Requirements of Orbital Phase Continuity Revisited: A FMO Approach

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Keywords: Cyclic Orbital Interaction; Requirements of Orbital Phase Continuity; Delocalization; FMO Theory

Cyclic orbital interaction, in which a series of orbitals interact with each other so as to make a monocyclic system, affords stabilization if the requirements of orbital phase continuity are satisfied.[1] We have demonstrated that the phase-continuous cyclic orbital interaction determines the selectivity, especially the diastereoselectivity in the electrophilic addition of α-substituted ethylenes[2] and Felkin-Anh model for the nucleophilic addition.[3]

Requirements of orbital phase continuity consist of five terms: (i) donating orbitals are out-of-phase; (ii) a donating orbital and an accepting orbital are in-phase; and (iii) accepting orbitals are in-phase (Figure). When the number of corresponding orbitals in the interaction is more than three, two additional requirements should also be satisfied: (iv) interaction among the orbitals is monocyclic, and (v) the series of orbital interactions should be divided into two, a donor part and an acceptor part, and not into four, six or more. Note that the overlap between the orbitals is less than 1; |S| < 1, cyclic orbital interaction with fewer orbitals is often preferred.

These requirements are initially derived from consideration of three-body system. The perturbation term of the third order in the orbital interaction results in stabilization when all the requirements are satisfied.

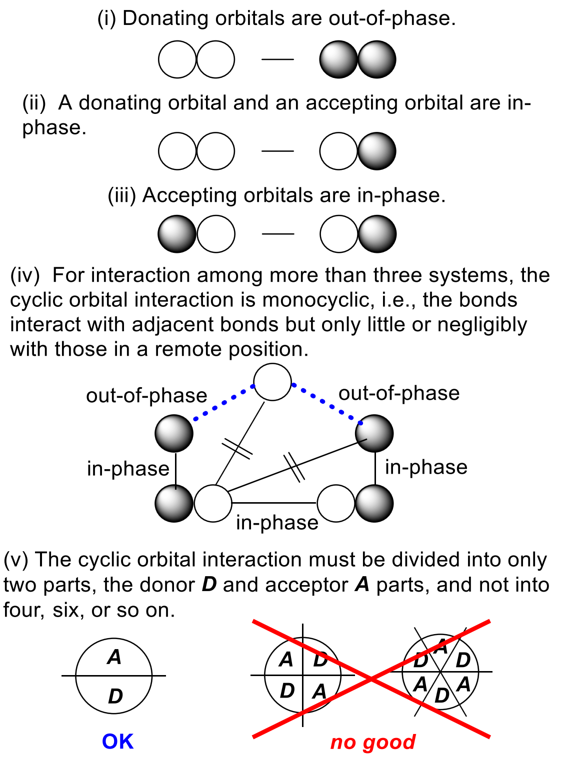

Figure. Requirements of orbital phase continuity

Here I present that these conditions are readily obtained from the FMO theory, and show some further applications.

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