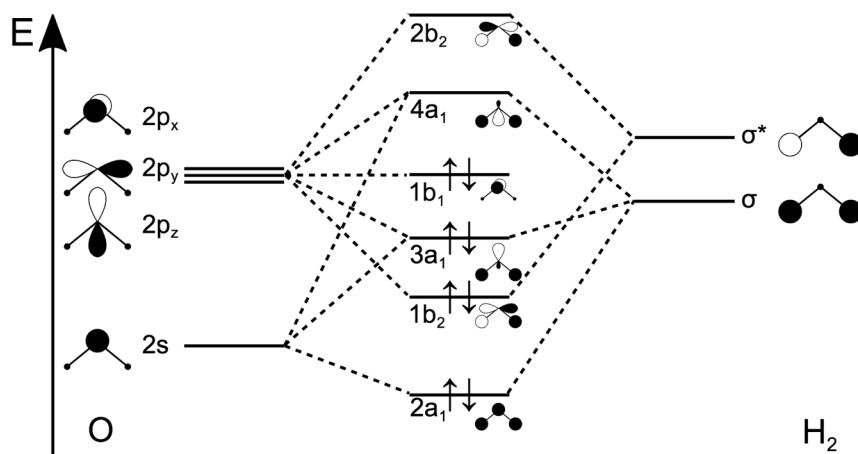
A schematic sketch of how the HOMO-LUMO gap decreases with increase of *L* or the value of *k*:



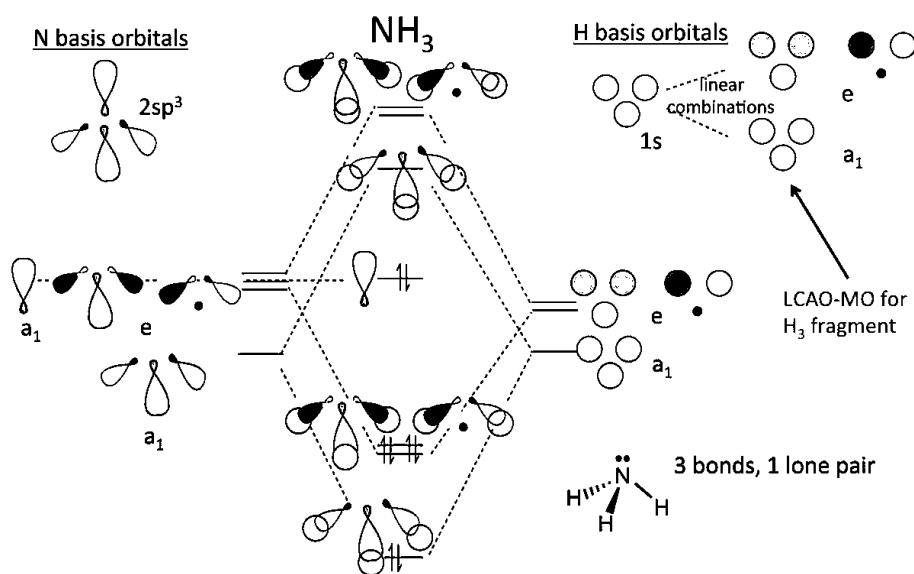
One can make a neat table or a graph for the system given above. The energy levels of HOMO and LUMO and the difference are (ΔE) shown here in two graphs. Note that the energy is scaled to 10^5 in the units of $(\hbar^2/2m)$.



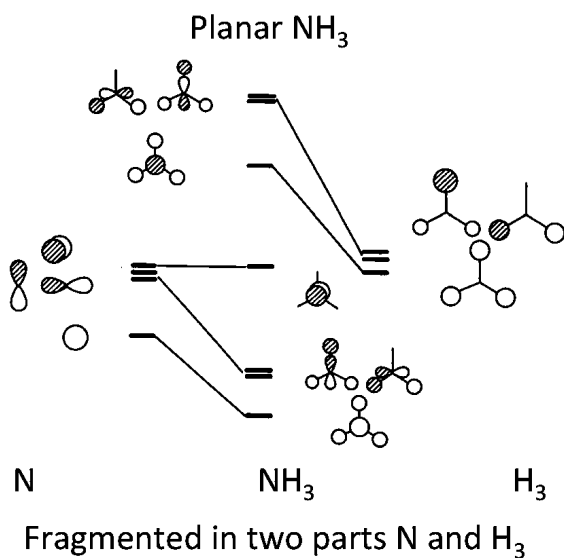
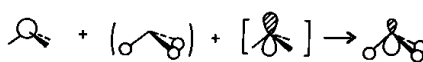
II. Construct molecular orbital energy level diagram for H_2O in its ground state using fragment molecular orbitals.



III. 3. Construct molecular orbital energy level diagrams for NH_3 when it is trigonal planar and pyramidal molecular arrangements. Notice the differences in the HOMO and LUMO levels in each case.



Mixing of the orbitals
Example:



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