

Is Theoretical Justification given to the Electronic Structure of the Molecule Obtained by the Molecular Orbital Method?

We compare chemical phenomena with electronic structures due to molecular orbital calculation, i.e., electron density of molecules, bond order, population, energy and energy density between atoms, and so on. I felt doubtful as to whether these indices really have rationale.

What I immediately found was that those electronic structures have no theoretical basis. Strictly speaking, it means that tremendous amount of electronic structure analyses so far done were meaningless. The main point is that when obtaining the molecular orbital, the coefficients of the basis functions are determined to optimize the energy of the molecular orbital (which spreads throughout the molecule) to become a standing wave, and as for the part in the molecule, those coefficients are not optimized.

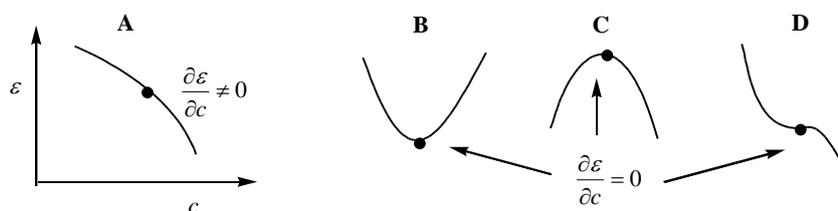


Figure 1. So as to the molecular orbital is a standing wave, ϵ must have the condition **B**, **C**, or **(D)** with respect to the change of c .

Many texts describe as "partial differentiation of ϵ with respect c is to minimize ϵ ", but this is not necessarily correct (because there is no judgment by the sign of the second derivative). Correctly, that is "to find the wave function of a standing wave".

Repeatedly, based on the coefficients (c 's) of the basis functions, electron density or atomic population, bond order or atomic bond population, furthermore, energy density on atom and attribution of all energy to atom and atom have been carried out. As mentioned above, c 's are optimized with respect to the energy concerning the whole molecule and are not optimized for every part of the molecule. As a conclusion, the molecular indices based on c 's have no meaning (this is a severe problem!).

Although it may be an unnecessary addition, the atomic orbital population of the basis function sometimes becomes 2 or more. I think this may be a typical example that c 's are not optimized with respect to the intramolecular part.