Localization of Electrons: Blue-shifting Hydrogen Bonds

Satoshi Inagaki* and Takahiro Takeuchi
Department of Chemistry, Faculty of Engineering, Gifu University, Yanagido, Gifu 501-1193

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A theory of electron localization is developed. Localization is caused by the interaction of an occupied orbital with a vacant orbital. Electrons localize in the occupied orbital rather than delocalize from the occupied orbital to the overlap region. The localization is substantiated by the contraction of the CH bond length of H_nCF_{4-n} with the fluorination and successfully applied to the blue-shifting hydrogen bonding of fluoroform with dimethyl ether.

Delocalization of electrons is one of the important factors of the stability and the reactivity of molecules. For example, the stability of cyclic conjugated molecules or the Hückel $4n + 2\pi$ electron rules[1] is associated with the delocalization of π electrons.[2] The frontier orbital theory[3] for chemical reactions lays an emphasis on the delocalization at the transition states.

In this work, we develop a theory of electron localization and substantiate the theory by applying to the C–H bond lengths of H_nCF_{4-n} and the blue-shifting hydrogen bonds[4] where the contact between the A–H bond of a proton donor and the Y atom with lone pairs in a proton acceptor gives rise to an unexpected blue shift of the A–H stretching frequency.

The localization of electrons is here shown to be expressed by applying the perturbation theory to the interaction of an occupied orbital χ_1 and a vacant orbital χ_2 (Figure 1).

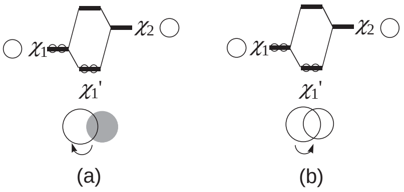

Figure 1. (a) The localization of electrons ($|sh_{11}| > |h_{12}|$) and (b) the delocalization of electrons ($|sh_{11}| < |h_{12}|$).

The perturbed orbital χ_1' and the electron distribution $\chi_1'^2$ are given by Eqs 1 and 2, respectively:[5]

$$\chi_1' \approx \left\{1 - s\frac{h_{12} - sh_{11}}{h_{11} - h_{22}}\right\}\chi_1 + \left\{\frac{h_{12} - sh_{11}}{h_{11} - h_{22}}\right\}\chi_2 \qquad (1)$$

$$\chi_1'^2 \approx \left\{1 - 2s\frac{h_{12} - sh_{11}}{h_{11} - h_{22}}\right\}\chi_1^2 + 2\left\{\frac{h_{12} - sh_{11}}{h_{11} - h_{22}}\right\}\chi_1\chi_2 + \left[\left\{\frac{h_{12} - sh_{11}}{h_{11} - h_{22}}\right\}^2\chi_2^2\right] \qquad (2)$$

where the conventional notations, h_{11} (< 0), h_{22} (> 0), h_{12} (< 0), and s (>0) are employed. The change in the electron population of χ_1 on the $\chi_1 - \chi_2$ interaction is expressed by the second term, $-2s(h_{12} - sh_{11})/(h_{11} - h_{22})$, in the coefficient of χ_1^2 in Eq 2. The term is positive when $h_{12} - sh_{11} > 0$ since $h_{11} - h_{22} < 0$ and $-2s < 0$. This implies that the population of χ_1 increases when $|sh_{11}| > |h_{12}|$ because h_{12} and sh_{11} are negative. The increment is equal to the population $2s(h_{12} - sh_{11})/(h_{11} - h_{22})$ which disappears in the overlap region, as the coefficient of $\chi_1\chi_2$ in Eq 2. shows. It follows that electrons localize in χ_1 on the interaction when $|sh_{11}| > |h_{12}|$. The coefficients of χ_1 and χ_2 in Eq 1 are positive and negative, respectively since $h_{12} > sh_{11}$ and $h_{11} < h_{22}$. The orbitals, χ_1 and χ_2, are combined out of phase with each other. The energies, h_{12} and sh_{11}, are supposed to represent the energy of the electrons in the overlap region and the change in the energy of the electrons in the occupied orbital χ_1, respectively. When $|sh_{11}| > |h_{12}|$, electrons localize in the occupied orbital to gain the stabilization $|sh_{11}|$ greater than the destabilization $|h_{12}|$ of the electrons in the overlap region. The relative magnitude of $|h_{12}| > |sh_{11}|$ has been supposed so far for the donor–acceptor interactions. Only electron delocalizaton from the donor to the overlap region and the acceptor to gain the stabilization $|h_{12}|$ greater than $|sh_{11}|$ has been applied to molecular science so far.

The localization is substantiated by the trends of the CH bond length of fluorinated methanes. Fluorination of CH_4 shortens the C–H bond (the values calculated at RHF/6-31G* level:[6] 1.0837 Å in CH_4, 1.0818 Å in H_3CF, 1.0781 Å in H_2CF_2, 1.0742 Å in HCF_3). The bond model analysis[7,8] at RHF/6-31G* level[6] shows that the population of the σ_{CH} orbital increases (BOP:[7] 2.1923 in CH_4, 2.2394 in H_3CF, 2.2867 in H_2CF_2, 2.3097 in HCF_3) with the fluorination. The σ_{CH} bonding electrons localize.

The localization is caused by the interaction of the bonding orbital of the C–H bond (σ_{CH}) with the antibonding orbital of the C–F bonds (σ^*_{CF}). The overlap integral ($S_{\sigma\sigma^*} = 0.0977$) and the off-diagonal element ($F_{\sigma\sigma^*} - S_{\sigma\sigma^*}F_{\sigma\sigma} = 0.0346$) for the σ_{CH} and σ^*_{CF} orbitals in fluoroform unusually have the same signs because $|F_{\sigma\sigma^*}(= -0.0470)| < |S_{\sigma\sigma^*}F_{\sigma\sigma}(= -0.0816)|$, as was reported for the interaction between the σ and σ^* orbitals of geminal bonds.[9] This implies that the orbital where σ and σ^* are combined out of phase ($c_\sigma c_{\sigma^*} S_{\sigma\sigma^*} < 0$) is stabilized (Figure 2). The electron population is excluded from the overlap region to localize in the C–H bonding (σ_{CH}) orbital. The coefficient (1.0019) of σ_{CH} is greater than 1.0.

We investigated the blue-shifting hydrogen bond between $(CH_3)_2O$ and HCF_3 and the hydrogen bond in water dimer as a reference. Calculations at RHF/6-31G* level[6] reproduced the

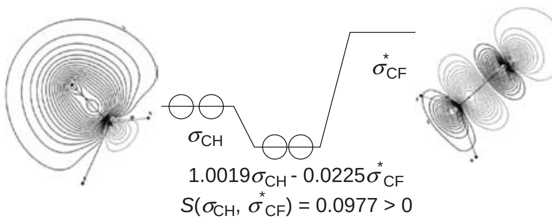

Figure 2. The interaction between the σ_{CH} and $\sigma_{CF}{}^*$ orbitals of fluoroform.

contraction of the C–H bond from 1.0742 Å in free fluoroform to 1.0712 Å in the hydrogen bonded fluoroform. In contrast, the O–H bond is elongated from 0.9474 Å in the monomer to 0.9519 Å in the dimer. The bond model analysis[7,8] shows that the localization in σ_{CH} of HCF_3 is enhanced by the hydrogen bond with $(CH_3)_2O$. The σ_{CH} population increases from 2.3097 to 2.3180 on the hydrogen bonding. The localization occurs and contracts the C–H bond. The localization does not result from the C–H bond shortening. In the fluoroform of the same geometry as in the complex (BOP = 2.3010) the C–H bonding electrons localize less than those in the free fluoroform (BOP = 2.3097). The localization does not occur in the water dimer where the corresponding σ_{OH} population decreases from 2.1090 to 2.0971 on the hydrogen bonding. As a result, the blue-shifting is caused by the enhancement of the localization of the σ_{CH} bonding electrons.

The enhancement of the localization by the hydrogen bonding is caused by the interaction of the σ_{CH} orbital with the n_O orbital of dimethyl ether. The σ^*_{CF}–σ_{CH}–n_O interaction was calculated by using the overlap integrals and the Fock matrix elements of free fluoroform and dimethyl ether. The overlap integral $S(n_O, \sigma_{CH})$ was changed to evaluate the effect of the magnitude of the n_O–σ_{CH} interaction. The $F(n_O, \sigma_{CH})$ value is supposed to be proportional to be the overlap integral or to be given by multiplying the Fock matrix element $F_c(n_O, \sigma_{CH})$ in the complex by $S(n_O, \sigma_{CH})/S_c(n_O, \sigma_{CH})$. The σ_{CH} population is found to increase with the overlap between the σ_{CH} and n_O orbitals (Figure 3). Localization is enhanced by the σ_{CH}–n_O interaction.

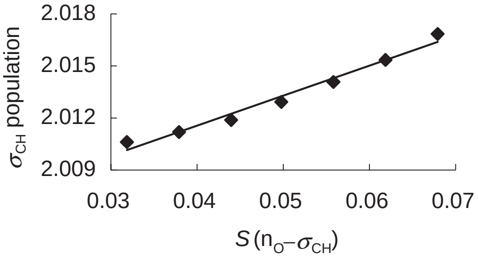

Figure 3. Effect of the interaction with the oxygen lone pairs on the localization in the σ_{CH} bond of $(CH_3)_2O\cdots HCF_3$.

The enhancement of the localization is also caused by the electrostatic effect of negative charge on the oxygen atom of dimethyl ether. The effect is investigated by increasing the Fock matrix element F_{HH} of the hybrid orbital on the hydrogen atom in the C–H bond. The σ_{CH} population is shown to increase with F_{HH} (Figure 4). The electrostatic effect also enhances the localization.

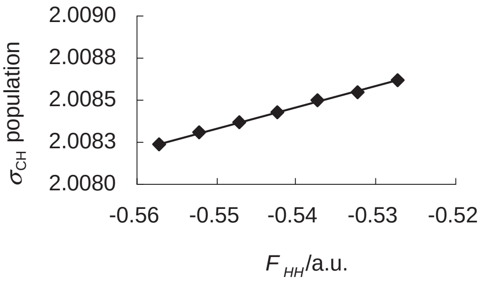

Figure 4. Electrostatic effect of the negative charged oxygen atom on the localization in the σ_{CH} bond of $(CH_3)_2O\cdots HCF_3$.

In conclusion, we developed a theory of electron localization. The localization is caused by the interaction between occupied and vacant orbitals or by localizing the electrons from the overlap region to the occupied orbital rather than by delocalizing electrons from the occupied orbital to the overlap region. Electrons occupy the out-of-phase combined occupied and vacant orbitals in the localization in contrast to the electron occupation of the in-phase combined orbitals in the delocalization. The localization gives an insight into the origin of the blue-shifting hydrogen bonds.

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7 A wave function (Ψ) is expanded into electron configurations:

$$\Psi = C_G\Phi_G + \Sigma\, C_T\Phi_T + \Sigma\, C_E\Phi_E + \cdots$$

In the ground configuration (Φ_G), a pair of electrons occupies each bonding orbital ϕ_i of the bonds. Electron-transferred configurations and locally excited configurations are denoted by Φ_T and Φ_E, respectively. A set of bond orbitals are optimized to give the maximum C_G value. A molecular orbital ψ_j is expressed by a linear combination of the bonding and antibonding orbitals ϕ_i and ϕ_i^*:

$$\psi_j = \sum_i (c_{i,j}\phi_i + c^*_{i,j}\phi^*_i).$$

The population of the bond (bonding and antibonding) orbitals are defined:

$$\mathrm{BOP}(\phi_i) = 2\sum_j^{occ} c_{i,j}{}^2, \quad \mathrm{BOP}(\phi_i^*) = 2\sum_j^{occ} c^{*}_{i,j}{}^2$$

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