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Application of the Locally Projected Molecular Orbital Perturbation Theory with Dispersion Correction to the Large Water Clusters

(Toyota Riken[1)], Jawaharlal Nehru University[2)]) ○S. Iwata[1)], S. Shanker[2)], P. Bandyopadhyay[2)]

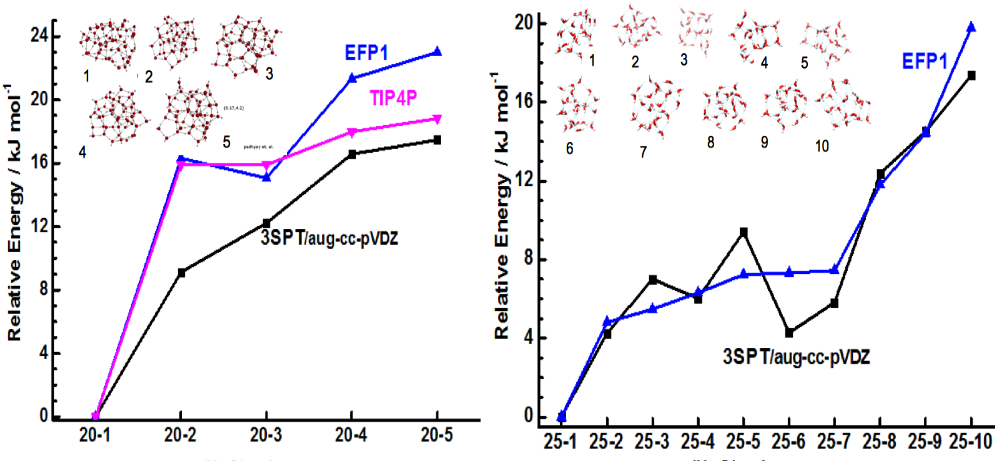
I. Introduction

The efficient evaluation of the weak molecular interaction in the clusters consisting of a large number of molecules is important in studying the structure and dynamics not only of the molecular clusters but also of the biomolecules. For the practical purpose, the empirical and semi-empirical potential energy functions are playing an important role in these studies. For the reliable functions the appropriate comparison with the ab initio MO calculations is necessary. Molecular interaction is essentially pair-wise, but the many-body effects sometimes unexpectedly large through the electrostatic and polarization interactions. Therefore, to examine the empirical functions, the ab initio calculations of realistically large clusters are desirable. However, the ab initio MO (and density functional) theories are not immune from the errors. The errors in evaluating weak molecular interaction are caused by the orbital basis and configuration basis inconsistencies (OBI & CBI) between the free constituents and the composite system. The ab initio computations should be carried out by avoiding these inconsistencies.

II. Theoretical

The perturbation expansion theory based on the locally projected molecular orbitals (LP MO) was developed and tested for various molecular interactions.[1] [2] It was demonstrated[1] that the binding energy evaluated by the third order single excitation perturbation theory (LP MO 3SPT) is very close to the counterpoise (CP) corrected Hartree-Fock (HF) binding energy, if the augmented basis sets are used. For instance, the average error is 0.31kJ mol^{-1} and the standard deviation is 0.14kJ mol^{-1} for various isomers of $(H_2O)_n$ (n=2~8) if aug-cc-pVDZ is used. The required computational resource is approximately same with a single iteration of HF calculations. The required user times on an ordinal Linux workstation for $(H_2O)_{20}$ and $(H_2O)_{25}$ are 200m and 350m, respectively. The results are shown in Figures 1 and 2.

Figure 1 Relative Binding Energy of $(H_2O)_{20}$ and $(H_2O)_{25}$



In LP MO, both occupied and excited MOs are locally defined on each constituent molecule. Therefore, only the dispersion type double excitations can be included in the second order perturbation theory, which ensures avoiding CBI. The rare gas dimers as well as some of complexes in S22 set were examined, and the applicability and limitation were discussed.[2]

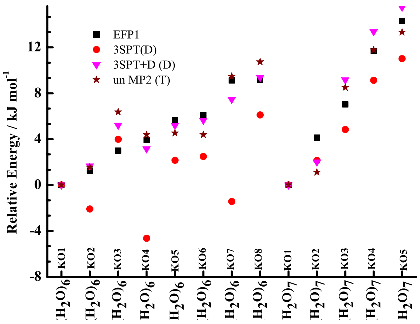
Comparison of halogen bond energies with those of Riley & Hobza [4] (/kJ mol^{-1})

	H_3CCl--OCH_3		F_3CCl--OCH_3		H_3CBr--OCH_3		F_3CBr--OCH_3	
aug-cc-pVxZ	x=D	x=T	x=D	x=T	x=D	x=T	x=D	x=T
SAPT^a	-3.14	-4.10		-8.20	-6.23	-7.11		-12.72
CCSD(T)^a	-3.26	-4.39		-7.70	-5.19	-6.23		-10.79
3SPT+D	-3.82	-4.55	-8.62	-8.84	-6.03	-6.62	-12.27	-12.36
SAPT Dispersion		-7.57				-8.28		
LP MO Dispersion	-6.62	-7.35	-6.02	-7.01	-6.86	-8.19	-6.59	-7.75
3SPT	+2.40	+2.80	-2.60	-1.83	+0.83	+1.57	-5.68	-4.61
CP corr HF	+2.69	+2.79	-2.01	-1.86	+1.27	+1.53	-5.08	-4.66
CT ($Y_3CX \rightarrow OCH_2$)	-0.58	-0.40	-0.62	-0.28	-0.92	-0.40	-0.90	-0.29
CT ($OCH_2 \rightarrow Y_3CX$)	-0.60	-0.41	-0.80	-0.52	-0.79	-0.57	-1.00	-0.73

III. **Results and Discussion**

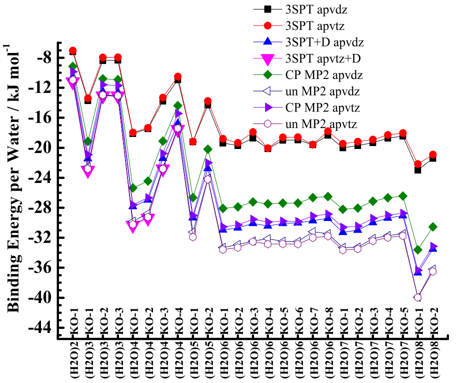
Figures 1 and 2 compare the relative energies of water cluster isomers $(H_2O)_{20}$ and $(H_2O)_{25}$. The geometries of the isomers are determined using Monte Carlo Basis Paving method[3] using Effective Fragment Potential 1 (EFP1). The energy ordering among the isomers approximately agrees with each other. But, there are some discrepancies, which might result from the dispersion term. LP MO 3SPT does not contain the dispersion energy, while the empirical potentials are parameterized to include it.

Figure 3. The relative isomer energy of $(H_2O)_6$ and $(H_2O)_7$



The dispersion correction is added to LP MO 3SPT (3SPT + D), and the test calculations of the method are given in Table for the halogen bonds. For a given basis set, the calculated binding energy and dispersion energy agree well with the reference values.[4] Figure 3 compares the relative isomer energies of EFP1, 3SPT/aug-cc-pVDZ, (3SPT + D)/aug-cc-pVDZ and uncorrected MP2/aug-cc-pVTZ. The figure clearly shows the dispersion force does contribute to the isomer energy. Figure 4 shows the hydrogen bond energy per water of various water isomers, where "un(CP) MP2 apvtz" stands for the uncorrected (CP corrected) MP2/aug-cc-pVTZ calculations. For n≦4, which is a limit of the present code, the 3SPT+D/apvtz energy agrees with the un MP2/apvdz and un MP2/apvtz. Note that uncorrected MP2 is much less basis-set-dependent than the CP MP2. The 3SPT+ D/apvdz *accidentally* agrees well with the CP MP2/apvtz.

Figure 4 Binding energy per water in $(H_2O)_n$



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[3] Bandyopadhyay, P., Chem. Phys. Letters 487 (2010) 133, [4] Riley,K.. and Hobza, P. J. Chem. Theory. Comp. 4 (2008) 232