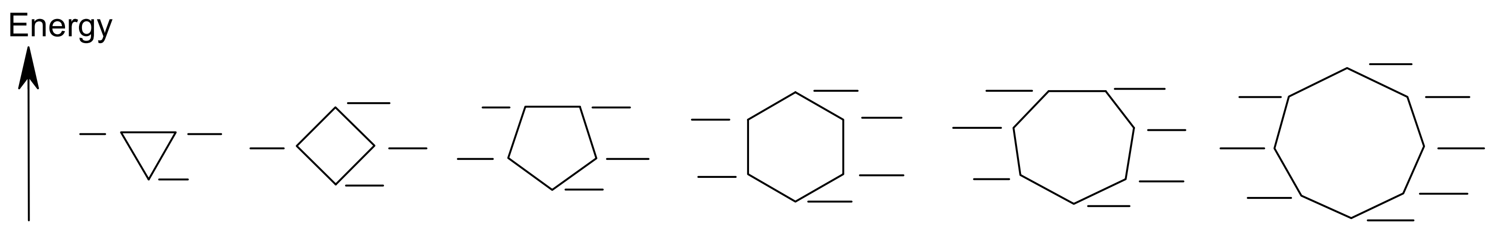
The Origin of the 4n+2 Rule

Huckel calculated the energies of the molecular orbitals of the cyclic hydrocarbons and got the patterns below. Later, another scientist noticed that, if you placed drawings of the rings oriented with their points down, the patterns and relative energies of the orbitals matched precisely the pattern and relative positions of the vertices. (The reason this works is that the pattern of the orbitals depends on the molecule's symmetry.) The original energies of the p-orbitals with no bonding is represented by a line though the center of gravity of the rings. Please add the p-orbital energy to this drawing by taking a ruler and drawing a line across the page that goes through the middle vertices of the 4- and 8-membered rings.



Take a moment to look at the even-carbon rings. How many π electrons are there in these molecules? Hint: each carbon contributes one p orbital with one electron. Don't forget to follow Hund's rule when you have orbitals of equal energy. Now - which molecules have all of their electrons in bonding orbitals, i.e. those with lower energy than the original p orbitals? And which of the molecules have all their electrons paired (molecules with unpaired electrons are very reactive)?

Obviously the rings with odd numbers of carbons would also have odd numbers of electrons, and would be radicals if they were neutral. Look at those rings and think - how many electrons could be put in their orbitals and still have all the electrons in bonding molecular orbitals? Let's look at the five-membered ring as an example. There are three MO's with energies lower than the line you drew to represent the energies of the p-orbitals. This the five-membered ring could take 6 electrons and put all of them in bonding orbitals. The anion formed is called cyclopentadienide, and it is very common, forming stable salts (complexes) with metals like iron! It is in fact very stable for a carbanion.

So where does the 4n+2 rule come from? Look at the number of electrons in the neutral molecules and ions. Those which have 2, 6, and 10 electrons have all the electrons paired and in bonding orbitals and are thus stable molecules; 2, 6, and 10 can be generated from the formula *4n+2* where *n* is an integer. Those which have 4 and 8 electrons have two electrons unpaired and in non-bonding orbitals (same energy as the p-orbitals) and thus have much less bonding (two electrons are not bonding) and are very reactive; 4 and 8 can be generated by the formula *4n* where *n* is an integer.

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