Chemical bonding in real (or position) space: the quantum theory of atoms in molecules and beyond

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Outline

1. Electron density & Atoms in Molecules.

2. A brief QTAIM introduction.

3. Interacting Quantum Atoms (IQA) & Chemical Bonds.

4. Examples.

1. Introduction.

- Quantum Chemistry is now near Dirac's reductionist goal:
  - Theoretical (DFT) & Computational achievements allow us to reach *chemical* accuracy in everyday molecules.

- Problems, however, if chemical insight is regarded:
  1. Wavefunction information.
  2. Epistemology of emergent phenomena.

- Chemistry has a language defined before Quantum Mechanics.
  - Chemists envision entities in interaction
  - These entities live in 3D space, and are embodied with properties: bonds, transferability, characteristic energies and reactivities...

- We need interpretations!.

- How do we extract chemically meaningful information from Ψ?

$$\Psi \rightleftharpoons \text{Chemistry}$$

Density and the chemical bond.

- As old as Quantum Chemistry.

- Properly put into context by Berlin (1950's): Hellmann-Feynman theorem and charge redistributions.
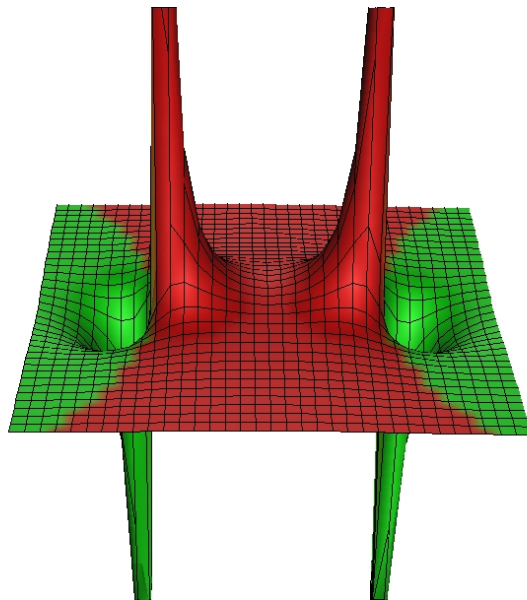
- Binding & antibinding regions ...,

- build–up of density in the binding region.

- Difficult to generalize to polyatomics.

- It leads naturally to study Difference maps: $\Delta\rho = \rho_f - \rho_i$

- Usually, $\rho_i = \sum_A \rho_A (in\ vacuo)$

- The reference problem is huge.

$\Delta\rho$ map for F_2.
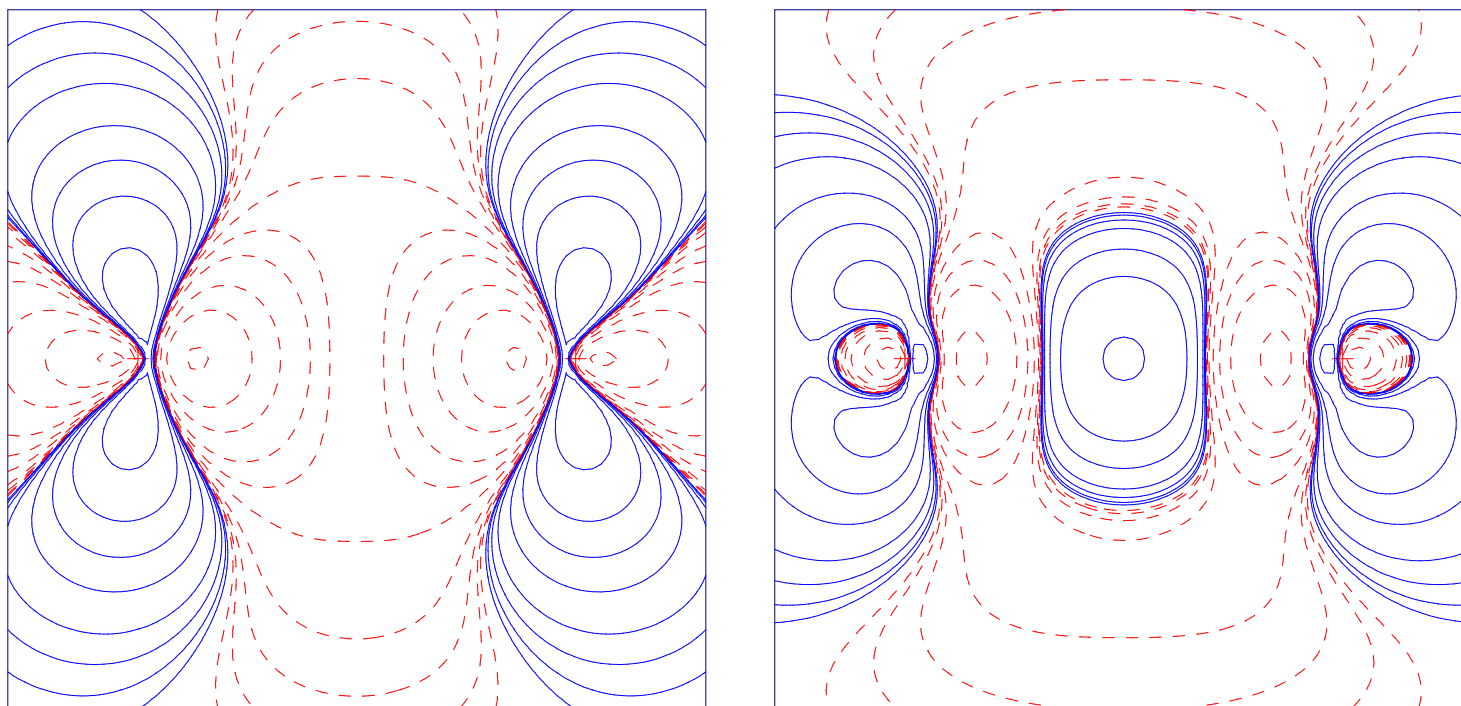
spherically averaged ^2P F's $2p_z$ aligned F's

- How to avoid the indefinitions? Look at derivatives.

  - Charge accummulation & charge depletion

- Topological Theories of the Chemical Bond.

- **The topology induced by many scalar fields constructed from reduced density matrices carry chemical information**

  1. Take a scalar field $f : D \to R$

  2. Construct its gradient field: ∇f

  3. Obtain its CPs, isolate local maxima (M) or minima (m).

  4. Build their attraction or repulsion basins: $D = \bigcup_{M(m)} D_{M(m)}$

- A number of them, according to the scalar studied: (ρ, ELF, ...)

- **The QTAIM is based on the attraction basins of ρ.**

  - Part of many standard chemistry curricula. Many advocates and detractors.
    - A theory without external reference
    - A theory of atoms in molecules, and groups of atoms or functional groups.
    - A theory of bonding: The CP's carry chemical information
    - An additive partition of observables into basin contributions
    - A theory of binding, through IQA.

A mathematical digression: Dynamical systems.

A **Dynamical system** is a vector field $\mathbf{y}$ defined over an n–dimensional variety M.

-If the field is differentiable, then the set of differential equations $d\mathbf{r}/dt = \mathbf{y}$ univocally defines the trajectories $\mathbf{r}(t)$ of the DS..

-Gradient fields:

Let us consider a *scalar function* ρ.

$$\begin{aligned}
\mathbb{R}^3 &\rightarrow \mathbb{R} \\
\boldsymbol{r} &\rightarrow \rho(\boldsymbol{r}),
\end{aligned}$$

that we will call potential.

The DS associated to ρ is the $\boldsymbol{\nabla}\rho = \boldsymbol{f}$ vector field, defined by the action of the gradient operator on the scalar field ρ:

$$\boldsymbol{\nabla}\rho = \boldsymbol{\imath}\,\frac{\partial\rho}{\partial x} + \boldsymbol{\jmath}\,\frac{\partial\rho}{\partial y} + \boldsymbol{k}\,\frac{\partial\rho}{\partial z} = \rho_x\boldsymbol{\imath} + \rho_y\boldsymbol{\jmath} + \rho_z\boldsymbol{k}.$$

The trajectories of this DS, also known as flux, force, field, or gradient lines, are defined by:

$$\boldsymbol{r}(t) = \boldsymbol{r}(t_0) + \int_{t_0}^{t} \boldsymbol{\nabla}\rho(\boldsymbol{r}(t))dt.$$

Some of their properties are:

1. One and only one trajectory of $\boldsymbol{\nabla}\rho$ passes through any point $\boldsymbol{r}$ of the domain space. This is equivalent to saying that field trajectories of $\boldsymbol{\nabla}\rho$ do never cross each other. The only exception to this rule is found at the so-called critical points of the field.

2. At each point $\boldsymbol{r}$, the vector $\boldsymbol{\nabla}\rho(\boldsymbol{r})$ is tangent to the field line passing through that point.

3. Given that the gradient field always points along the steepest ascent direction of ρ, the trajectories of $\boldsymbol{\nabla}\rho$ are *orthogonal to the isoscalar lines*.

4. *Each trajectory must originate or end up either at a point where* $\boldsymbol{\nabla}\rho(\boldsymbol{r}) = \boldsymbol{0}$, *or at infinity.*

Critical points of a field:

- Those points in $\mathbb{R}^3$ that satisfy the condition $\dot{r} = 0$ are called **critical points**.

- $\alpha-$ **and** $\omega-$**limits of a point** p:
  The geometrical locus of $\lim_{t \to -\infty} r$ y $\lim_{t \to +\infty} r$, respectively.

- Characterization: Based on the behavior of the DS in the vicinities of the CPs. That is why it is useful to study the linearized system (LS), a first order truncated approximation to the DS close to the critical point under scrutiny, r_c:

$$\dot{r} = f(r) \simeq f(r_c) + \mathbb{J}(r - r_c)$$
$$= \mathbb{J}(r - r_c),$$

  where $\mathbb{J}$ is the Jacobian matrix of the system at r_c,

$$\mathbb{J} = \frac{\partial f(x, y, z)}{\partial (x, y, z)}.$$

  In 3D gradient DS's, the jacobian of the vector field at the CP may be identified with the Hessian matrix:

$$\mathbb{J}(\boldsymbol{\nabla}\rho) = \mathbb{H},$$

$$\mathbb{H} = \begin{pmatrix} \frac{\partial^2 \rho}{\partial x^2} & \frac{\partial^2 \rho}{\partial x \partial y} & \frac{\partial^2 \rho}{\partial x \partial z} \\ \frac{\partial^2 \rho}{\partial y \partial x} & \frac{\partial^2 \rho}{\partial y^2} & \frac{\partial^2 \rho}{\partial y \partial z} \\ \frac{\partial^2 \rho}{\partial z \partial x} & \frac{\partial^2 \rho}{\partial z \partial y} & \frac{\partial^2 \rho}{\partial z^2} \end{pmatrix}_{r_c} .$$

Redefining the origin of the reference frame at the critical point,

$$\dot{\boldsymbol{r}} = \mathbb{H}\boldsymbol{r}. \tag{1}$$

Provided that $\mathbb{H}$ is a symmetric matrix, we may uncouple the DS easily.

If $\mathbb{U}$ is the orthogonal matrix that diagonalizes $\mathbb{H}$ at a CP:

$$\mathbb{U}^t \mathbb{H} \mathbb{U} = \mathrm{diag}(\lambda_i),$$

and $\boldsymbol{\eta}$ is the eigen reference frame of $\mathbb{H}$,

$$\boldsymbol{r} = \mathbb{U}\boldsymbol{\eta},$$

$$\dot{\boldsymbol{r}} = \mathbb{U}\dot{\boldsymbol{\eta}}.$$

$$\eta_i(t) = \eta_i(t_0)e^{\lambda_i(t-t_0)}, \{i = 1,3\}.$$

The λ_i coefficients are also called characteristic or Lyapunov exponents. And the eigen frame is usually known as the principal system of curvature, its axes the principal curvature axes, which coincide with the directions along which the field varies mostly.

- There exist 4 different types of non-degenerate CPs in $\mathbb{R}^3$. In this field it is customary to classify them according to a terminology with two integer indices (r, s). The *rank*, r, is defined as the number of non vanishing curvatures at the CP, and the *signature*, s, as the difference between the number of positive and negative curvatures.

- The set of points with field lines ending at a given CP is known as the **basin of attraction** of the CP.

- The set of points with field lines starting at a given CP is known as the **basin of repulsion** of the CP.

- Properties of the different types of CPs in $\mathbb{R}^3$:

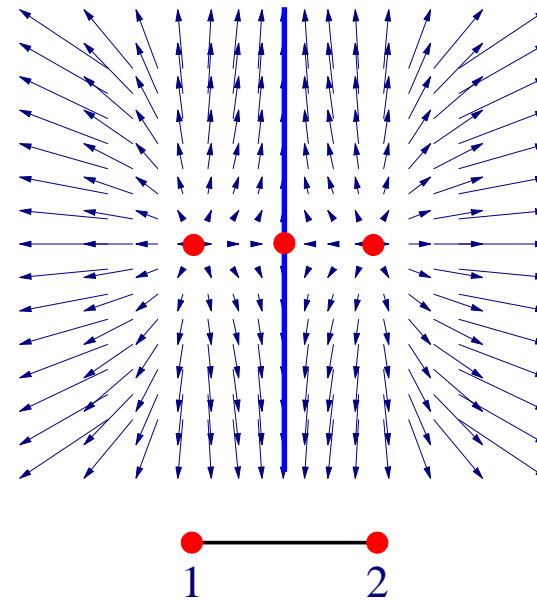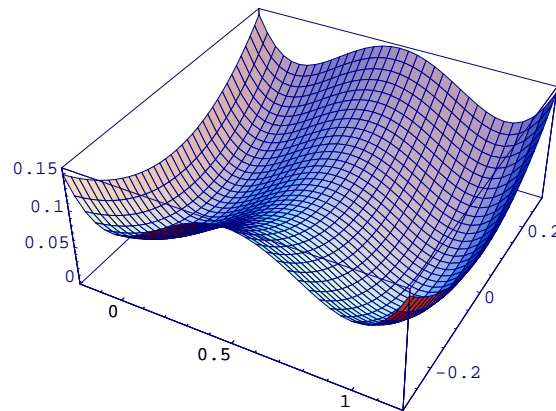| (r,s)	Curvatures	Description	AB	RB
$(3,-3)$	$\lambda_i < 0 \quad \forall i$	Local Maximum (attractor)	3D	0D
$(3,-1)$	$\lambda_1, \lambda_2 < 0; \lambda_3 > 0;$	First order saddle	2D	1D
		Maximum in $\boldsymbol{\eta}_1$ and $\boldsymbol{\eta}_2$; minimum in $\boldsymbol{\eta}_3$		
$(3,+1)$	$\lambda_1, \lambda_2 > 0; \lambda_3 < 0;$	Second order saddle	1D	2D
		Maximum in $\boldsymbol{\eta}_3$ and minimum in $\boldsymbol{\eta}_1$ and $\boldsymbol{\eta}_2$		
$(3,+3)$	$\lambda_i > 0 \quad \forall i$	Local Minimum (source)	0D	3D
$(2,-2)$	$\lambda_1, \lambda_2 < 0; \lambda_3 = 0;$	Local Maximum in $\boldsymbol{\eta}_1$ y $\boldsymbol{\eta}_2$	2D	0D
$(2,0)$	$\lambda_1 < 0; \lambda_2 = 0; \lambda_3 > 0$	Saddle point.	1D	1D
		Maximum in $\boldsymbol{\eta}_1$ and minimum in $\boldsymbol{\eta}_3$		
$(2,+2)$	$\lambda_1 = 0; \lambda_2, \lambda_3 > 0$	Local minimum in $\boldsymbol{\eta}_2$ y $\boldsymbol{\eta}_3$	0D	2D
$(1,-1)$	$\lambda_1 < 0; \lambda_2 = \lambda_3 = 0$	Local Maximum in $\boldsymbol{\eta}_1$	1D	0D
$(1,+1)$	$\lambda_1 = \lambda_2 = 0; \lambda_3 > 0$	Local Minimum in $\boldsymbol{\eta}_3$	0D	1D
$(0,0)$	$\lambda_1 = \lambda_2 = \lambda_3 = 0$		0D	0D

- **Image:**
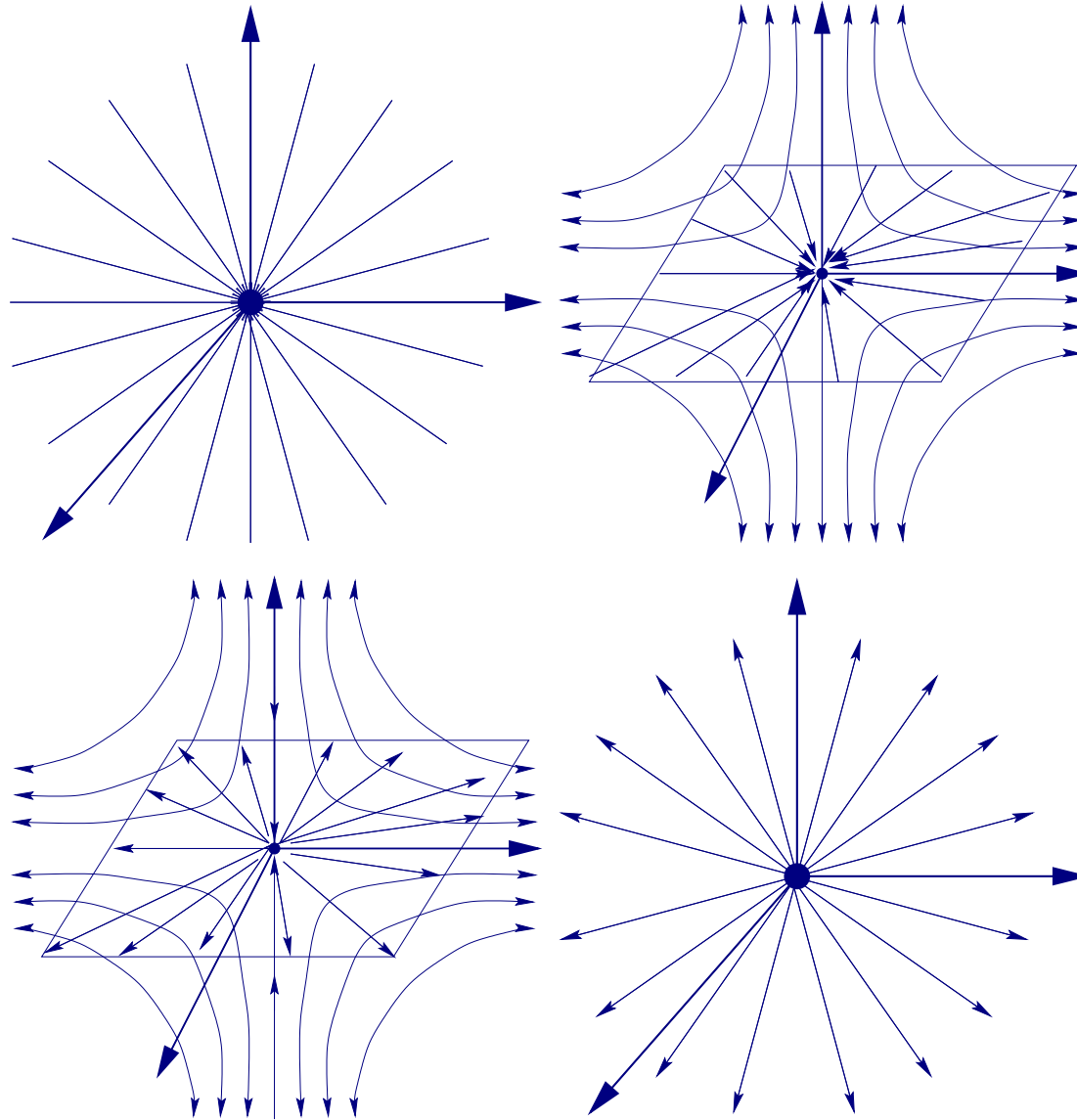
Basins, separatrices and induced topologies.

- We call **separatrix** to the set of points that do not belong to the AB(RB) of a critical point.

- It is possible to divide space $\mathbb{R}^3$ in a finite number of subsets, corresponding to the α- and ω-limits of the CPs of the potential function. We may choose two types of subsets:
  - Using the ABs of the maxima.
  - Using the RBs of the minima.

- We thus introduce in $\mathbb{R}^3$ a set of open subsets $\{A_j\}$, that we will call $(\mathbb{R}^3, A)$.

- This structure is called the topology induced by ρ.

- **Example: Topology of the RBs of a field.**
  $V(x, y) = x^2(x - 1)^2 + y^2$. A potential in $\mathbb{R}^2$.

$$\dot{\boldsymbol{x}} = \boldsymbol{\nabla} V = \begin{cases} \dot{x} & = & 2x(x-1)(2x-1) \\ \dot{y} & = & 2y. \end{cases}$$

- Critical points:

$$
\mathbb{H} = \begin{cases}
(0,0) & \begin{pmatrix} +2 & 0 \\ 0 & +2 \end{pmatrix} & \text{Minimum} \\[2em]
(1,0) & \begin{pmatrix} +2 & 0 \\ 0 & +2 \end{pmatrix} & \text{Minimum} \\[2em]
(\tfrac{1}{2},0) & \begin{pmatrix} -1 & 0 \\ 0 & +2 \end{pmatrix} & \text{Saddle}
\end{cases}
$$

- The **Separatrix** is a local zero flux surface:

$$\int_S \boldsymbol{\nabla} V(\boldsymbol{r}) \cdot \boldsymbol{n}(\boldsymbol{r}) ds = 0.$$

- The gradient field has generated a partition of the 2D space in three regions.

- A **binary relationship** between the two basins appears. Basin 1 is related to basin 2, since a saddle exists which AB connects both repulsors.

Topological invariants.

- The number and type of non-degenerate critical points of a field depends on the structure of the supporting variety.

- For instance, in a **ring**, S^1, the number of maxima must be equal to the number of minima.

- These relationships may be generalized using concepts from topology. The Betti number, R_n, of a veriety $\mathcal{D}$ is the number of n–dimensional topologically different regions that have no boundaries and are not boundaries of $(n+1)$–dimensional regions of $\mathcal{D}$.
  - in S^1: $R_0 = 1, R_1 = 1$.
  - in S^2: $R_0 = 1, R_1 = 0, R_2 = 1$.
  - in T^2: $R_0 = 1, R_1 = 2, R_2 = 1$.
  - in T^3: $R_0 = 1, R_1 = 3, R_2 = 3, R_3 = 1$.

- The Morse relationships establish that:

$$N^0 \geq R_0$$

$$N^1 - N^0 \geq R_1 - R_0$$

$$\vdots$$

$$\sum_{i=0}^{n} (-1)^{n-i} N^i \geq \sum_{i=0}^{n} (-1)^{n-i} R_i$$

$$\vdots$$

$$\sum_{i=0}^{l} (-1)^i N^i = \sum_{i=0}^{l} (-1)^i R_i,$$

where N^n is the number of maxima, N^{n-1} the number of first order saddles, etc.

- In S^1 $N^0 \geq 1$ y $N^0 - N^1 = 0$. As before.
- In S^2, $N^0 \geq 1$, $N^1 - N^0 \geq -1$, and $N^2 - N^1 = 2$.
- In T^3, $N^0 \geq 1$, $N^1 - N^0 \geq 2$, $N^2 - N^1 + N^0 \geq 1$, and $N^3 - N^2 + N^1 - N^0 = 0$.

In $\mathbb{R}^3$ n-b+r-c=1
In $\mathbb{T}^3$ n-b+r-c=0

2. QTAIM Quick Reference Guide

General features of ρ.

The stationary electron density is obtained from $\Psi(\boldsymbol{x}_1, \boldsymbol{x}_2, \ldots \boldsymbol{x}_N, \boldsymbol{R}_1, \ldots \boldsymbol{R}_M)$ as:

$$\rho(\boldsymbol{r}) \quad = \quad N \sum_{s_1} \int \ldots \int d\boldsymbol{x}_2 \ldots d\boldsymbol{x}_N \int \ldots \int d\boldsymbol{R}_1 \ldots d\boldsymbol{R}_M$$

$$\Psi^*(\boldsymbol{x}_1 \ldots \boldsymbol{x}_N, \boldsymbol{R}_1 \ldots \boldsymbol{R}_M)\Psi(\boldsymbol{x}_1 \ldots \boldsymbol{x}_N, \boldsymbol{R}_1 \ldots \boldsymbol{R}_M),$$

$\boldsymbol{x}$ being the spatial and spinorial coordinates of electrons, and $\boldsymbol{R}$ the spatial coordinates of the nuclei.

Under the BO approximation, $\Psi(\boldsymbol{x}_1, \boldsymbol{x}_2, \ldots \boldsymbol{x}_N; \boldsymbol{R})$, y

$$\rho(\boldsymbol{r}; \boldsymbol{R}) = N \sum_{s_1} \int \ldots \int d\boldsymbol{x}_2 \ldots d\boldsymbol{x}_N \Psi^*(\boldsymbol{x}_1 \ldots \boldsymbol{x}_N; \boldsymbol{R})\Psi(\boldsymbol{x}_1 \ldots \boldsymbol{x}_N; \boldsymbol{R}),$$

ρ is observable. For instance, from elastic X–Ray scattering,

$$I(\boldsymbol{k}) \simeq \left| \int \rho(\boldsymbol{r}) e^{2\pi i \boldsymbol{k} \cdot \boldsymbol{r}} d\boldsymbol{r} \right|^2 = |A(\boldsymbol{k})|^2,$$

where A is the Fourier transform of ρ.

Analytical properties of ρ.

- Cusp theorem:

$$\bar{\rho}(r) = \frac{1}{4\pi} \int \rho(\boldsymbol{r})\sin\theta d\theta d\phi$$

$$-2Z_\alpha = \left.\frac{\partial \ln \bar{\rho}(r)}{\partial |\boldsymbol{r} - \boldsymbol{R}_\alpha|}\right|_{r=R_\alpha}.$$

- Asymptotic behavior:

$$\lim_{r\to\infty} \bar{\rho}(r) \simeq r^{2\left(\frac{Z_{\text{total}} - N + 1}{\sqrt{2\text{IP}}}\right)} e^{-2r\sqrt{\text{IP}}},$$
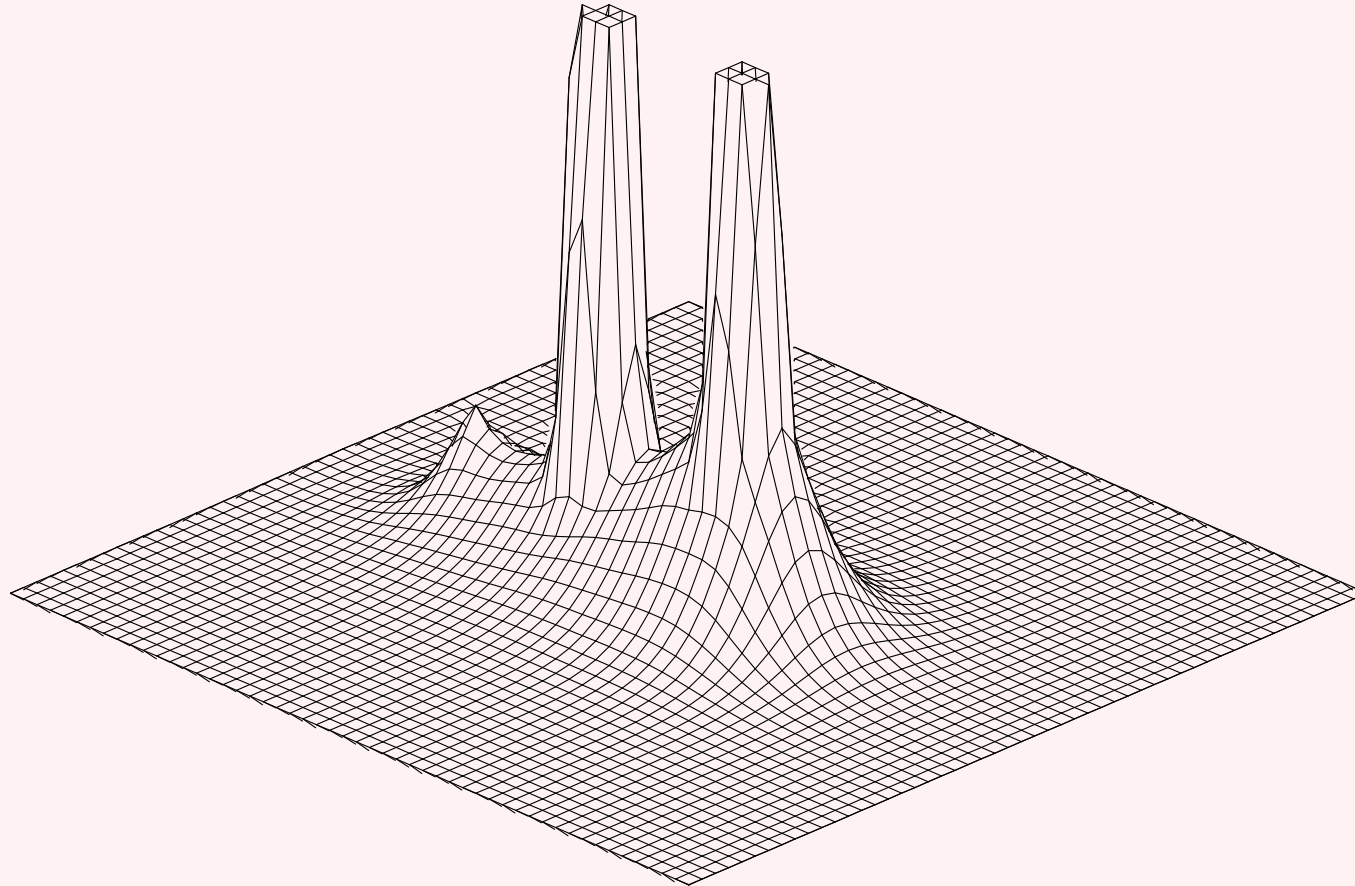
- Hoffmann-Ostenhof and Hoffmann-Ostenhof inequalities:

$$-\frac{1}{2}\boldsymbol{\nabla}^2\rho + (\text{IP} - \frac{Z}{r})\rho \leq 0.$$

- Monotonicity and convexity are not assured.

Basic Morphology of ρ.

HCN (HF/6-311G(p,d))

We rectify the ρ field.

Topological analysis of ρ.

In general, the number of attractors of the ρ field coincide in number and position with the nuclei.
There will be, therefore, as many attraction basins as atoms in the system.
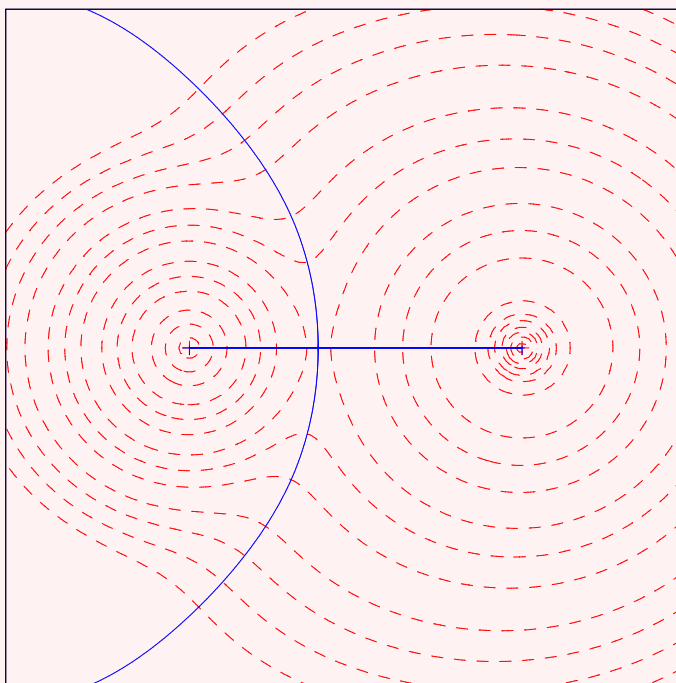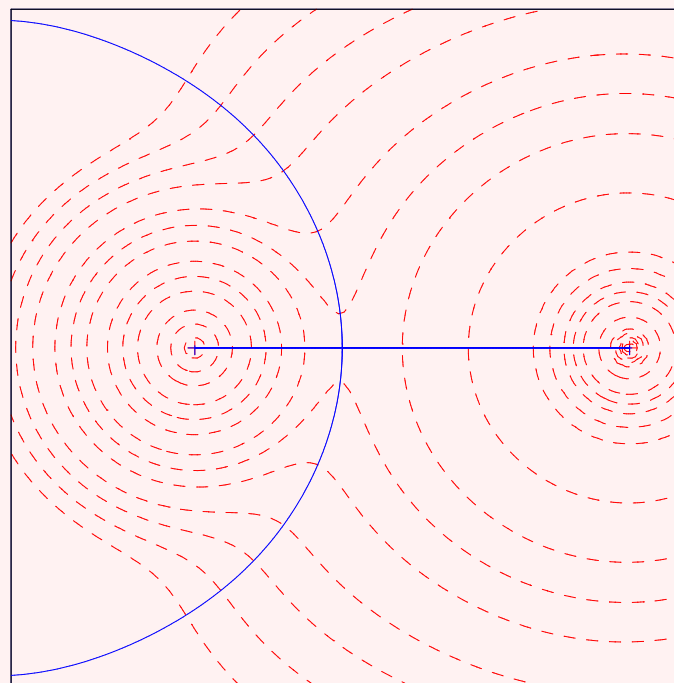
LiF (HF/6-311G*)   LiCl (HF/6-311G*)

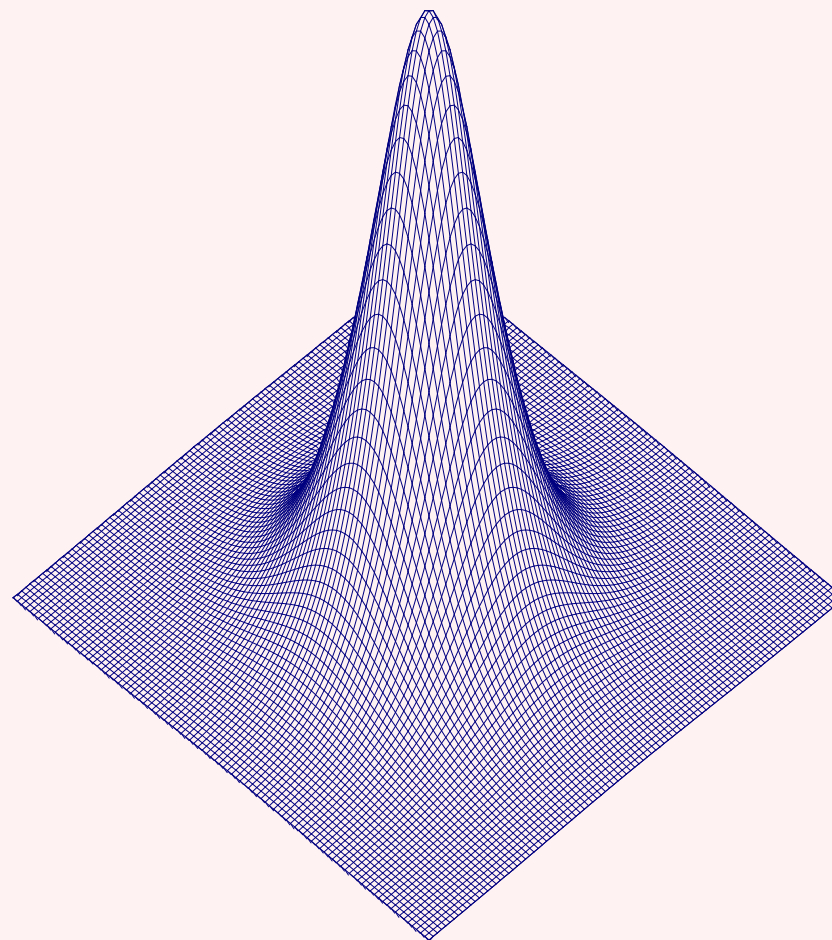**The basins** of equal atoms under similar bonding regimes seem to be **transferable.**
Critical points $\nabla\rho = 0$ are important, and classified according to the eigenvalues of the Hessian of
ρ: (3,-1) $\equiv$ two negative, one positive curvatures.

Usual representations. (LiH HF/TZV)

a) Projected relief diagrams.
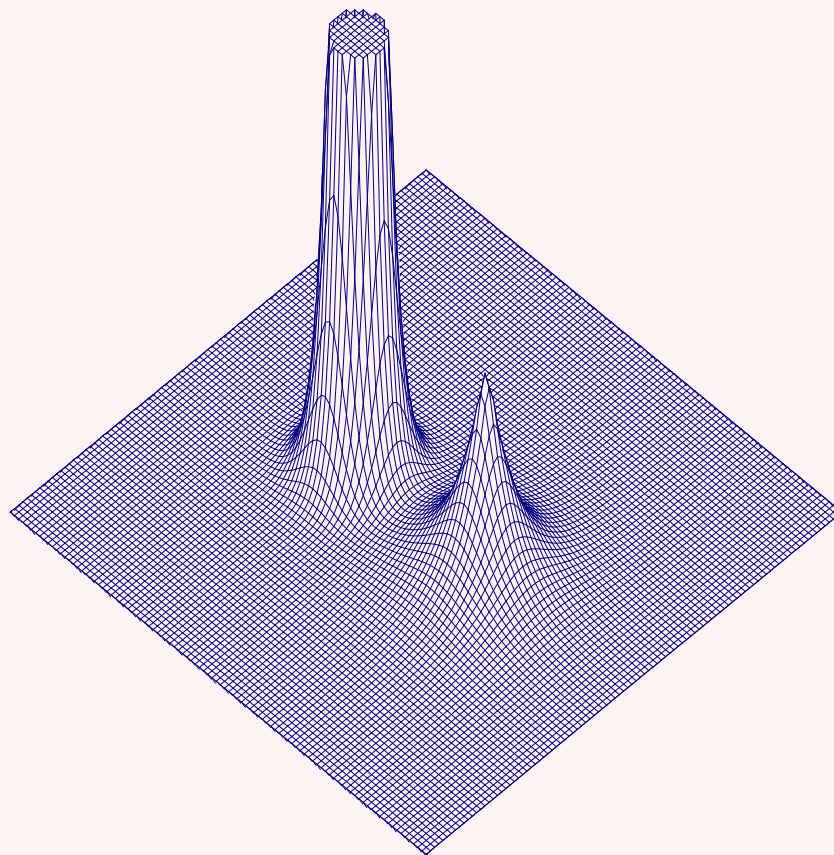
Nuclear plane   Perpendicular plane
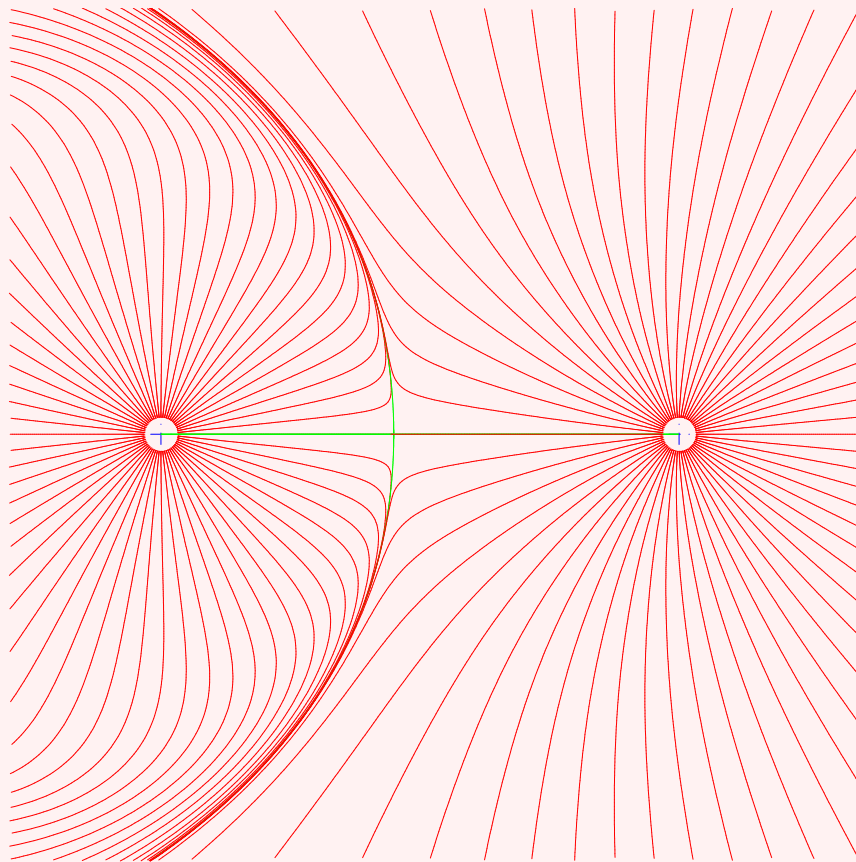
b) Projected contour diagrams.
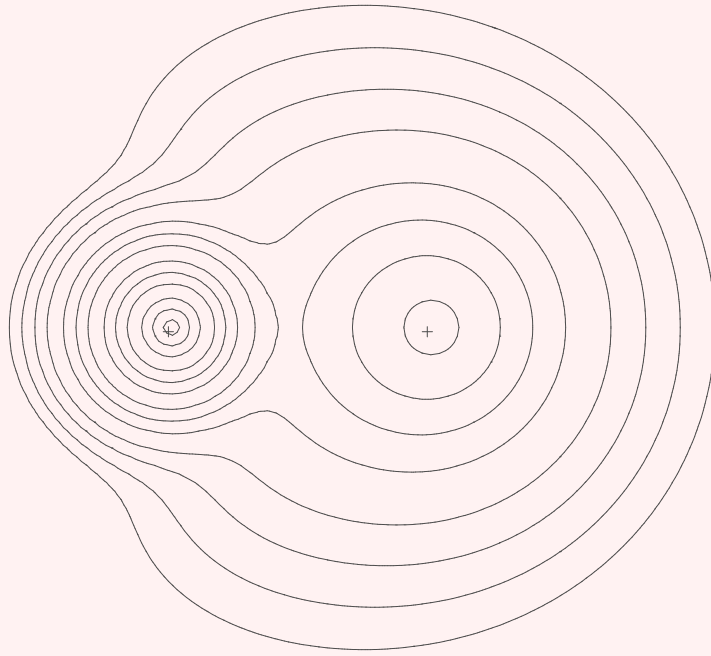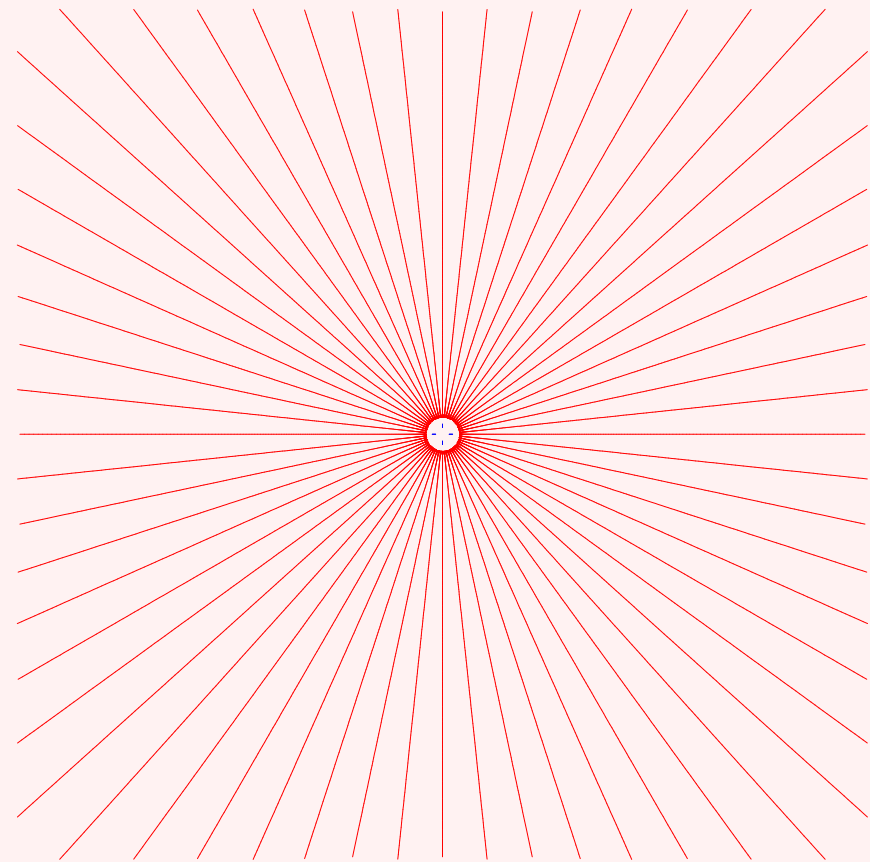
Nuclear plane
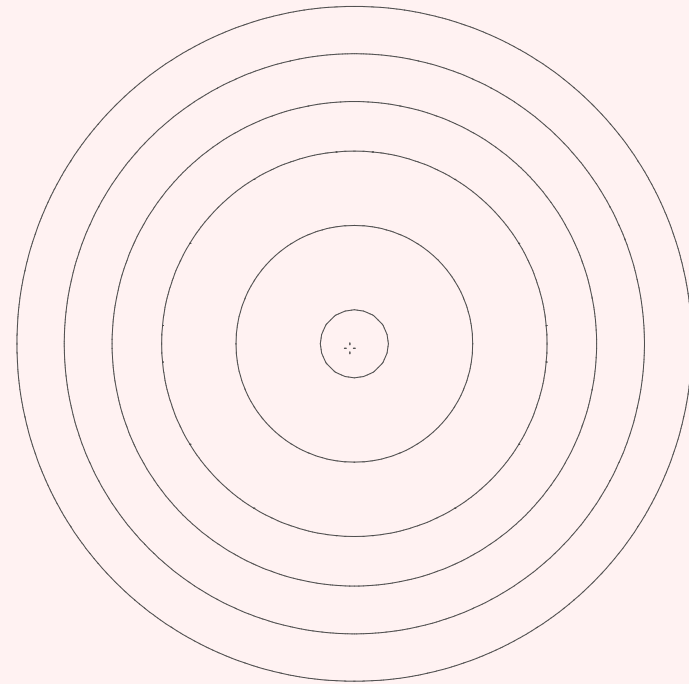
Perpendicular plane

c) Projected gradient field diagrams.
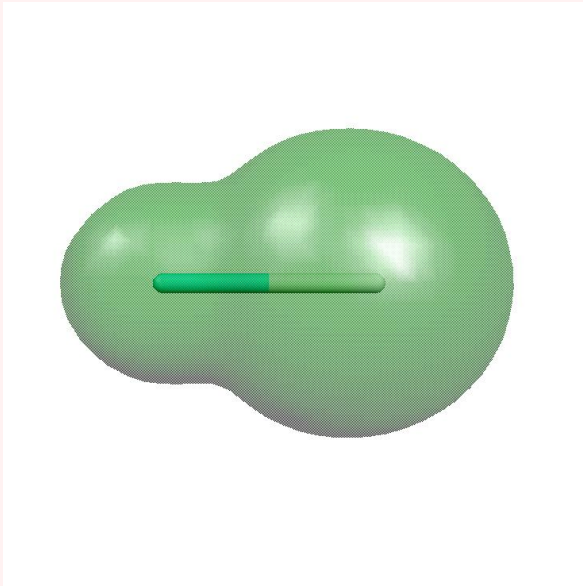

Nuclear plane   Perpendicular plane

(d) Isosurfaces.
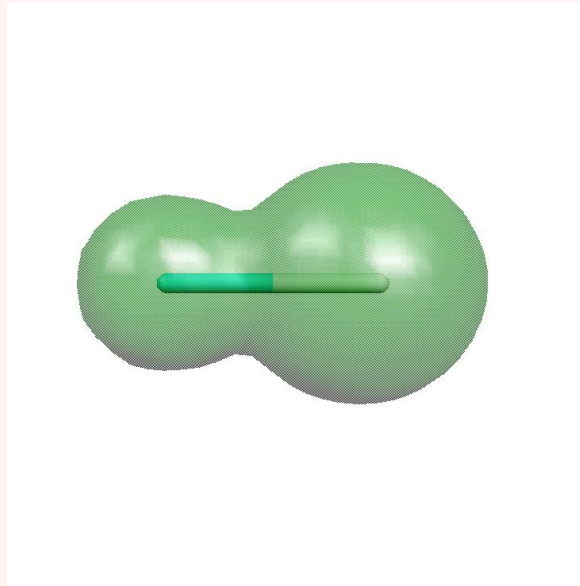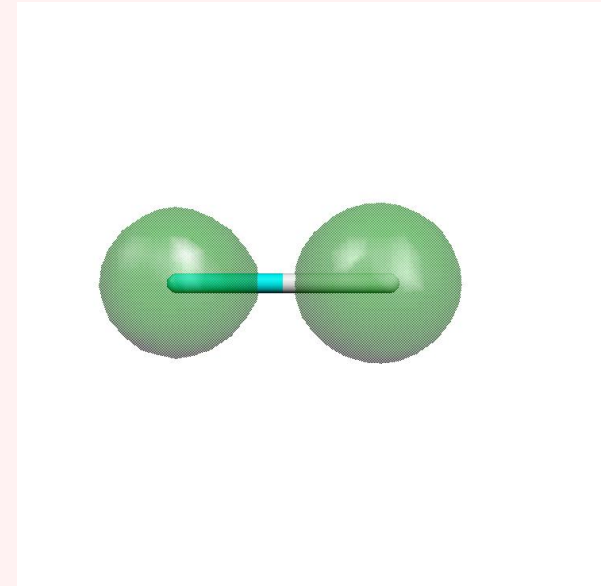
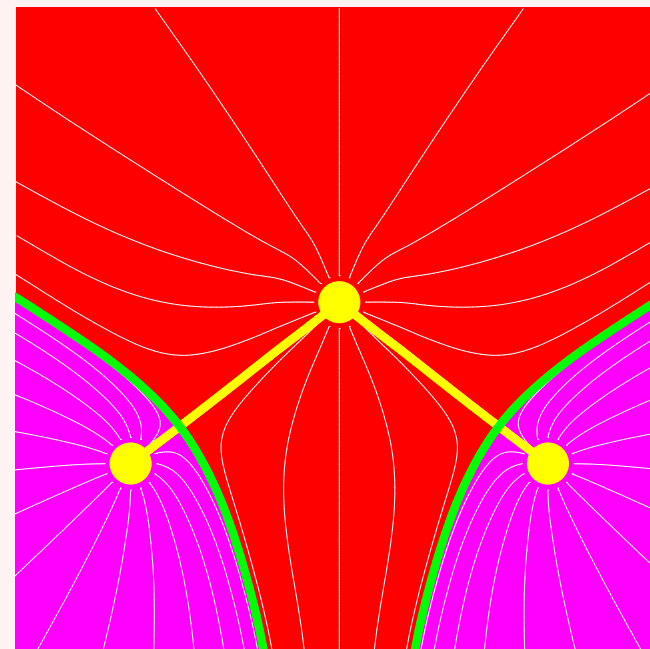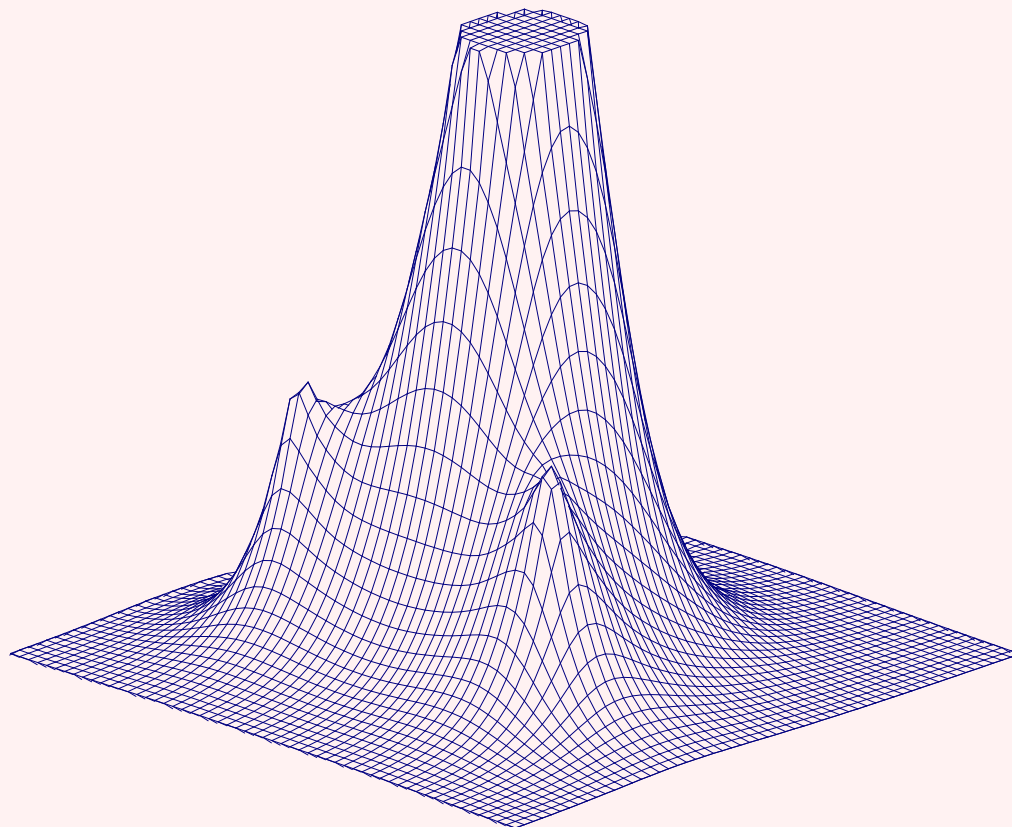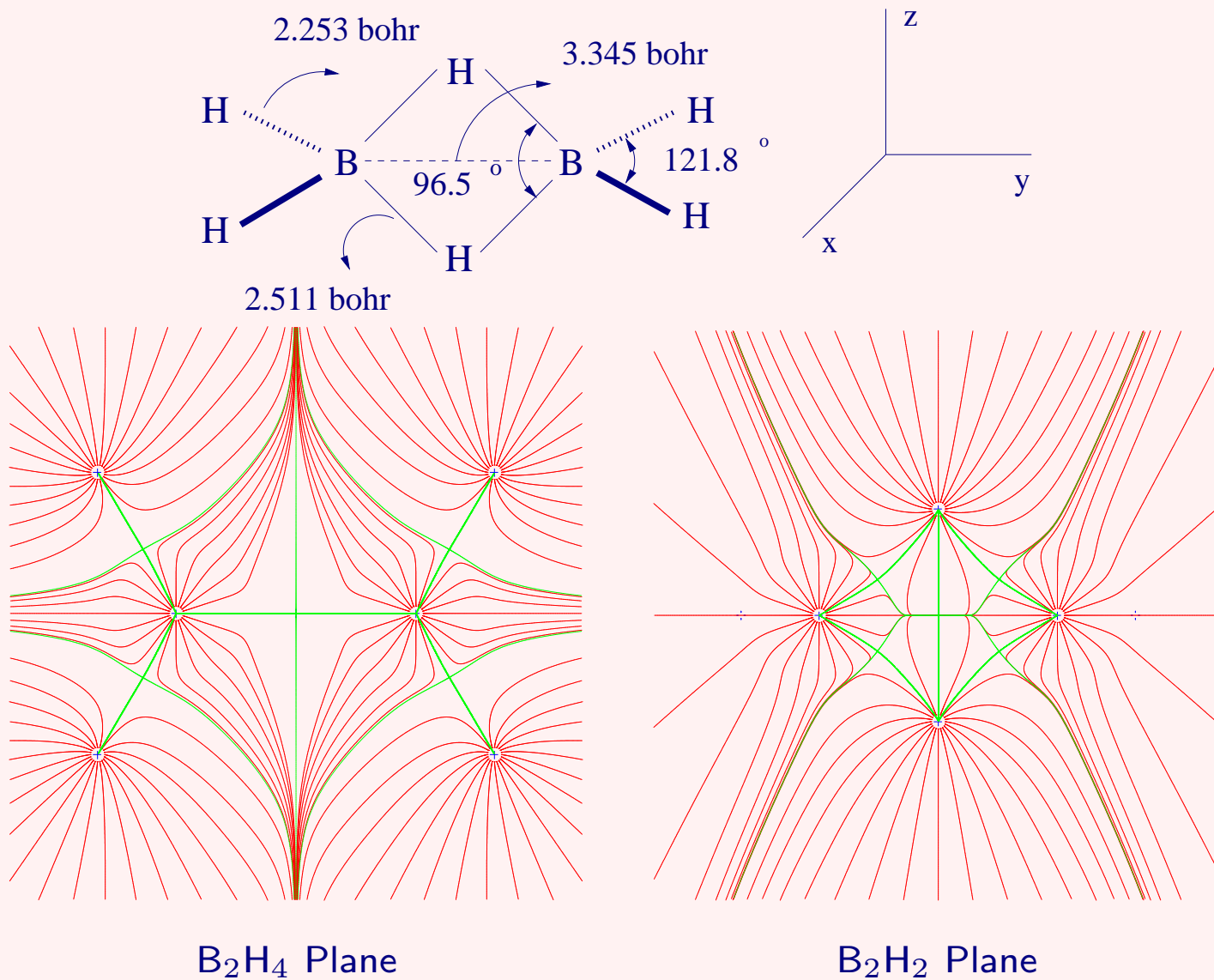$$\rho = 0.01 \qquad\qquad \rho = 0.02 \qquad\qquad \rho = 0.05$$

Bond critical points.

- $(3, -1)$ critical points are identified with chemical bonds. This is, in principle, an empirical assignment.

- However, they usually coincide with the objects defined in chemistry, even in rather strange situations.
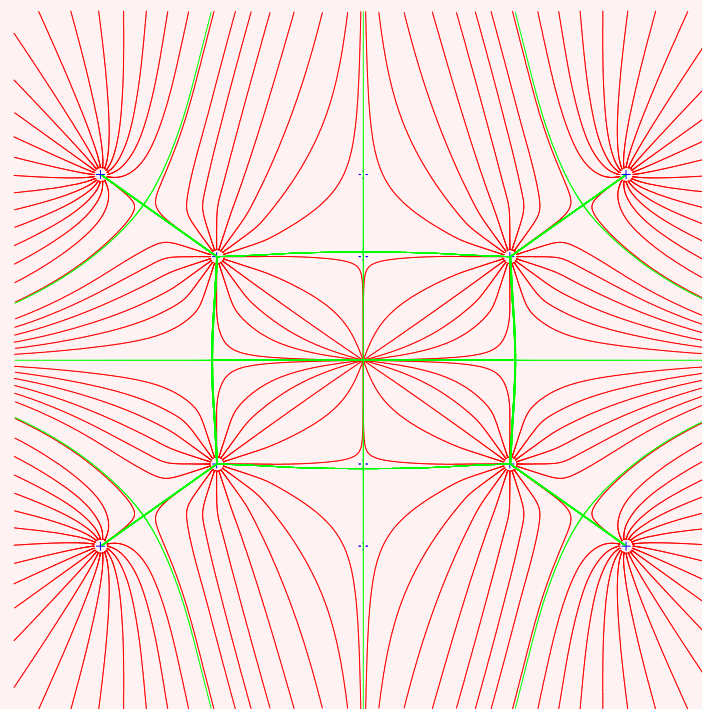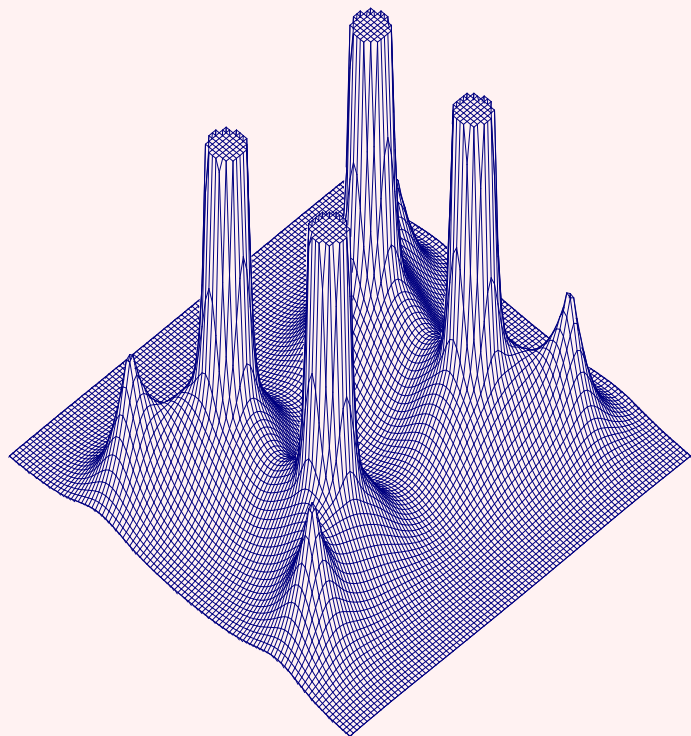
  H_2O

B_2H_6. Ring points.

2.253 bohr

3.345 bohr

H

H

H

B   B   H

96.5 °   121.8 °

H   H

H

2.511 bohr

z

y

x

B_2H_4 Plane

B_2H_2 Plane

C_8H_8. Cage points.

- ■ **Properties computed at critical points: The QTAIM local stance**

  - CPs provide a continuous $\Rightarrow$ discrete map: 3D to finite set of points.

  - Many kinds of scalar and tensor properties calculated at the CPs are easy to correlate with chemically relevant concepts.

    - ρ_b itself is a measure of bond strength for a given pair of bonded atoms.
    - It turns to be small in ionic compounds and large in covalent.
    - It correlates with bond order
    - It is not possible to simply compare values of ρ_b for different bonded pairs.
    - However, it is reasonable to compare ρ_b values for set of molecules that share a given pair of bonded atoms.

  - The distances from nuclei to BCP's are good indicators of atomic size.

  - The ratio of curvatures of the Hessian, ellipticity, has been used as a measure of something like π character of the bond.

  - etc...

- **Bond radius.**

  ○ The distance from the BCP to each of the bonded nuclei is called topological bonded radius.
  ○ It is basically the crystalline radius introduced by Shanon.
 ○ They depend on the effective nuclear charge and on the electronegativity.
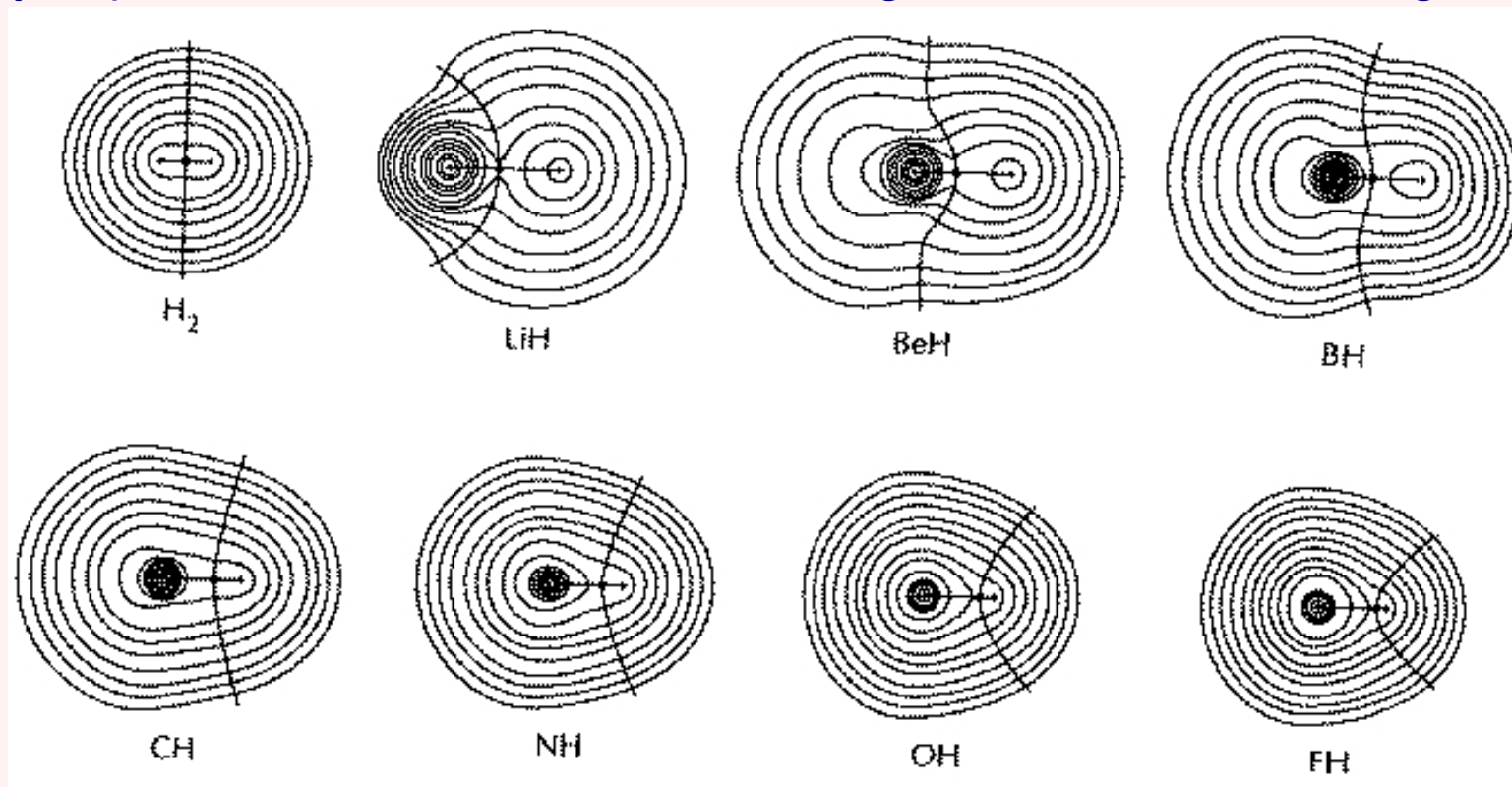
B3LYP/6-311+G(2d,2p)//HF/6-31(d) a.u.

Molecule	R_e	$r_b(H)$	ρ_b
HH	1.3792	0.6896	0.2700
HLi	3.0908	1.7234	0.0379
HBe	2.5469	1.4545	0.0952
HB	2.3163	1.2790	0.1916
HC	2.0941	0.7112	0.2807
HN	1.9347	0.5315	0.3360
HO	1.8111	0.3802	0.3717
HF	1.7211	0.2848	0.3801
HNa	3.6176	1.7091	0.0321
HMg	3.3043	1.6195	0.0500
HAl	3.1222	1.5896	0.0758
HSi	2.8634	1.4566	0.1171
HP	2.6655	1.3110	0.1670
HS	2.5134	0.9044	0.2175
HCl	2.3928	0.7071	0.2490

- The values of ρ_b for LiH, BeH y NaH, MgH are small. Ionic bonding.

- BCP density increases on advancing on a period.

- If we compare pairs of identical bonded atoms, ρ_b may be used to define a topological **bond order** n_b.

- For instance, in C-C bonds the values of ρ_b for the ethane, ethene, and ethyne series are approximately $0.249, 0.356$ y 0.426 a.u. A linear fit that recovers the classical 1, 2, and 3 bond orders gives $n_b = 1.6$ for the C-C bond in benzene.

- The n_b–ρ_b relations are different for each pair of bonded atoms.

- It has been proposed that the concept of bond order is actually an scaled measure of ρ_b.

- **Ellipticity.**

  - Let us call λ_1, λ_2, and λ_3 the 3 principal curvatures at the bcp, in ascending order.
  - In an A_2 molecule, $\lambda_1 = \lambda_2$.
  - We define the ellipticity at a BCP as $\epsilon = \lambda_1/\lambda_2 - 1$.
  - It measures the asymmetry of the perpendicular accumulation of charge, determining the facile, and non-facile directions of density accumulation.
  - In C_2H_4 $\epsilon = 0.3$. π character? In C_6H_6 $\epsilon = 0.23$.
  - Caution: the π character is not an observable.
  - In C_2H_2 $\epsilon = 0$. IN B_2H_6, $\epsilon = 0.33$
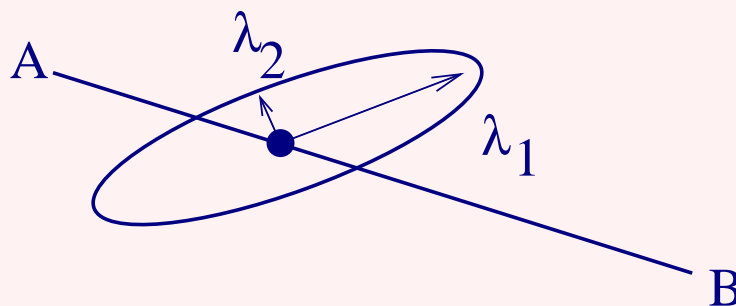
Other scalars: General Features of $\nabla^2 \rho$.

What other scalar fields may we study? Further order derivatives.

- $\nabla \rho \cdot \nabla \rho$. Its critical points are located where the condition $\mathbb{H}(r)\nabla\rho(r) = 0$. is satisfied.
- $\nabla^2 \rho$. Related to local charge accumulation or depletion.
- Since the trace of a matrix is invariant under an orthogonal transformation:

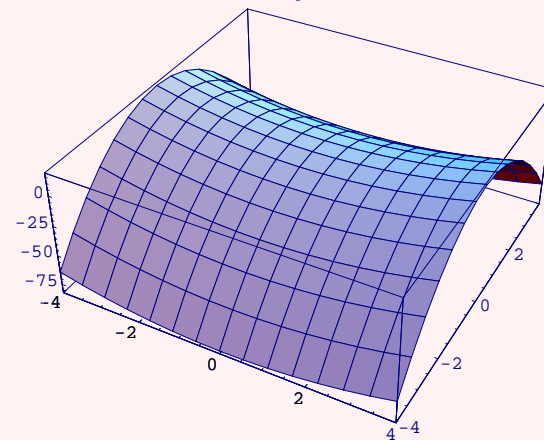$$\nabla^2 \rho = \lambda_1 + \lambda_2 + \lambda_3,$$

- $\circ$ $\nabla^2 \rho > 0$ The positive curvatures "win", and we have a point of charge **depletion** with respect to its neighbourhood.
- $\circ$ $\nabla^2 \rho < 0$ corresponds to charge **accumulation** with respect to its neighbourhood.

Example:
$z = x^2 - 5y^2$
A Critical Point at $(0, 0)$
$\nabla^2 \rho(0, 0) = -8$

- Morphology of $\nabla^2\rho$ in spherical atoms.
  - Given that $\rho = \rho(r)$

$$\nabla^2\rho(r) = \rho''(r) + 2\frac{\rho'(r)}{r}$$

  - Supposing an exponential behaviour: $\rho(r) = Ne^{-\zeta r}$, valid close to the nucleus as well as in the asymptotic limit,

$$\nabla^2\rho(r) = Ne^{-\zeta r}(\zeta^2 - 2\zeta/r)$$

 - There exits a cutoff radius $r_c = 2/\zeta$ for which a change of sign appears.

$$\nabla^2\rho < 0 \text{ if } r < r_c \text{ and viceversa.}$$

  - $\lim_{r\to 0} \nabla^2\rho = -\infty$ and $\lim_{r\to\infty} = 0^+$.
  - Atomic densities are reasonably appproximated by a series of exponentially decreasing segments, so we should expect a negative and positive region in the laplacian for each of these segments. These are usually identified with the classical atomic shells. This is correct until Ca, which shows only 3 shells. Other functions (ELF,...) allow for a more perfect match.
  - The (3,-3) points of $\nabla^2\rho$ are associated with important charge concentrations. The most exterior ones are the valence charge concentrations (VCC). They may be associated with bonds (BVCC), or with lone pairs (LVCC).

He (HF)
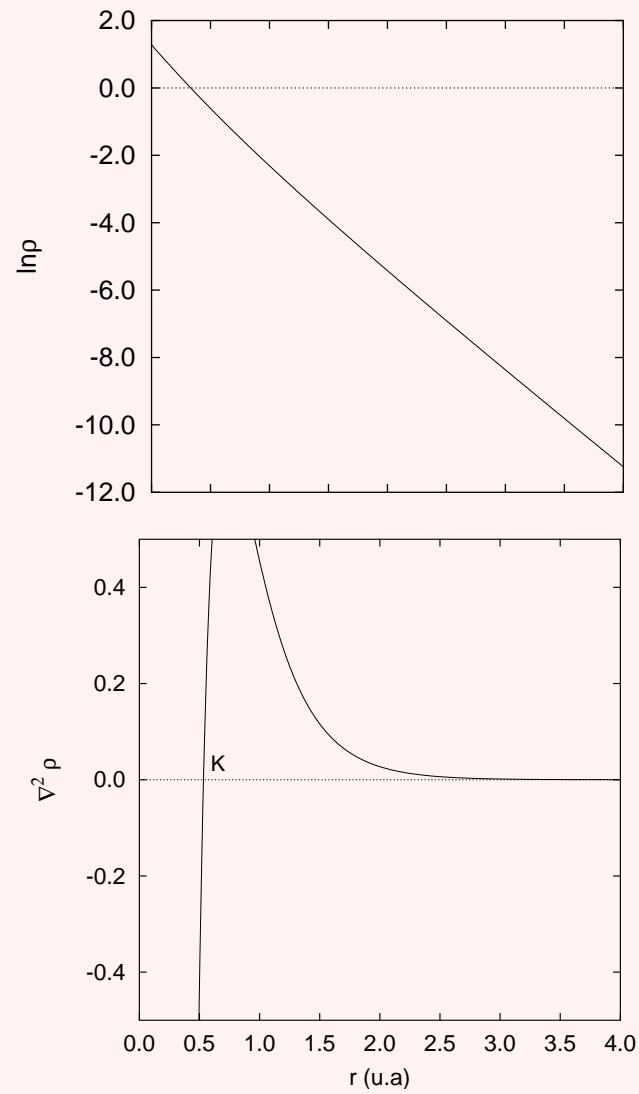
Ar (HF)
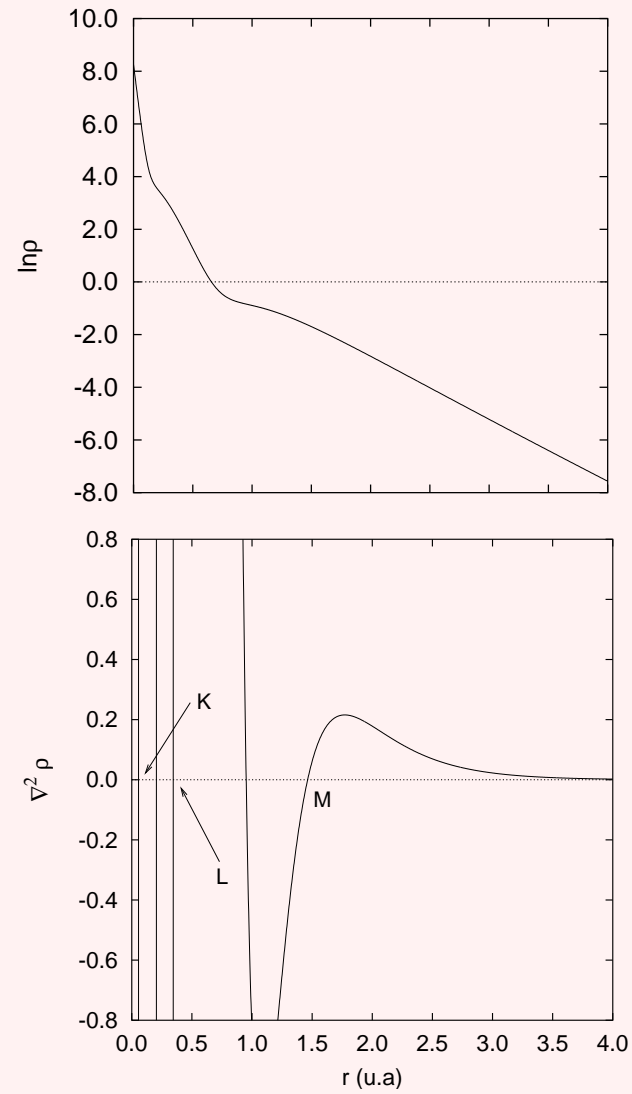
○ The position of the zeros, minima, and maxima of the laplacian in atoms has been successfully related to a other atomic size measures.

| Radius	Li	Be	B	C	N	O	F	Ne
r_2	2.49	1.59	1.19	0.94	0.78	0.66	0.57	0.50

Radius	Na	Mg	Al	Si	P	S	Cl	Ar
r_2	0.44	0.40	0.36	0.33	0.30	0.28	0.26	0.24
r_3	3.44	2.55	2.08	1.76	1.52	1.34	1.20	1.08

Radius	K	Ca	Ga	Ge	As	Se	Br	Kr
r_2	0.23	0.21	0.13	0.12	0.12	0.12	0.11	0.11
r_3	0.98	0.90	0.49	0.47	0.45	0.43	0.41	0.39
r_4	4.94	3.77			2.18	1.83	1.65	1.50

Radii of maximum charge concentration for the different atomic shells in some elements. Quasi-HF results from multi–ζ Clementi and Roetti basis set.

- $\nabla^2\rho$ suffers a restructuration upon molecule formation: Cl_2, NaCl HF//6-311G**
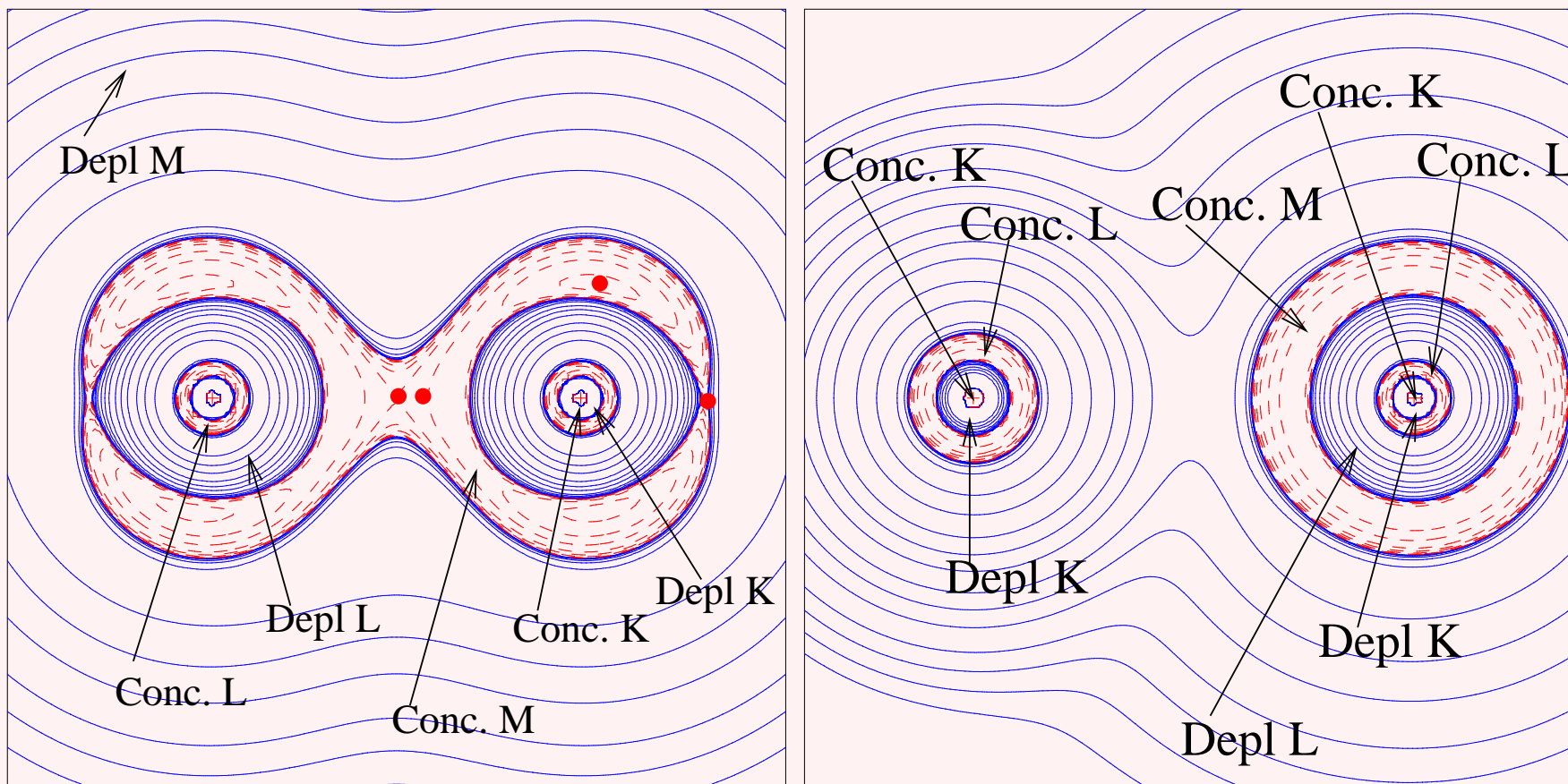
- $\nabla^2\rho$ changes more noticeably if symmetry breaks: H_2O:HF//6-311G**
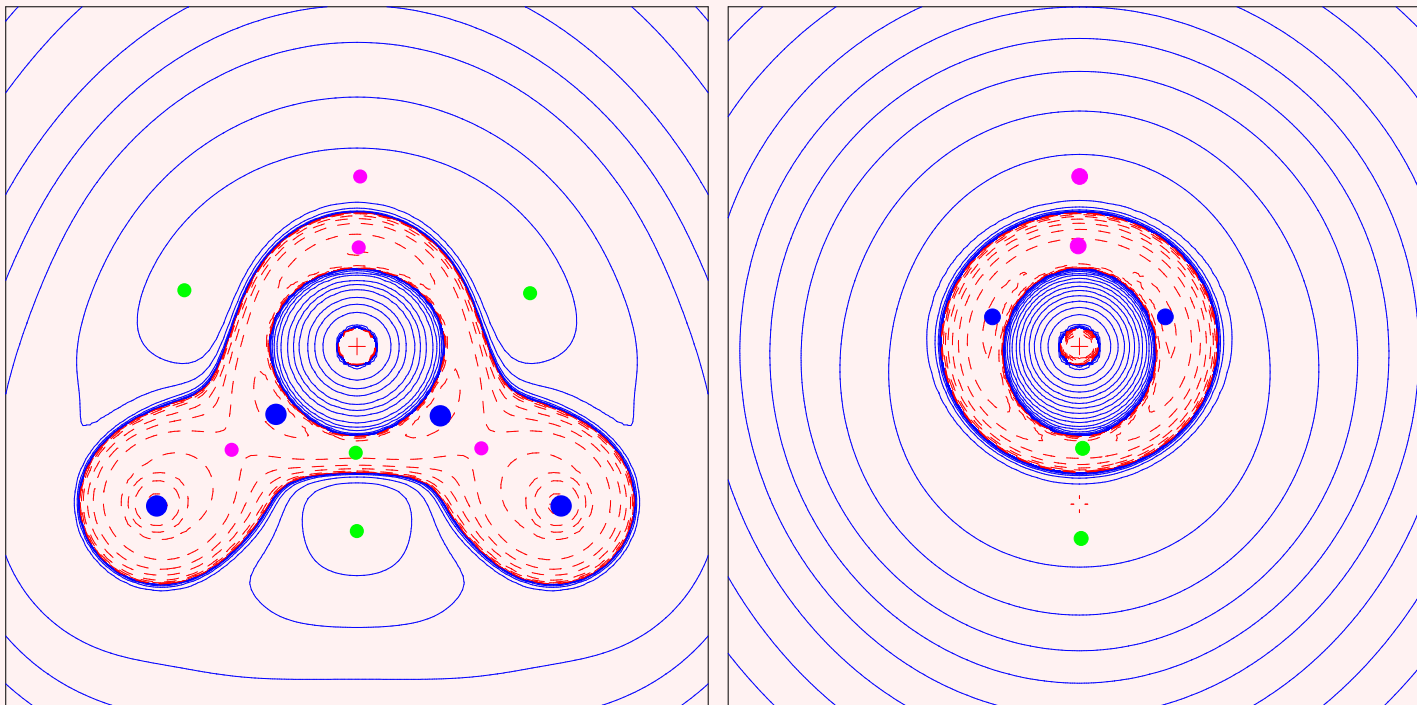
- ○ There are 4 tetrahedrally arranged VCC now.
- ○ Two BVCC's and two lone pairs.
- ○ They correspond to the VSEPR model: The angle between the two BVCC's is $103.8°$ and $138.6°$ for the lone pairs.

Atomic observables: The QTAIM global stance

- There exist well defined **operator densities** within QT subsystems. They may be integrated over atomic basins, but since the actual form of the operators depends on the structure of the basins, only in the case of QTAIM zero-flux separated basins, we will get physically meaningful results.

- Let $\hat{\mathcal{O}}$ be the density associated to 1-electron operator $\hat{O}$:

$$\langle \hat{O} \rangle = \sum_{\Omega} \int_{\Omega} \hat{\mathcal{O}} \, d\boldsymbol{r} = \sum_{\Omega} \hat{O}_{\Omega}, \tag{2}$$

so all global observables are additively reconstructed from the **atomic observables**. The transferability that the latter have shown to have is the origin of the constancy and experimental additivity of what we usually call **group properties.**

- Simple examples:

  - $\mathcal{O} = 1 \Rightarrow V_\Omega = \int_\Omega d\boldsymbol{r}$. In isolated molecules $V_\Omega \to \infty$ usually. It is common practice define an integration domain $\Omega' = \Omega \cap I(\rho = 0.002)$ u.a. These atomic volumes are trasnferable.

  - $\mathcal{O} = \rho \Rightarrow N_\Omega = \int_\Omega \rho \; d\boldsymbol{r}$. **Domain populations.**. They are usually transformed into **net atomic charges**, $Q_\Omega = Z - N_\Omega$. They are not observables. Their variances $\sigma^2(\Omega) = \langle N^2 \rangle_\Omega - N_\Omega^2$ determine the quantum mechanical uncertainty associated to electron populations.

- **Atomic moments**: Let us define the **real spherical harmonics**, S_{lm},

$$S_{lm}(\theta,\phi) = \begin{cases} \frac{(-1)^m}{\sqrt{2}}(Y_{lm} + Y_{lm}^*) & m > 0, \\ Y_{l0} & m = 0, \\ \frac{(-1)^m}{i\sqrt{2}}(Y_{l|m|} - Y_{l|m|}^*) & m < 0. \end{cases}$$

With this, $S_{00} = s$, $S_{1\bar{1}} = p_y$, $S_{10} = p_z$, $S_{11} = p_x$, $S_{2\bar{2}} = d_{xy}$, $S_{2\bar{1}} = d_{yz}$, $S_{20} = d_{z^2}$, $S_{21} = d_{xz}$, y $S_{22} = d_{x^2-y^2}$.

We define the **spherical multipolar atomic moments**, N_{Ω}^{lm}, as

$$N_{\Omega}^{lm} = \int_{\Omega} r^l S_{lm}(\theta,\phi)\rho(\boldsymbol{r})d\boldsymbol{r}.$$

N^{00} is the atomic population, the $(N^{11}, N^{1\bar{1}}, N^{10})$ trio determines the **atomic dipolar moment** vector, μ_{Ω}, and the $l = 2, 3, 4, \ldots$ moments are to be identified with the different atomic quadrupoles, octupoles, etc.

Atomic moments measure the atomic charge distribution distortion with respect to an ideal sphere.

With the N_Ω^{lm} we may reconstruct the molecular N^{lm} moments. For $l = 1$, for instance,

$$
\begin{aligned}
\boldsymbol{\mu} &= \int \boldsymbol{r}\rho d\boldsymbol{r} = \sum_A \int_{\Omega_A} \boldsymbol{r}\rho d\boldsymbol{r} = \sum_A \int_{\Omega_A} (\boldsymbol{r} - \boldsymbol{R}_A)\rho d\boldsymbol{r} + \sum_A \int_{\Omega_A} \boldsymbol{R}_A\rho d\boldsymbol{r} \\
&= \sum_A \boldsymbol{\mu}_A + \sum_A N_A \boldsymbol{R}_A = \boldsymbol{\mu}_{\mathrm{pol}} + \boldsymbol{\mu}_{\mathrm{TC}}
\end{aligned}
$$

- **Energetic components:**

  - Kinetic energy: Very problematic outside the QTAIM. $T_\Omega = G_\Omega = K_\Omega$, with $T = \sum_A T_A$.

$$T_A = \frac{1}{2} \int_{\Omega_A} \nabla\nabla'\rho(\boldsymbol{r}; \boldsymbol{r}')d\boldsymbol{r},$$

  - Atomic energy: Using the virial Th.: $E_\Omega = -T_\Omega$. ! Equillibrium configurations only.

  - Nucleus-electron potential energy:

$$V_{AB}^{en} = -Z_B \int_{\Omega_A} \frac{\rho(\boldsymbol{r})}{|\boldsymbol{r} - \boldsymbol{R}_B|} d\boldsymbol{r},$$

$V_{AB}^{ne} = V_{BA}^{en}.$

$$V^{en} = -\sum_A Z_A \int \frac{\rho(\boldsymbol{r})}{|\boldsymbol{r} - \boldsymbol{R}_A|} d\boldsymbol{r} = \sum_{A,B} V_{AB}^{en}.$$

- **Digression: Why the QTAIM?**

  - Only the atoms of the QTAIM have well defined energetic components:
    - Only if the separatrices are of ρ is the domain T quasi-unique.

  - The QTAIM is a quantum theory of subsystems.
    - Open quantum regions

3. A world beyond $\rho(r)$: IQA

- Chemically partitioning ρ_2 introduces a energetic viewpoint in QTAIM.

- The energy depends only on the second-order reduced density matrix (2RDM):

$$\rho_2(\boldsymbol{r}_1, \boldsymbol{r}_2; \boldsymbol{r}_1', \boldsymbol{r}_2') = N(N-1) \int d\boldsymbol{r}_3, \ldots, d\boldsymbol{r}_N \ \Psi^*(\boldsymbol{r}_1', \boldsymbol{r}_2', \ldots, \boldsymbol{r}_N)\Psi(\boldsymbol{r}_1, \boldsymbol{r}_2, \ldots, \boldsymbol{r}_N)$$

  Its diagonal part is the two-particle density. Integrating one particle, we get the 1RDM,

$$\rho(\boldsymbol{r}_1; \boldsymbol{r}_1') = N \int d\boldsymbol{r}_2, \ldots, d\boldsymbol{r}_N \ \Psi^*(\boldsymbol{r}_1', \ldots, \boldsymbol{r}_N)\Psi(\boldsymbol{r}_1, \ldots, \boldsymbol{r}_N)$$

  Its diagonal part is the electron density. With this,

$$\hat{H}_{\text{el}} = \sum_i \hat{h}_i + \sum_{i>j} \frac{1}{r_{ij}} \Rightarrow E = \text{Tr}(\rho_1 \hat{h}) + \frac{1}{2}\text{Tr}(\rho_2 r_{12}^{-1}) + V_{nn}$$

- Now let us partition all the integrals into domain contributions...

$$T_A = \int_{\Omega_A} d\boldsymbol{r}\ \hat{t}\rho_1(\boldsymbol{r}';\boldsymbol{r});\ V_{en}^{AB} = -Z_B \int_{\Omega_A} d\boldsymbol{r}\ \frac{\rho_1(\boldsymbol{r})}{|\boldsymbol{R}_B - \boldsymbol{r}|};\ V_{ee}^{AA} = \tfrac{1}{2}\int_{\Omega_A} d\boldsymbol{r}_1 \int_{\Omega_A} d\boldsymbol{r}_2\ \frac{\rho_2(\boldsymbol{r}_1,\boldsymbol{r}_2)}{r_{12}}$$

$$V_{nn}^{AB} = \frac{Z_A Z_B}{R_{AB}} \qquad\qquad\qquad\qquad\qquad V_{ee}^{AB} = \int_{\Omega_A} d\boldsymbol{r}_1 \int_{\Omega_B} d\boldsymbol{r}_2\ \frac{\rho_2(\boldsymbol{r}_1,\boldsymbol{r}_2)}{r_{12}}$$

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

- Since $\rho_2 = \rho_2^C + \rho_2^{xc}$, with $\rho_2^C = \rho(\boldsymbol{r}_1)\rho(\boldsymbol{r}_2)$, $V_{ee}^{AB} = V_C^{AB} + V_{xc}^{AB}$
$$E_{int}^{AB} = V_{clas}^{AB} + V_{xc}^{AB}$$

- If binding with respect to a reference is needed, then

$$E_{bind} = \sum_A \left(E_{self}^A - E^{A,0} \right) + \sum_{A>B} E_{int}^{AB} = \sum_A E_{def}^A + \sum_{A>B} \{ V_{clas}^{AB} + V_{xc}^{AB} \}$$

- $\lambda^A = \int_{\Omega_A} d\boldsymbol{r}_1 \int_{\Omega_A} d\boldsymbol{r}_2\ \rho_{xc}(\boldsymbol{r}_1,\boldsymbol{r}_2)$,
$\delta^{A,B} = 2\int_{\Omega_A} d\boldsymbol{r}_1 \int_{\Omega_B} d\boldsymbol{r}_2\ \rho_{xc}(\boldsymbol{r}_1,\boldsymbol{r}_2)$, localization and delocalization indices. They measure the number of localized electrons, and the number of delocalized pairs ($\approx$ covalent bond order)
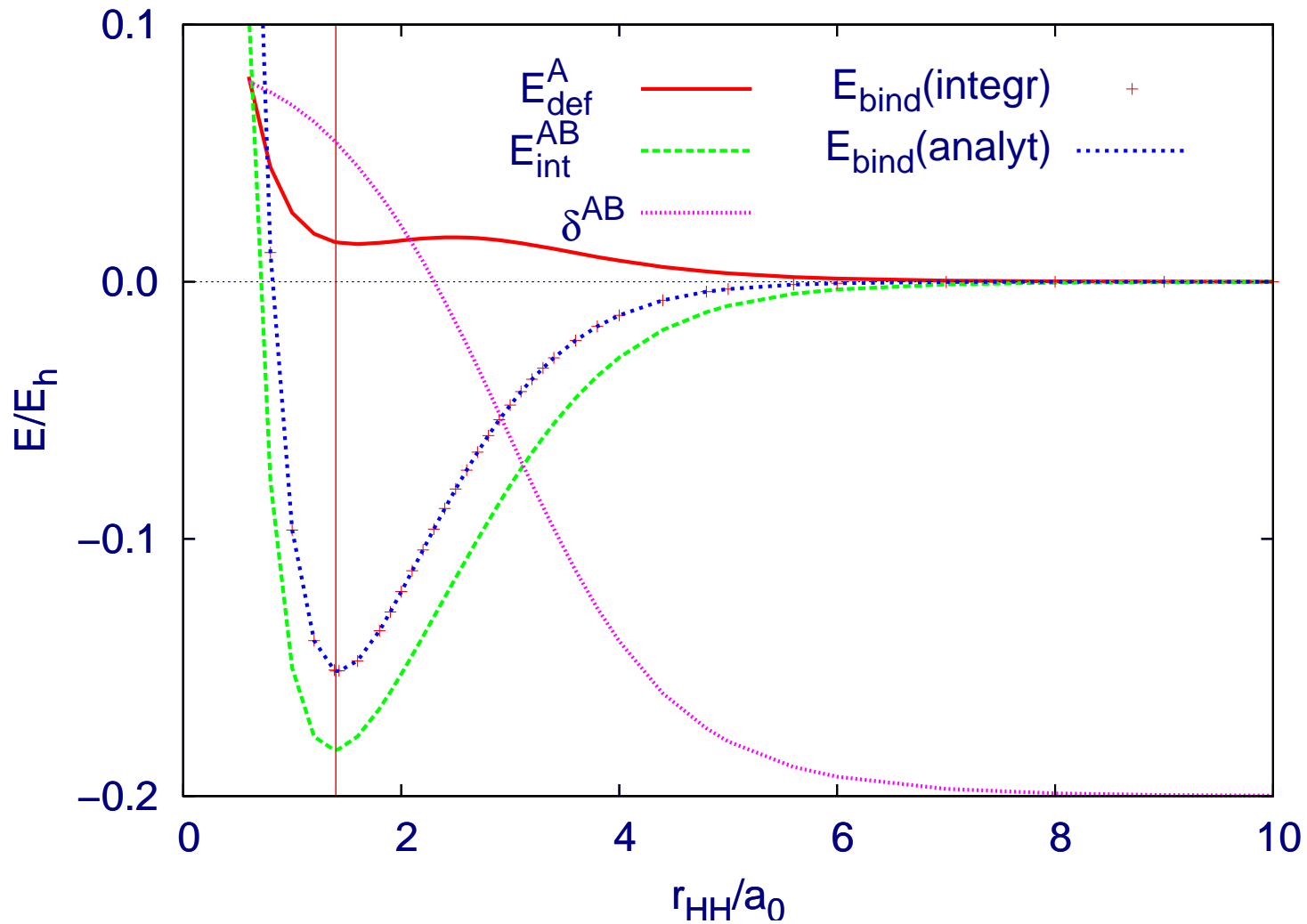
3. IQA in the H_2 molecule I. The $^1\Sigma_g^+$ state

■ FCI//TZV(p,d) calculations. True chemical bond.
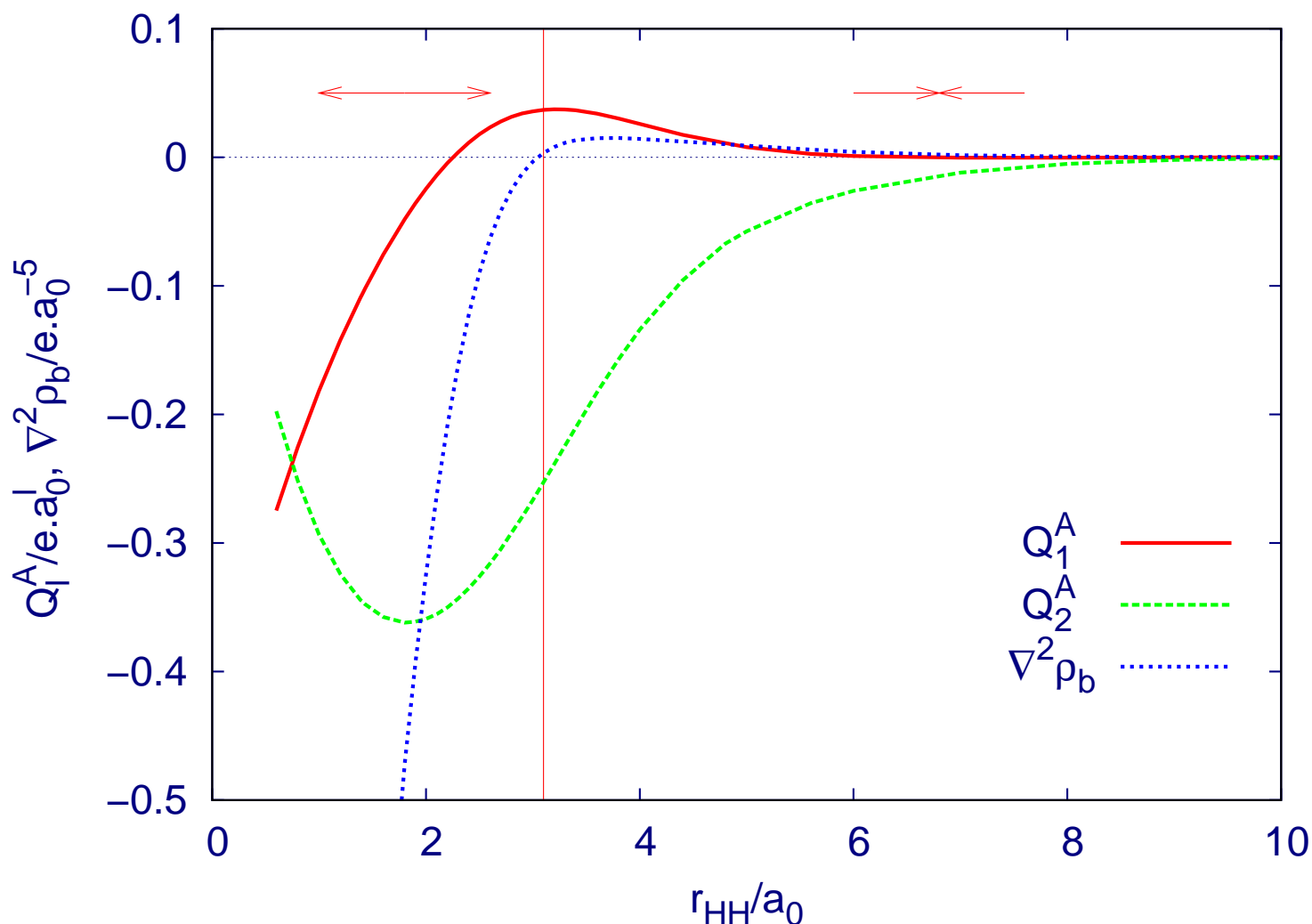
- The atomic dipole Q_{10} changes sign.

- Its maximum almost coincides with $\nabla^2\rho$ crossing the axis.

- The atomic quadrupole $Q_{20} < 0$.

- Many energetic contributions follow the dipole.

- IQA analysis of E_{bind}

- $\lim_{R \to \infty} E_{self} = E(H)$

- E_{def} is very small (8 kcal/mol) at R_e.

- E_{def} increases steeply at short distances.

- Binding is basically interaction.

- Two deformed H atoms interact strongly.

- Delocalization is large.

■ Self–Energy: A balance of large components.
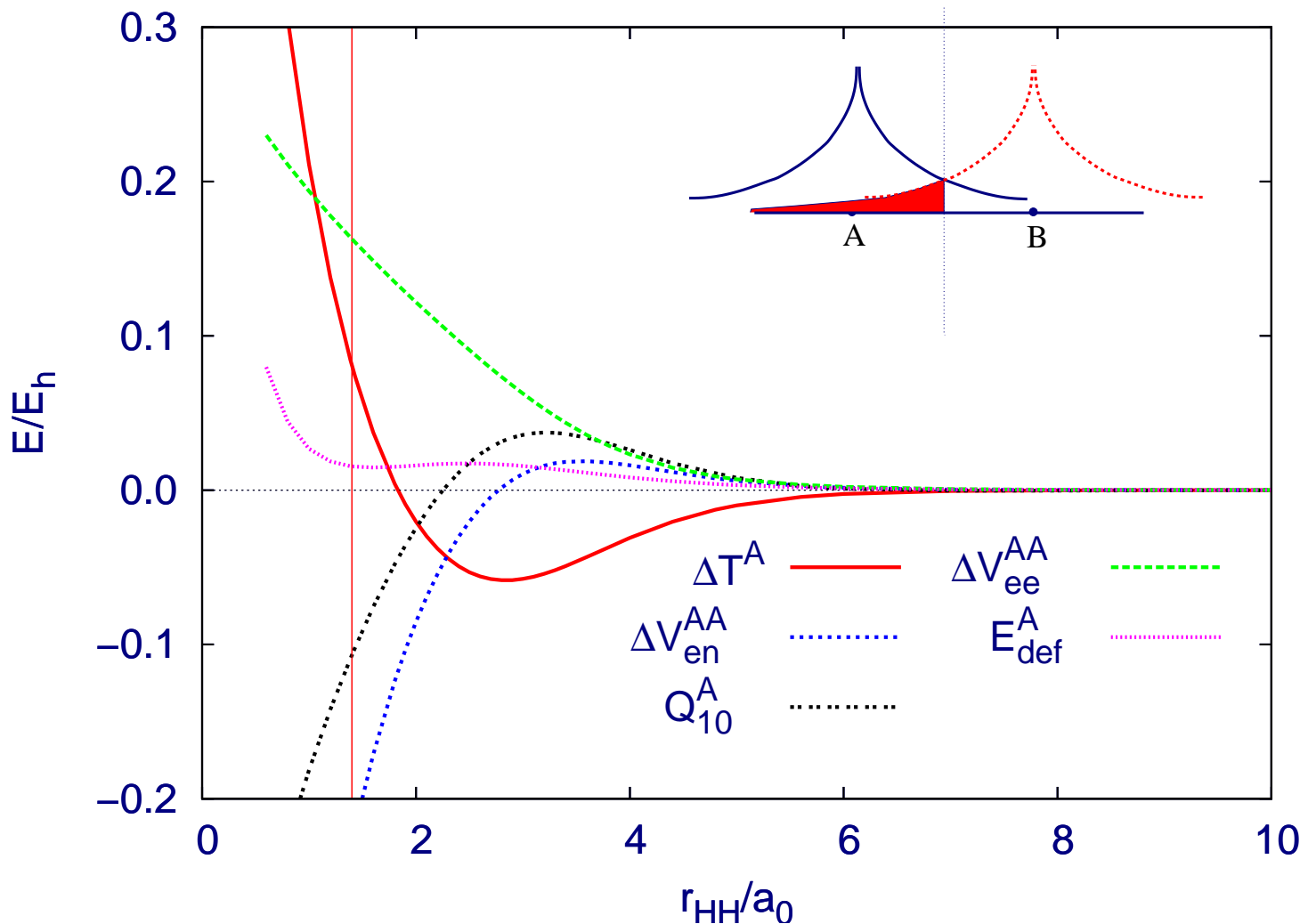
- $E_{def} > 0$: from a restricted variational principle.

- T^A follows Q_{10}, the atomic dipole.

- V_{ne} has an important contribution from the delocalized electrons from atom B

- $V_{ee}^{AA} \neq 0$. A <mark>direct</mark> measure of electron delocalization

- Delocalization changes all energetic components. The total energetic change is very small.

- The environment $\simeq$ perturbation $\Rightarrow \Delta E_{eff} \simeq \int \Delta \hat{V} \rho^{A,0} \Rightarrow \Delta E_{self} \simeq 0$.

- Interaction energy decomposition.
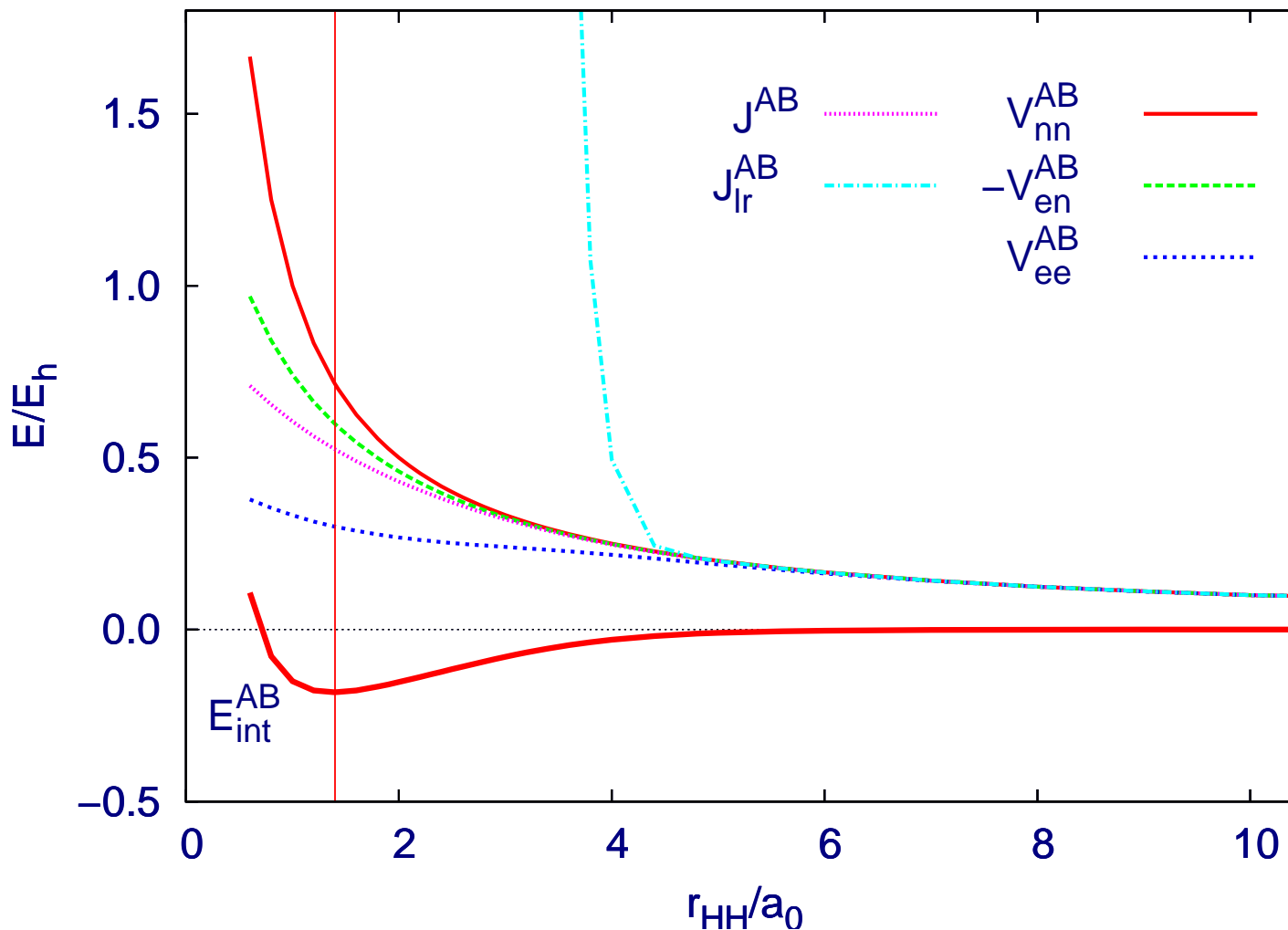
- For $R \geq 4.5$ All components basically converge to Coulombic $1/R$ behavior.

- For $R \leq 4.5$ the series diverges. Overlap (Delocalization) is felt. (Multipolar regime *vs.* short–range regime.

- $V_{ee} < J$. An important part of the interelectron repulsion has **become monocentric**. Not a big E_{self} penalty, a **big** decrease in E_{int} $\Rightarrow$ signature of covalency.

■ Interaction energy decomposition II.
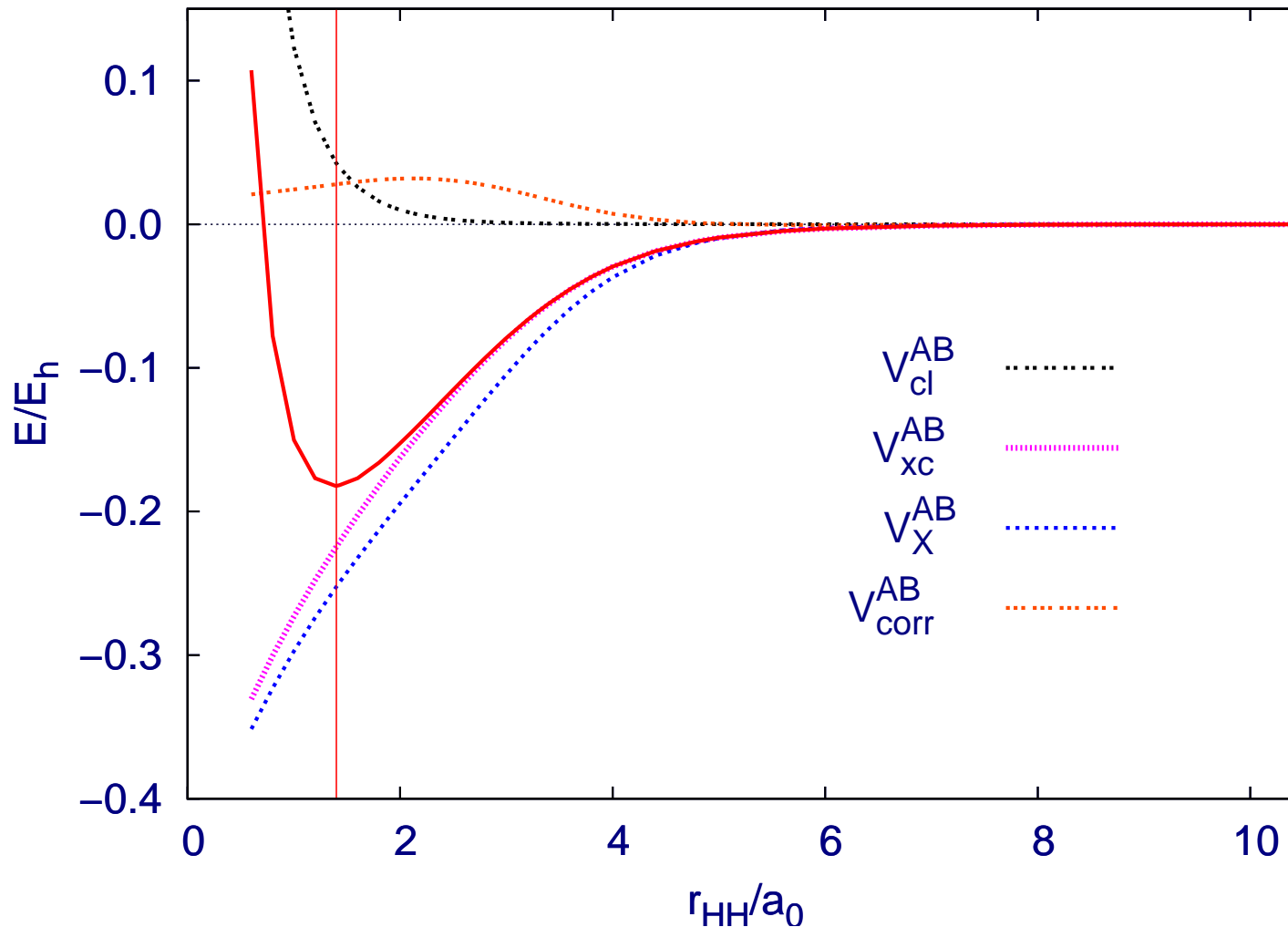
- $V_{clas} > 0$. Small even at R_e. At variance with other analysis.

- E_{int} is the only stabilizing contribution. ==Interaction binded molecule==

- $E_{int} = V_{clas} + V_{xc}$. V_{xc} is the stabilization mechanism. ==Exchange–correlation== binded molecule.

- $V_{xc} = V_X + V_{corr}$:
  - At $R \simeq R_e$, $V_{corr}^{AB} > 0$, $|V_X| \gg |V_{corr}|$. Exchange $\equiv$ Resonance binding.
  - At $R \gg R_e$, $V_{corr}^{AB} < 0$, and $V_{corr}^{AB} \to V_X$. Cannot separate exchange from correlation. Dissociation problem & Static correlation.

Some numbers at the exp. geometry:

Prop.	HF	CAS[2,2]	FCI
Q_1^A	-0.1021	-0.1068	-0.1064
Q_2^Q	-0.3617	-0.3452	-0.3488
T_A	0.5608	0.5805	0.5849
V_{en}^{AA}	-1.2153	-1.2277	-1.2251
V_{ee}^{AA}	0.1979	0.1628	0.1532
J^{AA}	0.3957	0.3994	0.3984
V_{xc}^{AA}	-0.1979	-0.2366	-0.2452
V_X^{AA}	-0.1979	-0.1988	-0.1967
V_{corr}^{AA}	0.0000	-0.0378	-0.0486
E_{def}^{A}	0.0432	0.0154	0.0128
V_{en}^{AB}	-0.5974	-0.5975	-0.5975
V_{ee}^{AB}	0.2619	0.2993	0.2871
J^{AB}	0.5236	0.5237	0.5236
V_{xc}^{AB}	-0.2619	-0.2244	-0.2365
V_X^{AB}	-0.2619	-0.2522	-0.2510
V_{corr}^{AB}	0.0000	0.0279	0.0145
E_{int}^{AB}	-0.2193	-0.1820	-0.1942

- The sensitivity of magnitudes to calculation level **is very dependent** on the type of magnitude.
  - Intraatomic: J (0.9 %, 0.2 %); V_{ne} (1, 0.2); T (5, 1); V_{xc} (20, 4). Those related to xc more sensitive, in general. However, V_X (0.4, 1) relatively stable.
  - Interatomic: Similar behavior. J stable, V_{xc} sensitive through correlation.

- Correlation has different behavior for intra–, interatomic magnitudes. Correlation stabilizes intra-, destabilizes inter-.

- HF delocalizes too many electrons.

- E_{int} (FCI) is about 120 kcal/mol. The resonance energy $V_X \simeq 160$ kcal/mol. In agreement with **chemical wisdom** E_{def} decreases on increasing electron correlation.
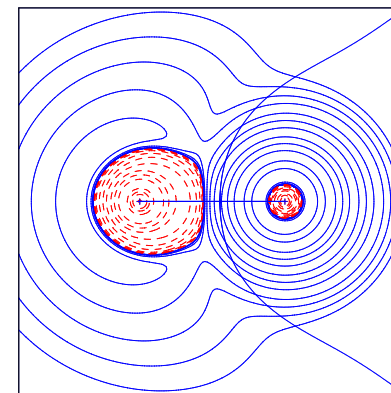
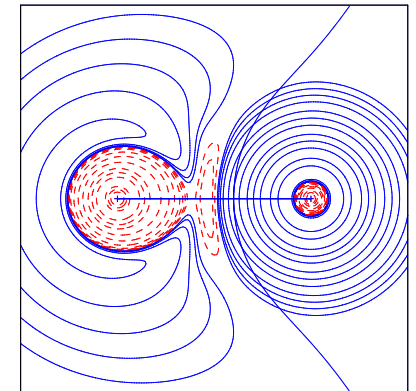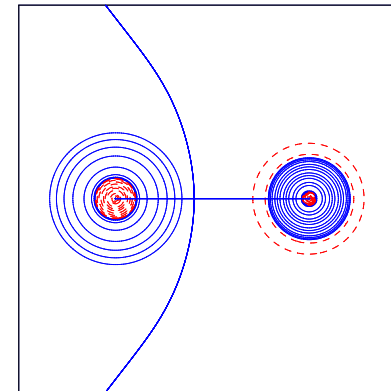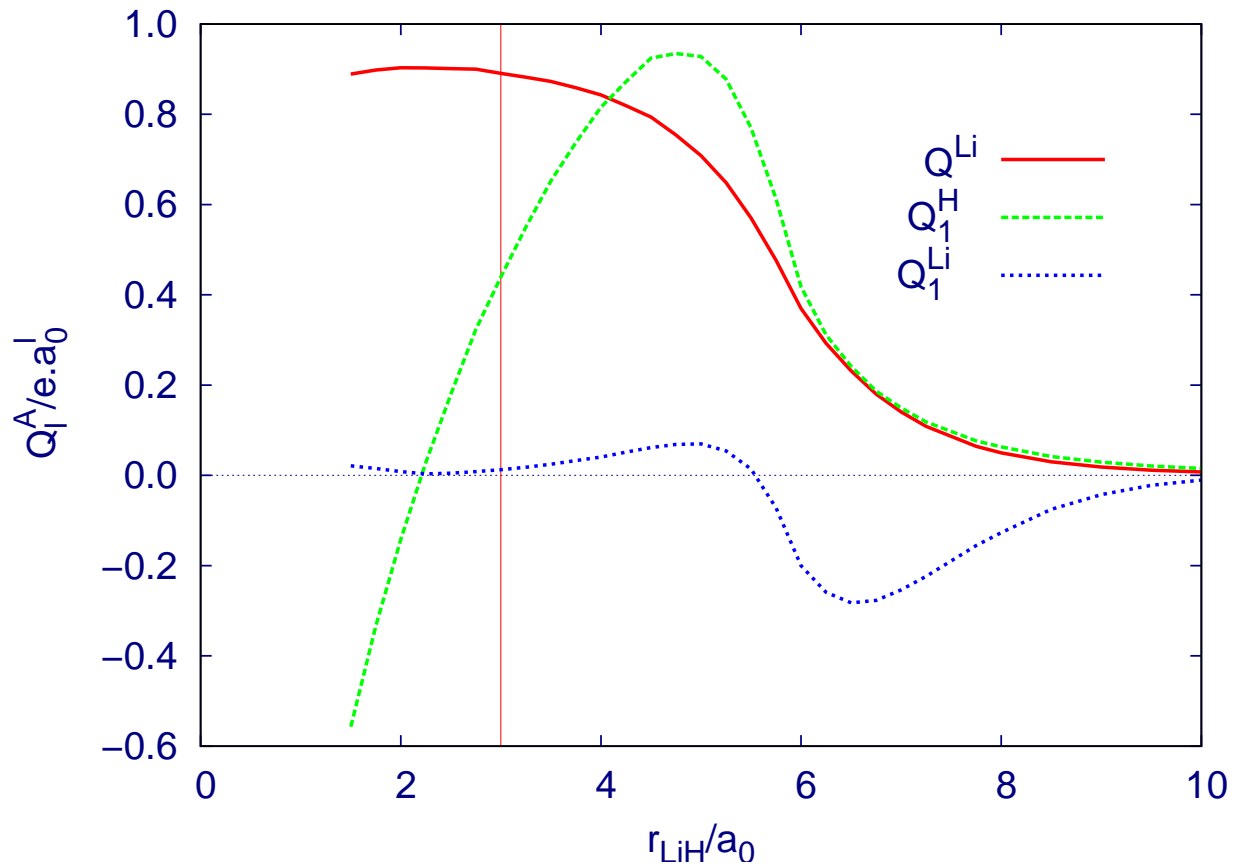# The H_2 molecule II. The $^3\Sigma_u^+$ state

- FCI//TZV(p,d) calculations.
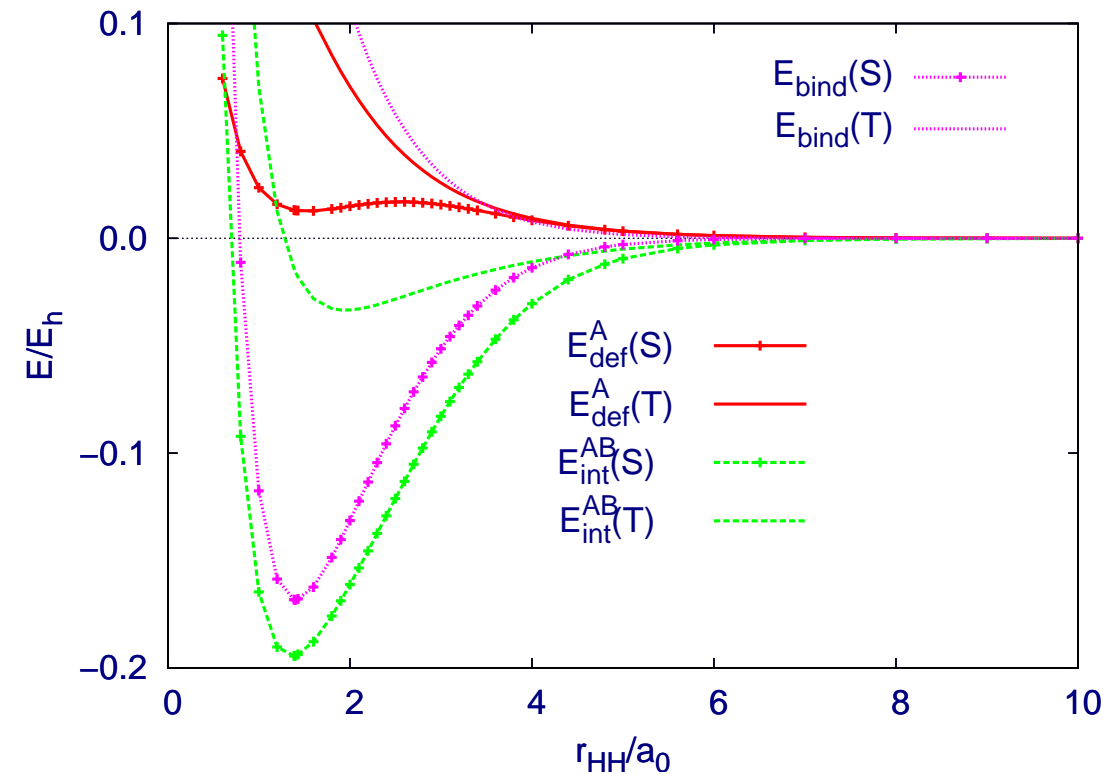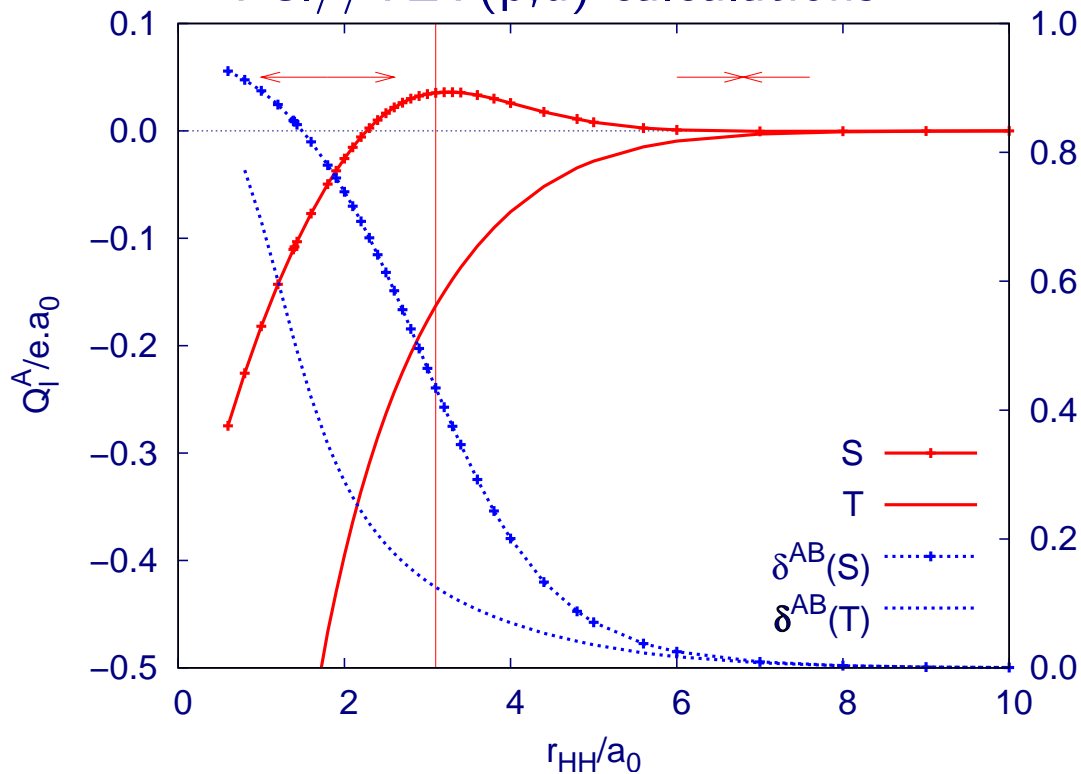
- The triplet does not accummulate bonding charge. Delocalization is smaller.

- A much smaller, but stabilizing, E_{int}. Why?

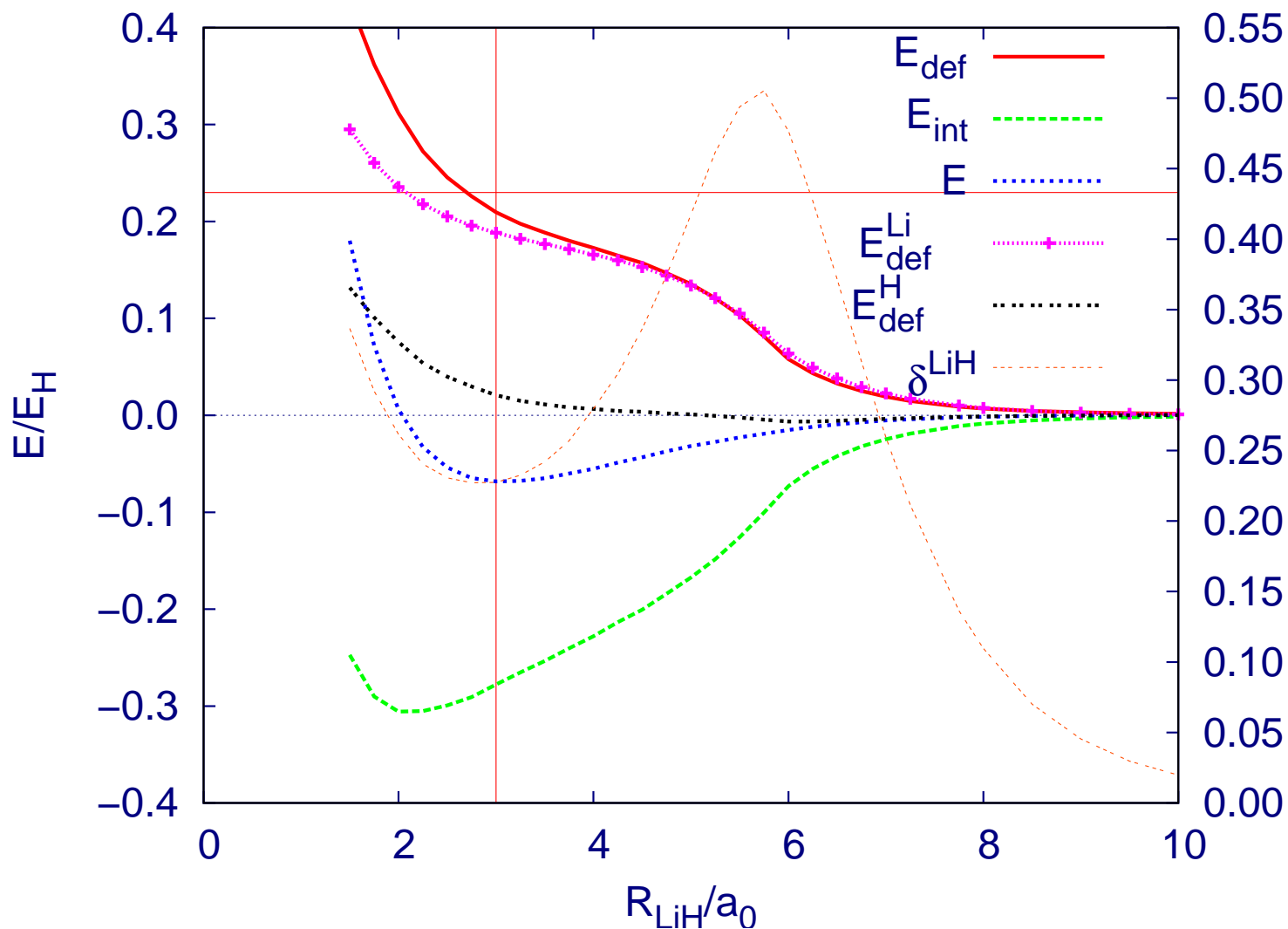- The triplet has a much larger deformation energy. Why?

Charge Transfer. The LiH molecule.

- CAS[2,2]//6-311G* calculations.

$R = 10, 5.5, 3$ bohr.

Hook Ionization.

Forward & backwards

polarization.

- Binding energy Analysis: The reference.

- E_{def}/neutral atoms $\simeq$ 140 kcal/mol.

- E_{def}/ions $\simeq$ -12 kcal/mol. Negative due to incomplete ionization.

- Everything has two regimes. Atomic, Ionic.

- E_{def} due to E_{self}^{Li}.

- E_{self}^{Li} $-$ E^{Li^+} just -5 kcal/mol.

- δ^{LiH} describes beautifully the ionization.

- Interaction Energy. Classical Behavior
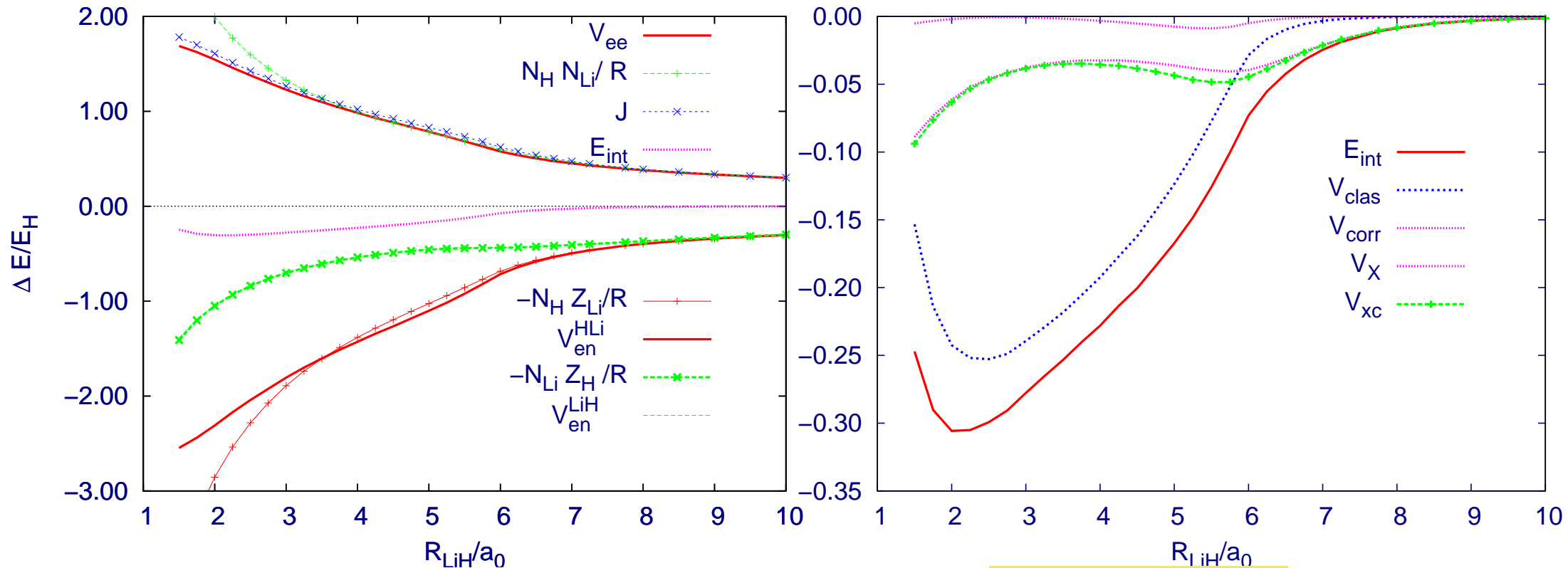
- All the interaction terms are very well represented by their classical expressions

- V_{clas} is 86 % E_{int} at R_e! Electrostatically binded system.

- $V_{xc} \simeq$ resonance. Two regimes with a plateau. Weakly correlated system.

Polar bonds: the $^1A_1$ H_2O molecule.

- CAS[6,5]//6-311G** calculation.
  - 3 Quantum Atoms, 2 bond paths; 2 bonded, 1 non–bonded interactions.
  - A summary of the topological properties:

Prop.	Value
ρ_b	0.3896
$\nabla^2\rho_b$	-2.7361
G	0.0897
$Q(H)$	0.5598
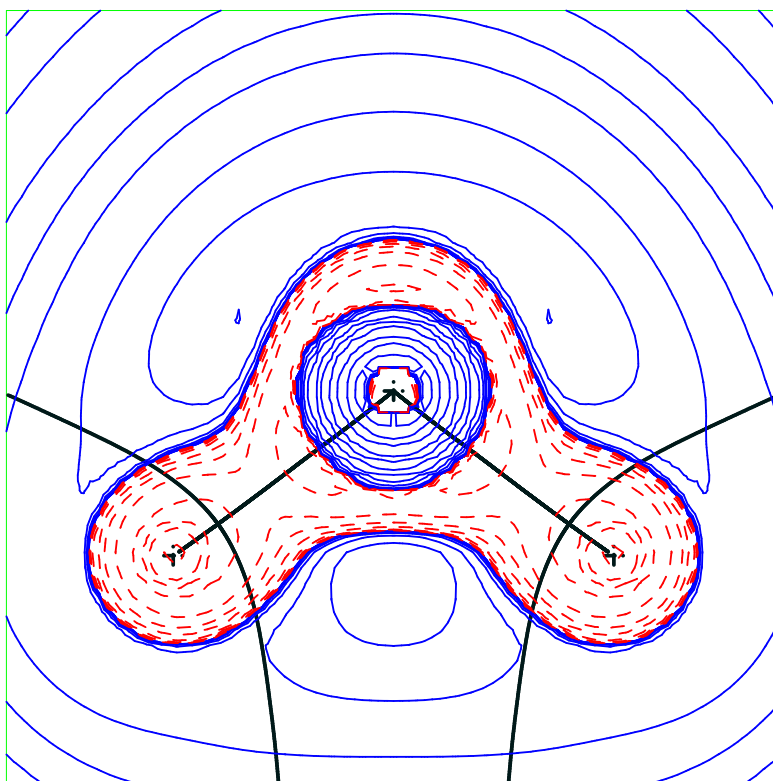
- Large density at BCP.
- Large negative Laplacian.
- Considerable CT.
- Shared interaction.
- Two non–bonded VCC's

What do we expect on physical grounds?

- O–H interactions with $\begin{cases} \text{large Exchange/Resonance contributions.} \\ \text{large Electrostatic terms.} \end{cases}$

- H–H interaction with important classical repulsion.

Property	O	H
ΔT^A	0.6349	-0.1060
ΔV_{en}^{AA}	-6.5823	0.1187
ΔV_{ee}^{AA}	6.1149	0.0431
E_{def}^A	0.1675	0.1956

	OH	HH
E_{int}^{AB}	-0.4897	0.1239
V_{xc}^{AB}	-0.1976	-0.0055
V_{clas}^{AB}	-0.2921	0.1295
J_{lr}^{AB}	diverges	0.1376
δ^{AB}	0.6148	0.0404

- A reference is difficult to find.

- The H atom looses charge $\Rightarrow \Delta T < 0, \Delta V_{en} > 0$.

- OH delocalization very large $\Rightarrow \Delta V_{ee} > 0$.

- E_{int} for OH very large. 60/40 partition into class cal/QM
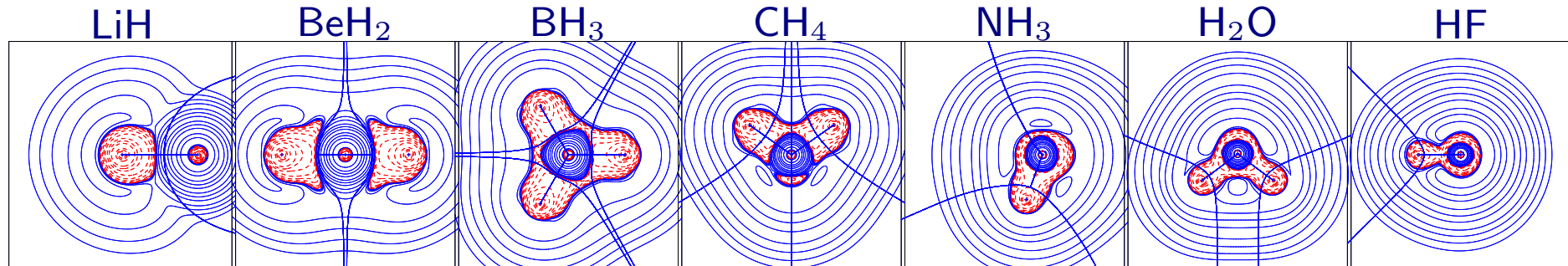
- V_{xc} for OH similar to the single bond in H_2.

- HH interaction dominated by classical, multipolar repulsion.

- Negligible HH delocalization.

- Clear partition into bonded & non–bonded interactions.

4. Other IQA examples.

- Ionicity, Polarity, Covalency. HF//TZV(p,d)

	LiH	BeH$_2$	BH$_3$	CH$_4$	NH$_3$	H$_2$O	HF
Q(H)	-0.9111	-0.8684	-0.6973	-0.0394	0.3611	0.6035	0.5800
δ^{AH}	0.2040	0.2651	0.5143	0.9835	0.8816	0.6450	0.6762
δ^{HH}	-	0.0904	0.1416	0.0434	0.0173	0.0077	-
E_{int}^{AH}	-0.2886	-0.7009	-0.8791	-0.2530	-0.4062	-0.5551	-0.2652
E_{clas}^{AH}	-0.2518	-0.6389	-0.7361	0.0347	-0.1384	-0.3548	-0.1395
V_X^{AB}	-0.0367	-0.0620	-0.1429	-0.2877	-0.2679	-0.2002	-0.1257
$\nabla^2\rho_b$	0.1420	1.4354	-0.3101	-1.0595	-1.9089	-3.0992	-3.8719

- Bond formation and bond breaking. H_2O CAS[6,5]//6-311G** calculation.
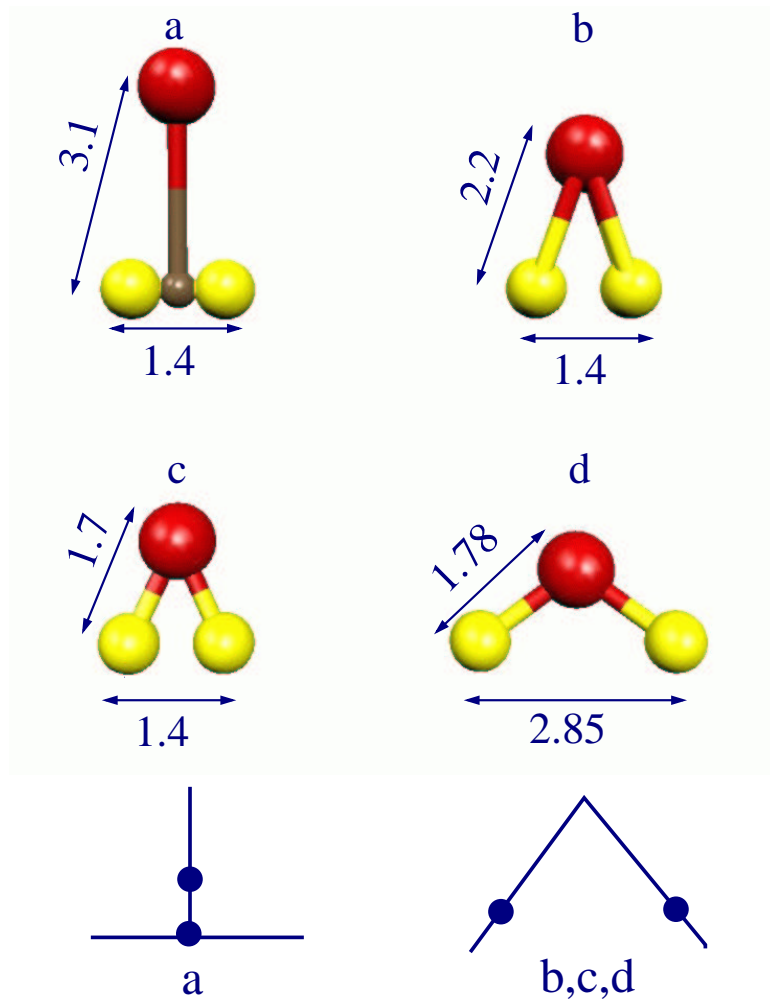
Property	a	b	c	d
Q_{H}	0.088	0.312	0.546	0.560
$E_{\mathrm{int}}^{\mathrm{OH}}$	-0.059	-0.227	-0.518	-0.490
$V_{\mathrm{clas}}^{\mathrm{OH}}$	0.001	-0.052	-0.304	-0.292
V_{xc}^{OH}	-0.060	-0.175	-0.214	-0.198
$E_{\mathrm{int}}^{\mathrm{HH}}$	-0.138	0.016	0.252	0.124
$V_{\mathrm{clas}}^{\mathrm{HH}}$	0.050	0.117	0.278	0.130
V_{xc}^{HH}	-0.188	-0.098	-0.026	-0.006
$E_{\mathrm{H_2}}$	-1.018	-0.722	-0.345	-0.485
E_{O}	-74.731	-74.783	-74.577	-74.633

- **Isomers & Functional Groups:** HCN *vs.* CNH. [HF//TZV(p,d)]

CNH

Net charge

δAB

R(bohr)

E_{self}

0.022

1.742   0.664

1.174   2.168   −1.749   1.857   0.575

−36.8493   −53.3398   −0.3028

0.084

0.916   2.291

0.212   1.999   +1.200   2.128   −1.411

−0.4175   −36.8044   −53.5601

HCN

- Isomers & Functional Groups: HCN *vs.* CNH. [HF//TZV(p,d)]

CNH
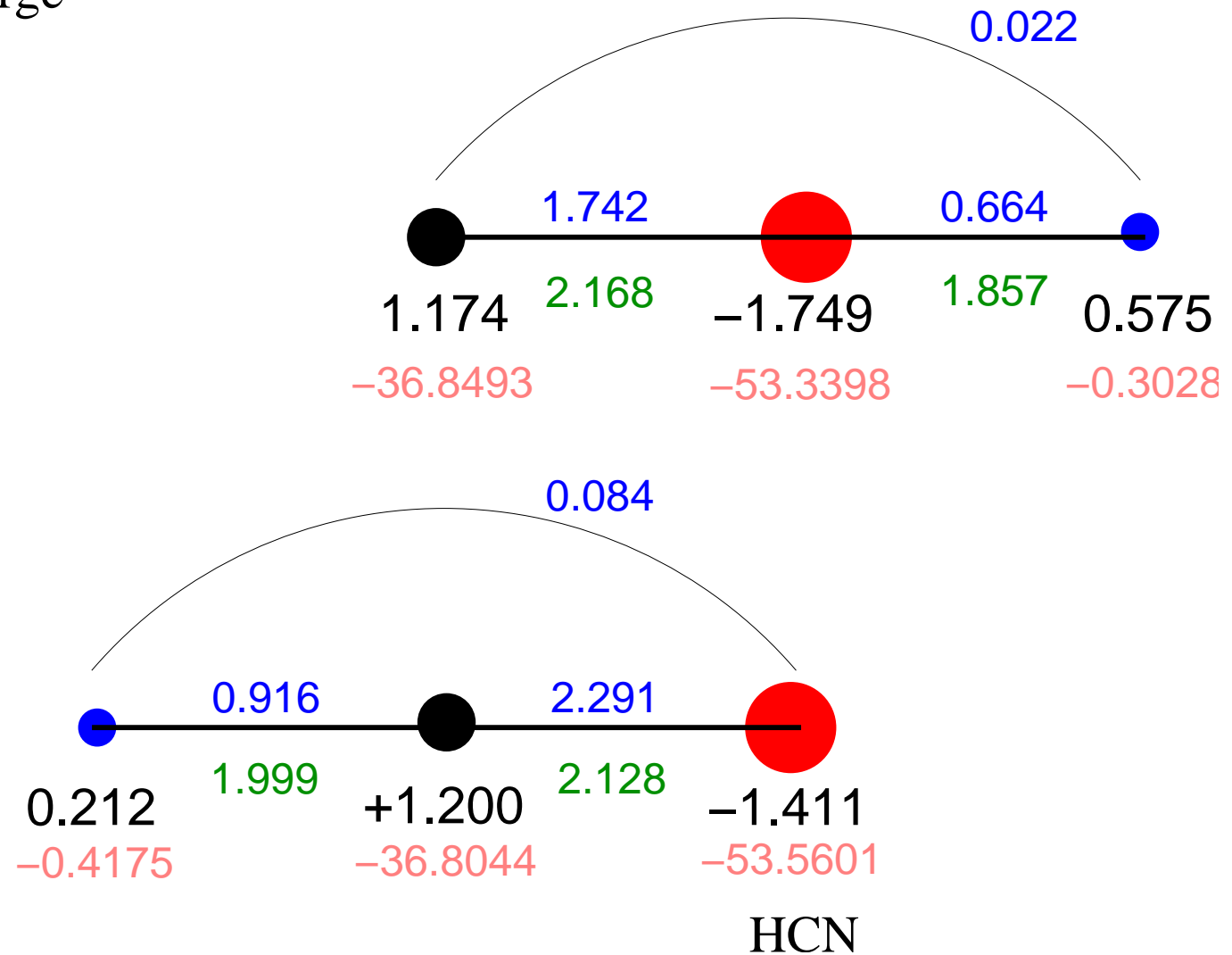
Net charge
E_{int}^{AB}
V_{xc}^{AB}
E_{self}

0.2425
−0.0023

−2.0702   −0.5710
1.174 −0.4632 −1.749 −0.2091 0.575
−36.8493   −53.3398   −0.3028

−0.1060
−0.0104

−0.1240   −1.8862
0.212 −0.2774 +1.200 −0.5763 −1.411
−0.4175   −36.8044   −53.5601

HCN

- Isomers & Functional Groups: HCN *vs.* CNH. [HF//TZV(p,d)]
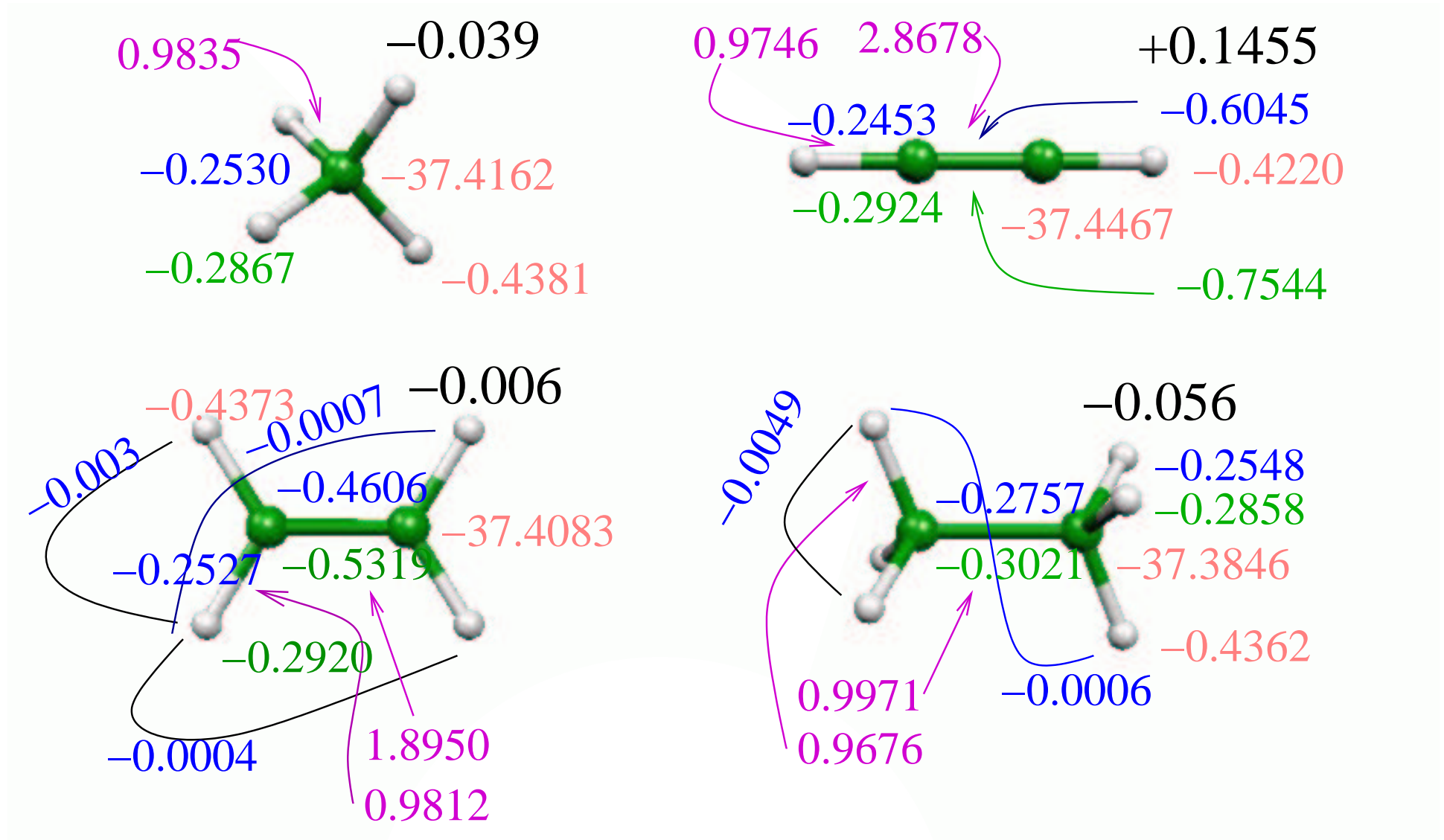
CNH

Net charge

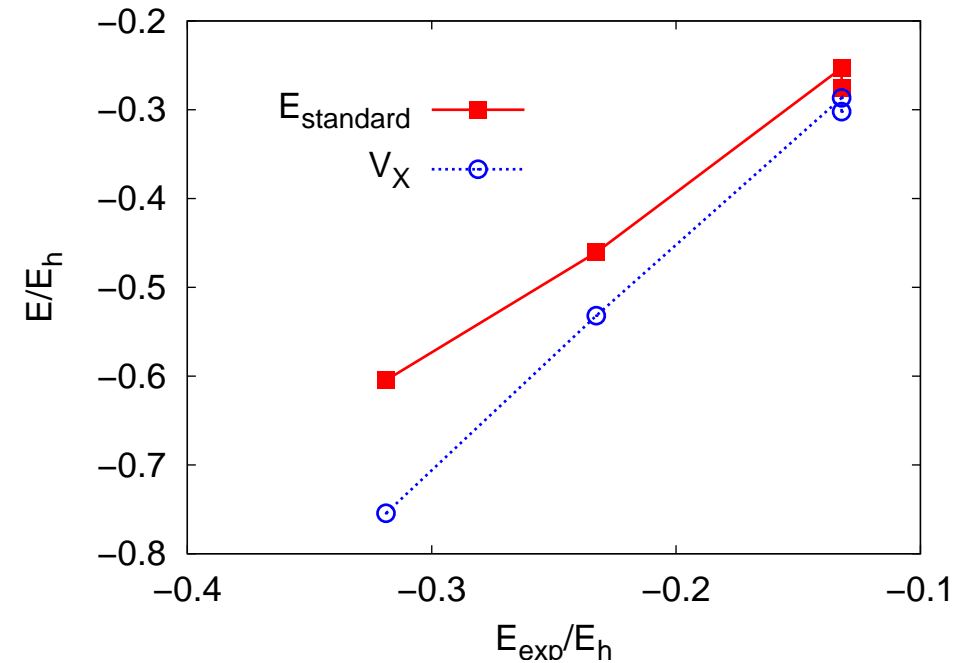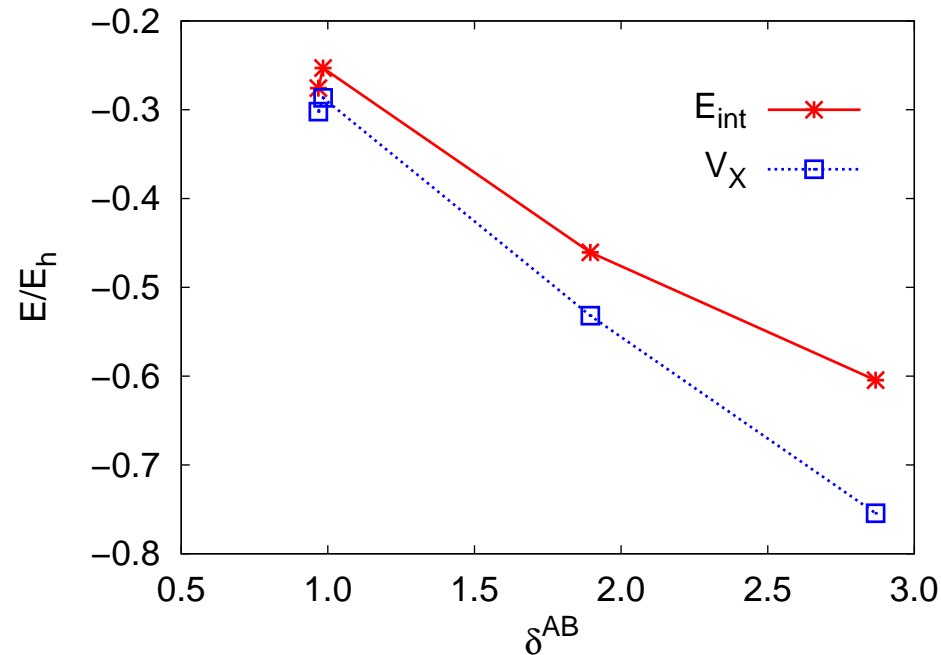E^{AB}_{int}

V^{AB}_{xc}

E_{self}

- $\Delta E \simeq 10$ kcal/mol.

- $\Delta E_{self}(CN) < 6$ kcal/mol.

- E_{self} (CN/HCN) within 1 kcal/mol of extrapolated value using the E.A. of CN (0.1420).

−0.3285

−0.2114

0.575

−92.2593   −0.3028

−0.2300

−0.2878

0.212

−0.4175   −92.2507

HCN
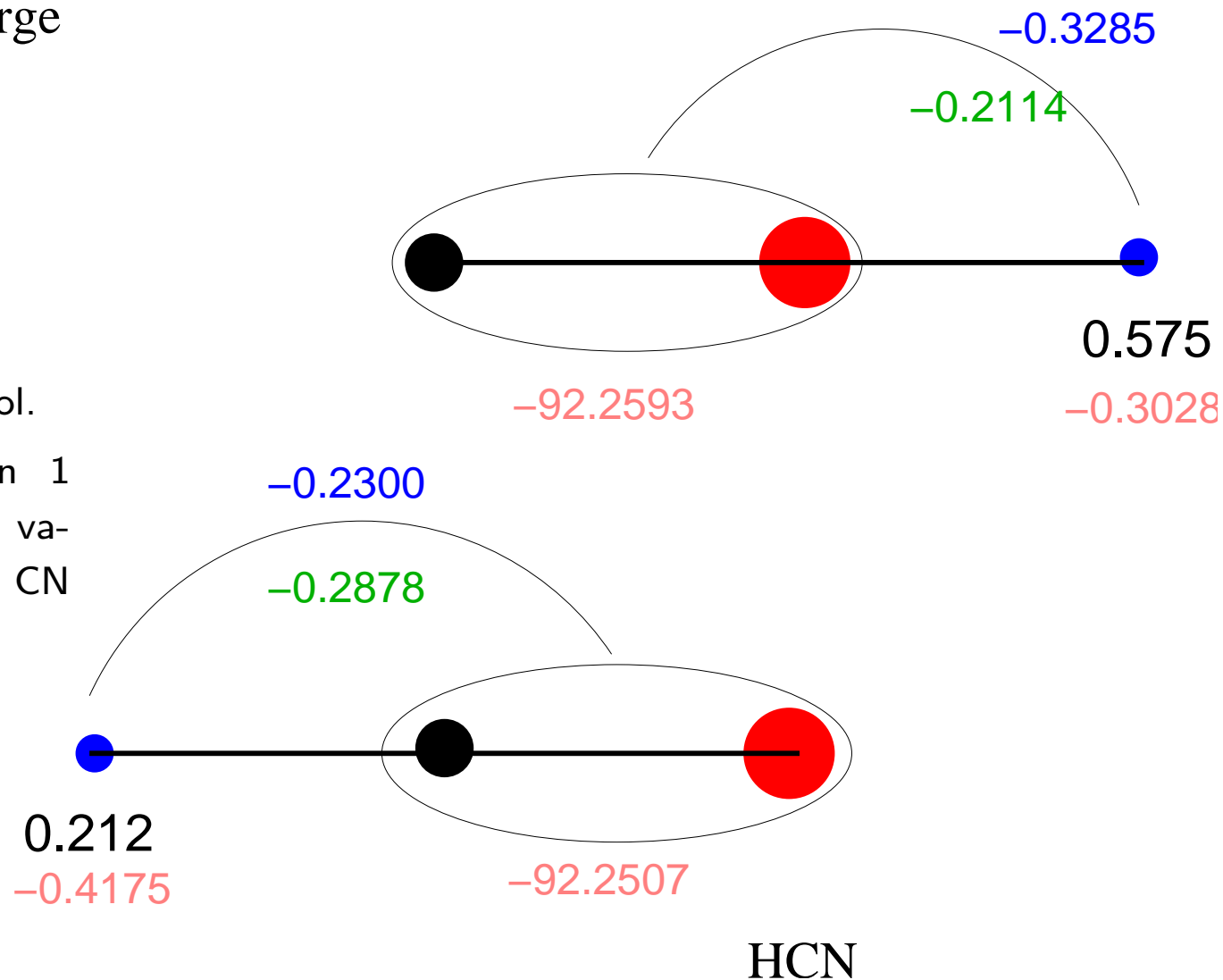
- Multiple bonds. Ethane-Ethyne HF//TZV(p,d)

- Multiple bonds. HF//TZV(p,d)

- E_{int}^{AB} changes by a few kcal/mol for equivalent bonds.

- Interaction energies are proportional to delocalization indices.

  ○ The correlation is best for V_{xc}^{AB}.

- Standard Bond energies are proportional to Interaction Energies.

  ○ The correlation is best for V_{xc}^{AB}.

Bibliography:

- R. F. W. Bader, Atoms in Molecules. A Quantum Theory. Oxford 1990.

- C. Gatti, P. Macchi, Eds. Modern Charge density analysis. Springer 2012.

- R. Chauvin, C. Lepetitt, B. Silvi, E. Alikhani, Eds. Applications of Topological Methods in Molecular Chemistry. Springer, 2016.

- A. Martín Pendás, M. A. Blanco, E. Francisco, *J. Chem. Phys.* **120**, 4581 (2004)

- M. A. Blanco, A. Martín Pendás, E. Francisco, *J. Chem. Theory Comput.* **1**, 1096 (2005)

- A. Martín Pendás, M. A. Blanco, E. Francisco, *J. Comput. Chem.* **2**, 90 (2006)

- A. Martín Pendás, E. Francisco, M. A. Blanco, and C. Gatti, *Chem. Eur. J.* **13**, 9362 (2007)