Structure Optimization of Molecules Consisting of up to Period 5 Elements by Discrete Variational Xα Method

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Discrete variational method utilizes very natural and adaptive basis functions[1], which will be advantageous to calculate various chemical and physical quantities. But numerical integration accompanying this method causes rather serious numerical errors. Especially energy gradient seemed to be very difficult to calculate with practical accuracy. The author succeeded to cancel major part of its numerical error by the following way.

$$F_B = \left(F_B^{H-F} + F_B^{LCAO}\right)_{MOL} - \left(F_B^{H-F} + F_B^{LCAO}\right)_B$$

Here F_B denotes a force acting on atom B in the molecule, $(F_B^{H\text{-}F}+F_B^{LCAO})_{MOL}$ denotes Hellmann-Feynman force and the correction for LCAO approximation calculated in the molecule and $(F_B^{H\text{-}F}+F_B^{LCAO})_B$ denotes the counterpart calculated in only atom B. As no force can act on the isolated atom, calculated value of the latter part must be just numerical error and it cancels mostly numerical errors included in the former part.

By applying this way to MOs obtained by DV-Xα method[2], the force acting on each atom in the molecule consisting of up to period 3 elements could be calculated. Further by the procedure adopted by McIVER and KOMORNICKI[3], those molecules could be optimized with practical accuracy. But there still remained large numerical errors for molecules including period 4 and 5 elements.

The author has developed the new numerical integration method, where sample points are arranged like the face centered cubic lattice instead of quasi random number distribution in the unit cube and are mapped into the real 3D space. Further the mapping function is adjusted to distribute sample points far more densely near nuclei in the real 3D space. By these improvements, molecules consisting of up to period 5 elements can be optimized. The followings are its small examples, where 37600 points/atom for I atom and Sb atom and 56400 points/atom for In atom were used.

This method can be applied also for calculations of other quantities and will add new applications to Discrete Variational method.

AB_3	InI_3 (D_{3h})		SbI_3 (C_{3V})	
	Experimental	Optimized	Experimental	Optimized
R(AB)	2.64Å	2.67～2.68Å	2.719Å	2.730～2.789Å
∠BAB	120.0°	117.2～122.4°	99.1°	99.4～102.3°

[1] A.Rosen, D.E.Ellis, H.Adachi and F.W.Averill, *J. Chem. Phys.* **65**, 9, 3629, 1976
[2] The DV-Xα program distributed by the Society for Discrete Variational Xα
[3] K.Nakagawa, *J. Comput. Chem. Jpn.*, **11**, 4, 194, 2012 doi:10.2477/jccj.2012-0011
[4] J.W.McIVER Jr., A.KOMORNICKI, *Chem. Phys. Letters*, **10**, 3, 303, 1971