σ, π (sigma, pi)

The terms are symmetry designations, π molecular orbitals being antisymmetric with respect to a defining plane containing at least one atom (e.g. the molecular plane of ethene) and σ molecular orbitals symmetric with respect to the same plane. In practice the terms are used both in this rigorous sense (for orbitals encompassing the entire molecule) and also for localized two-centre orbitals or bonds, and it is necessary to make a clear distinction between the two usages. In the case of two-centre bonds, a π-bond has a nodal plane that includes the internuclear bond axis, whereas a σ-bond has no such nodal plane. (A δ-bond in organometallic or inorganic molecular species has two nodes.) Radicals are classified by analogy into σ- and π-radicals. Such two-centre orbitals may take part in molecular orbitals of σ- or π-symmetry. For example, the methyl group in propene contains three C–H bonds, each of which is of local σ-symmetry (i.e. without a nodal plane including the internuclear axis), but these three 'σ-bonds' can in turn be combined to form a set of group orbitals one of which has π-symmetry with respect to the principal molecular plane and can accordingly interact with the two-centre orbital of π-symmetry (π-bond) of the double-bonded carbon atoms, to form a molecular orbital of π-symmetry. Such an interaction between the CH_3 group and the double bond is an example of what is called hyperconjugation. This cannot rigorously be described as 'σ–π conjugation' since σ and π here refer to different defining planes, and interaction between orbitals of different symmetries (with respect to the same defining plane) is forbidden.

Source:
PAC, 1994, *66*, 1077 *(Glossary of terms used in physical organic chemistry (IUPAC Recommendations 1994))* on page 1163