Fluctuation of electron populations and chemical bonding

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Kathmandu 2012

Outline

Introduction

What drives chemical bonding?

- $E(\mathrm{A}-\mathrm{B}) < E(\mathrm{A}) + E(\mathrm{B})$
  - $E = T + V_{ne} + V_{ee}$. Subtle effects: $\Delta E \ll E$.
  - Solutions? Large contributions to E remain dominated by nuclei $\approx$ constant.
  - Partitioning E in chemically meaningful ways.
- Orbital paradigm: 1e picture.
  - $\Psi \approx |\phi_1 \ldots \phi_N|$. $\phi_i = \sum_\mu c_{i\mu}\chi_\mu$.
  - $T = \sum t_i \ldots$.

Lesson: No bonding without overlap, $\langle \chi_\nu | \chi_\mu \rangle = S_{\nu\mu} \neq 0$

Introduction

What drives chemical bonding? (In real space) CEJ 13, 9362, (2007)

- Real space analyses: 3D regions with chemical meaning. $R^3 = \bigcup_A \Omega_A$

$$E = \sum_A \overbrace{\{T_A + V_{ee}^{AA} + V_{en}^{AA}\}}^{E_{self}^A} + \sum_{A>B} \overbrace{\{V_{en}^{AB} + V_{ne}^{AB} + V_{nn}^{AB} + V_{ee}^{AB}\}}^{E_{int}^{AB}}$$

$$V_{ee}^{AB} = \int_{\Omega_A} \int_{\Omega_B} d\boldsymbol{r}_1 d\boldsymbol{r}_2 \; \rho_2(\boldsymbol{r}_1, \boldsymbol{r}_2)/r_{12}, \quad \rho_2 = \rho(\boldsymbol{r}_1)\rho(\boldsymbol{r}_2) - \rho_{xc}$$

$$E_{int}^{AB} = V_{cl}^{AB} + V_{xc}^{AB}, \qquad E = \sum_A E_{self}^A + \sum_{A>B} E_{int}^{AB}$$

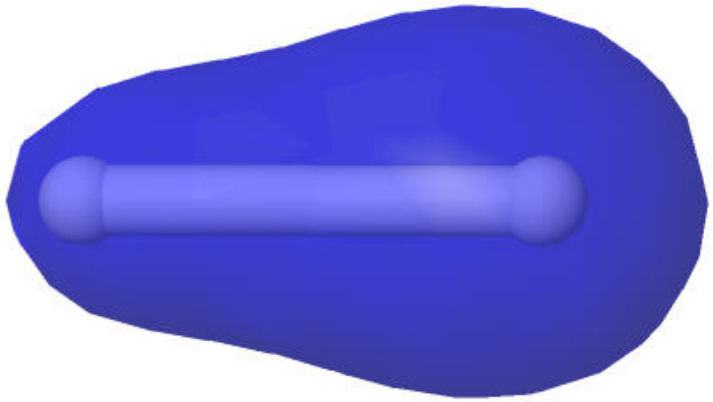
Lesson: No bonding without $V_{xc}^{AB} = \int_{\Omega_A} \int_{\Omega_B} d\boldsymbol{r}_1 d\boldsymbol{r}_2 \; \rho_{xc}(\boldsymbol{r}_1, \boldsymbol{r}_2)/r_{12}$

Introduction

What drives chemical bonding? (In real space)

- $\rho_{xc}(1,2) = \rho(1)(\rho(2) - \rho(2|1)) = \rho(1)\rho_h(2|1)$
- $V_{xc}^{AB} = \int_{\Omega_A} \int_{\Omega_B} d1d2\ \rho(1)\rho_h(2|1)/r_{12}$
- The hole has to be delocalized.
  No bonding without (hole) delocalization

H_2 $\rho_h(2|\text{rightH})$ $r = 1.4$ a.u.



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$H_2\ \rho_h(2|\mathrm{rightH})\ r = 6.0$ a.u.

Introduction

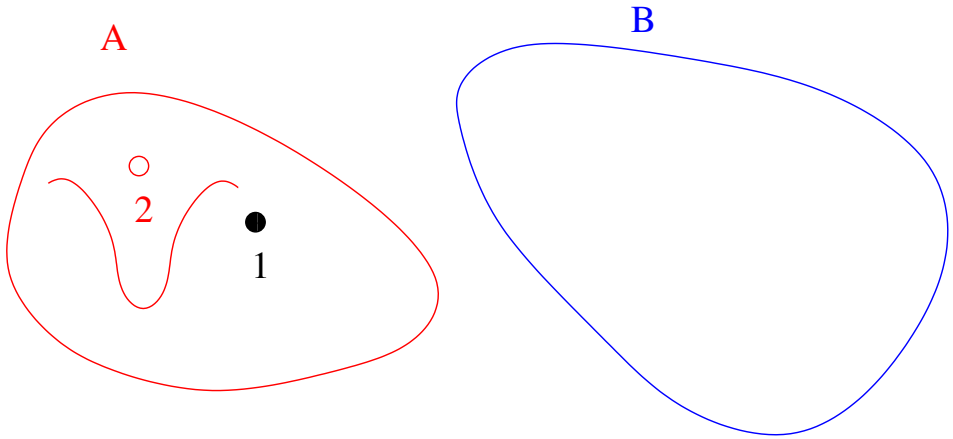
What drives chemical bonding? (In real space)

- ρ_{xc} admits a probabilistic interpretation (infinitesimal $d1, d2$).
  - $\rho(1)d1 \equiv$ P. of finding one and only one electron in $d1$.
  - $\rho_2(1,2)d1d2 \equiv$ P. one and only one electron in $d1$, one and only one electron in $d2$
  - Sample space in $d1, d2$?: $S = \{(0_{d1}, 0_{d2}), (1_{d1}, 0_{d2}), (0_{d1}, 1_{d2}), (1_{d1}, 1_{d2})\}$.
  - $\rho_{xc}(1,2)d1d2 = (\rho(1)\rho(2) - \rho_2(1,2))d1d2 = p(1_{d1})p(1_{d2}) - p(1_{d1}, 1_{d2})$
  - $\rho_{xc}(1,2)d1d2 = \sum_S p(S)n_1(S) \sum_S p(S)n_2(S) - \sum_S p(S)n_1(S)n_2(S)$
  - $\rho_{xc}(1,2)d1d2 = \langle n_1 \rangle \langle n_2 \rangle - \langle n_1 n_2 \rangle = -\mathrm{cov}(n_1, n_2)$.
  - ρ_{xc} is a covariance density.
- General: $\int_{\Omega_A} \int_{\Omega_B} d1d2 \; \rho_{xc}(1,2) = -\mathrm{cov}(n_A, n_B) = -\langle (n_A - \langle n_A \rangle)(n_B - \langle n_B \rangle) \rangle$
  - Fluctuation of population: $\mathrm{cov}(n_A, n_B) = \langle \delta_A \delta_B \rangle$
  - Similarly, $\int_{\Omega_A} \int_{\Omega_A} d1d2 \; \rho_{xc}(1,2) = \langle n_A \rangle - \mathrm{var}(n_A)$

Introduction

Delocalization & statistical independence

- Imagine two regions A, B.
- $\rho_h(2|1) \in A \; \forall 1 \in A$ (hole strictly localized in A)
  - Knowing an electron lies in A decreases p of finding another only in A.
  - $\mathrm{cov}(n_A, n_B) = 0$, $\mathrm{var}(n_A) = 0$.
  - A and B populations are statistically isolated.
  - $\rho_h(2|1) = 0 \Rightarrow \rho(1,2) = \rho(1)\rho(2) \equiv p(1_{d1})p(1_{d2}) = p(1_{d1}, 1_{d2})$

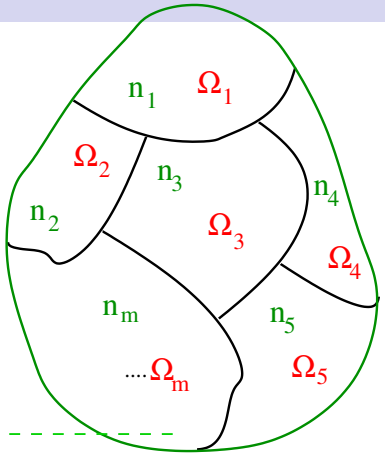


- Despite general **dependence** $\Rightarrow$ blocks of independent e's.
- Study the distribution of electron population in coarse-grained regions.
- Finding such regions $\equiv$ finding chemically distinctive blocks.

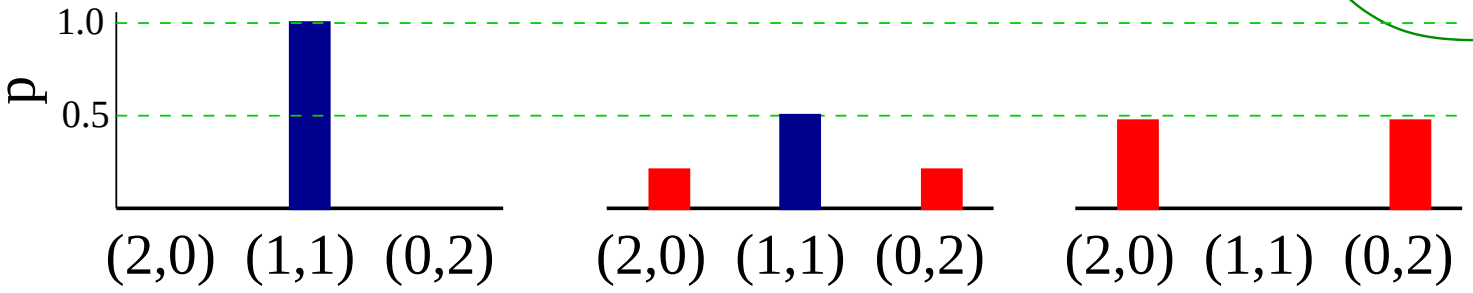
Electron Population Distribution Functions

Population Statistics

PCCP 9, 1087 (2007)



- N electrons distributed in m regions. $R^3 = \Omega_1 \bigcup \Omega_2 \bigcup \cdots \bigcup \Omega_m$
- $p(n_a, n_b, \ldots n_m) = \frac{N!}{n_a! n_b! \ldots n_m!} \int_a d1 \int_a d2 \ldots \int_m dN \, \Psi^*(1,\ldots,N)\Psi(1,\ldots,N)$
- Two equivalent boxes: $N = 2,\ m = 2$



$\mathrm{var}(n_a) = \mathrm{cov}(n_a, n_b) = 0$ $\mathrm{var}(n_a) = -\mathrm{cov}(n_a, n_b) = 0.5$ $\mathrm{var}(n_a) = -\mathrm{cov}(n_a, n_b) = 1.0$

- $N_a = \langle n_a \rangle,\ N_{aa} = N_a - \mathrm{var}(n_a),\ N_{ab} = -\mathrm{cov}(n_a, n_b),\ \delta^{AB} = 2N_{ab}$
- H_2?
  - Simple partition
  - Hartree-Fock exactly binomial (0.25,0.5,0.25)
  - From holes to models: Two independent electrons.
  - Full-CI: (0.21,0.57,0.21).

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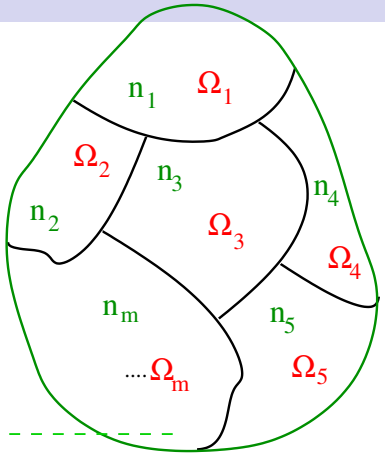

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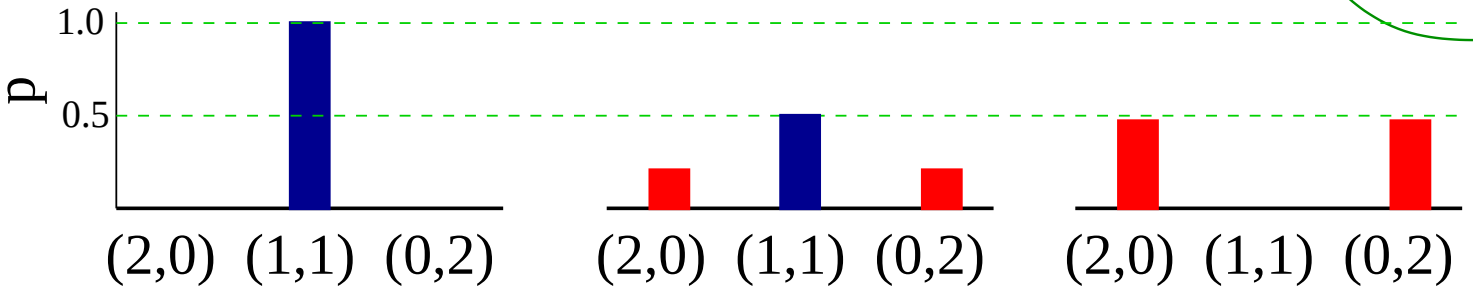

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$N_a = N_{aa} = 1, N_{ab} = 0$ $\quad N_a = 1, N_{aa} = N_{ab} = 0.5$ $\quad N_a = 1, N_{aa} = 0, N_{ab} = 1$

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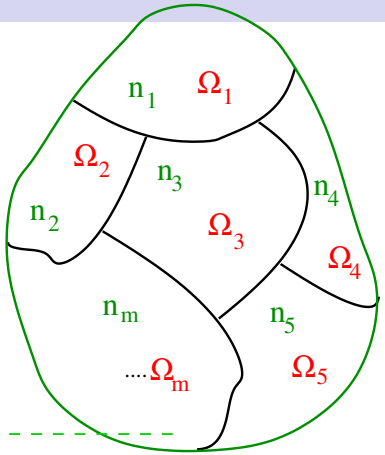

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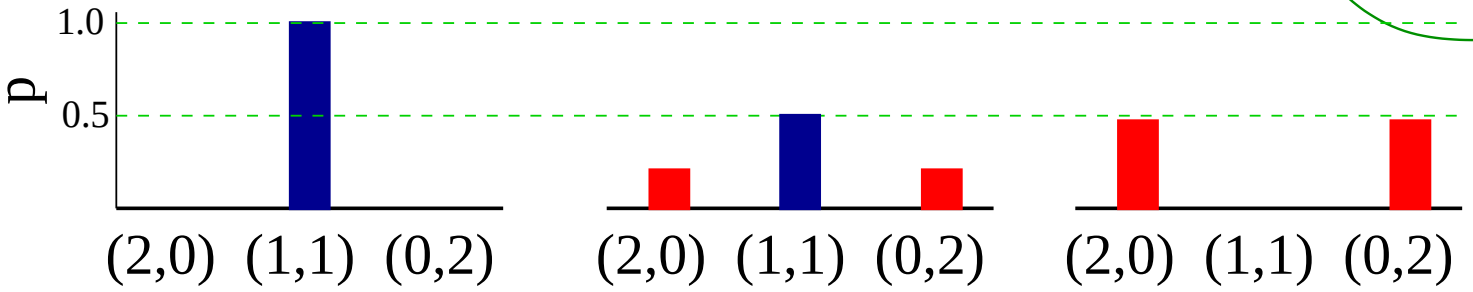

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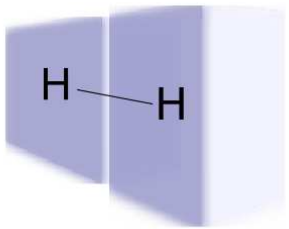
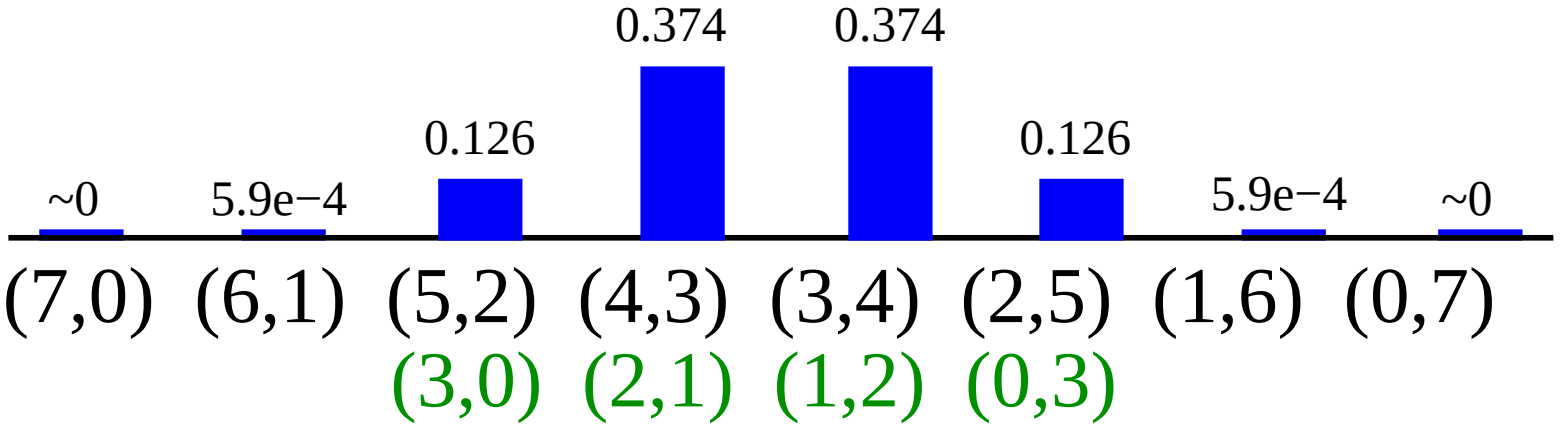


EDF examples: $^1\Sigma_g^+$ N_2

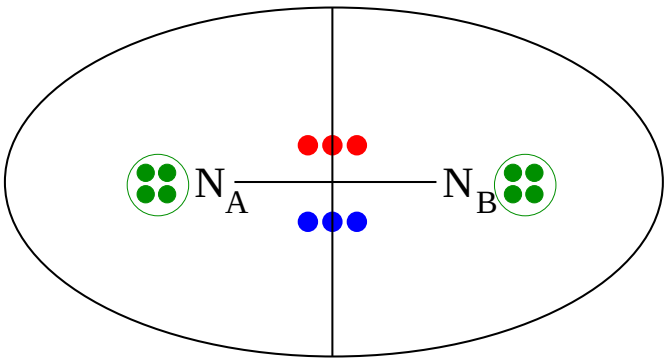
JCP 126, 094102 (2007)

- At the HF level, $p(n_a, n_b) = p^\alpha \otimes p^\beta$



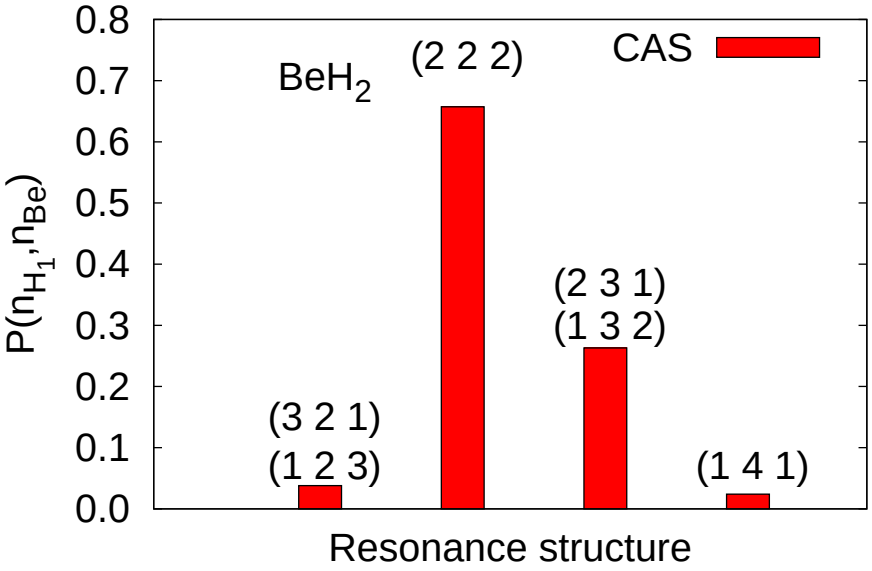
- 3 independent $1e$ p's ($p_1(0,1) = p_1(1,0) = 0.5$) provide: $p_3 = p_1 \otimes p_1 \otimes p_1$

$$p(3,0) = p(0,3) = (1/2)^3 = 0.125,\ p(2,1) = p(1,2) = 0.375$$



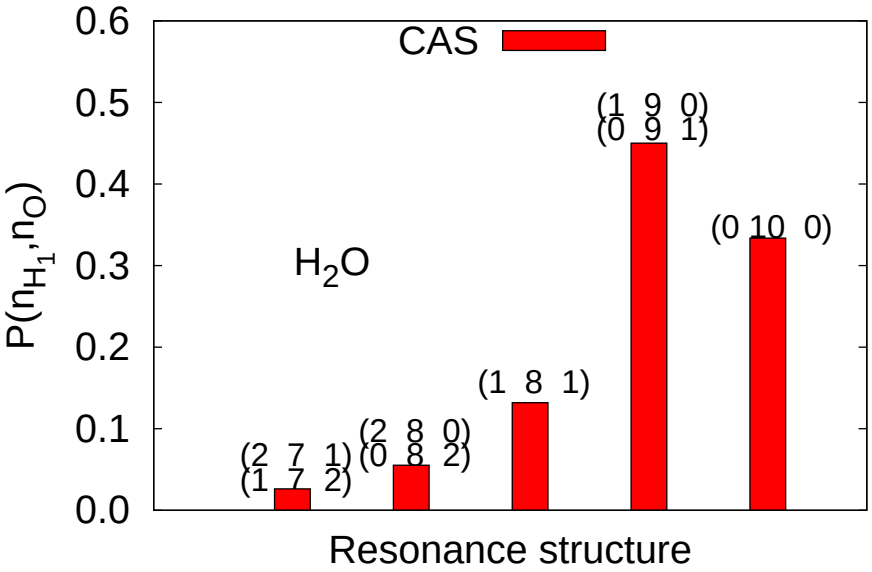
- 4 extremely localized electrons in each basin.
- 3 α, 3 β fully delocalized electrons.
- Thus... 3 bonding pairs:
  $\delta = -2\mathrm{cov}(n_a, n_b) = 3.038$
- Correlation (CAS[10,10]) hinders delocalization :$\delta = 1.987$

EDF examples: Simple QTAIM full EDFs



BeH_2

- 7:3 $H^-Be^{2+}H^-$: H-Be^+H^- $\leftrightarrow$ H^-Be^+-H
- (2 3 1) very different from (3 2 1): Chemistry
- Partial statistics available:
  - $\delta^{\mathrm{Be,H}} = 0.302$, but $\delta_0^{\mathrm{Be,H}} = 0.522$
- in diatomic BeH, $\delta^{\mathrm{Be,H}} = 0.460$



H_2O

- Less ionic than BeH_2
- 1e transfers dominate.. $q(O) = -1.087$
- but the O^{2-} contribution is important.
- Partial statistics
  - $\delta^{\mathrm{O,H}} = 0.637$, and $\delta_0^{\mathrm{O,H}} = 0.640$

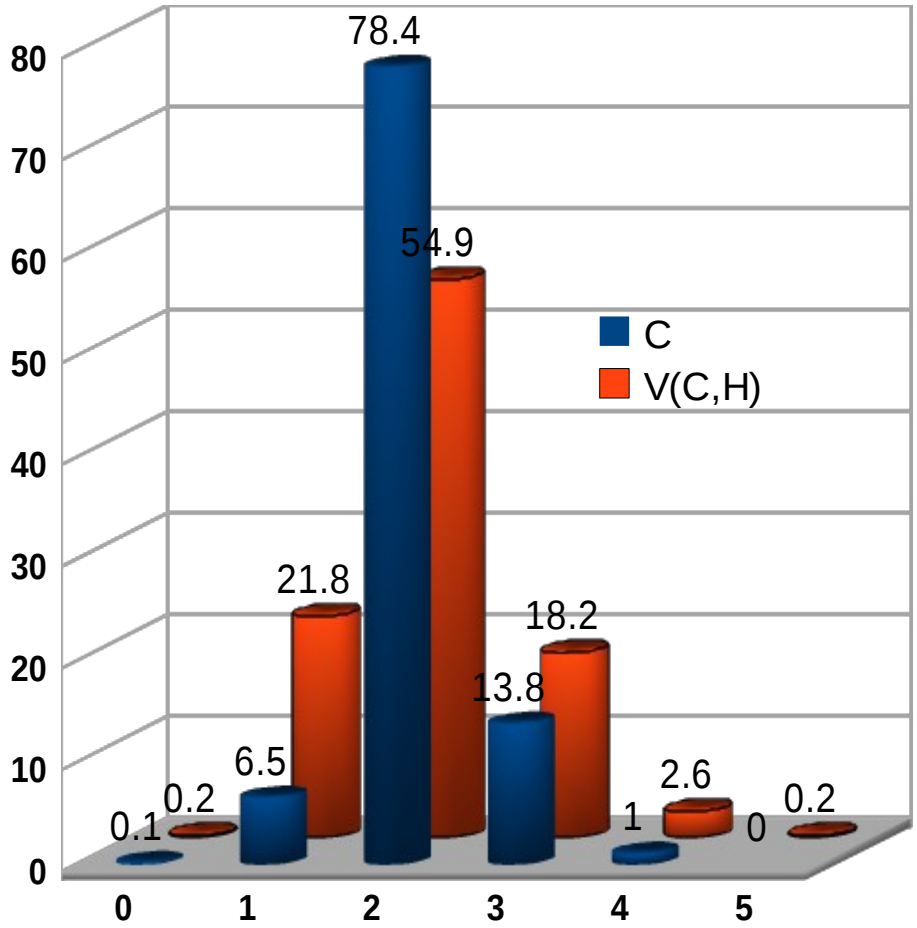
Lego example

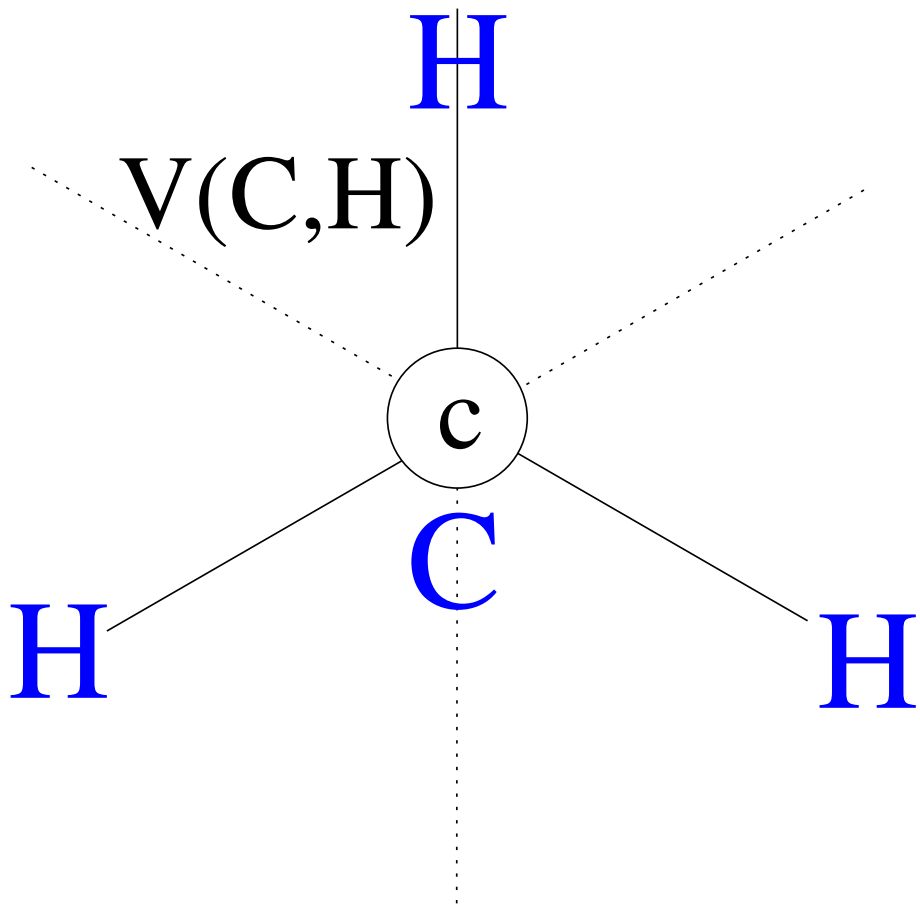
C_2H_n ($n = 6, 4, 2$)

- Examine bonding between the CH_3, CH_2 or CH groups.
- Hypothesis: non-polar single, double, triple bonds.
- The modeled α or β EDFs are easily constructed:
  C_2H_6: $(\frac{1}{2}, \frac{1}{2}) = (0.5, 0.5)$
  C_2H_4: $(\frac{1}{2}, \frac{1}{2}) \times (\frac{1}{2}, \frac{1}{2}) = (0.25, 0.50, 0.25)$
  C_2H_2: $(\frac{1}{2}, \frac{1}{2}) \times (\frac{1}{2}, \frac{1}{2}) \times (\frac{1}{2}, \frac{1}{2}) = (0.125, 0.375, 0.375, 0.125)$
- ... to be compared with the computed HF data.
  C_2H_6: $(\cdots, 0.0187, 0.4811, 0.4811, 0.0187, \cdots)$
  C_2H_4: $(\cdots, 0.061, 0.250, 0.4878, 0.250, 0.061, \cdots)$
  C_2H_2: $(\cdots, 0.1251, 0.3747, 0.3747, 0.1251, \cdots)$
- Atomic (or group) regions **seem to isolate quite well groups of localized and delocalized electrons in agreement with chemical wisdom**

EDFs for other space partitions: ELF domains

- CH_4: $p(n_a)$

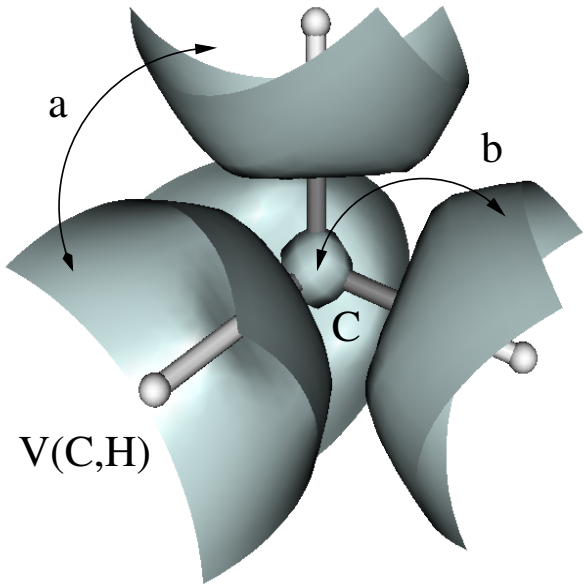




How large is delocalization among localized domains?

- $\delta(\mathrm{CV}, \mathrm{VV}) = 0.12, 0.37$.
- QTAIM $\delta(\mathrm{CH}, \mathrm{HH}) = 0.98, 0.04$. Where is simplicity hidden?

p	Core	V(C,H1)	V(C,H2)	V(C,H3)	V(C,H4)
0.2069	2	2	2	2	2
0.0347	2	1	2	2	3
0.0161	3	1	2	2	2
0.0079	2	3	3	1	1
0.0065	1	3	2	2	2
0.0044	2	1	1	2	4
0.0039	3	3	1	2	1
0.0024	2	3	3	2	0
0.0016	1	3	3	2	1
0.0012	3	3	2	2	0
0.94					



- Build a model: α set, forget the core
  - 4 α electrons in the 4 V(C,H) regions.
  - Elementary events: inter V jumps.
  - Each electron has a probability j of jumping to any of the other V's
  - Each electron has a probability s of staying in its own V.
  - $s + 3j = 1$.

How large is delocalization among localized domains?

JCP 131, 124125 (2009)

- α probs. without core (HF).

p	V1	V2	V3	V4
0.4960	1	1	1	1
0.0377	2	0	1	1
0.0041	2	2	0	0
0.0021	3	1	0	0
0.0000	4	0	0	0

- $s = 0.832,\ j = 0.056$. (Only one parameter).
- Very good fit. **Lessons:**
  - The small $p(2,2,2,2,2) \approx 0.21$ value is due to the large number of elementary events. (In the model, $256 = 4^4$).
  - Each V electron is quite rigidly sit in its V region. p(moving)=0.168.
  - Rigid $\alpha + \beta$ tetrahedra give rise to the 4 α, β pairs.
  - Including the core, a 3-parameter model (C-V jumps are asymmetric) reproduces extremely well the distribution.

How large is delocalization among localized domains?

JCP 131, 124125 (2009)

- α probs. without core (HF).

p	V1	V2	V3	V4	Model	p(Model)
0.4960	1	1	1	1	$s^4 + 6s^2j^2 + 8sj^3 + 9j^4$	0.4930
0.0377	2	0	1	1	$s^3j + 2s^2j^2 + 5sj^3 + 4j^4$	0.0374
0.0041	2	2	0	0	$2s^2j^2 + 2sj^3 + 2j^4$	0.0046
0.0021	3	1	0	0	$s^2j^2 + 2sj^3 + j^4$	0.0024
0.0000	4	0	0	0	j^4	0.0000

- $s = 0.832,\ j = 0.056$. (Only one parameter).
- Very good fit. **Lessons:**
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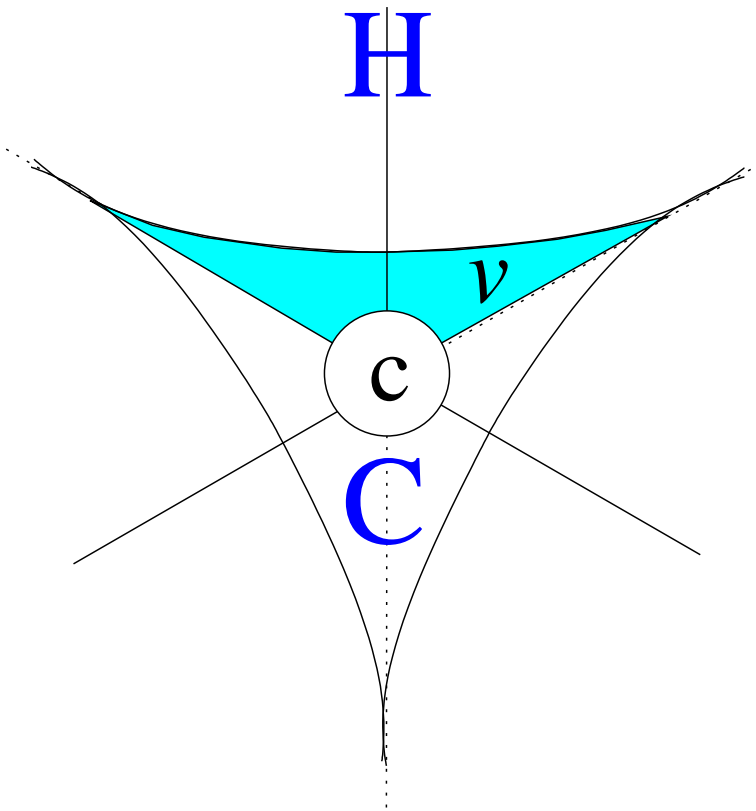
  - Including the core, a 3-parameter model (C-V jumps are asymmetric) reproduces extremely well the distribution.

Is deeper insight possible? Joint atomic & localization regions analysis.

- What happens inside a localization basin? (e.g. V(c,H))
  - Part of the bond valence is in C, part in H
  - V(C,H1)=V=H1$\cup v1$; C=Carbon atom=$c \cup v1 \cup v2 \cup v3$



- Populations: $\langle n \rangle_A$ & δ's ($\delta \equiv -2\mathrm{cov}$)

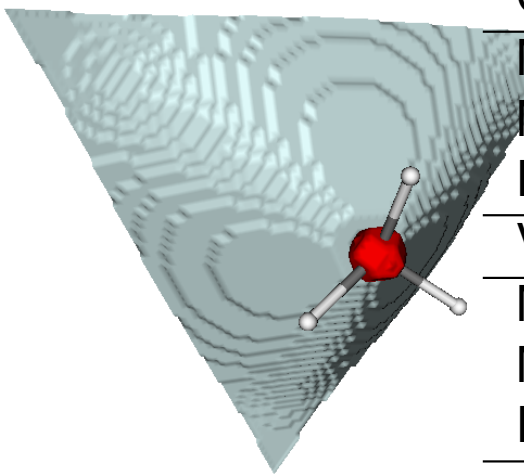
C	H	c	V	v
5.816	1.034	2.083	1.967	0.933
cv	cH	$v1, v2$	$v1$,H1	$v1$,H2
0.075	0.048	0.125	0.632	0.099

- δ(c,V)$= 0.125 = 0.075 + 0.049$
- δ(V1,V2)$=0.371 = 0.043 + 2 \times 0.099 + 0.125$
- δ(C,H)$=0.977 = 0.048 + 3 \times 0.099 + 0.632$
- Rigid tetrahedra with mobile e's within lobes.

- For the isolated C atom, $\delta(c, v) \approx 0.10, \quad \delta(v1, v2) \approx 0.37$

Are other localization regions possible? JCC 28, 442 (2007)

- Use p's to build domains:
  - Maximum probability domains (MPD's): Shape optimization $\max(p(n))$.
  - Minimum variance domains (MVD's): Shape optimization $\min(\text{relvar})$



Core	$p(0)$	$p(1)$	$p(2)$	$p(3)$	$p(4)$
MPD	0.003	0.090	0.785	0.118	0.008
MVD	0.003	0.090	0.785	0.115	0.007
ELF	0.001	0.065	0.784	0.138	0.001
V(C,H)	$p(0)$	$p(1)$	$p(2)$	$p(3)$	$p(4)$
MPD	0.024	0.224	0.552	0.174	0.024
MVD	0.023	0.219	0.552	0.179	0.025
ELF	0.002	0.218	0.549	0.182	0.026

  - In CH_4, $p(2)$ MPD's very close to ELF basins (symmetry). MPD's & MVD's may overlap.

Conclusions, References

- More quantitative ELF analyses are possible and useful.
- Precise meaning of ELF EDFs?
- Even though ELF basin populations provide nice Lewis values in many cases... their statistical decomposition shows fairly wide distributions.
- Some papers:
  - *Chem. Phys. Lett.* **454**, 396 (2008);
  - *J. Phys. Chem.* A **111**, 1084 (2007);
  - *J. Chem. Phys.* **126**, 094102 (2007);
  - *Phys. Chem. Chem. Phys.* **9**, 1087 (2007);
  - *J. Chem. Phys.* **127**, 144103 (2007);
  - *J. Chem. Phys.* **131**, 124125 (2009);.
  - *Theor. Chem. Acc.*, DOI:10.1007/s00214-010-0809-4 (2010).