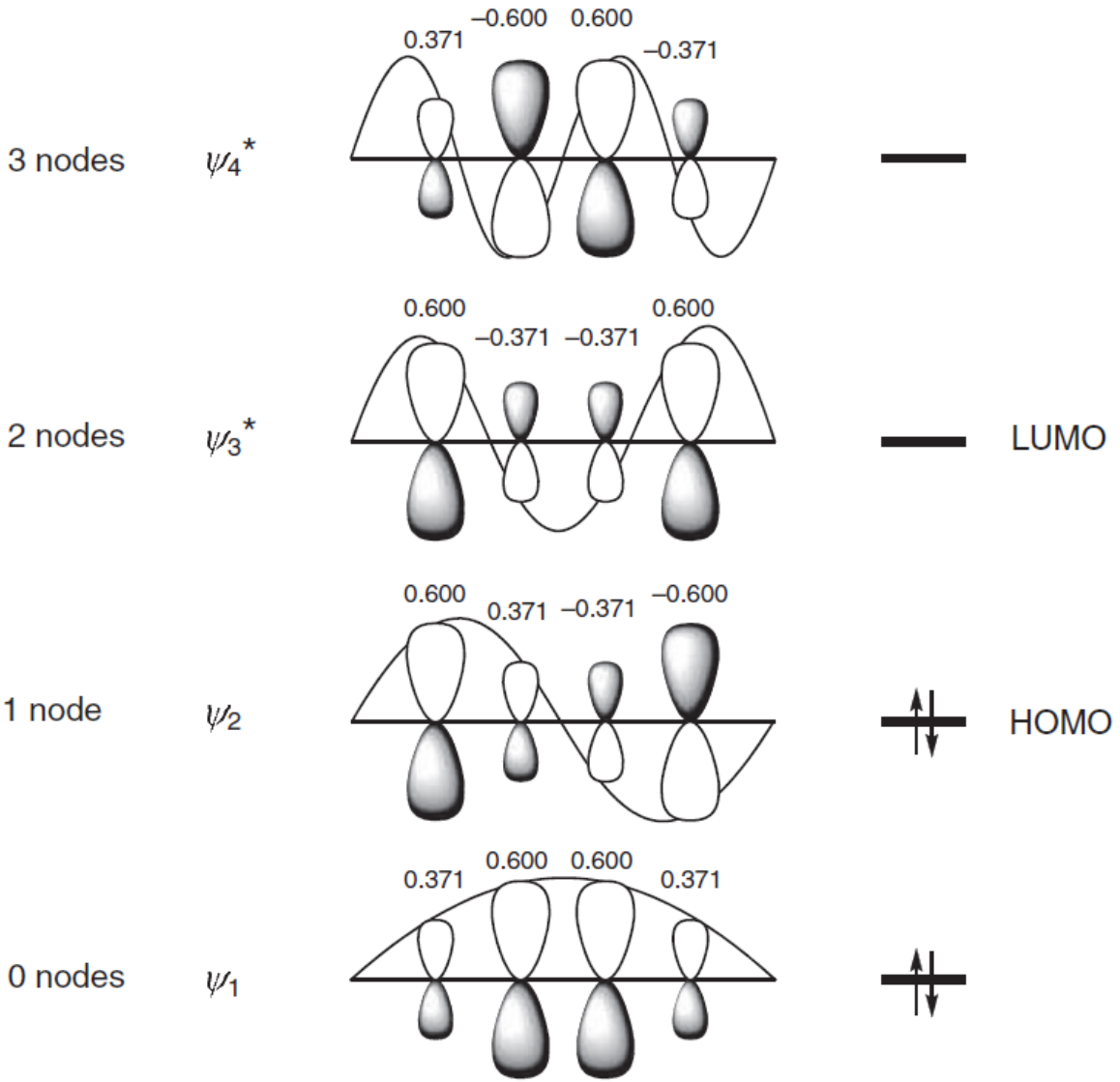
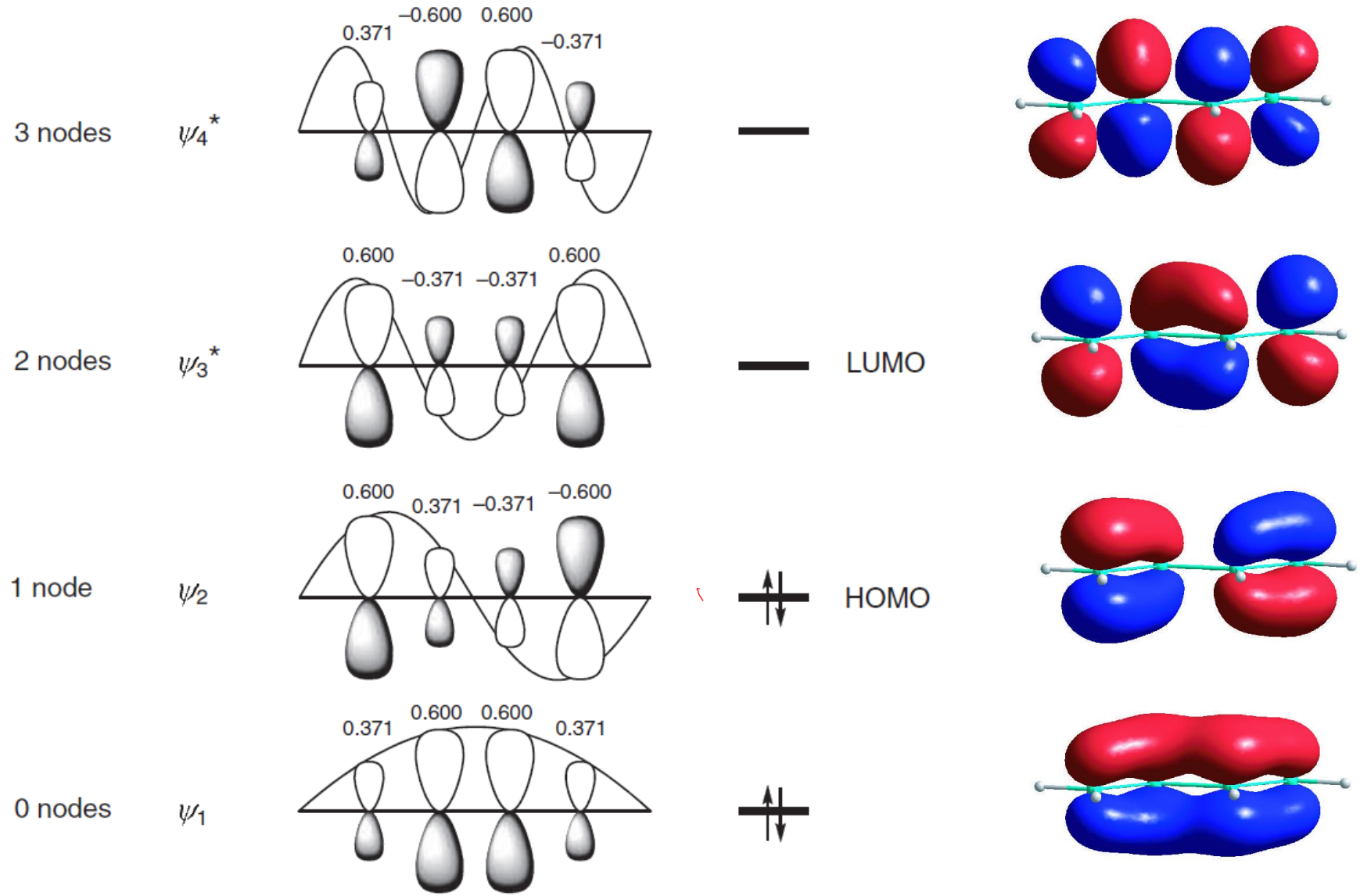
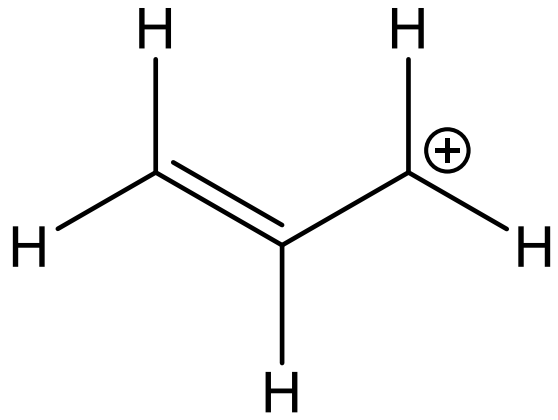
π-Molecular Orbitals of Butadiene

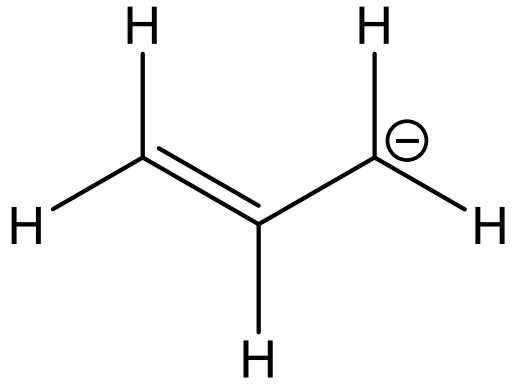


- ✓ *The molecular orbitals (ψ) are one-electron wave functions (electron in a box)*
- ✓ *The coefficients (C) are the weights of the contributions of the atomic orbitals to the molecular orbitals*
- ✓ *4 MOs spread all over 4 carbon atoms*
- ✓ *Bonding electrons reside on ψ_1 and ψ_2*

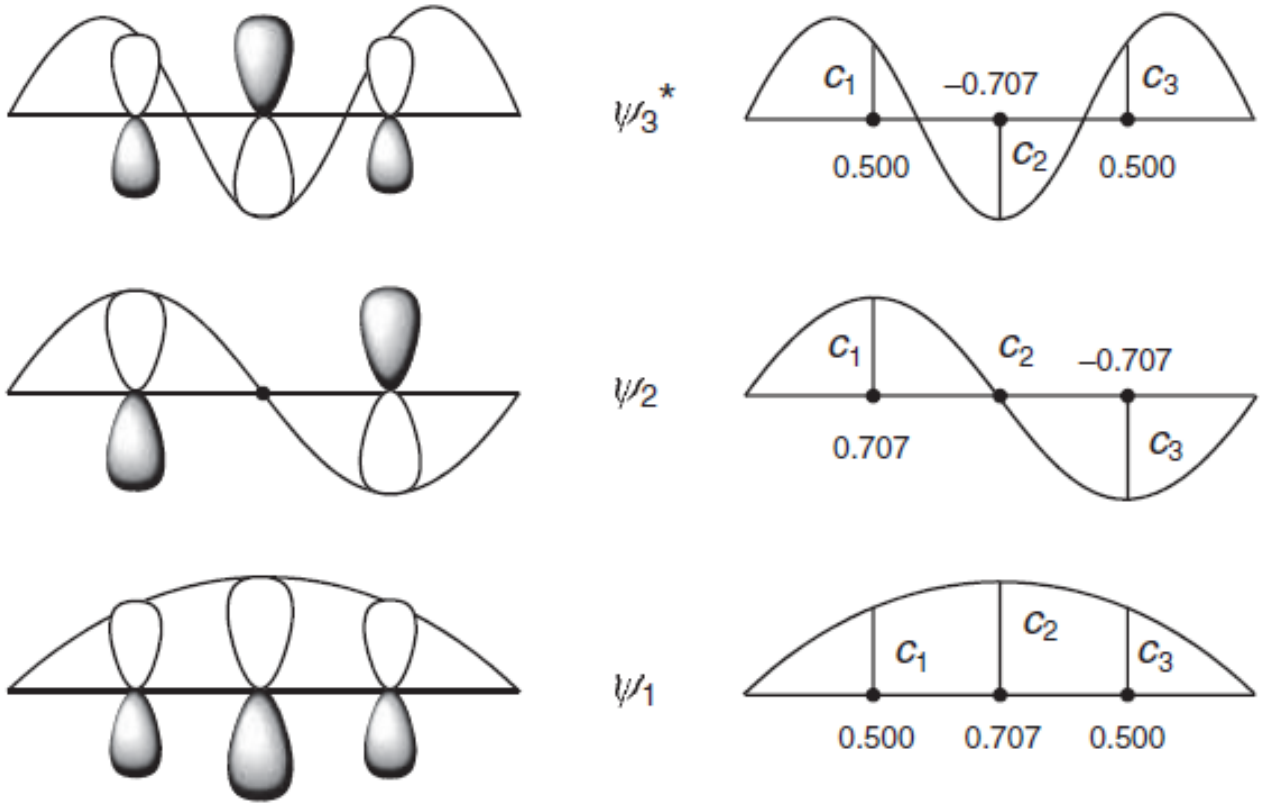

3 nodes
ψ_4^*
0.371
−0.600
0.600
−0.371
2 nodes
ψ_3^*
0.600
−0.371
−0.371
0.600
LUMO
1 node
ψ_2
0.600
0.371
−0.371
−0.600
HOMO
0 nodes
ψ_1
0.371
0.600
0.600
0.371

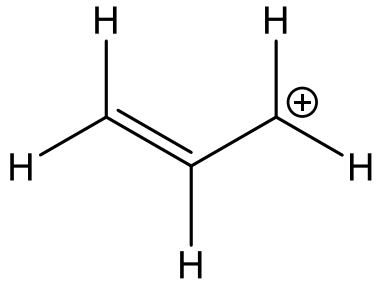
π-Molecular orbitals of allyl cation/anion

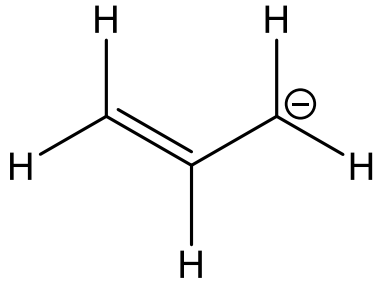


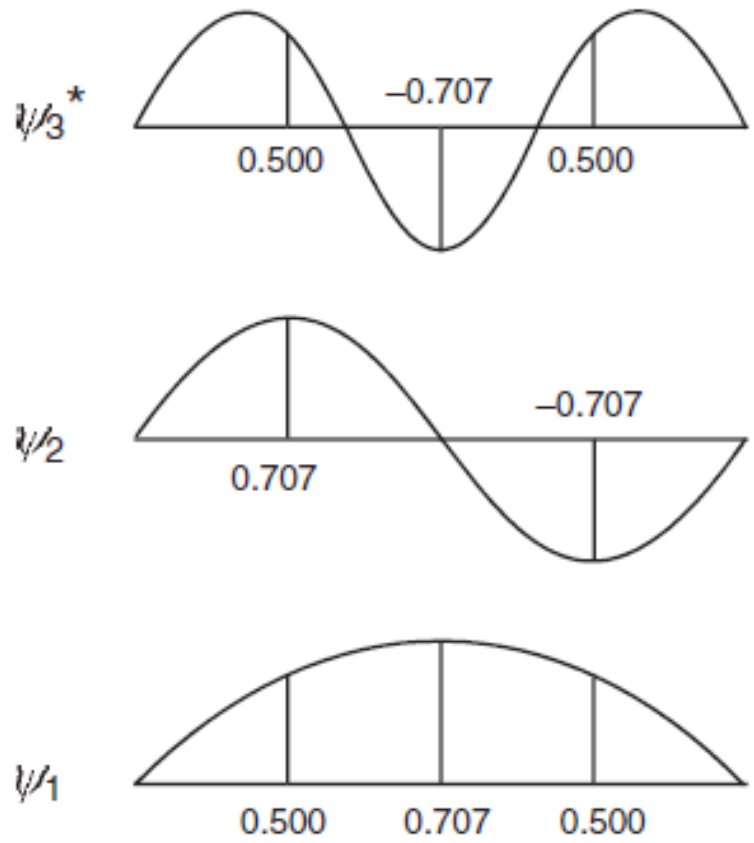


- ✓ *Both the allyl cation and anion are planar and symmetrical*
- ✓ *Two end carbons are same (however the above representations do not suggest that)*

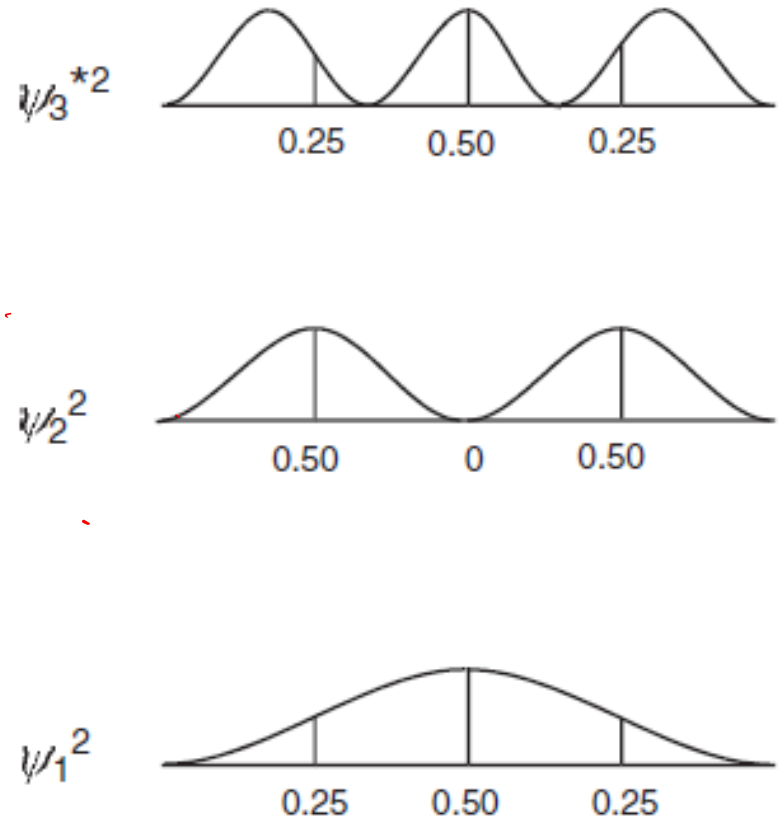

ψ_3^*
c_1
−0.707
c_3
0.500
c_2
0.500
ψ_2
c_1
c_2
−0.707
0.707
c_3
ψ_1
c_1
c_2
c_3
0.500
0.707
0.500


H
H
H
H
H

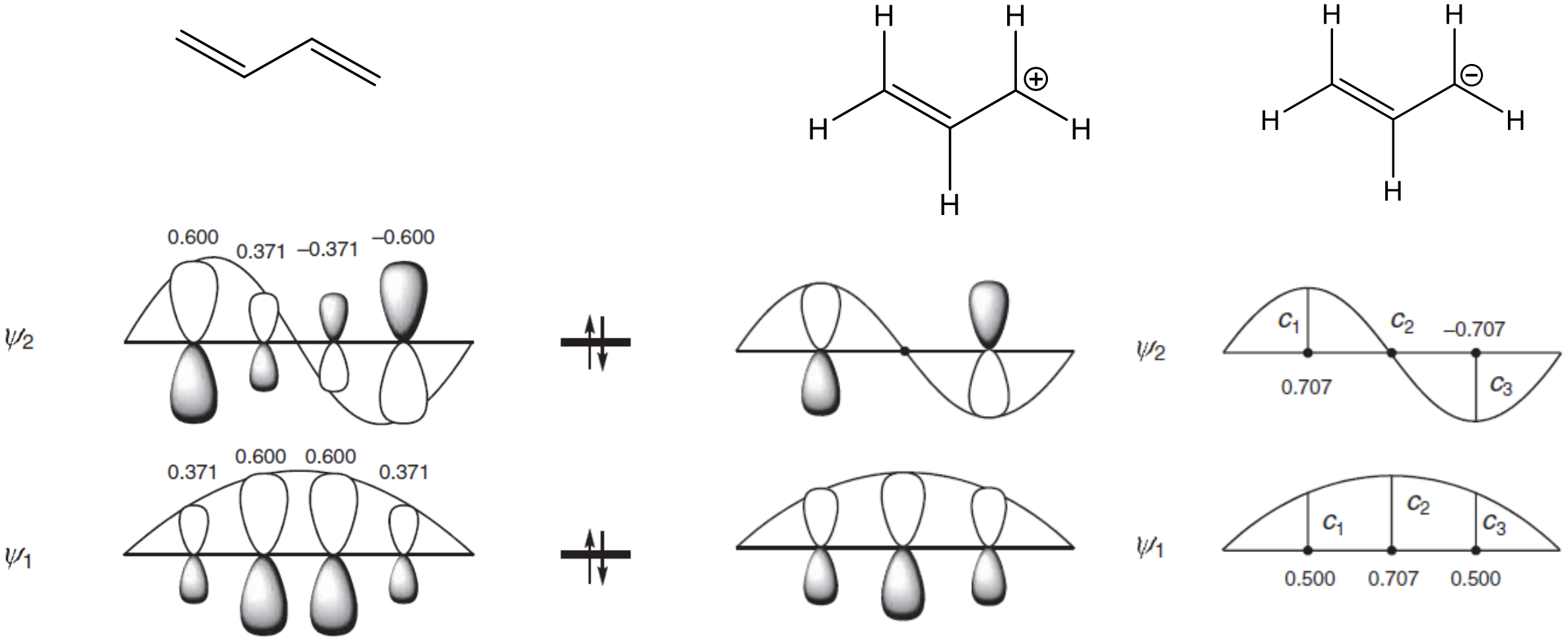

H
H
H
H
H



(a) Wave functions



(b) Electron populations for one electron

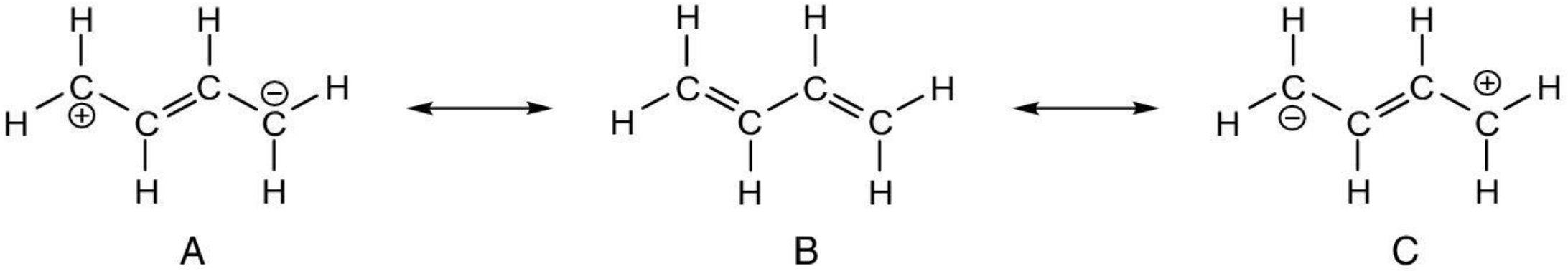


MO approach can explain: a) partial double bond character in the C2-C3 bond in butadiene

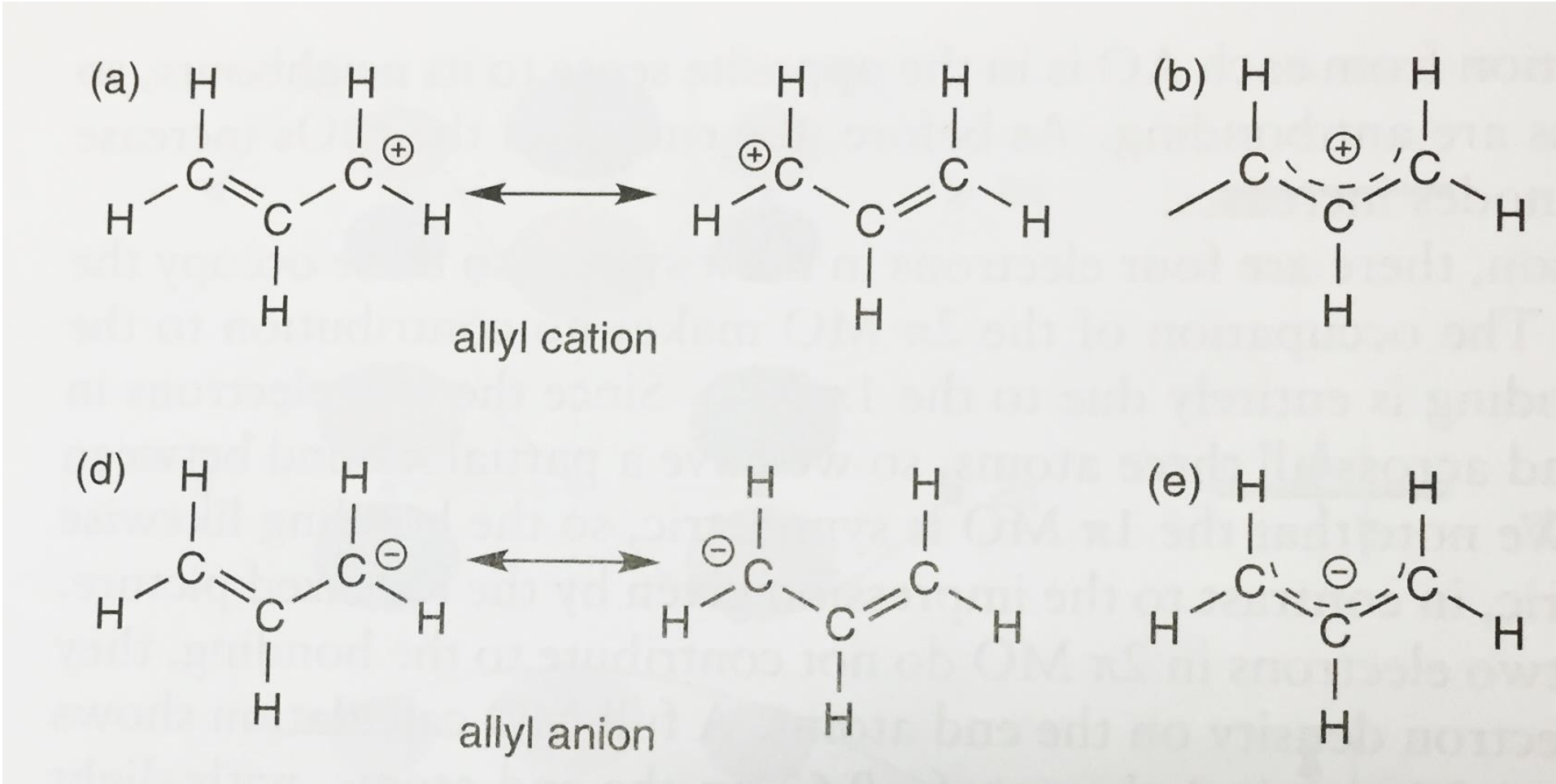
b) the equivalence of C1 and C3 carbons in allyl cation and anion

How do we explain these observations from hybridization approach (localized bonding)?

Resonance Structures

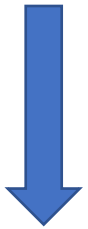


- *Resonance*: More than one possible Lewis structures for a molecule
- **A, B** and **C** are resonance structures; *they don't exist in reality*
- Butadiene is a combination of all the resonating structures-Resonance Hybrid


(a)
(b)
allyl cation
(d)
(e)
allyl anion

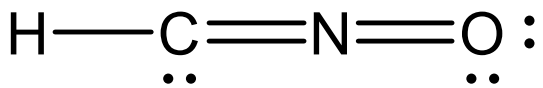
Formal Charge

Formal charge: (Number of valence electrons in the neutral atom) – (number of valence electrons around the atom in molecule)



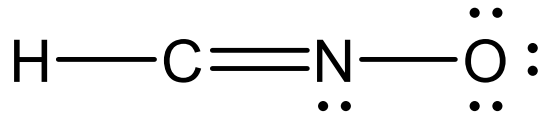
(Number of valence electrons in the neutral atom) – ½ (number of electrons in covalent bonds) - (number of electrons in lone pairs)

1. Calculate the formal charges on each atom in each structure.
2. Which are resonance structures?

A) 

B) 

C) 

D) 

Q. Two resonance forms can be written for each of the following structures:

(i) $(CH_3)_2BN(CH_3)_2$ (ii) $(CH_3)_2BOCH_3$ (iii) $(CH_3)_2BF$

(A) Write the resonance structures

(B) Which forms in each pair of resonance forms is more important?

A few key points regarding resonance structures

- ✓ Only electrons move. Atoms never move
- ✓ Only π-electrons (electrons in π-bonds) and lone-pair electrons can move; never move σ-electrons

- ✓ Resonance forms with filled octets are more stable
- ✓ Negative charge should reside on more electronegative atom, positive charge on electropositive atom