

## A Molecular Orbital Study of the Dipole Moment of HF, LiH, and HeH<sup>+</sup>

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The threshold bond distances of electron transfer in the typical heteronuclear diatomic molecules, HF, LiH, and HeH<sup>+</sup> have been studied in conjunction with the dipole moments by using ab initio molecular orbital method. The electron transfer begins at 3Å for HF, 6Å for LiH, and 4Å for HeH<sup>+</sup>, and the dipole moments have their maxima at 1.2Å for HF, 2.4Å for LiH, and 0.8Å after the electrostatic correction for HeH<sup>+</sup>.

The heteronuclear diatomic molecules with strongly ionic character play very important roles in chemistry.<sup>1</sup> In our previous work, the orbital correlation diagrams of LiH and HF molecules on the basis of ab initio molecular orbital calculations were far from those in the typical textbook of chemistry.<sup>2,3</sup> We also reported that the chemical bond of HeH<sup>+</sup> is considered to be a coordination bond.<sup>4</sup>

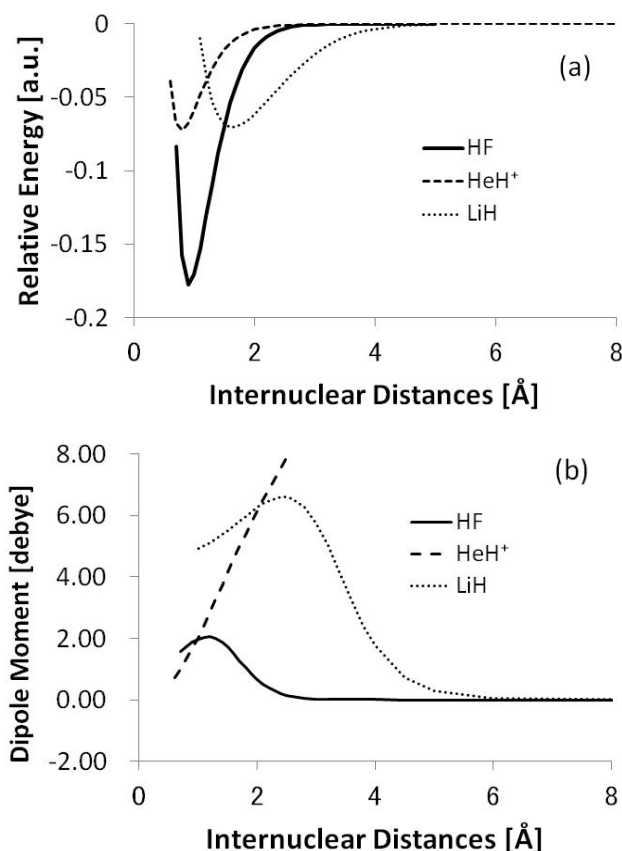
In HF and LiH, each atom is electrically neutral at the dissociation limit, but the two atoms in their equilibrium geometry are polarized depending on the difference of their electronegativity. It is difficult to experimentally study how the polarization occurs and how the polarization relates to the interaction region between two atoms. Therefore, it is very interesting to discuss these from the results of the theoretical calculations.

In the present communication, using ab initio molecular orbital calculations we discuss the bond length of the heteronuclear diatomic molecule where the electron transfer starts. We select HF and LiH molecules as covalent bond type molecules with strong ionicity and HeH<sup>+</sup> molecule as a coordination bond type molecule. The quantum chemistry of LiH and HeH<sup>+</sup> is still a topic of current interest.<sup>5,6</sup>

In the ab initio molecular orbital calculations, the widely used 6-311G\*\* basis sets are adopted throughout this study.<sup>7,8</sup> We use the MCSCF wave functions in order to treat the dissociation limit correctly. We use CASSCF within the configuration of 2 electrons in 2 orbitals for LiH, full-CI for HeH<sup>+</sup>, and CASSCF within the configuration of 6 electrons in 4 orbitals for HF. We abbreviate these calculations just as MCSCF/6-311G\*\* in this study. We put both atoms on z-axis and the left-hand-side atoms of H-F, Li-H, and H-He are on the minus side of z-axis. We set the center of gravity of molecules at the origin. All the calculations are carried out using Gaussian09 program package.<sup>9</sup>

Figure 1(a) shows the plot of the MCSCF/6-311G\*\* total energy vs the internuclear distance in HF, LiH, and HeH<sup>+</sup> molecules. The energy values are shown as the relative energy with respect to the energies at the internuclear distance of 10 Å. The total energies become almost constant above the internuclear distance greater than 5 Å. The optimized

internuclear distances are 0.915 Å for HF, 1.647 Å for LiH, and 0.789 Å for HeH<sup>+</sup>.



**Figure 1** (a) Plot of relative total energies in a.u. and (b) z-component of dipole moment in debye versus internuclear distance in HF, LiH, and HeH<sup>+</sup>.

Figure 1(b) also shows the plot of the z-axis component of the dipole moment (hereafter we simply refer it to “dipole moment”) in HF, LiH, and HeH<sup>+</sup> molecules vs the internuclear distances. The calculated dipole moments of HF and LiH at their optimized geometries are 1.888 debye and 5.724 debye, respectively, which reasonably agree with the experimental results, 1.796 debye<sup>10</sup> and 5.881 debye.<sup>11</sup> With decrease of the internuclear distance the dipole moment of HF starts to increase around 3 Å and reaches the maximum around 1.2 Å. The value of the dipole moment of LiH shows a change similar to that of HF, but increases from 6 Å and reaches the maximum at 2.4 Å because the optimized bond

length of LiH molecule is longer than that of HF molecule and the amount of these polarized charges induced by the electron transfer of LiH is larger than that of HF. The electron transfer does not occur in the region of long internuclear distances but occurs in the vicinity of the optimized internuclear distance in the case of HF and LiH molecules.

Note that the optimized bond length does not coincide with the internuclear distance for the maximum dipole moment. With decreasing the internuclear distance, the electron once transfers from H and Li to F and H, respectively, with simple Coulomb interaction. Then the electron back transfer to H and Li occurs at the optimized bond lengths with the reorganization of the molecule. Note that the electron transfer is caused by sp coupling in HF, whereas by ss coupling in LiH. However, the expectation value for the radial function  $\langle r \rangle$  is 1.5 a.u. for H, 3.874 a.u. for the 2s AO (atomic orbital) of Li, and 1.084 a.u. for 2p AO of F.<sup>12</sup> The sum of  $\langle r \rangle$  for HF is 2.584 a.u. and that for LiH is 5.374 a.u. The maximum of dipole moment of LiH occurs at 4.54 a.u. (2.4 Å) and that of HF at 2.27 a.u. (1.2 Å) as shown before, which reflects the difference of  $\langle r \rangle$ . The overlap of the orbitals of HF is considered to be almost the same as that of LiH, and the difference in  $\langle r \rangle$  between the 2pAO of F and the 2s AO of Li is, therefore, the reason for the large difference in the internuclear distance for the maximum dipole moment.

On the other hand in the case of HeH<sup>+</sup>, the dipole moment does not have the maximum and monotonically decreases along with decreasing the internuclear distance. The dipole moment of HeH<sup>+</sup> is classically zero at the united atom, linearly increases with increasing the internuclear distance, and becomes infinity at the dissociation limit. Since such electrostatic change of the dipole moment, however, does not take the interatomic electron transfer into account, the correction for the electrostatic effect should be considered in order to reveal the electron transfer clearly.

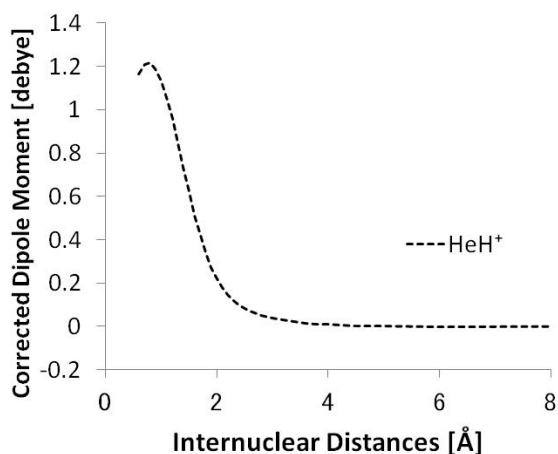


Figure 2. Plot of z-component of dipole moment after electrostatic correction in debye versus internuclear distance in HeH<sup>+</sup>.

When the distance between the proton and He atom is long enough, there is no interatomic electron transfer and the dipole moment linearly depends on the interatomic distance.

From the dipole moments at the internuclear distances of 5 Å and 10 Å, the linear relationship is expressed as,

$$\mu'(r) = 0.0316 - 3.20484r \quad (1)$$

where  $r$  denotes the internuclear distance. We have estimated the corrected dipole moment as the difference of this  $\mu'(r)$  and the calculated dipole moment  $\mu(r)$ .

$$\mu_{corr.}(r) = \mu(r) - \mu'(r) \quad (2)$$

Figure 2 shows the plot of this corrected dipole moment of HeH<sup>+</sup>. The corrected dipole moment clearly shows a behavior similar to those of HF and LiH molecules. The corrected dipole moment starts to increase from 4 Å being about five times as long as the optimized bond length. Furthermore, the corrected dipole moment has the maximum at the vicinity of 0.8 Å, which is almost the same as the optimized bond length. The result is totally different from the plot of the dipole moment in HF and LiH. This dissociation would be a feature of the coordination bond against the covalent bond.

In conclusion, in the present communication, we have studied the threshold bond distances of electron transfer in the typical heteronuclear diatomic molecules, HF, LiH, and HeH<sup>+</sup> in conjunction with the dipole moments by using ab initio molecular orbital method. In the cases of HF and LiH, the electron transfer begins at the bond length being three times (3 Å for HF) and 3.7 times (6 Å for LiH) as long as the optimized bond length, and the dipole moments have its maxima at the bond lengths being 1.3 times (HF, 1.2 Å) and 1.5 times (LiH, 2.4 Å) as long as the optimized bond lengths. On the other hand, in the case of HeH<sup>+</sup>, the dipole moment decreases monotonically with decrease of the internuclear distance, and it is impossible to determine the bond length where the electron transfer begins. A result similar to those of HF and LiH is, however, obtained for HeH<sup>+</sup> after the electrostatic correction on the dipole moment. The electron transfer begins at the bond length being five times as long as the optimized bond length (4 Å), and the dipole moment has its maximum at its optimized bond length.

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**NOTE** The diagram is acceptable in a colored form. Publication of the colored G.A. is free of charge. For publication, electronic data of the colored G.A. should be submitted. Preferred data format is EPS, PS, CDX, PPT, and TIFF. If the data of your G.A. is "bit-mapped image" data (not "vector data"), note that its print-resolution should be 300 dpi.

