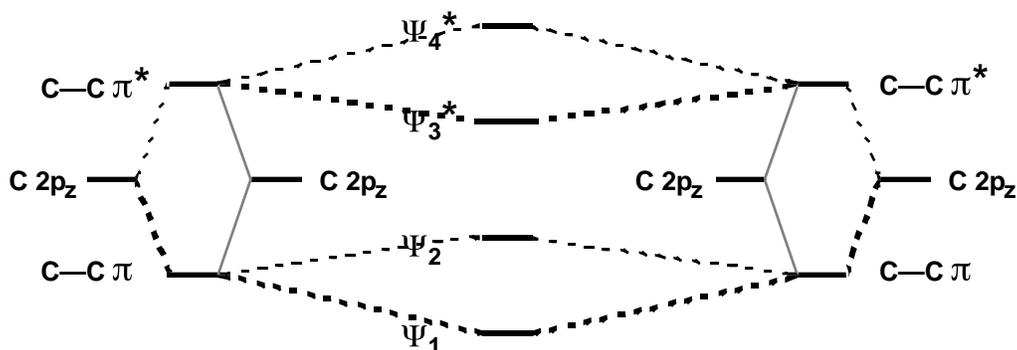


### Text Related to Segment 8.01 ©2002 Claude E. Wintner

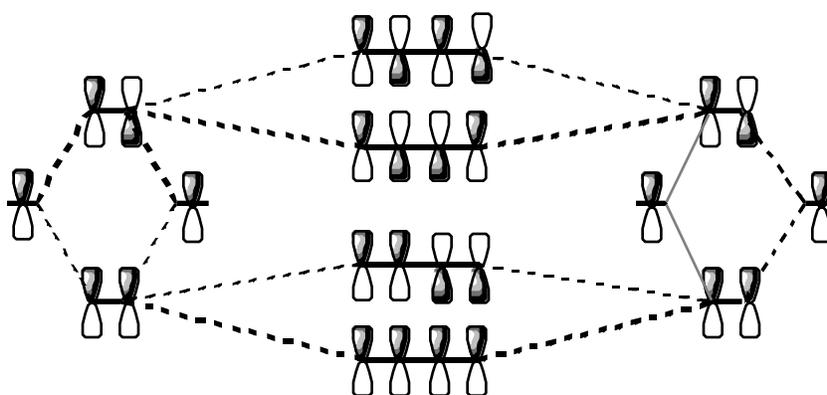
The ideas developed up to this point, concerning stereochemistry on the one hand and delocalization on the other, can be instructively exemplified and extended in a treatment of polyene systems. Starting with 1,3-butadiene, for the moment we consider only constitution, leaving stereochemistry aside. As the molecule is written in a standard Lewis structure, there is a framework of three  $\sigma$  bonds that form the underlying  $C_1-C_2-C_3-C_4$  linkages, and in addition a pair of  $\pi$  bonds joining  $C_1$  to  $C_2$  and  $C_3$  to  $C_4$ . Each  $\pi$  bond comes about as a consequence of the delocalization of two electrons in a  $\pi$  molecular orbital that is the result of a linear combination of two atomic (p) orbitals. In the Lewis structure these two  $\pi$  bonds are pictured as themselves localized and without further mutual interaction:



However, we now know enough to realize that we should look for further interaction to take place, and that we will err in characterizing the total system — by predicting too high an energy — if we do not take into account the full delocalization possible:



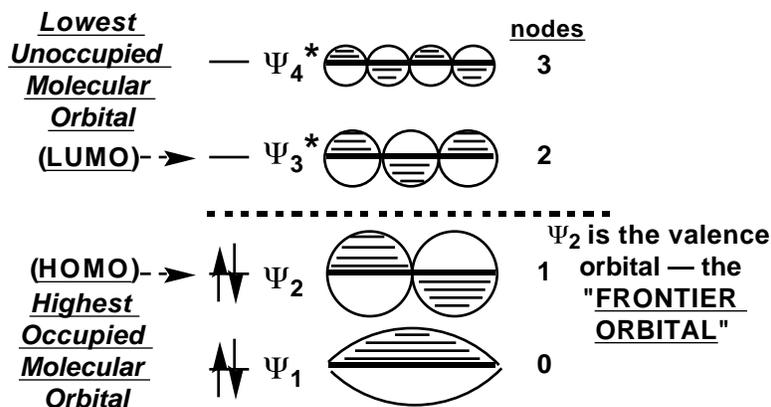
From the two molecular orbitals we have constructed two new, more fully delocalized, molecular orbitals,  $\psi_1$  and  $\psi_2$ , and from the two  $\psi^*$  orbitals we have obtained  $\psi_3^*$  and  $\psi_4^*$ . How can we visualize these new, more fully delocalized molecular orbitals of 1,3-butadiene? A rendering of the orbital mixing, construed as a set of linear combinations of the  $\psi$  and  $\psi^*$  orbitals (which are themselves, as we already have emphasized, linear combinations of the original p atomic orbitals) gives a pictorial answer to the question:



$\psi_1$  is constructed by bringing together the two  $\psi$  orbitals in a bonding sense. In  $\psi_2$  the interaction between the two  $\psi$  orbitals is antibonding.  $\psi_3^*$  brings together the two  $\psi^*$  orbitals in bonding fashion;  $\psi_4^*$  does this in the antibonding mode. It is clear that  $\psi_1$  is a fully bonding orbital. However, while  $\psi_2$  has one antibonding interaction, it nevertheless maintains *overall* bonding character (bonding, antibonding, bonding). On the other hand,  $\psi_3^*$  is antibonding overall (antibonding, bonding, antibonding), while  $\psi_4^*$  is only antibonding in its interactions. Note that, as always, the number of orbitals is conserved throughout the mixing process. We started with four localized p atomic orbitals, and we have ended with four highly delocalized ( $\psi$ ) molecular orbitals, by way of four ( $\psi^*$ ) molecular orbitals.

As the number of nodes in the orbitals increases, the orbitals increase in energy, and vice versa. (Think, once again, of the frequency of a vibrating string; this

is also a connection in which physicists invoke the so-called "particle in a box" model.) Indeed, we can simplify the pictures, to emphasize these nodal properties:

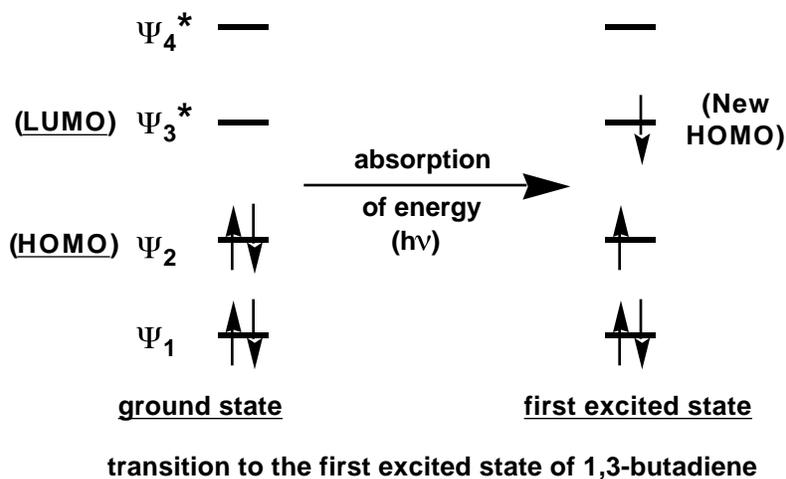


**delocalized  $\pi/\Psi$  molecular orbitals of 1,3-butadiene**

Finally, we have four electrons to distribute in these orbitals, and we place them in  $\Psi_1$  and  $\Psi_2$ , both of which are *bonding* molecular orbitals. A more quantitative analysis suggests that in terms of energy the real molecule 1,3-butadiene achieves an advantage of some 15 kcal/mole compared to a model of the same molecule that is localized in the sense of neglecting interaction between the two bonds.  $\Psi_2$  is higher in energy than the two  $\Psi_1$  orbitals, but  $\Psi_1$  is more than correspondingly lower.

It is extremely important to grasp that  $\Psi_2$  is the critical orbital in (the ground state of) 1,3-butadiene. To draw on general chemical experience, it should be the valence electrons of a system that are most determinative of its properties.  $\Psi_2$  as the *highest occupied molecular orbital*, or HOMO, is, in fact, the valence orbital, the so-called "*frontier orbital*" of the ground state. In this connection, we immediately should stress once again the existence of excited states. For example, to reach its first excited state, 1,3-butadiene need only absorb energy in the form of electromagnetic radiation of the proper frequency (in this case, in the ultraviolet region

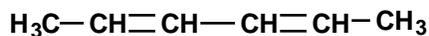
of the spectrum) to promote an electron from  $\psi_2$  to  $\psi_3^*$ , the *lowest unoccupied molecular orbital*, or LUMO. This transition is observed as an absorption band in the ultraviolet spectrum of 1,3-butadiene, and its existence is an important piece of evidence in support of the model we just have outlined.



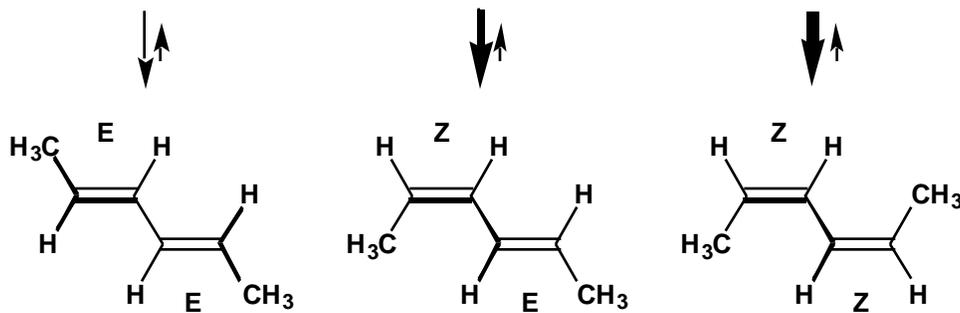
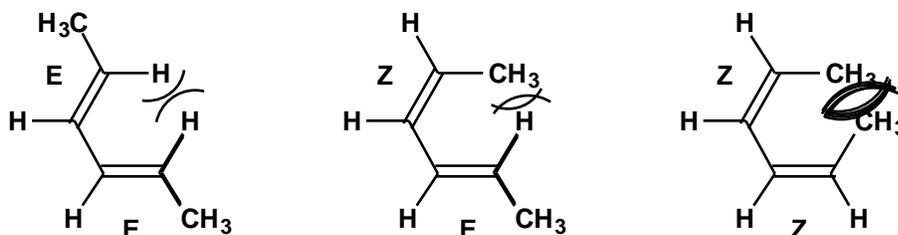
Must we discard the Lewis structure for ground state 1,3-butadiene as a useful model? In fact, *not at all*; and to see that this is so, let us now consider conformational changes in the ground state molecule. The following figure depicts two planar conformations of 1,3-butadiene (termed *s-trans* and *s-cis*, to distinguish that it is orientation about the *single* bond of the Lewis structure which is being considered), as well as the intermediate  $90^\circ$  case. The Lewis structure implies free rotation about the  $C_2-C_3$  bond, but no rotation about the  $C_1-C_2$  or  $C_3-C_4$  bonds. On the other hand, the implication of  $\psi_1$ , in order to allow the orbital overlap on which its construction is based, is that there also should not be rotation about the  $C_2-C_3$  bond. To take the extreme case, when the dihedral angle between the two planes defined by the two  $CH_2-CH-$  groupings is  $90^\circ$ , there can be no overlap whatsoever of the  $\psi_1$  type between the  $C_1-C_2$  bond and the  $C_3-C_4$  bond, because then the orbitals are orthogonal as well:



atoms in the *E,E* isomer in its *s-cis* form just miss interaction, for the *E,Z* isomer in the same conformation there is a mandatory clash between a corresponding hydrogen atom and the hydrogen atoms of a methyl group; and for the *Z,Z* isomer in its *s-cis* form the hydrogens of two methyl groups would have to be at the same place at the same time, so that the conformation effectively cannot exist as written.



*s-cis* conformations



*s-trans* conformations

planar conformations of the three configurational isomers having the constitution 2,4-hexadiene