

ELF解析 メモノート

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参考文献 (読みかけも含む)

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Electron Localization Function (ELF)

分子・固体での

Lone pairs

Single, double, triple bonds

これらを議論する方法

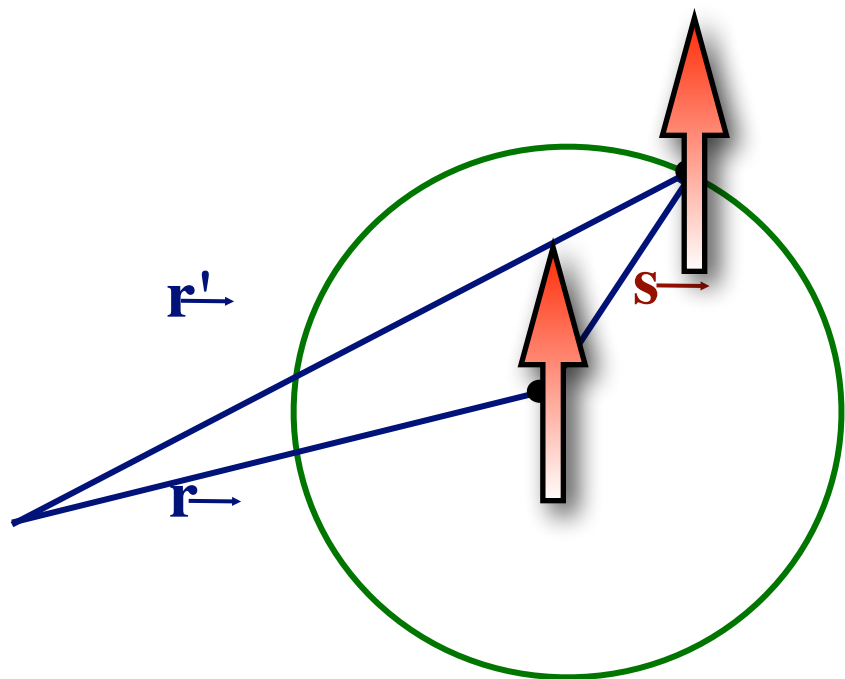
電子密度 $\rho(r)$ は議論に向かない

二体の密度行列

$$D_{\sigma}(\vec{r}, \vec{r}') = \sum_{\sigma_3 \sigma_4 \dots \sigma_N} \int d^3 r_3 \dots \int d^3 r_N |\Psi(\vec{r}\sigma, \vec{r}'\sigma, \vec{r}_3\sigma_3, \dots, \vec{r}_N\sigma_N)|^2$$

ペア電子密度を定義する

$$P_{\sigma}(\vec{r}, \vec{r}') := \frac{D_{\sigma\sigma}(\vec{r}, \vec{r}')}{\rho_{\sigma}(\vec{r})} \quad \text{スピン } \sigma(r), \text{ スピン } \sigma(r')$$



A.D.Becke, N.E.Edgecombe,
J. Chem. Phys. 1990,92,5397

ペア電子密度を一体で展開すると

$$P_{\sigma}(r, r') = p_{\sigma}(r, 0) + \underbrace{\frac{dp_{\sigma}(r, s)}{ds} \bigg|_{s=0}}_{=0} + \frac{1}{3} \boxed{C_s(r)} s^2 + \dots$$

$$C_s(r) = \boxed{\frac{1}{2} \sum_i n_i |\nabla \varphi_i|^2} - \frac{1}{8} \frac{|\nabla \rho|^2}{\rho}$$

運動E項

電子密度の二回微分項

$$\rho = \sum_i n_i |\varphi_i|^2$$

ELF を定義する

$$\text{ELF} = \left\{ 1 + \left[\frac{C(r)}{C_h(\rho(r))} \right]^2 \right\}^{-1}$$

$$C_h(r) \sim \rho^{5/3}$$

$$0 \leq \text{ELF} \leq 1$$

一様電子ガスのペア電子密度

ELF ($0.5 < \text{ELF}$) : $C(r) \rightarrow$ 大きい

perfectly delocalized

ELF (0.5)

$$C(r) = C_h(r)$$

ELF ($0.5 > \text{ELF}$) : $C(r) \rightarrow$ 小さい

localized (ELFが大きいと局在化)

ELF の値が大きい領域（白色）

電子が多く局在化 → 原子間に電子が局在化していると
→ 共有結合（図ではGeの三角形は共有結合）

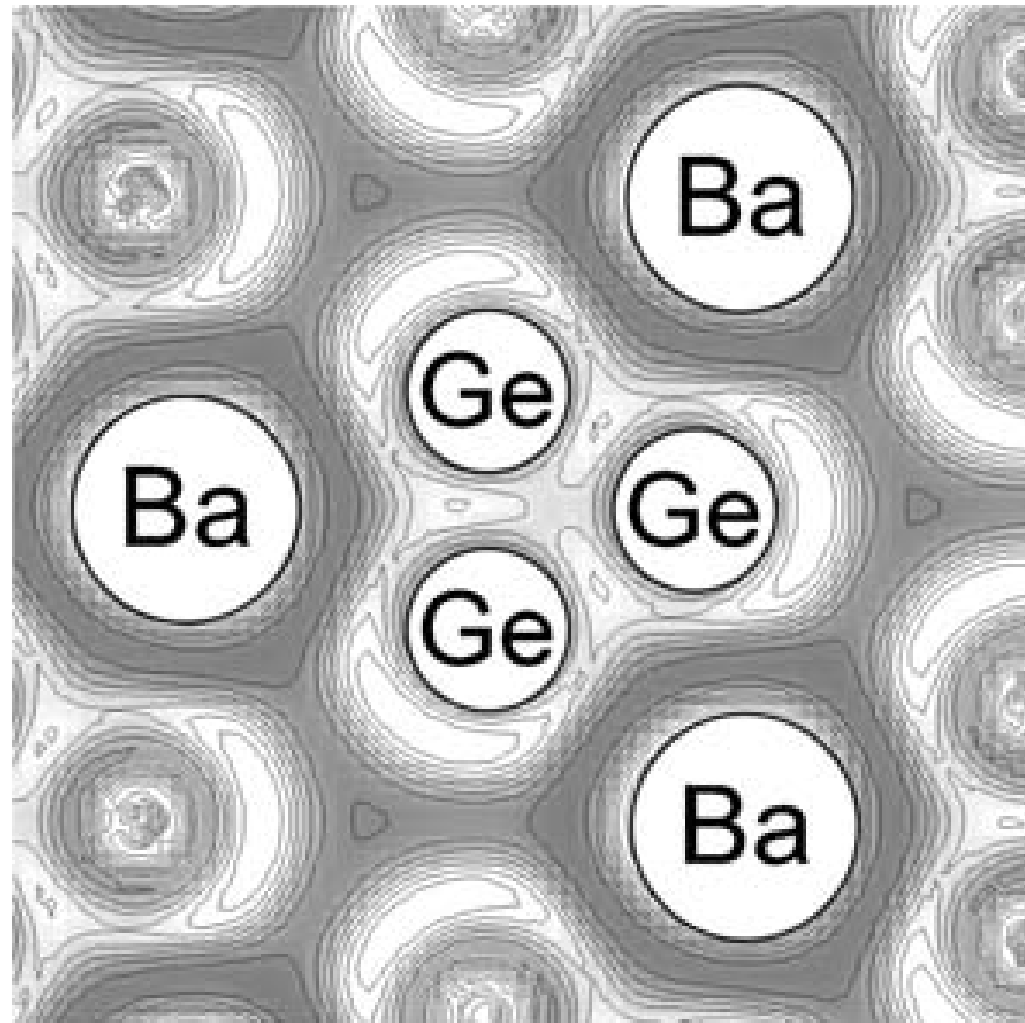


Fig. 9. Electron localization function (ELF) diagram of BaGe_3 .

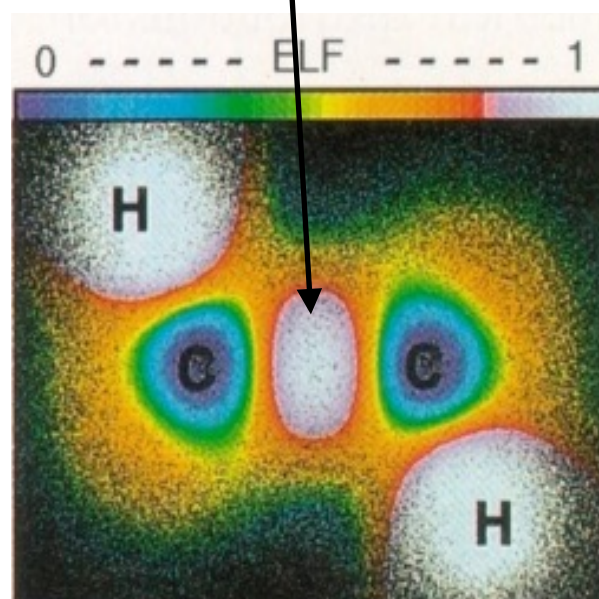
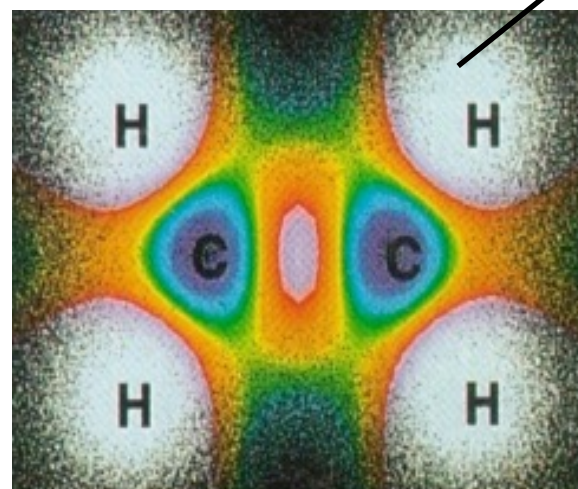
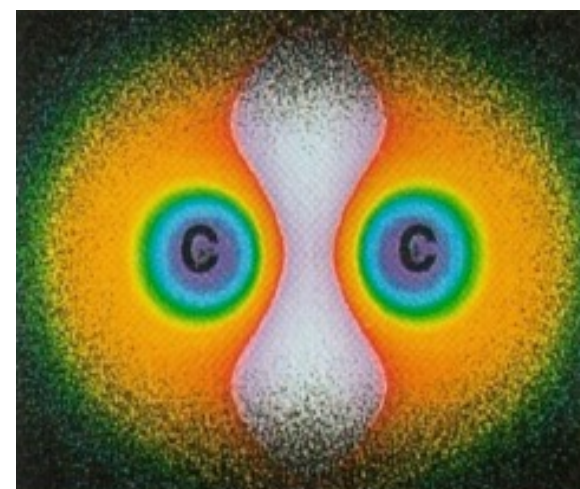
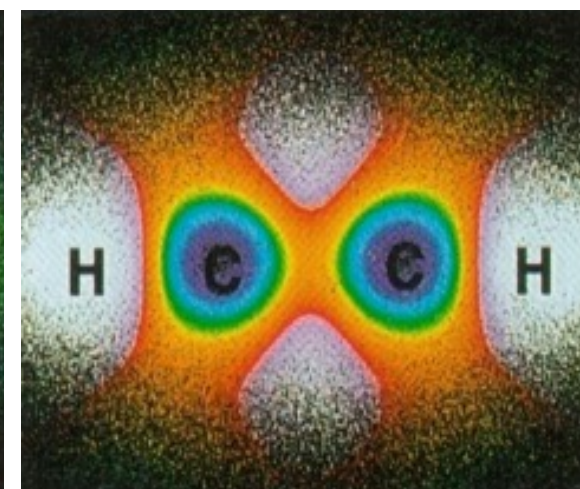
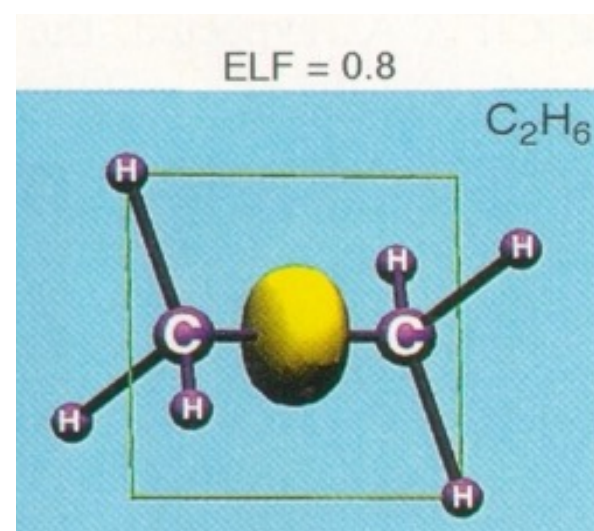
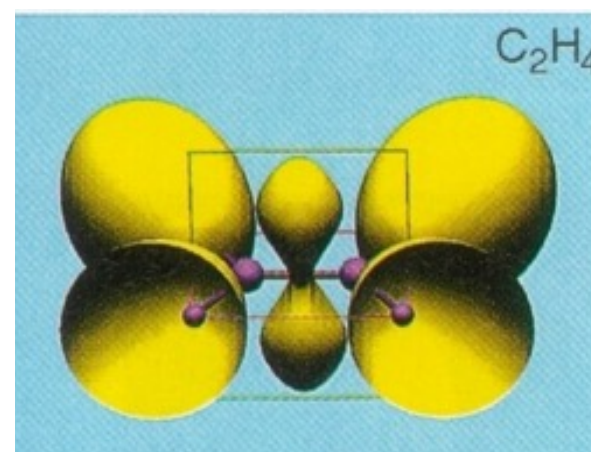
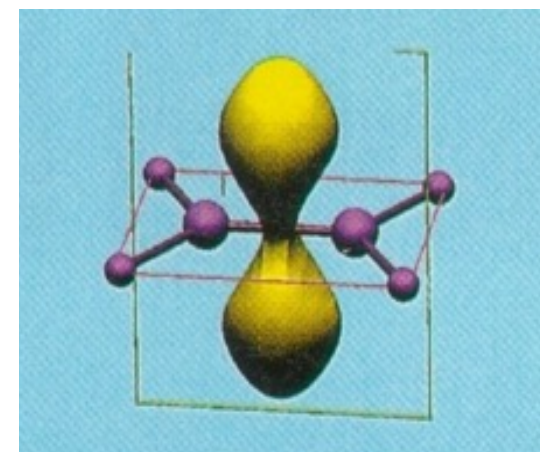
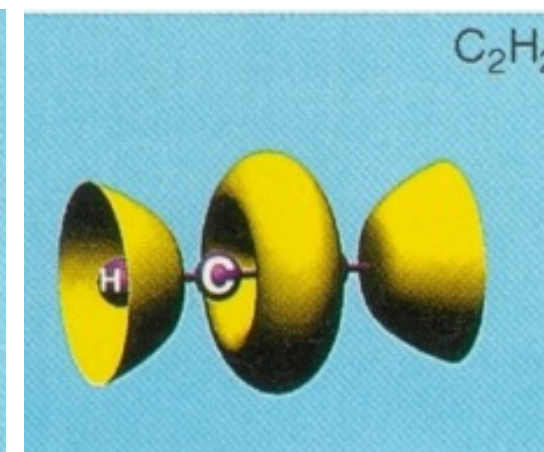
局在している電子が原子の間にいる(共有結合)

localized (ELFが大きいと局在化)

ELF

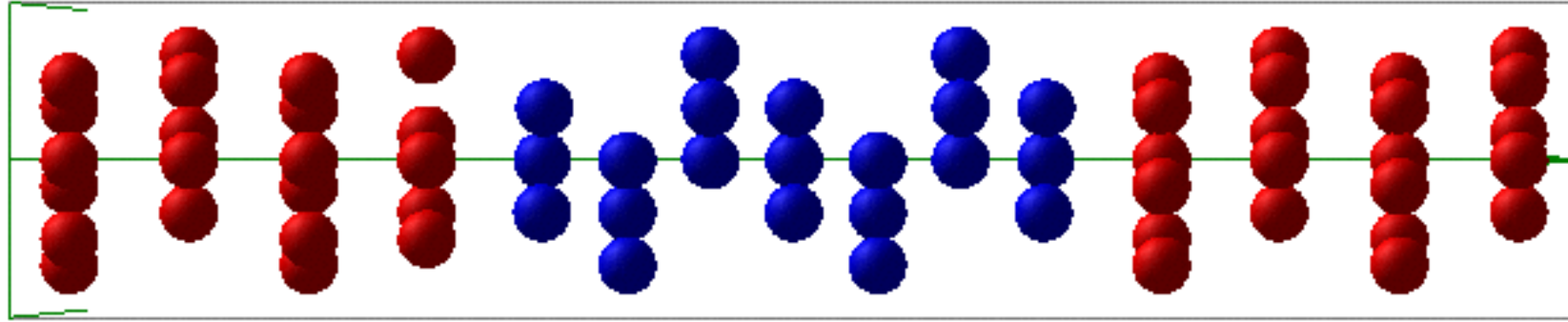
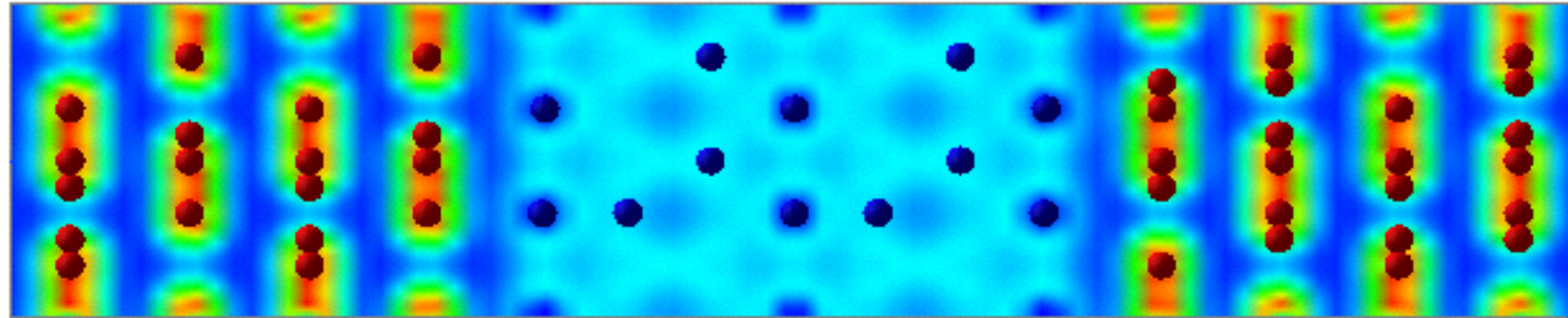
Lone pairs

局在している電子が孤立にいる

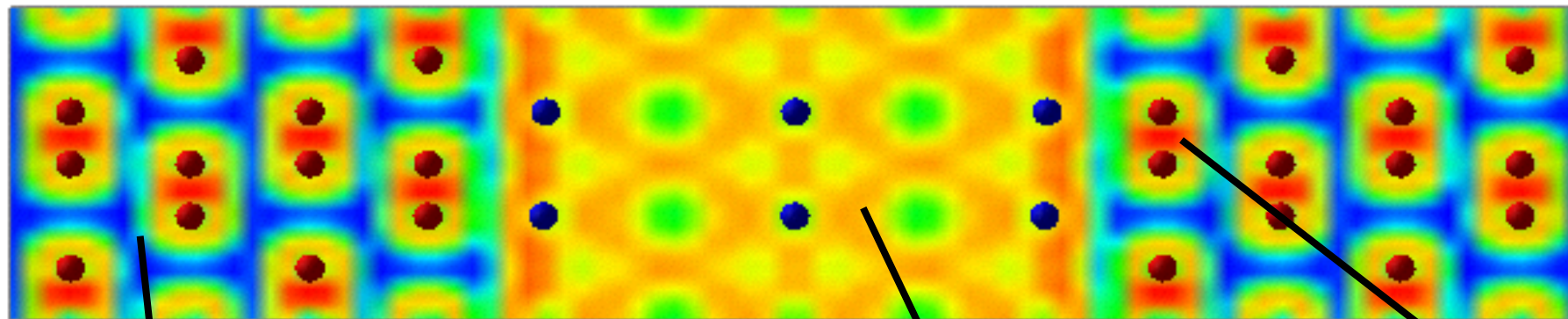


A. Savin, R. Nesper, S. Wengert, and T. F. Fässler, *Angew. Chem. Int. Ed.* **36**, 1808 (1997)

Graphite-Al-Graphite



Charge Density

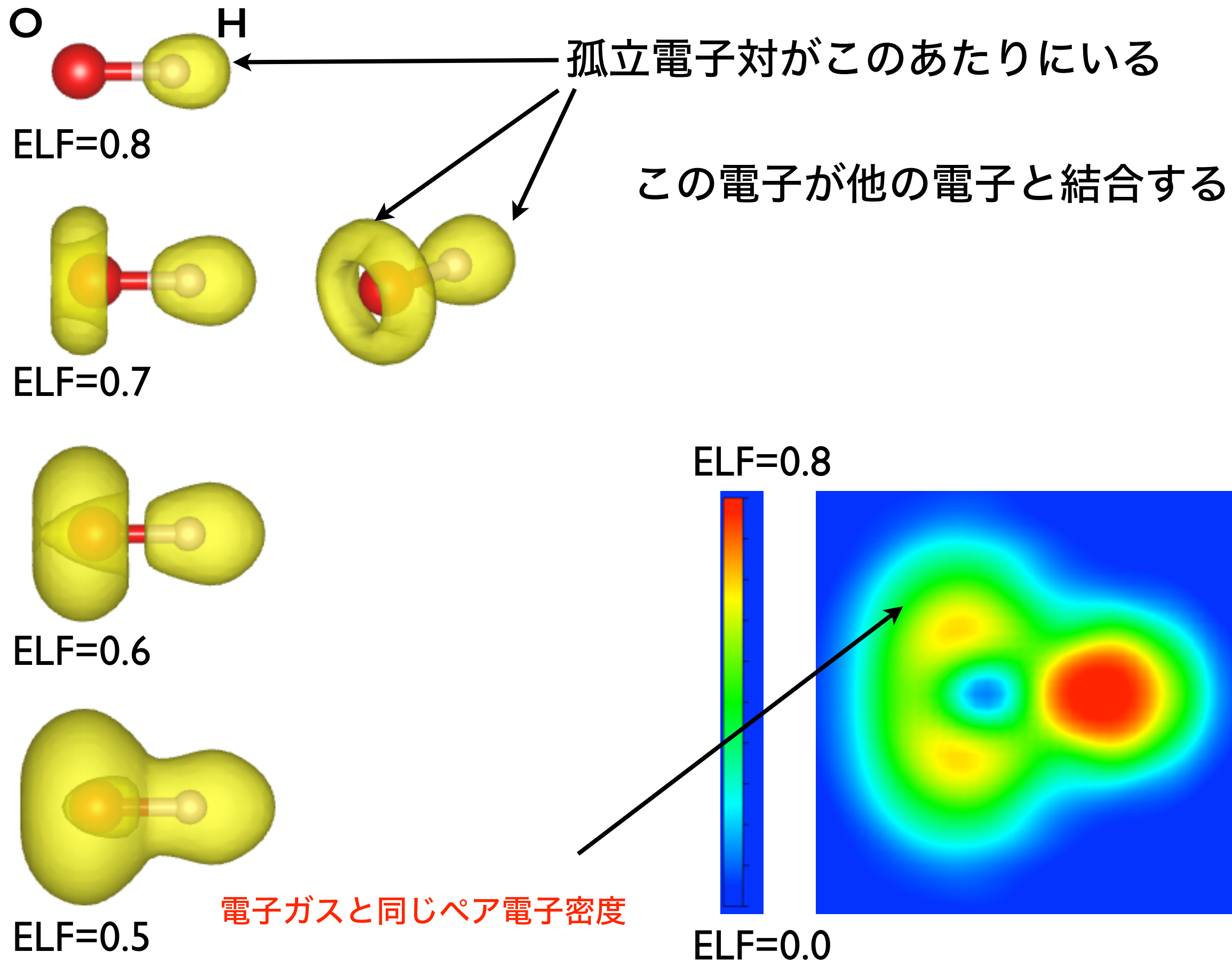


blue
unpaired electrons
(ELFが小さい)

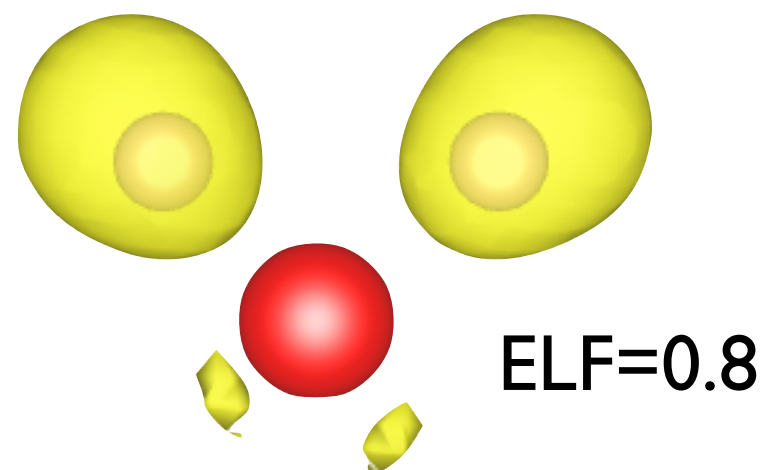
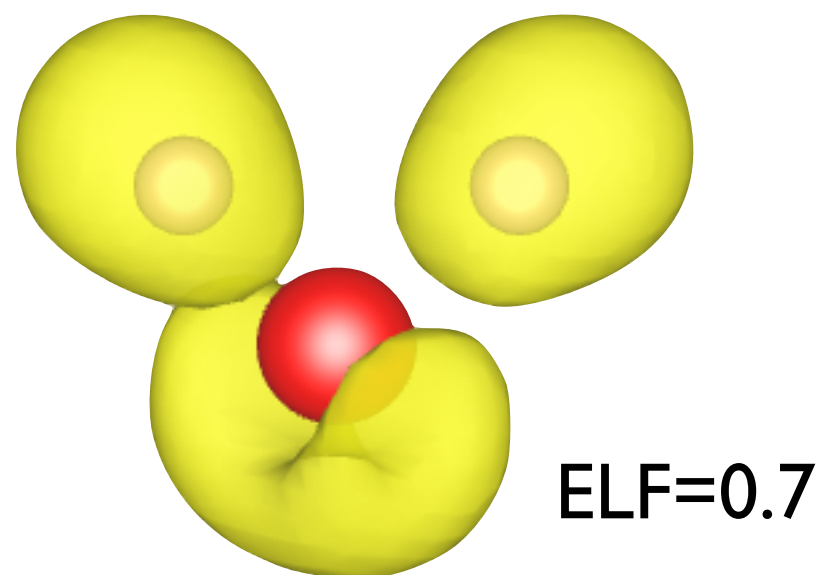
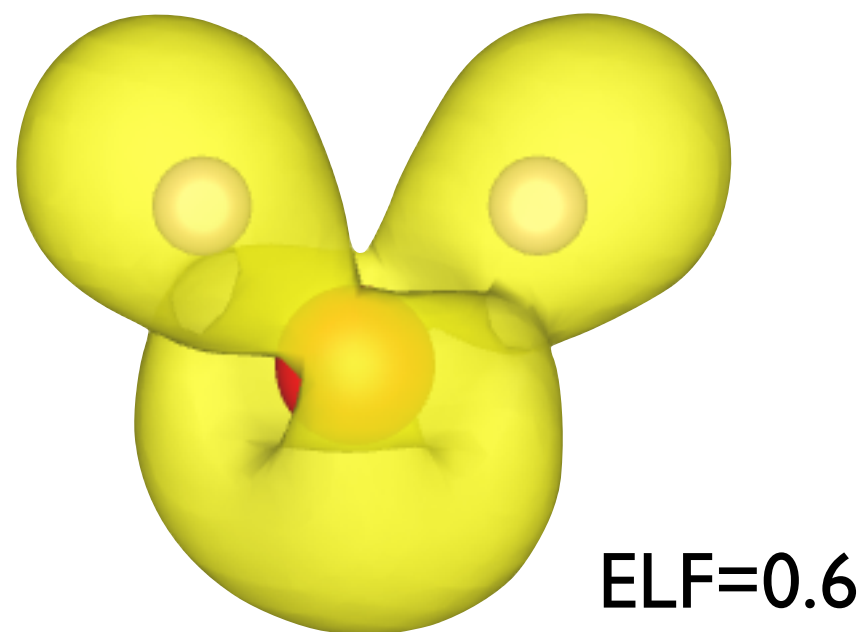
Yellow or Orange
metallic bonding

red
(localized bonding)
covalent
(ELF が大きい)

OH分子のELF



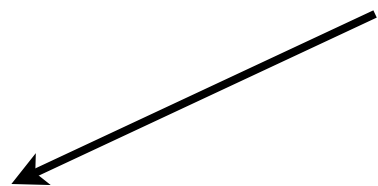
H₂O分子のELF



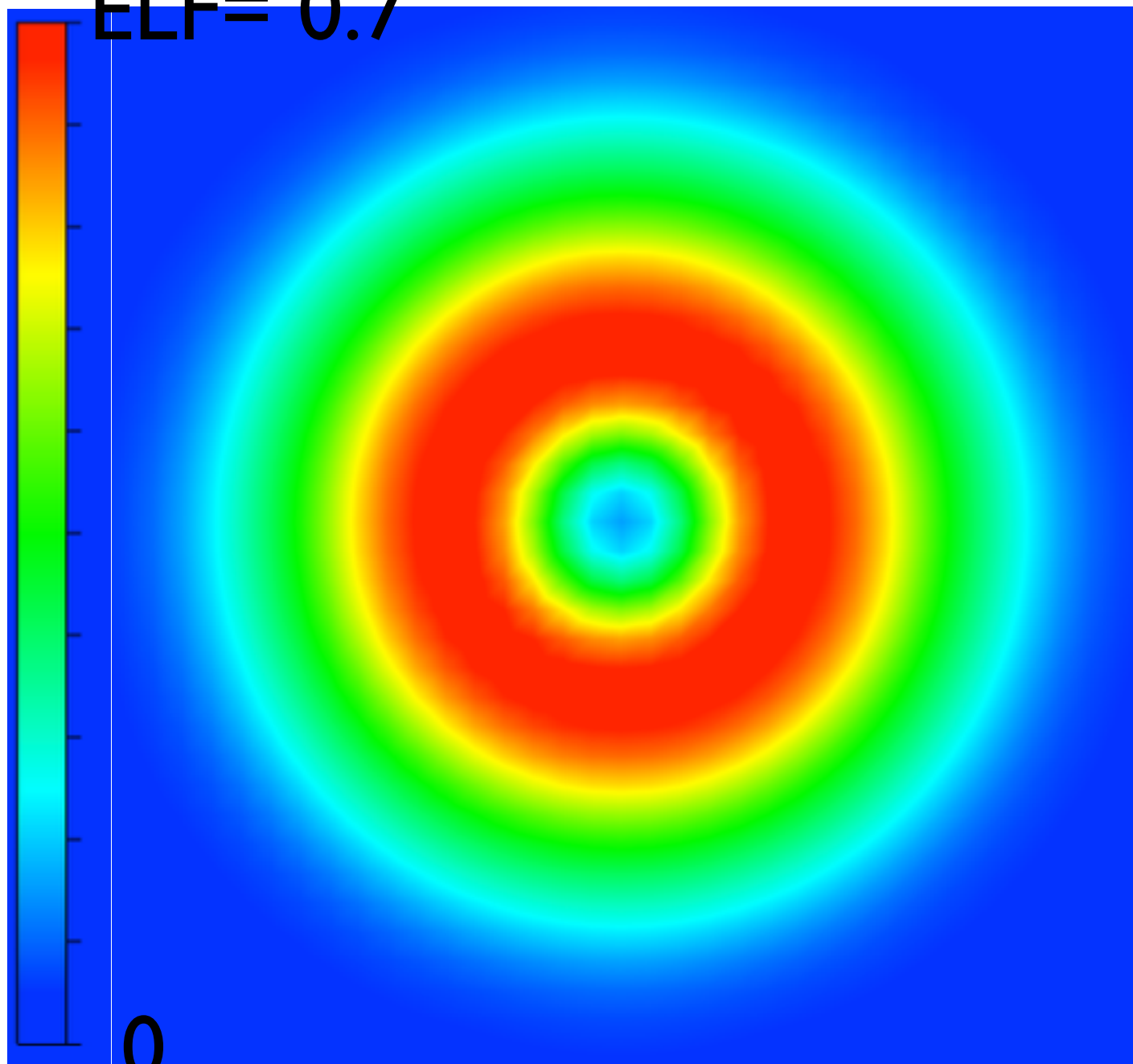
欠陥グラフェンの孤立電子対

○原子($2s^2 2p^4$)

孤立化:大



ELF = 0.7



0

Kr (クリプトン)原子 $4s^2 4p^6$

