

## Notes

### Examination of Gaussian-Type Basis Sets on Alkali Metal Iodides

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In theoretical studies using *ab initio* or density functional theory (DFT) methods, adequate choices of a theoretical method and a basis set are very important in obtaining reliable results. Unfortunately, basis sets, especially for elements beyond the 4<sup>th</sup> row in the periodic table, are relatively limited, although various accurate theoretical methods such as MPn, QCISD and B3LYP etc. have been currently developed. Theoretical studies on compounds containing iodine, the 4<sup>th</sup> row halogen atom, are less abundant compared to those containing F, Cl or Br. However, compounds containing iodine atom play important roles in many chemical reactions.

Currently, three kinds of basis sets on iodine (STO-3G, 3-21G and Midi! basis sets)<sup>1</sup> without using effective core potential (ECP) have been implemented in most of quantum mechanical programs. However any results obtained from theoretical works using these basis sets or the ECP basis sets might not be so accurate for reactions containing iodine atom, because these basis sets are relatively low-grade in quality. Especially, an iodide ion is considered as an intermediate or a product in many reactions, but none of these basis sets have incorporated a diffuse function. Therefore, any theoretical results obtained by using these basis sets could not be accurate due to incorrect nature of iodide anions.

On the other hand, Andzempl *et al.*<sup>2</sup> have reported the contracted Gaussian basis sets for halogen elements. These basis sets have similar quality to the basis sets generated earlier by Huzinaga *et al.*<sup>3</sup> but Andzempl *et al.* have argued that their basis sets after splitting of valence orbitals and augmented with polarization function, have given better atomic total energies and properties of atomic valence orbitals. Recently, Wiberg *et al.*<sup>4</sup> have also reported works for organometallic compounds containing iodine. In the work, they have used a TZ-quality basis set with two D polarization functions and one SP diffuse function for iodine. Therefore, in order to obtain reliable results on the reactions containing iodide anion, various types of basis set are re-examined in this work.

#### Calculations

Restricted Hartree-Fock (RHF) and B3LYP hybrid density

functional theory (DFT) calculations were carried out by using Gaussian 98 series of program.<sup>5</sup> In this work, a 64-node linux cluster system which consists of Intel Pentium IV 3.0 CPUs, 2 GB of RAM, and 80 GB of HDD were used. The 6-31G(d) and 6-311++G(d,p) basis sets have been used for all elements except iodine. For iodine, a standard all-electron TZ-quality basis set,<sup>6</sup> augmented by two D polarization functions with exponents of 0.30 and 0.08, respectively, and one SP diffuse function with exponent of 0.025 were used.<sup>4</sup> In this case, two types of split valences (SV) for 5s and 4p-electrons of iodine have been examined; one is named as a SV2PPD basis set with a split valence of 432211/42211/42 and another as SV4PPD with a split valence of 433321/43321/43. In the basis sets, PP stands for two polarization functions (exponents: 0.105 and 0.334).<sup>2</sup> The 3-21G(d) basis set have been also examined for all elements including iodine to make comparison with the results obtained by using the SV2PPD and SV4PPD basis sets.

The geometries were fully optimized, and characterized by vibrational frequency calculations. Calculated geometries and reaction enthalpies ( $\Delta H$ ) have been compared with experimental results.

#### Results and Discussion

To examine the accuracy of basis sets for iodine, bond lengths (d) of alkali-metal iodides, LiI, NaI and KI, were calculated by using several combinations of basis sets. The average absolute percentage-errors for the calculated bond lengths,  $\%d_{\text{Err}} = (|d_{\text{Calc}} - d_{\text{Exp}}|/d_{\text{Exp}}) \times 100$ , were summarized in Table 1. Examination of Table 1 shows that the  $\%d_{\text{Err}}$  at B3LYP levels are much smaller than those at RHF levels, and the result at B3LYP level with the combination of 6-311+G(d) for alkali metal and 3-21G(d) for iodine, which is designated as 6-311+G(d)/3-21G(d), is the most accurate. This indicates that the results at the B3LYP levels are more accurate than those at RHF levels, as is generally expected. Indeed, the experimental bond lengths<sup>7</sup> are 2.392, 2.711 and 3.048 Å for LiI, NaI and KI, respectively, and the calculated values in this work are 2.382, 2.695 and 3.041 Å at B3LYP level with combination of 6-311+G(d)/3-21G(d) basis sets. These are quite well consistent with the literature values

**Table 1.** Averaged values of absolute percentage-errors (%d<sub>Er</sub>) of the calculated bond lengths for alkali-metal iodides

RHF		Basis Sets for Alkali Metals		
		3-21G(d)	6-31G(d)	6-311+G(d)
Basis Sets For Iodine	3-21G(d)	2.7	2.2	1.2
	SV2PPD	2.4	3.3	2.6
	SV4PPD	3.1	3.1	2.5
B3LYP		Basis Sets for Alkali Metals		
		3-21G(d)	6-31G(d)	6-311+G(d)
Basis Sets For Iodine	3-21G(d)	1.7	0.9	0.4
	SV2PPD	1.9	1.8	0.9
	SV4PPD	2.7	1.5	0.8

considering the experimental uncertainties of  $\pm 0.01$  Å.<sup>8</sup> However the bond lengths calculated at RHF level with the same combination, 6-311+G(d)/3-21G(d) basis set, are 2.409, 2.731 and 3.113 Å for LiI, NaI and KI, respectively, and these are deviated by 0.017 (LiI)-0.065 Å (KI) from the experimental values.

The %d<sub>Er</sub> values at B3LYP level with combined 6-311+G(d)/SV2PPD and 6-311+G(d)/SV4PPD basis sets are also relatively small within 1% error range; the absolute errors in the calculated bond lengths are 0.009-0.04 Å as compared to the experimental values. Therefore, it could be expected that the calculated bond lengths at B3LYP level with combinations of 6-311+G(d)/SV2PPD and 6-311+G(d)/SV4PPD basis sets are also sufficiently reliable for neutral alkali-metal iodides, although the %d<sub>Er</sub> values are slightly larger than combination of 6-311+G(d)/3-21G(d) basis set.

On the other hand, in order to examine energetics for reactions including an iodide anion, reaction enthalpies ( $\Delta H$ ) for dissociation processes of alkali-metal iodides,  $MI \rightarrow M^+ + I^-$  where  $M = Li, Na$  and  $K$ , have been calculated at both the RHF and B3LYP levels with the same combinations of basis sets as discussed above. The average absolute errors for the calculated reaction enthalpies,<sup>7</sup> % $\Delta H_{Er} = (|\Delta H_{Calcd} - \Delta H_{Exp}|/\Delta H_{Exp}) \times 100$ , were summarized in Table 2. As can be seen in Table 2, the % $\Delta H_{Er}$  values at B3LYP levels are, in general, smaller than those at RHF levels indicating that the

**Table 2.** Averaged values of absolute percentage-errors (% $\Delta H_{Er}$ ) of the calculated reaction enthalpies for dissociation processes of alkali-metal iodides

HF		Basis Sets for Li, Na, and K		
		3-21G(d)	6-31G(d)	6-311+G(d)
Basis Sets For Iodine	3-21G(d)	5.1	5.6	6.8
	SV2PPD	3.6	4.1	3.2
	SV4PPD	4.4	4.2	3.4
B3LYP		Basis Sets for Li, Na, and K		
		3-21G(d)	6-31G(d)	6-311+G(d)
Basis Sets For Iodine	3-21G(d)	11.3	11.7	13.6
	SV2PPD	3.0	2.3	1.2
	SV4PPD	4.0	2.2	1.2

results are more accurate at the former. For example, the % $\Delta H_{Er}$  value is 2.2% at B3LYP level with 6-31G(d)/SV4PPD basis sets, but becomes 4.2% at RHF level with the same basis sets. However, the % $\Delta H_{Er}$  values at B3LYP level with combinations of 3-21G(d) basis set for iodine are much larger than those at RHF level. Moreover the % $\Delta H_{Er}$  values at both the B3LYP and RHF levels with 3-21G(d) basis set are the worst when compared to those with SV2PPD and/or SV4PPD basis sets. These results could be obviously caused by inaccurate description of product ion at 3-21G(d) level due to lack of a diffuse function for iodine. Therefore use of 3-21G(d) basis set could be inadequate for energetics on the dissociation process of alkali-metal iodides, even though the combined basis set of 6-311+G(d)/3-21G(d) at B3LYP level gave the best results for bond lengths of neutral molecules (*vide supra*).

The % $\Delta H_{Er}$  values at B3LYP levels with combined 6-311+G(d)/SV2PPD and 6-311+G(d)/SV4PPD basis sets are the same, and are much better than those with other combined basis sets. For example, the % $\Delta H_{Er}$  value at B3LYP levels with 6-311+G(d)/SV2PPD basis sets is only 1.2%. This is about a half of that with 6-31G(d)/SV2PPD basis sets. Indeed, the  $\Delta H$  values experimentally reported are 139.1, 118.3 and 106.3 kcal mol<sup>-1</sup> for LiI, NaI and KI, respectively, and the calculated  $\Delta H$  values are 139.2, 121.9 and 105.8 kcal mol<sup>-1</sup> at B3LYP levels with combination of 6-311+G(d)/SV2PPD basis sets.

In summary, the bond lengths for neutral alkali-metal iodides calculated at B3LYP level with combinations of 6-311+G(d) for alkali metals and 3-21G(d) for iodine seem to be the most reliable among combinations of basis sets employed. However this combination could be inadequate for description of reactions with iodide anion, since a diffuse function is not incorporated in the 3-21G(d) basis set. Instead, use of combinations of 6-311+G(d) for alkali metals and/or SV2PPD and SV4PPD basis sets for iodine at B3LYP level are much more reliable in obtaining reliable energetics on reactions with iodide anion, and the bond lengths obtained by using these combinations of basis sets are sufficiently accurate within 1% error ranges. Therefore choice of the SV2PPD or SV4PPD basis set for iodine could give a superior result than that of the 3-21G(d) basis set for reactions including iodide anion.

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