Molecular Orbital Theories for Molecular Interaction
Based on Locally Projected Molecular Orbital

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The non-covalent molecular interaction energy is by more than one order of magnitude smaller than the normal covalent bonds which make the backbone of the molecule. There are two sources of the errors in evaluating the weak molecular interaction energy. One is the orbital basis inconsistency (OBI) caused by the incompleteness of the one-electron basis sets, and the other is the configuration basis inconsistency (CBI) caused by the many-electron basis functions. The basis set superposition error (BSSE) should be referred to both of them. In the closed shell Hartree-Fock theory, only the OBI is the source of the BSSE, which can be removed by the counterpoise (CP) procedure. For the clusters consisting of many molecular units, however, the CP procedure is very time-consuming. For the direct MD/MC simulation, the use of the CP procedure is not practical.

  Last few years, to circumvent this difficulty, we have been developing the perturbation theory based on the locally projected molecular orbital (LP MO) for the molecular interaction.[1] Because the LP MO is absolutely local and not canonical, the single excitation perturbation theory (SPT) using appropriately determined excited MOs is required to compare the calculated binding energy with the corresponding CP corrected SCF energy. The efficient 3rd order SPT (3SPT) code was developed. It requires only one more two-electron integral handling after LP SCF calculation. The calculations for various isomers of water clusters and HF clusters demonstrate that the binding energy evaluated by LP MO 3SPT agrees well with the CP corrected energy, even for small basis set such as cc-pVDZ if a set of empirical scaling factor is introduced. For the basis set with the diffuse functions, such empirical factor is unnecessary. One of the advantages of the LP MO SPT is that the charge-transfer (CT) contribution to the binding energy can be clearly defined by using the absolute local nature both of the occupied and excited MOs. Figure shows the basis set dependence for strong hydrogen bond systems $F^-(H_2O)$ and $Cl^-(H_2O)$. Because the LP SCF MO does not allow the electron delocalization over the molecular units, the stabilization from the up-directed triangle in the figure is the CT contribution. The numbers of the inserted figure are evaluated with the aug-cc-pVTZ. The plots of 'ALEx' are evaluated using only the absolutely local excited MOs, and those of 'all' are evaluated using all of the excited MOs. The figure shows that if all of the excited MOs are used with the cc-pVDZ set, the BSSE is almost *recovered*. On the other hand, if only the absolutely local MOs are used with the same basis set, the binding energy is underestimated. As a compromise, a set of empirical factors, shown as [0.97, 0.77] and [0.8, 0.6] in the figure are introduced.

  To take into account the dispersion interaction, the double excitations (LP DPT) have to be carried out. Here care is needed not to introduce the CBI. With the local occupied and excited MOs, the proper selection of the excited configurations is required. The logical as well as numerical analyses are important, which is in progress.   [1] S. Iwata, J. Phys. Chem. B 112, 16104 (2008)