Quantifying Electron Delocalization in Stretched Bonds

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Introduction

- Electron delocalization, a versatile tool to understand the nature of bond, stability, chemical reactivity and novel bonding situation
- Bond formation delocalizes electron, bond stretching increases the delocalization and bond breaking re-localizes the electrons on atoms
- The study of bond stretching is important to understand the bond dissociation during reaction
- One way to get the understanding of bonding situation on stretched chemical system is by looking at real space picture of what is happening to delocalized electrons in a particular molecular system as the bond is stretched[1].

$EDR(\vec{r};d)$

- The Electron Delocalization Range function $EDR(\vec{r};d)$ quantifies how much electrons at $\vec{r}$ delocalizes over distance "d" [2-4]

$$EDR(\vec{r};d) = \int d^3\vec{r}' g_d(\vec{r},\vec{r}')\,\gamma(\vec{r},\vec{r}')$$

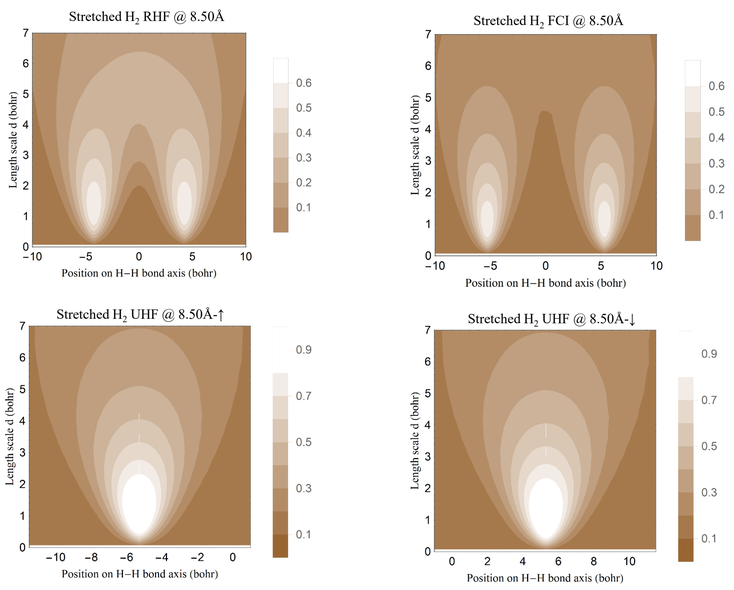
$$g_d(\vec{r},\vec{r}') \equiv \rho^{-1/2}(\vec{r})\left(\frac{2}{\pi d^2}\right)^{3/4} exp\left(-\frac{|\vec{r}-\vec{r}'|^2}{d^2}\right)$$

$$\langle EDR(d)\rangle = \int d^3\vec{r}'\rho(\vec{r})EDR(\vec{r};d)$$

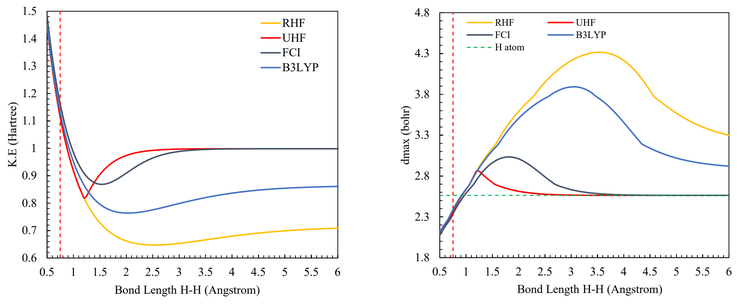
- EDR reduces the function of 6 variables γ(r, r′) to a more tractable functions of 4 variables
- Bond stretching makes it 5 variable function.

Visualizing $EDR(\vec{r};d)$

1. For point "x" along the bond

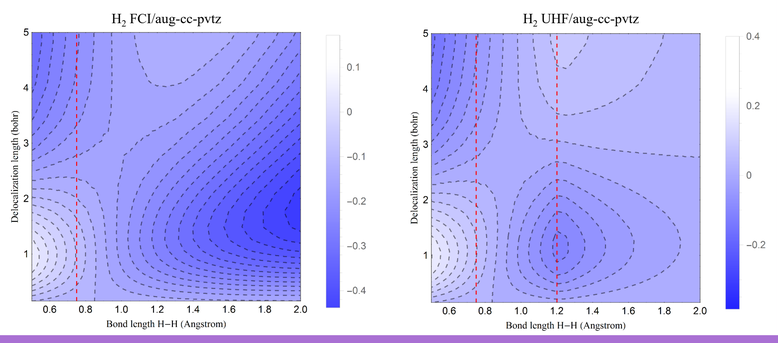


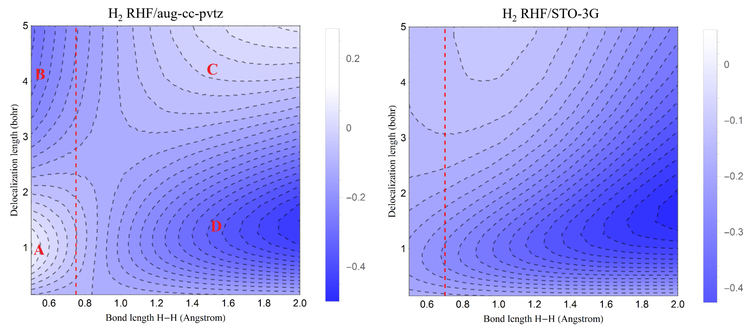
2. System averaged delocalization length d_{max}



3. Bond delocalization shifts: $\Delta EDR(A-B;d)$

- $\Delta EDR(H_2-2H;d)$ with reference to Isolated H atom
- Dotted line at 0.75Å indicates the equilibrium bond length and at 1.2Å indicates the Coulson–Fischer point





- ***Region A:*** More <u>localized</u> than isolated H atom
- ***Region B:*** More <u>delocalized</u> than isolated H atom
- ***Region C:*** More <u>delocalized</u> than isolated H atom
- ***Region D:*** More <u>localized</u> than isolated H atom
- **RHF:** Over-delocalizes at stretched bond length.
- **UHF:** First delocalizes till Coulson–Fischer point then starts localizing to separate atoms relative to the FCI
- **FCI**: The accurate one. Dissociate completely into isolated atoms
- In the absence of <u>cluster promotion or contractive promotion</u>[5] (RHF/STO-3G), formation of bond delocalizes electrons relative to the isolated atom.

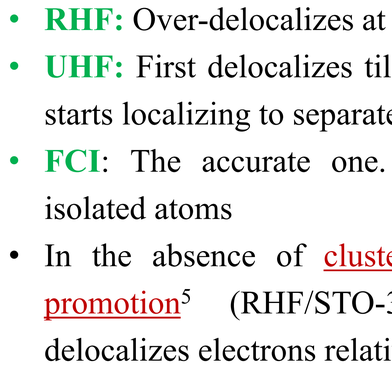
4. Real Space EDR

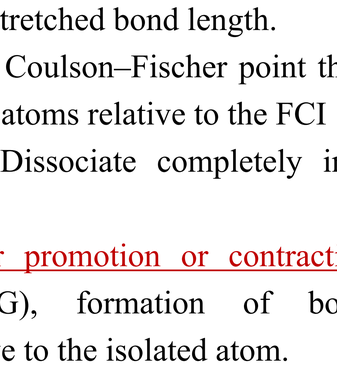
H_2 RHF $EDR(\vec{r}, d = 4.0\ bohr)$ @ 1.40Å

H_2 FCI $EDR(\vec{r}, d = 4.0\ bohr)$ @ 1.40Å

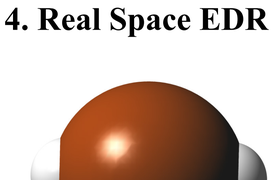
H_2^+ Molecule

- $\Delta EDR(H_2^+-H;d)$



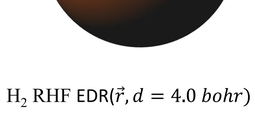


- Real Space EDR

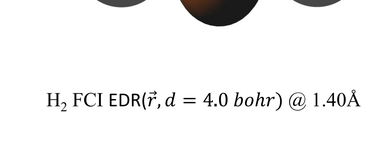


H_2^+ UHF $EDR(\vec{r}, d = 1.0\ bohr)$ @ R°

H_2^+ UHF $EDR(\vec{r}, d = 4.0\ bohr)$ @ 1.40Å



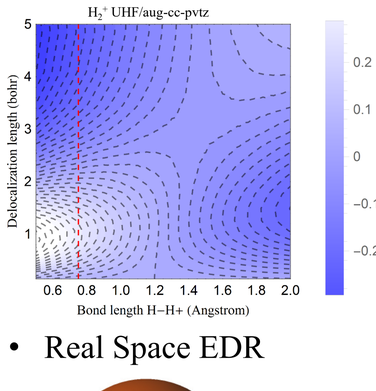
H_2^+ UHF $EDR(\vec{r}, d = 4.0\ bohr)$ @ R°

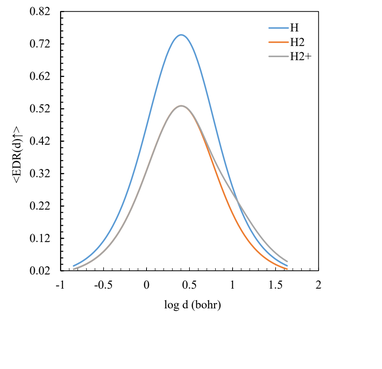


H_2^+ UHF $EDR(\vec{r}, d = 1.0\ bohr)$ @ 1.40Å

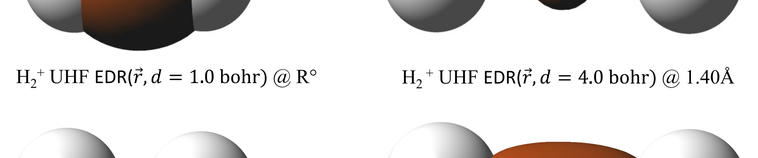
Closed-shell interactions: He_2

- $\Delta EDR(He_2-2He;d)$





- Real Space EDR

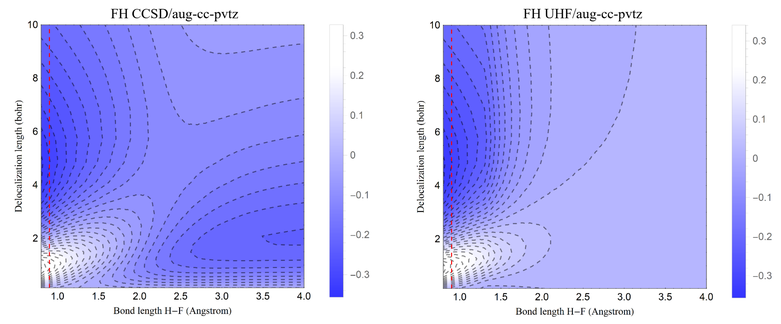


He_2 CCSD $EDR(\vec{r}, d = 0.8\ bohr)$ @ R°

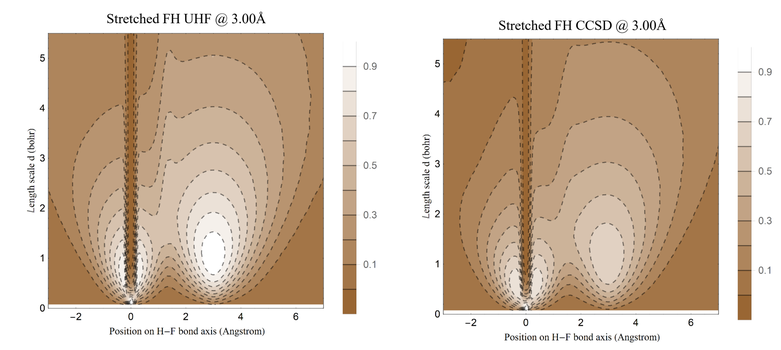
He_2 CCSD $EDR(\vec{r}, d = 0.8\ bohr)$ @ 2.0Å

Polar covalent bond: FH

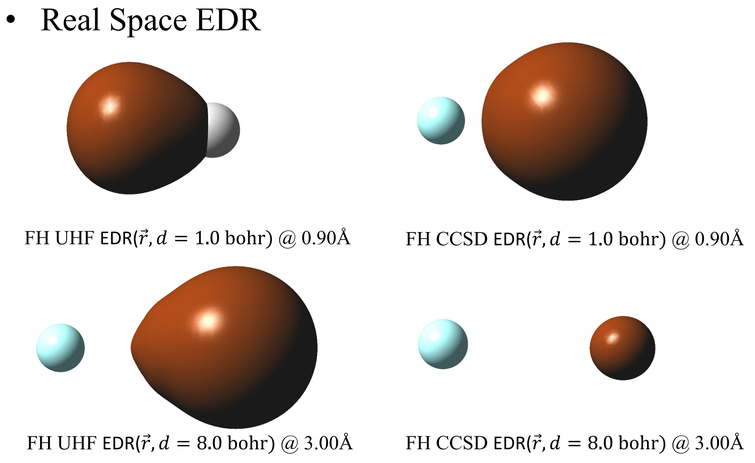
- $\Delta EDR(FH-(F+H);d)$



- For point "x" along the bond



- Real Space EDR



FH UHF $EDR(\vec{r}, d = 1.0\ bohr)$ @ 0.90Å

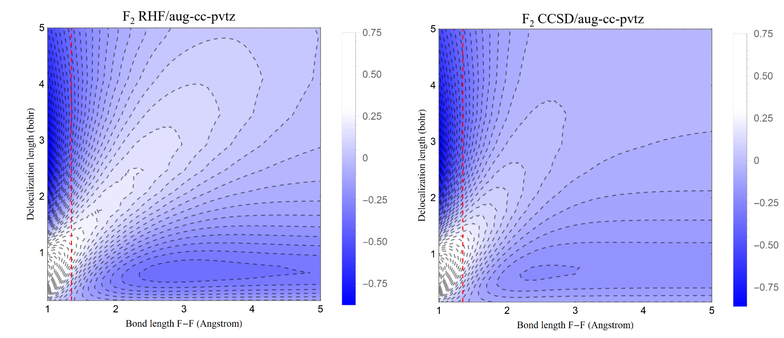
FH CCSD $EDR(\vec{r}, d = 1.0\ bohr)$ @ 0.90Å

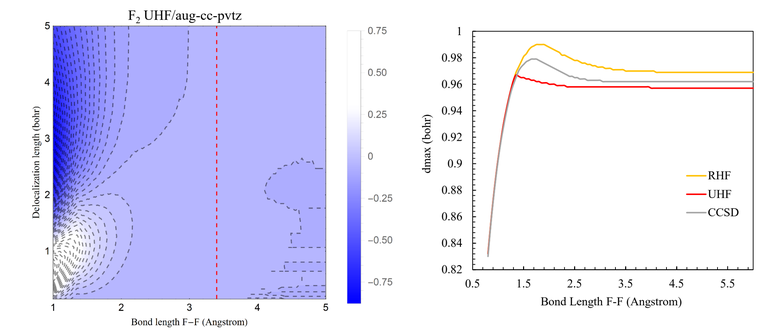
FH UHF $EDR(\vec{r}, d = 8.0\ bohr)$ @ 3.00Å

FH CCSD $EDR(\vec{r}, d = 8.0\ bohr)$ @ 3.00Å

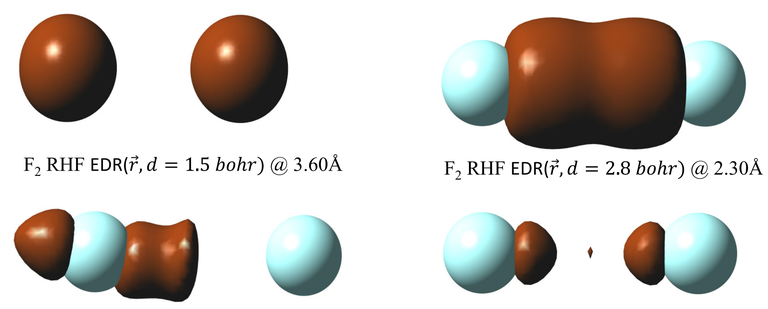
Charge-shift Bond: F_2

- $\Delta EDR(F_2-2F;d)$





- Real Space EDR



F_2 RHF $EDR(\vec{r}, d = 1.5\ bohr)$ @ 3.60Å

F_2 RHF $EDR(\vec{r}, d = 2.8\ bohr)$ @ 2.30Å

F_2 UHF $EDR(\vec{r}, d = 2.8\ bohr)$ @ 2.30Å

F_2 CCSD $EDR(\vec{r}, d = 2.8\ bohr)$ @ 2.30Å

References

1. A. J. Cohen *et al*., *Chem. Rev*., 2012, 112, 289–320.
2. B. G. Janesko *et al*., *J. Chem. Phys*., 2014, 141, 144104.
3. B. G. Janesko *et al*., *Phys. Chem. Chem. Phys*., 2015, 28, 18305-17.
4. B. G. Janesko *et al*., *J. Chem. Theory Comput*., 2016, 12,79–91.
5. K. Ruedenberg, *Rev. Mod. Phys.,* 1962, 34, 326-376.