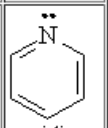
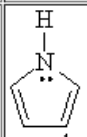
Heteroatom parameters in Hückel Theory

While Hückel theory is basically obsolete as tool for use in any kind of quantitative analysis of experimental data, it is still useful to have a qualitative tool that is simple to apply and simple to interpret – it also doubles as a good "teaching tool" for symmetry and group theory because it allows one to focus on symmetry aspects of molecular orbital theory without getting bogged down any more than necessary on the quantitative physics. Since the range of π-system examples one can examine in the pure hydrocarbons is fairly limited, is useful to be able to extend the qualitative applicability of Hückel theory by including parameters for heteroatoms. The table below shows one set of α and β parameters for various heteroatomic systems. More than one α parameter can apply to a heteroatom, depending on the number of electrons the formally neutral heteroatom donates to the π system. For example, in pyridine the nitrogen has four σ electrons; two electrons come from the two shared C–N σ bonds and two electrons reside in the sp^2 lone-pair. That leaves one electron in the pπ orbital when the N atom has no formal charge. On the other hand, the N atom in pyrrole has three σ electrons; all three from shared C–N and C–H σ bonds. That leaves two electrons in the pπ orbital when the N atom has no formal charge. The α parameter for pyrrole is at a lower energy (–1.5 in units of $|\beta|$) than the α parameter for pyridine (–0.5) because sharing of π electron density by the nitrogen atom in pyrrole necessitates the build-up of *positive* charge on the N atom. Likewise, ethereal oxygen atoms have a deeper α parameter (–2.0) than carbonyl oxygen atoms (–1.0). The SHMO program has a number of similar heteroatom parameters built in, but you do have to specify which "kind" of oxygen or nitrogen you are using.

π-Atom	Number of π-electrons	α	β	Bond	Ref	Example
B	0	1	-0.7	B - C	1, 2	
			-0.8	B - N	1, 2	
·C	1	0	-1	C - C	1, 2	
·N	1	-0.5	-0.8	N - C	1, 2	 pyridine
:N	2	-1.5	-1	N - C	1, 2	 pyrrole
N^+	2	2	-0.7	N - O	1, 2	
·O	1	-1	-0.8	N - C	1, 2	
:O	2	-2	-1	N = O	1, 2	
O^+		-2.5	-1	N - C	1, 2	
·F	2	-3	-0.7	F - C	1, 2	
·Cl	2	-2	-0.4	Cl - C	1, 2	
·Br	2	-1.5	-0.3	Br - C	1, 2	
$\cdot CH_3$	2	-2	-0.7	C - CH_3	a)	
$\cdot C_a$	1	0.1	-0.8	C_a - C ≡	b)	
·C ≡	1	0.1	-3	C ≡ CH_3	b)	
≡ H_3	1	0.5	-3	C ≡ CH_3	b)	