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# A real space perspective of how energy and electrons distribute in molecules: Interacting quantum atoms and electron distribution functions



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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.

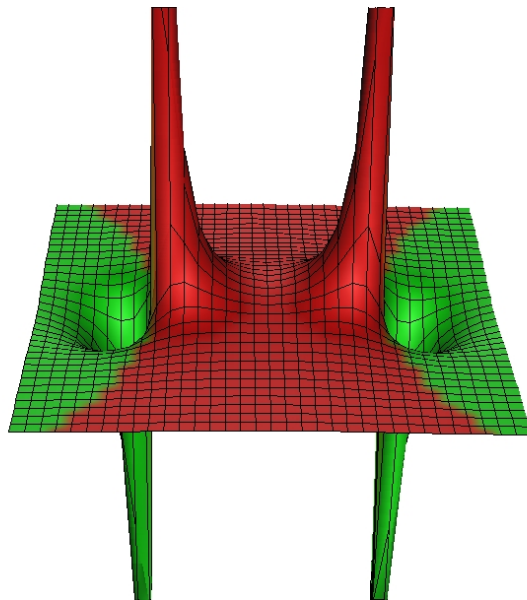
# 1. Introduction.

- 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  $\Psi$ ?**

$$\Psi \Leftrightarrow \text{Chemistry}$$

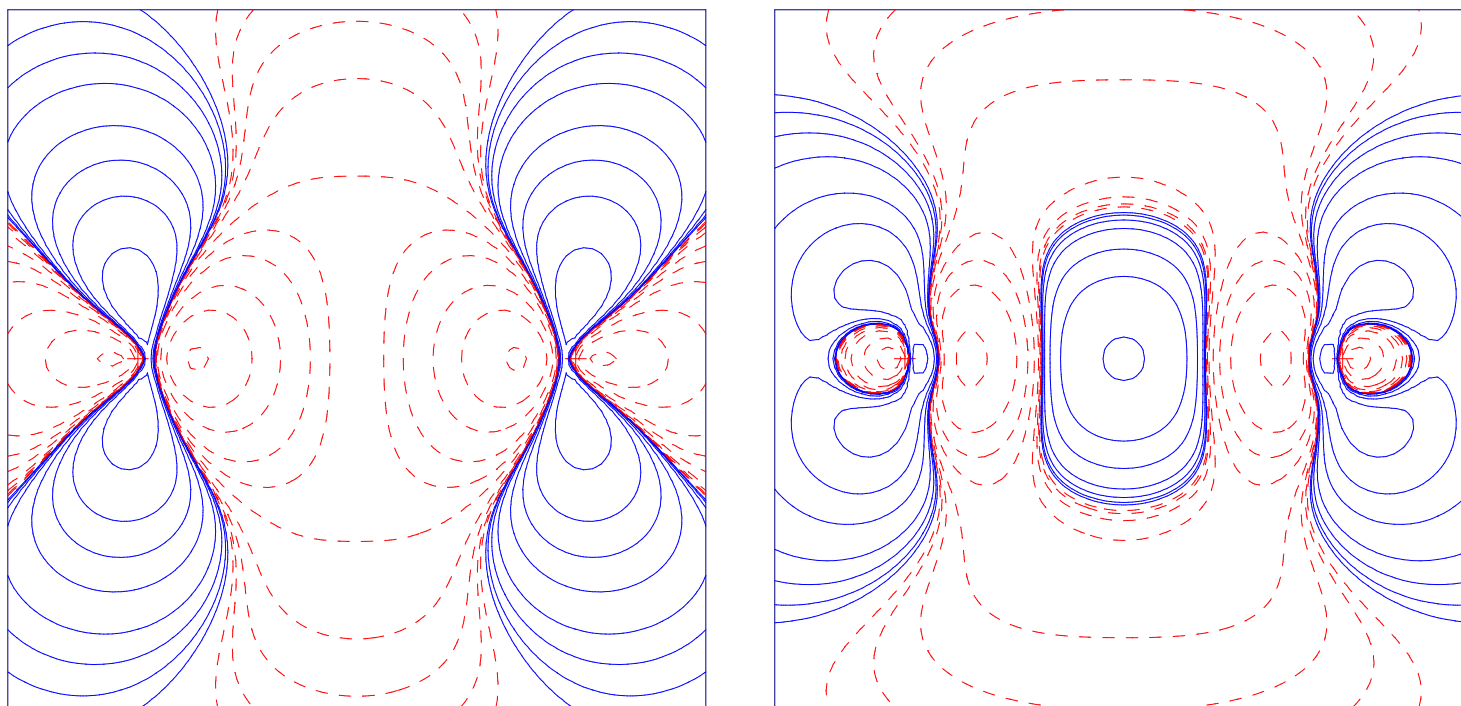
## Density and the chemical bond.

- 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 indefinities? Look at derivatives.
  - Charge accumulation & 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  $f : D \rightarrow R$
  2. Construct its gradient field:  $\nabla f$
  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:  $(\rho, \text{ELF}, \dots)$
- **The QTAIM is based on the attraction basins of  $\rho$ .**
  - 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*  $\rho$ .

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

that we will call potential.

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

$$\nabla\rho = \mathbf{i} \frac{\partial\rho}{\partial x} + \mathbf{j} \frac{\partial\rho}{\partial y} + \mathbf{k} \frac{\partial\rho}{\partial z} = \rho_x \mathbf{i} + \rho_y \mathbf{j} + \rho_z \mathbf{k}.$$

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

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

Some of their properties are:

1. One and only one trajectory of  $\nabla\rho$  passes through any point  $\mathbf{r}$  of the domain space. This is equivalent to saying that field trajectories of  $\nabla\rho$  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  $\mathbf{r}$ , the vector  $\nabla\rho(\mathbf{r})$  is tangent to the field line passing through that point.
3. Given that the gradient field always points along the steepest ascent direction of  $\rho$ , the trajectories of  $\nabla\rho$  are *orthogonal to the isoscalar lines*.
4. *Each trajectory must originate or end up either at a point where  $\nabla\rho(\mathbf{r}) = \mathbf{0}$ , or at infinity.*



## Critical points of a field:

- Those points in  $\mathbb{R}^3$  that satisfy the condition  $\dot{\mathbf{r}} = \mathbf{0}$  are called **critical points**.
- **$\alpha$ - and  $\omega$ -limits of a point  $p$ :**  
The geometrical locus of  $\lim_{t \rightarrow -\infty} \mathbf{r}$  y  $\lim_{t \rightarrow +\infty} \mathbf{r}$ , 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,  $\mathbf{r}_c$ :

$$\begin{aligned}\dot{\mathbf{r}} &= \mathbf{f}(\mathbf{r}) \simeq \mathbf{f}(\mathbf{r}_c) + \mathbb{J}(\mathbf{r} - \mathbf{r}_c) \\ &= \mathbb{J}(\mathbf{r} - \mathbf{r}_c),\end{aligned}$$

where  $\mathbb{J}$  is the Jacobian matrix of the system at  $\mathbf{r}_c$ ,

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

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

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

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

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

$$\dot{\mathbf{r}} = \mathbb{H}\mathbf{r}. \quad (1)$$

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:

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

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

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

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

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

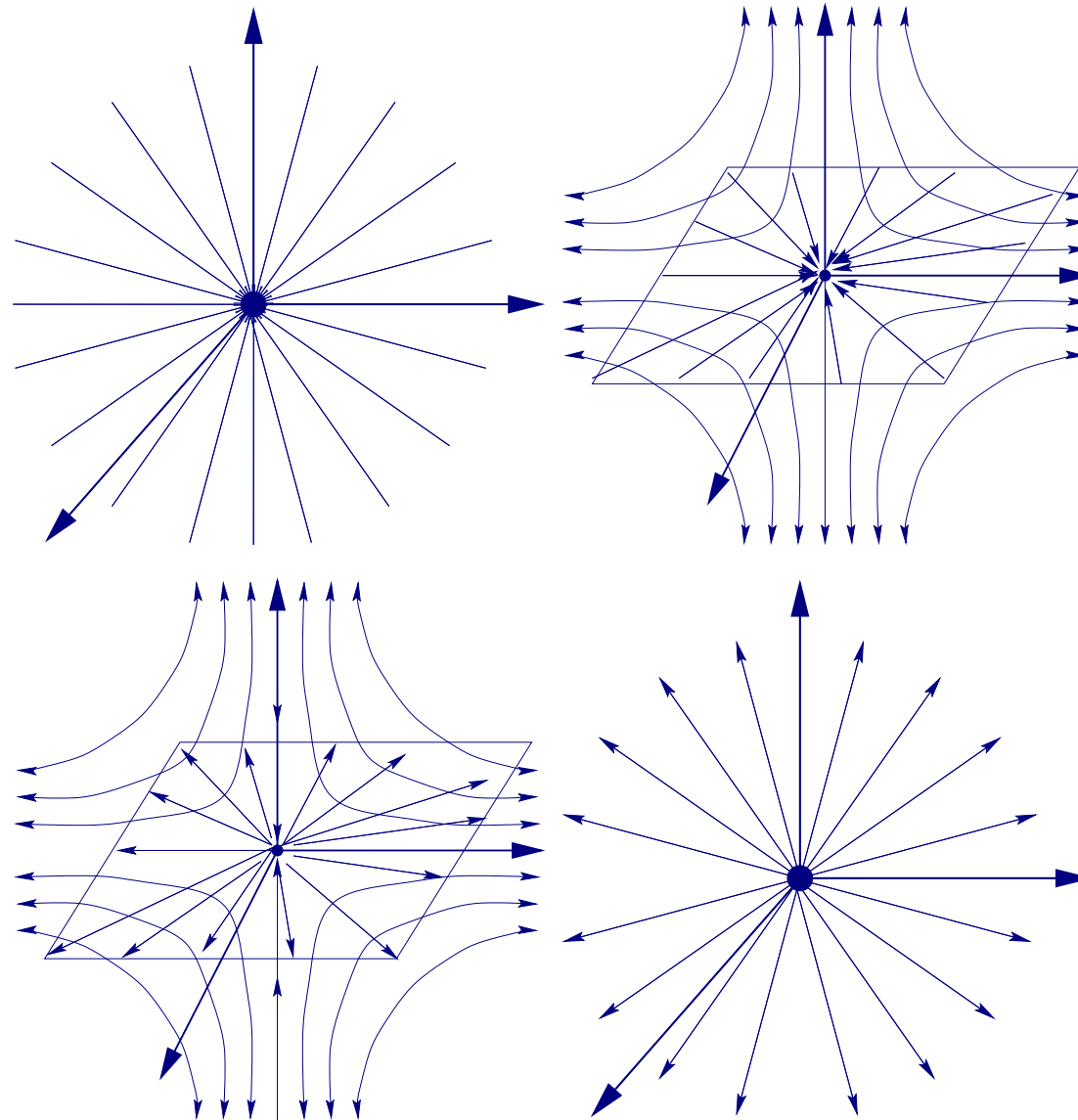
The  $\lambda_i$  coefficients are also called characteristic or Lyapunov exponents. And the eigen frame is usually known as the principal system of curvature, its axes the principal curvature axes, which coincide with the directions along which the field varies mostly.

- 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 Maximum in $\eta_1$ and $\eta_2$ ; minimum in $\eta_3$	2D	1D
$(3, +1)$	$\lambda_1, \lambda_2 > 0; \lambda_3 < 0;$	Second order saddle Maximum in $\eta_3$ and minimum in $\eta_1$ and $\eta_2$	1D	2D
$(3, +3)$	$\lambda_i > 0 \quad \forall i$	Local Minimum (source)	0D	3D
$(2, -2)$	$\lambda_1, \lambda_2 < 0; \lambda_3 = 0;$	Local Maximum in $\eta_1$ y $\eta_2$	2D	0D
$(2, 0)$	$\lambda_1 < 0; \lambda_2 = 0; \lambda_3 > 0$	Saddle point. Maximum in $\eta_1$ and minimum in $\eta_3$	1D	1D
$(2, +2)$	$\lambda_1 = 0; \lambda_2, \lambda_3 > 0$	Local minimum in $\eta_2$ y $\eta_3$	0D	2D
$(1, -1)$	$\lambda_1 < 0; \lambda_2 = \lambda_3 = 0$	Local Maximum in $\eta_1$	1D	0D
$(1, +1)$	$\lambda_1 = \lambda_2 = 0; \lambda_3 > 0$	Local Minimum in $\eta_3$	0D	1D
$(0, 0)$	$\lambda_1 = \lambda_2 = \lambda_3 = 0$		0D	0D

- **Image:**



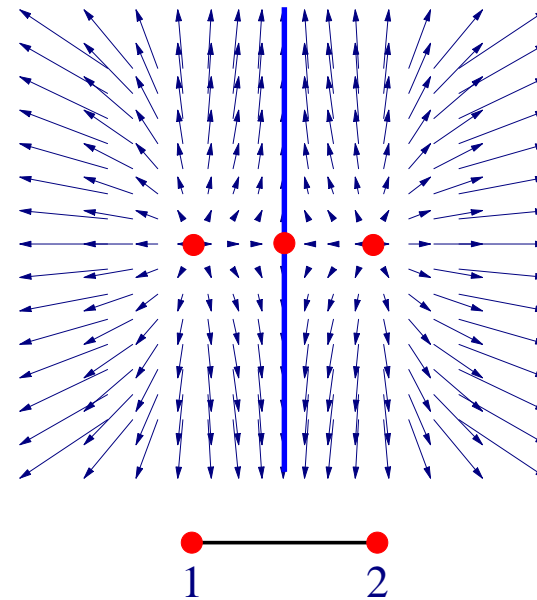
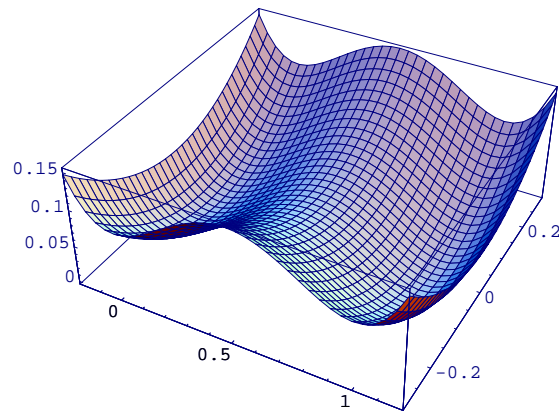
## Basins, separatrices and induced topologies.

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

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

■ Critical points:

$$\mathbb{H} = \left\{ \begin{array}{l} (0, 0) \\ (1, 0) \\ (\frac{1}{2}, 0) \end{array} \right. \left\{ \begin{array}{l} \begin{pmatrix} +2 & 0 \\ 0 & +2 \end{pmatrix} \\ \begin{pmatrix} +2 & 0 \\ 0 & +2 \end{pmatrix} \\ \begin{pmatrix} -1 & 0 \\ 0 & +2 \end{pmatrix} \end{array} \right. \begin{array}{l} \text{Minimum} \\ \text{Minimum} \\ \text{Saddle} \end{array}$$



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

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

- 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 variety  $\mathcal{D}$  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:

$$\begin{aligned}
 N^0 &\geq R_0 \\
 N^1 - N^0 &\geq R_1 - R_0 \\
 &\vdots \\
 \sum_{i=0}^n (-1)^{n-i} N^i &\geq \sum_{i=0}^n (-1)^{n-i} R_i \\
 &\vdots \\
 \sum_{i=0}^l (-1)^i N^i &= \sum_{i=0}^l (-1)^i R_i,
 \end{aligned}$$

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  $N^3 - N^2 + N^1 - N^0 = 0$ .

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

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

## 2. QTAIM Quick Reference Guide

General features of  $\rho$ .

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

$$\rho(\mathbf{r}) = N \sum_{s_1} \int \dots \int d\mathbf{x}_2 \dots d\mathbf{x}_N \int \dots \int d\mathbf{R}_1 \dots d\mathbf{R}_M \Psi^*(\mathbf{x}_1 \dots \mathbf{x}_N, \mathbf{R}_1 \dots \mathbf{R}_M) \Psi(\mathbf{x}_1 \dots \mathbf{x}_N, \mathbf{R}_1 \dots \mathbf{R}_M),$$

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

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

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

$\rho$  is observable. For instance, from elastic X-Ray scattering,

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

where  $A$  is the **Fourier transform** of  $\rho$ .

## Analytical properties of $\rho$ .

- Cusp theorem:

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

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

- Asymptotic behavior:

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

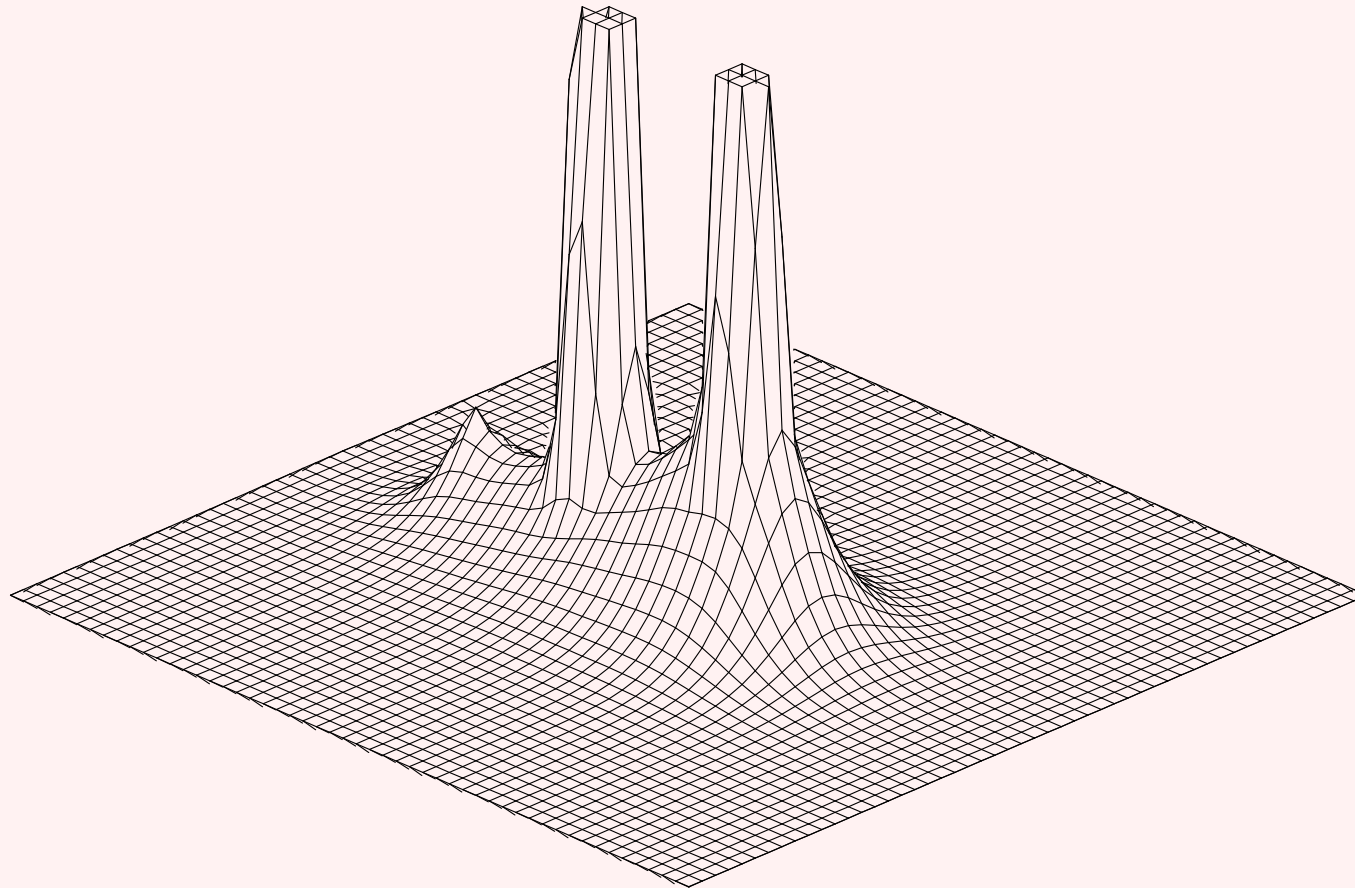
- Hoffmann-Ostenhof and Hoffmann-Ostenhof inequalities:

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

- Monotonicity and convexity are not assured.

## Basic Morphology of $\rho$ .

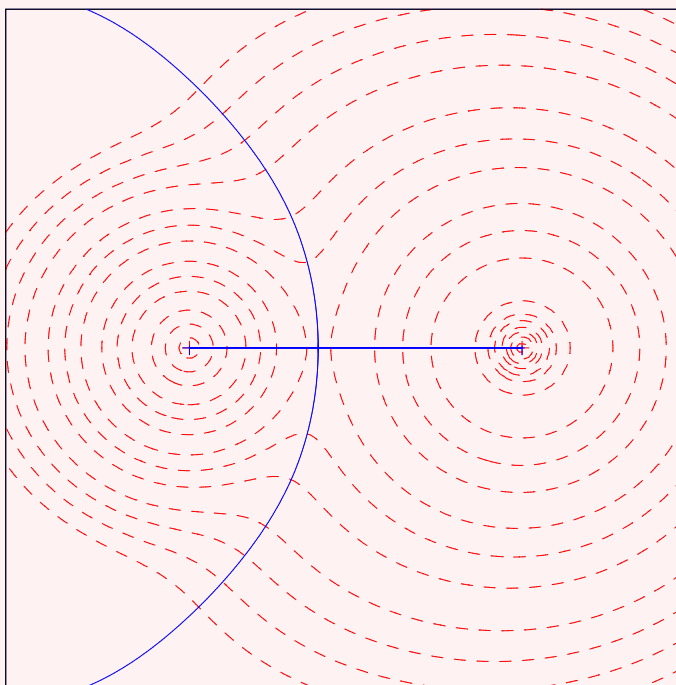
HCN (HF/6-311G(p,d))



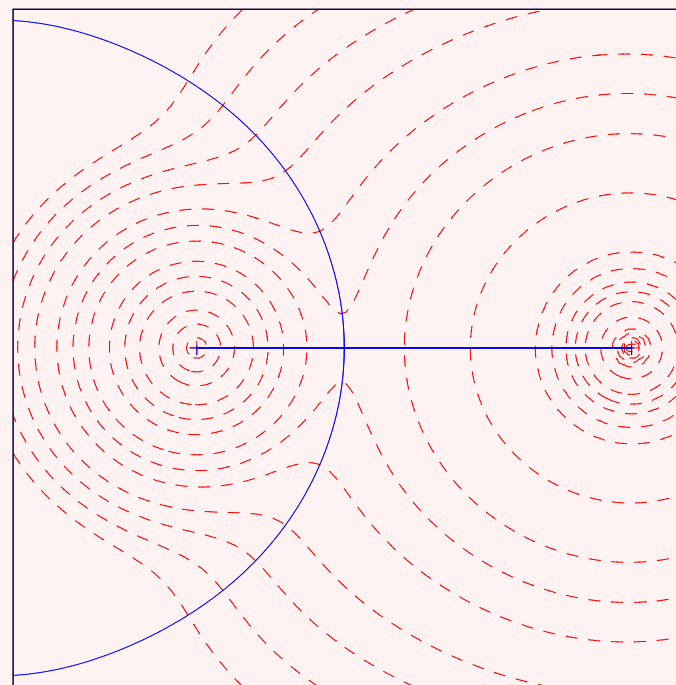
We rectify the  $\rho$  field.

## Topological analysis of $\rho$ .

In general, the number of attractors of the  $\rho$  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\*)



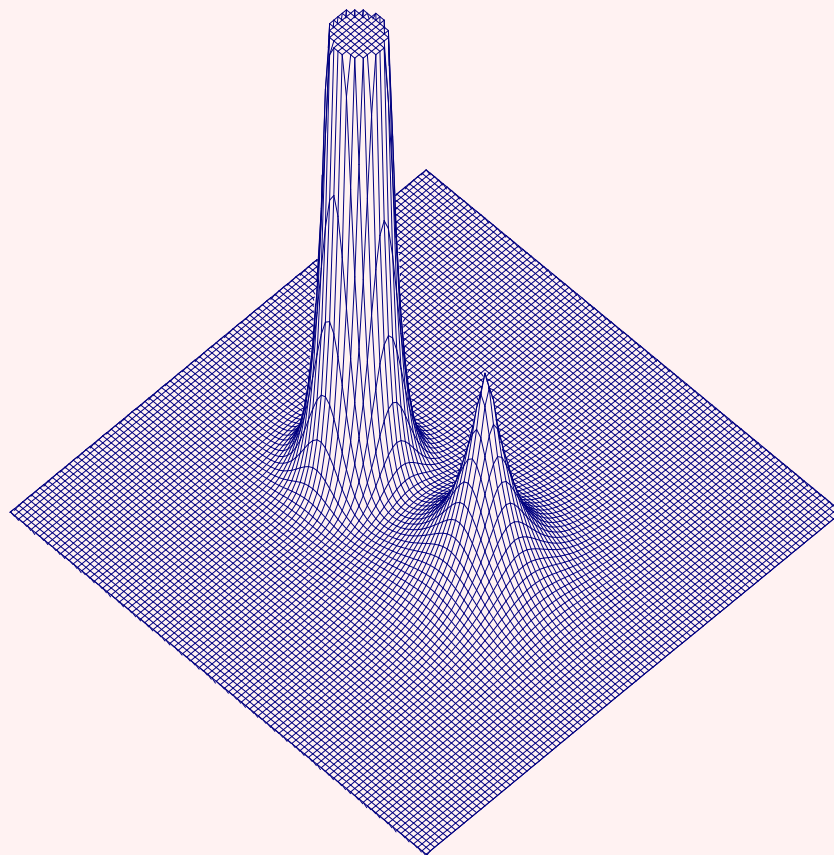
LiCl (HF/6-311G\*)

**The basins** of equal atoms under similar bonding regimes seem to be **transferable**.

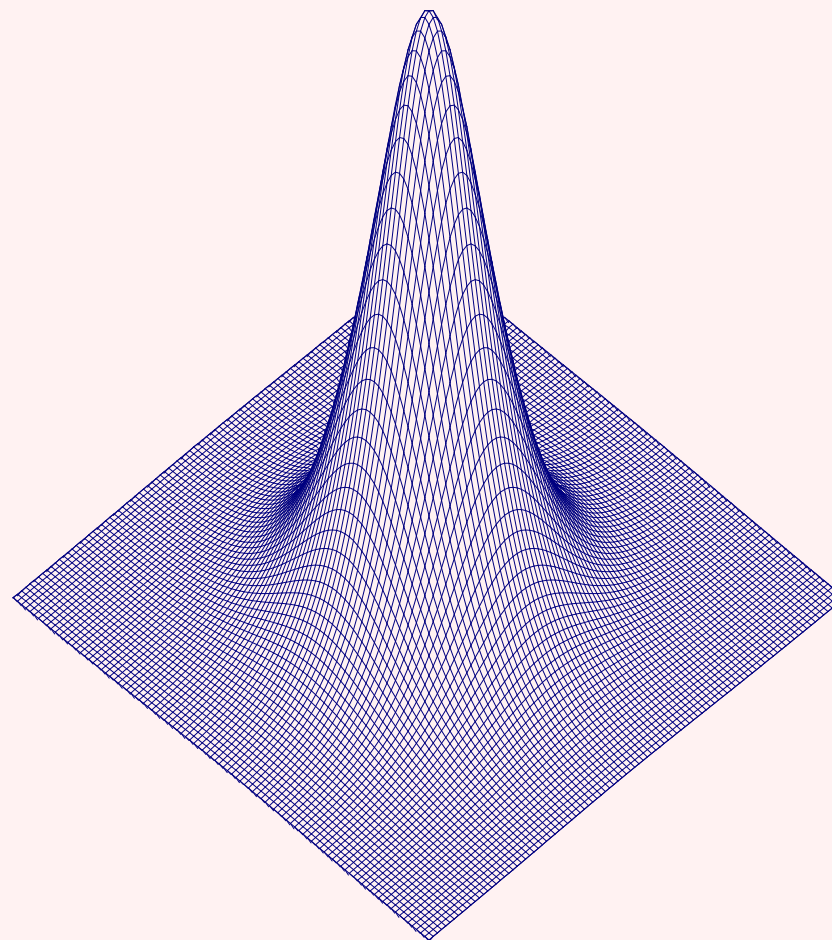
Critical points  $\nabla\rho = 0$  are important, and classified according to the eigenvalues of the Hessian of  $\rho$ :  $(3,-1) \equiv$  two negative, one positive curvatures.

## Usual representations. (LiH HF/TZV)

a) Projected relief diagrams.

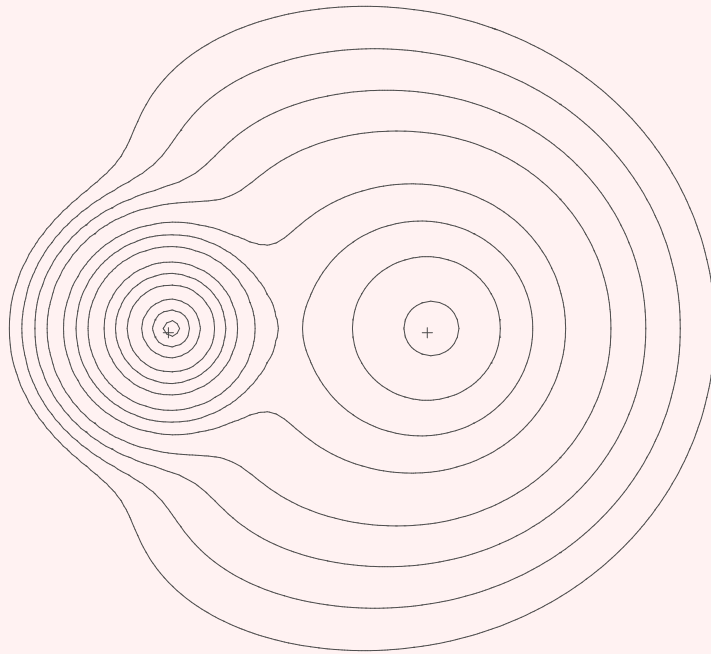


Nuclear plane

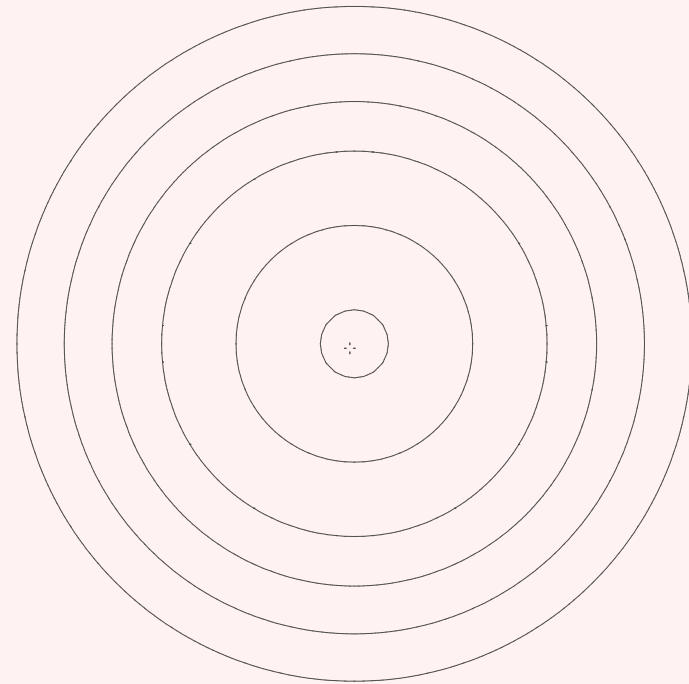


Perpendicular plane

b) Projected contour diagrams.

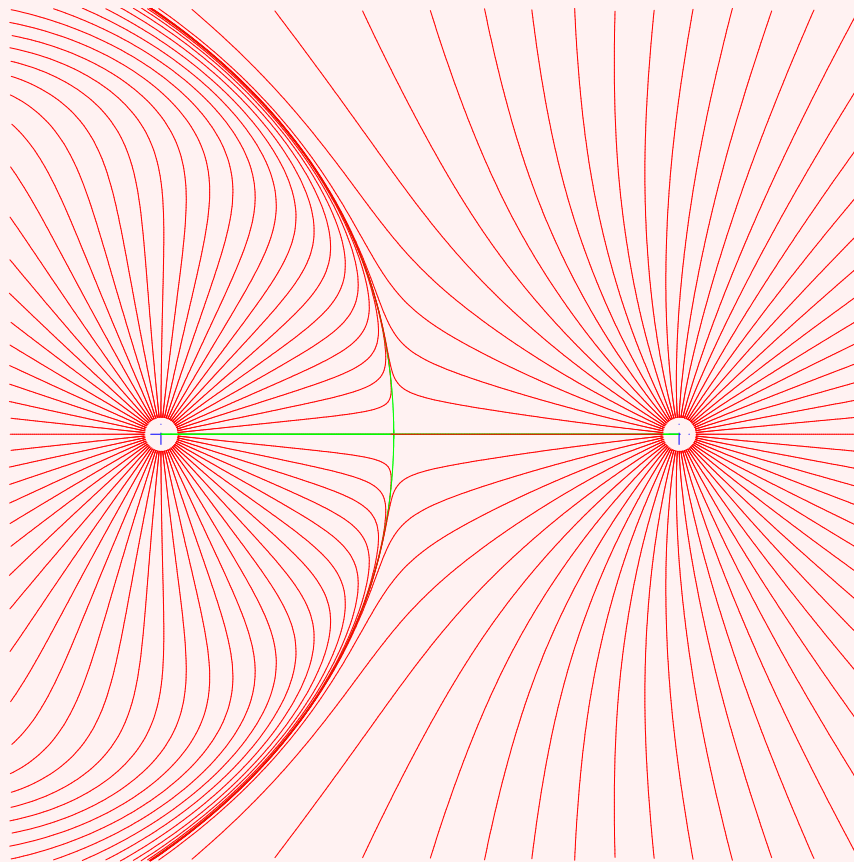


Nuclear plane

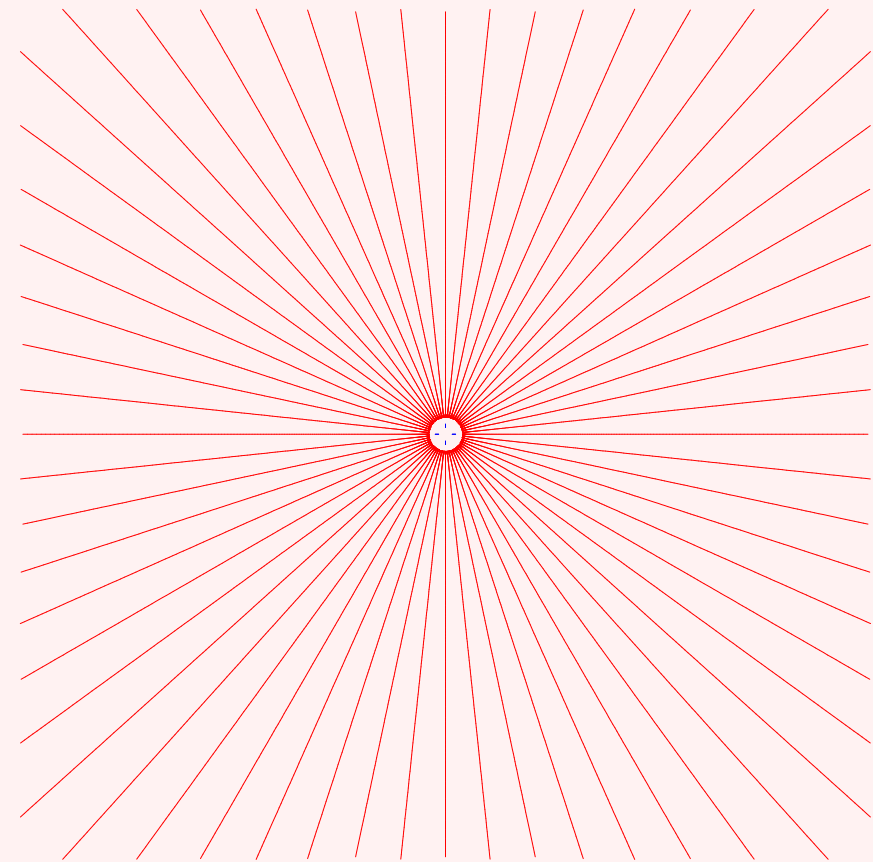


Perpendicular plane

c) Projected gradient field diagrams.



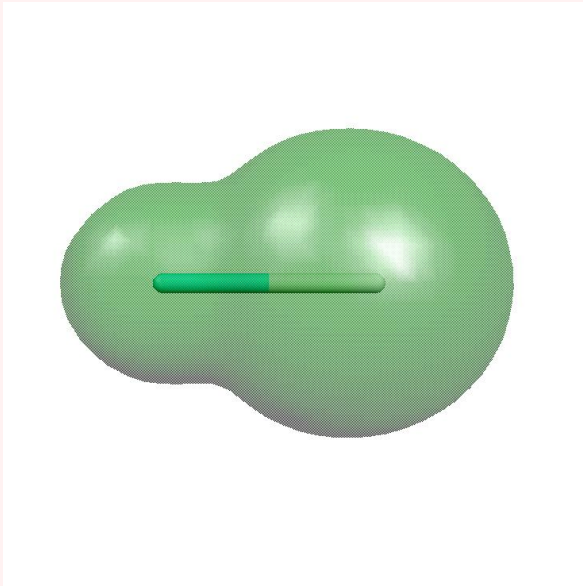
Nuclear plane



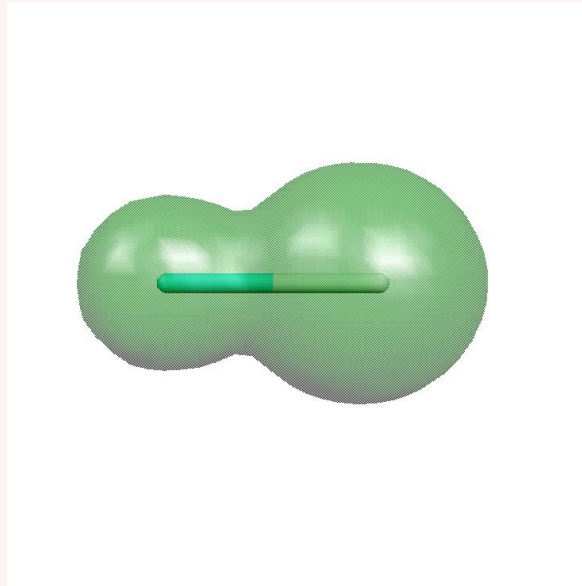
Perpendicular plane



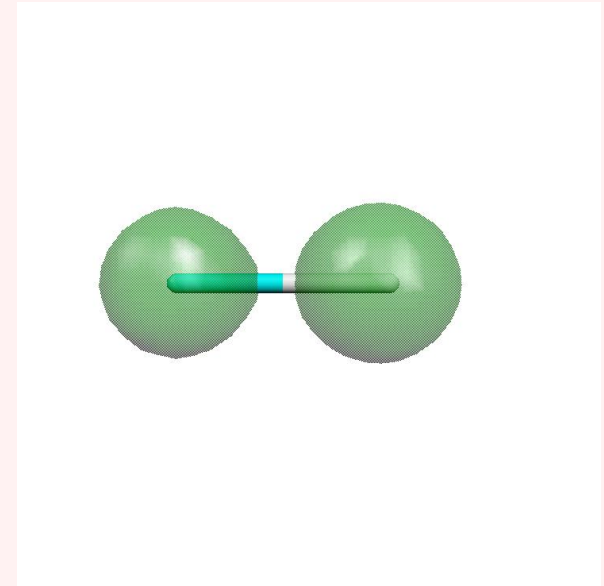
## (d) Isosurfaces.



$$\rho = 0.01$$



$$\rho = 0.02$$

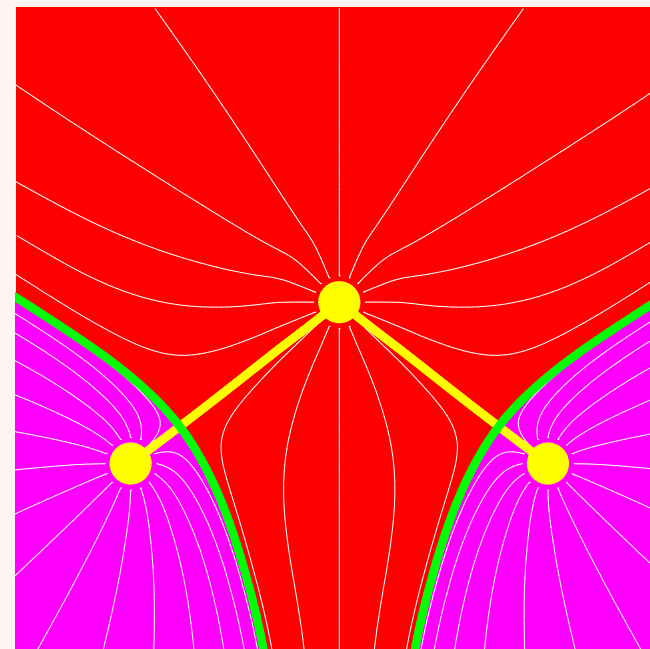
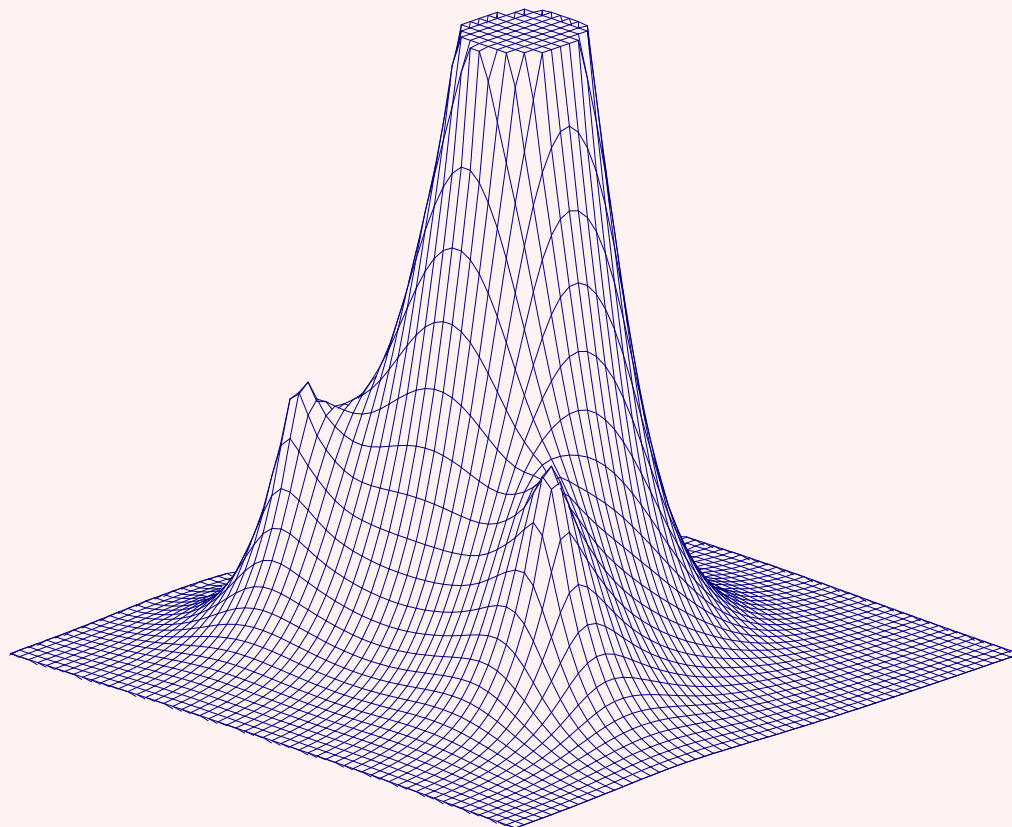


$$\rho = 0.05$$

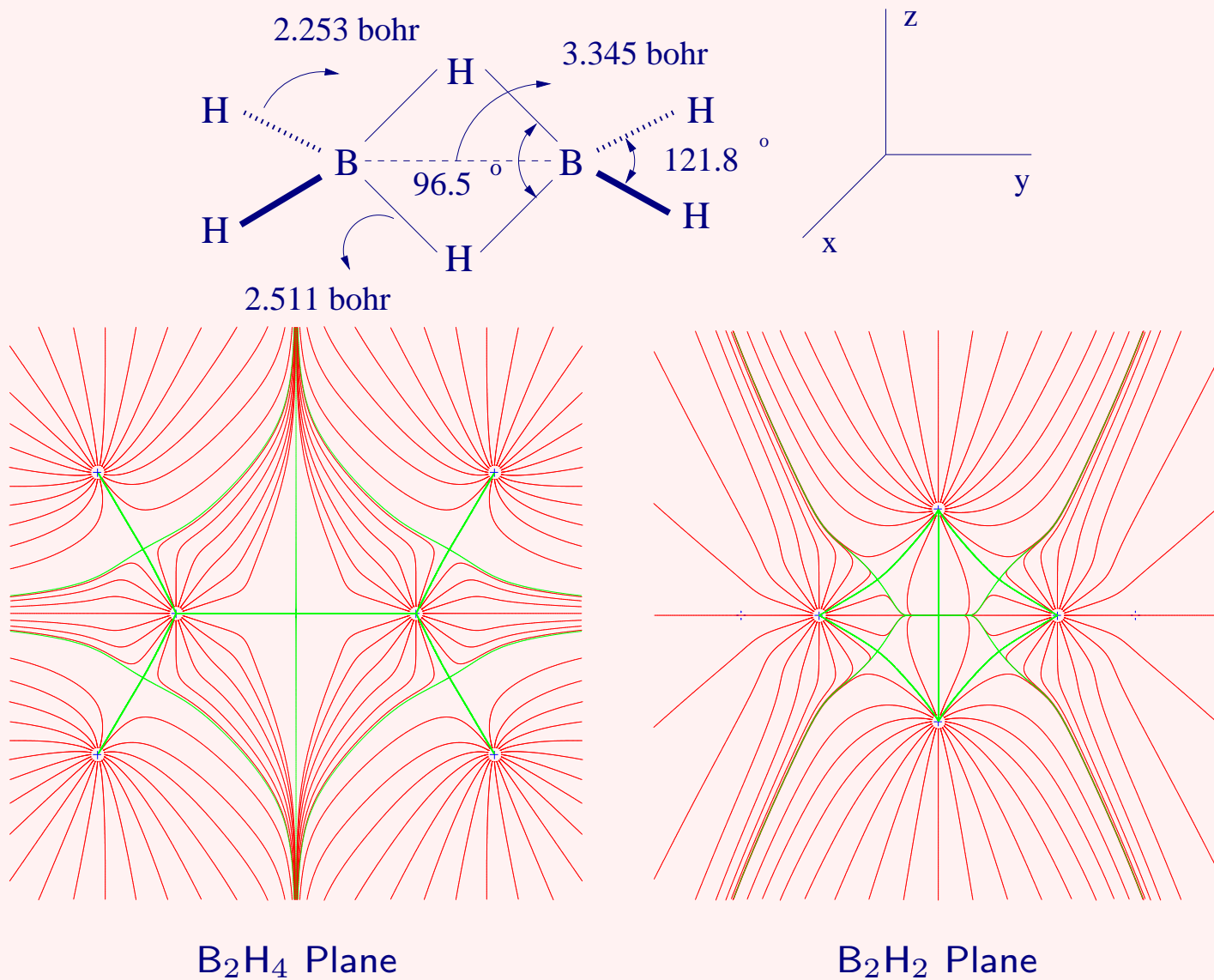
## Bond critical points.

- $(3, -1)$  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.

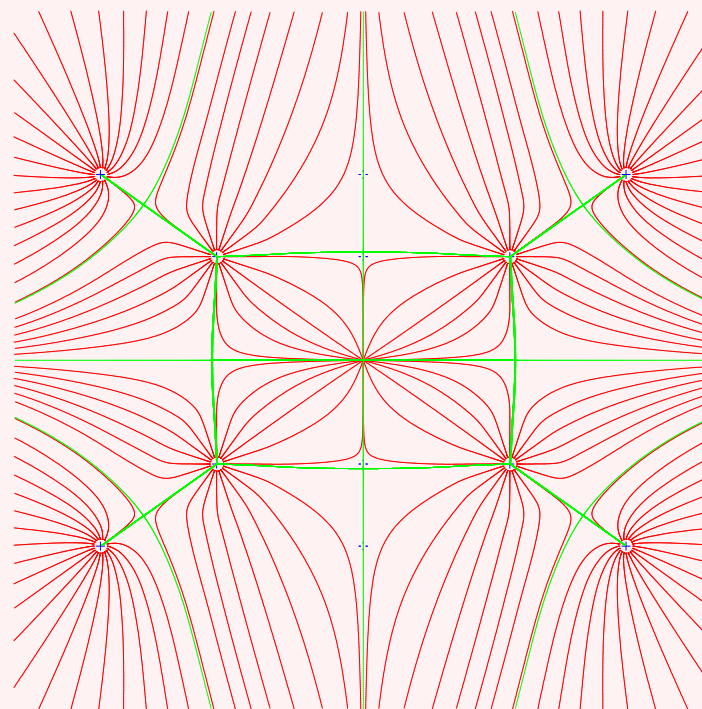
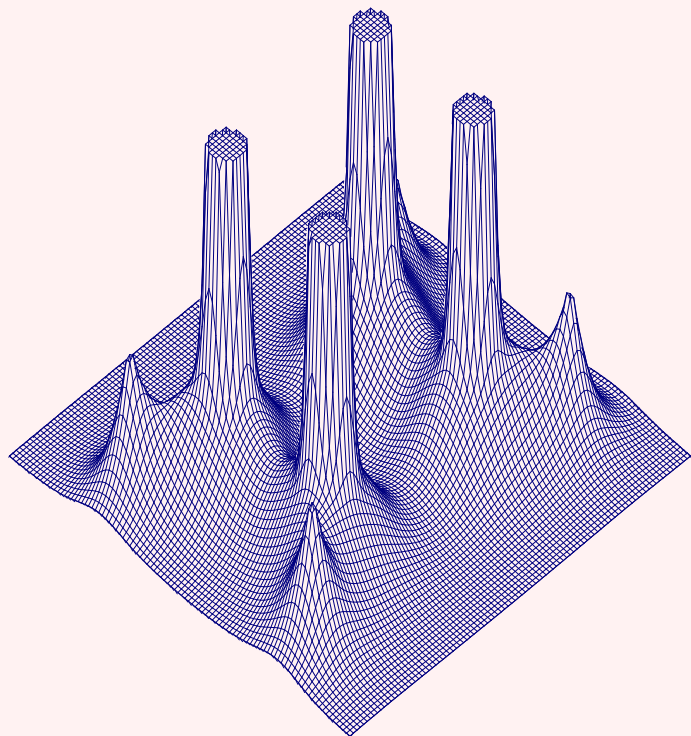
**H<sub>2</sub>O**



## $B_2H_6$ . Ring points.



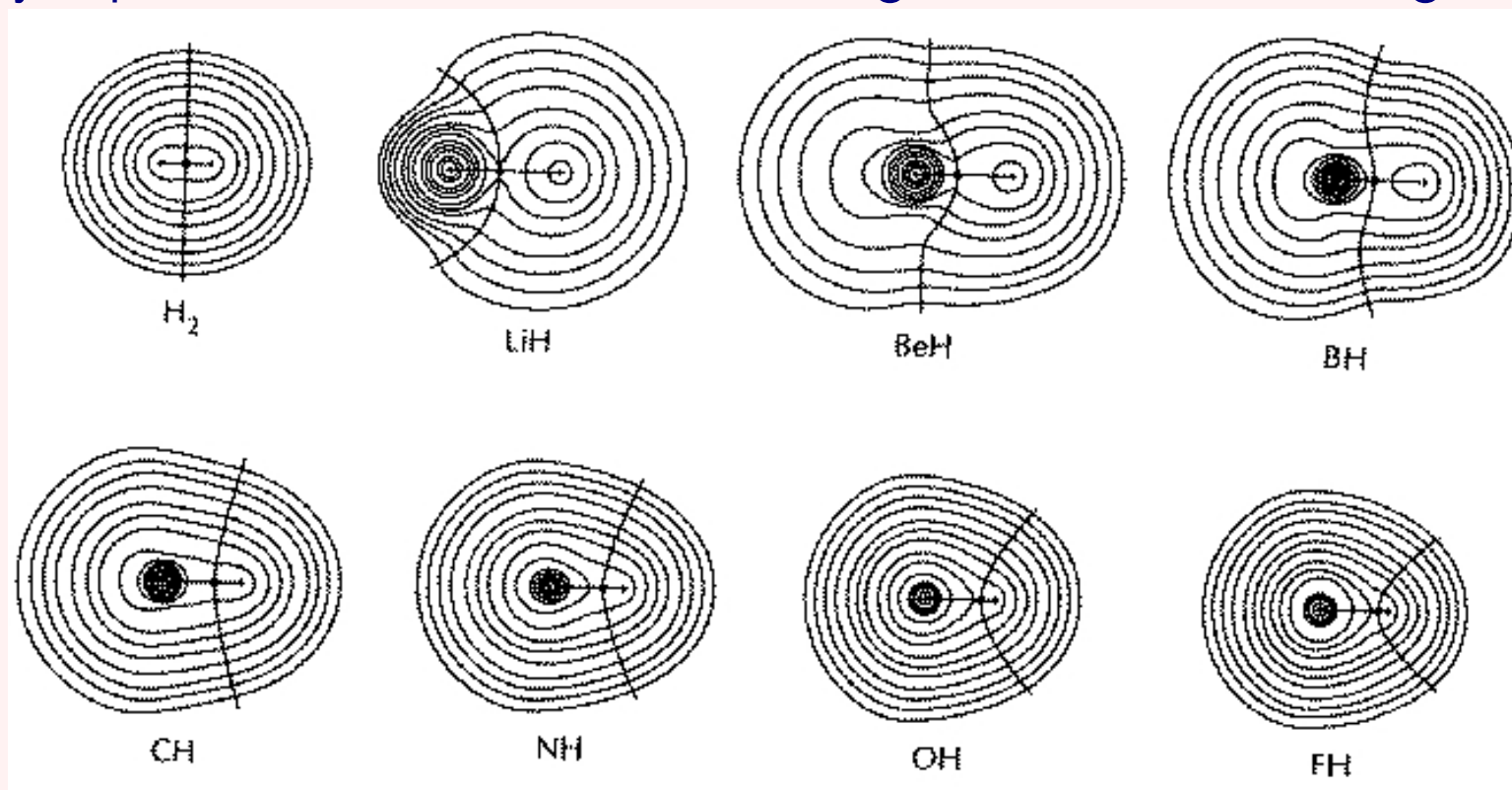
## $C_8H_8$ . Cage points.



- **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.
    - $\rho_b$  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  $\rho_b$  for different bonded pairs.
    - However, it is reasonable to compare  $\rho_b$  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  $\pi$  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.



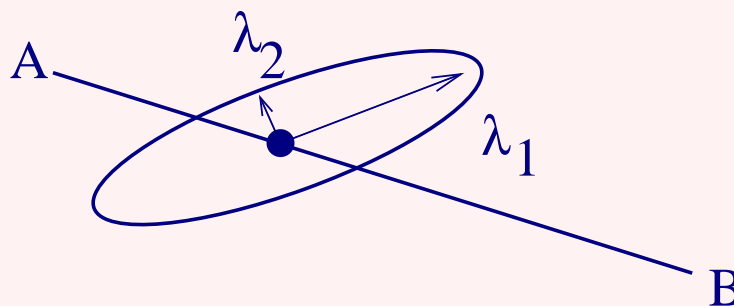
B3LYP/6-311+G(2d,2p)//HF/6-31(d) a.u.

Molecule	$R_e$	$r_b(\text{H})$	$\rho_b$
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  $\rho_b$  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,  $\rho_b$  may be used to define a topological **bond order**  $n_b$ .
- For instance, in C-C bonds the values of  $\rho_b$  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  $n_b-\rho_b$  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  $\rho_b$ .

## ■ Ellipticity.

- Let us call  $\lambda_1$ ,  $\lambda_2$ , and  $\lambda_3$  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  $C_2H_4$   $\epsilon = 0.3$ .  $\pi$  character? In  $C_6H_6$   $\epsilon = 0.23$ .
- Caution: the  $\pi$  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  $\mathbb{H}(\mathbf{r})\nabla\rho(\mathbf{r}) = \mathbf{0}$ . is satisfied.
- $\nabla^2\rho$ . Related to local charge accumulation or depletion.
- Since the trace of a matrix is invariant under an orthogonal transformation:

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

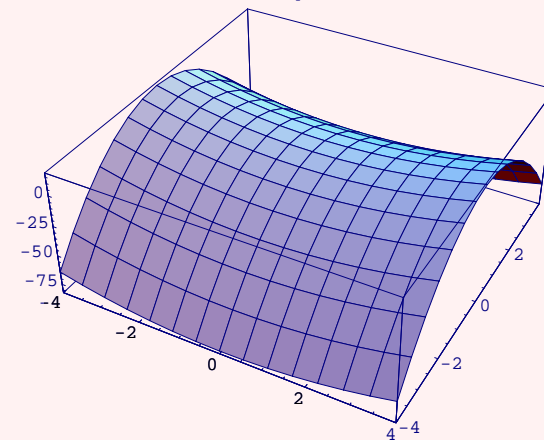
- $\nabla^2\rho > 0$  The positive curvatures "win", and we have a point of charge **depletion** with respect to its neighbourhood.
- $\nabla^2\rho < 0$  corresponds to charge **accumulation** with respect to its neighbourhood.

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,

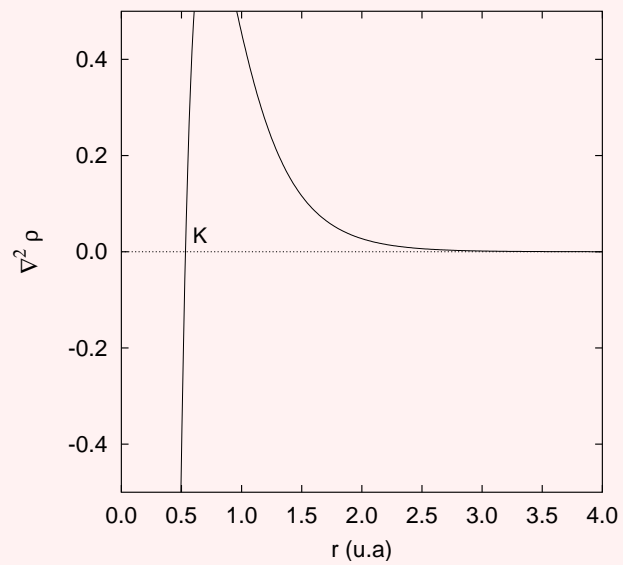
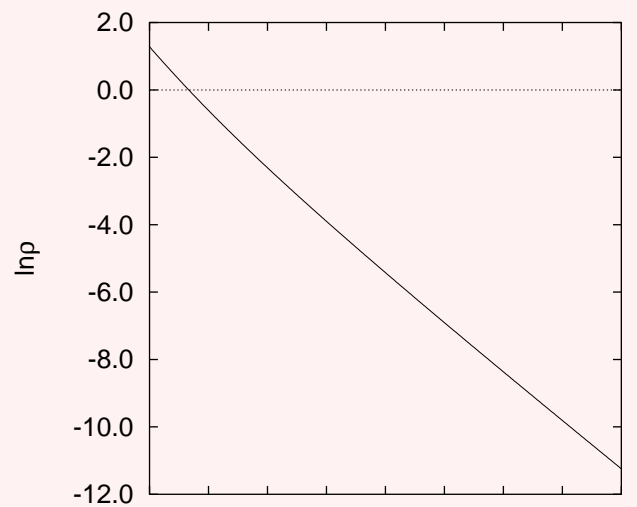
$$\nabla^2\rho(r) = Ne^{-\zeta r}(\zeta^2 - 2\zeta/r)$$

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

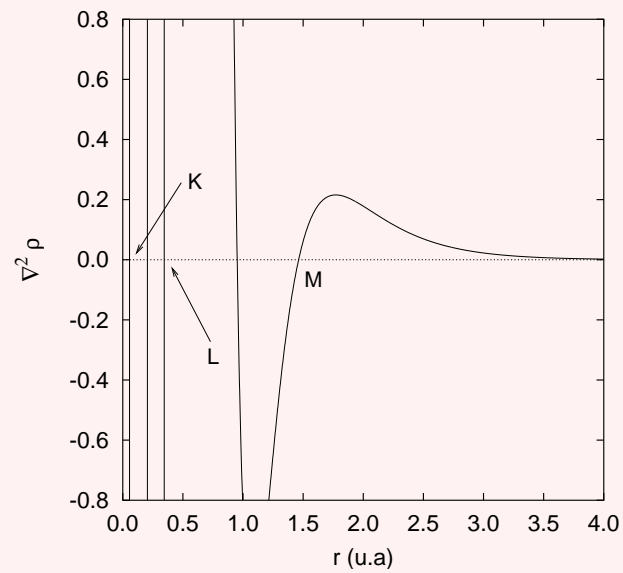
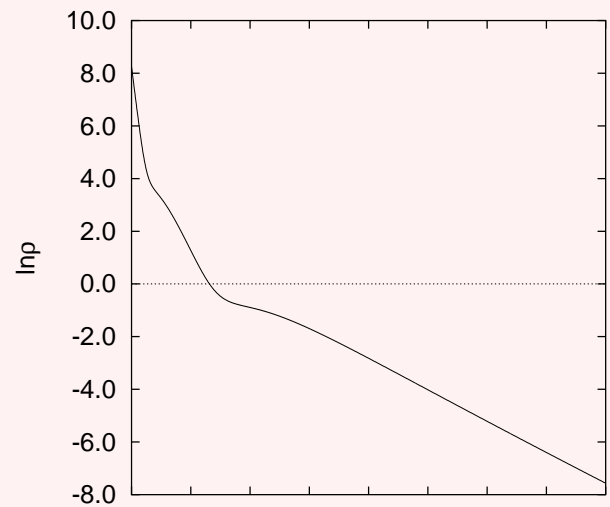
$$\nabla^2\rho < 0 \text{ if } r < r_c \text{ and viceversa.}$$

- $\lim_{r \rightarrow 0} \nabla^2\rho = -\infty$  and  $\lim_{r \rightarrow \infty} = 0^+$ .
- Atomic densities are reasonably approximated 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)

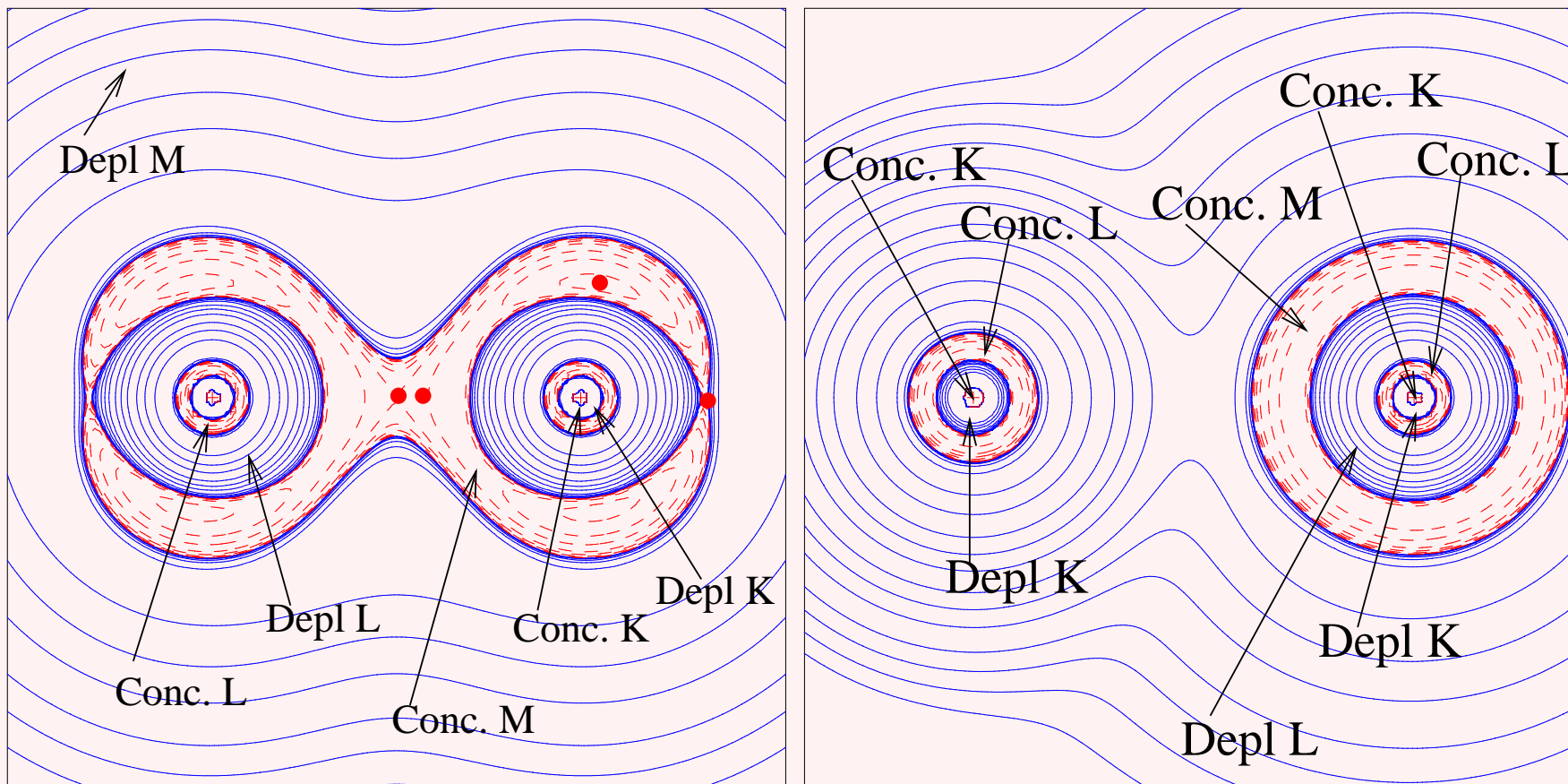


- The position of the zeros, minima, and maxima of the laplacian in atoms has been successfully related to a other atomic size measures.

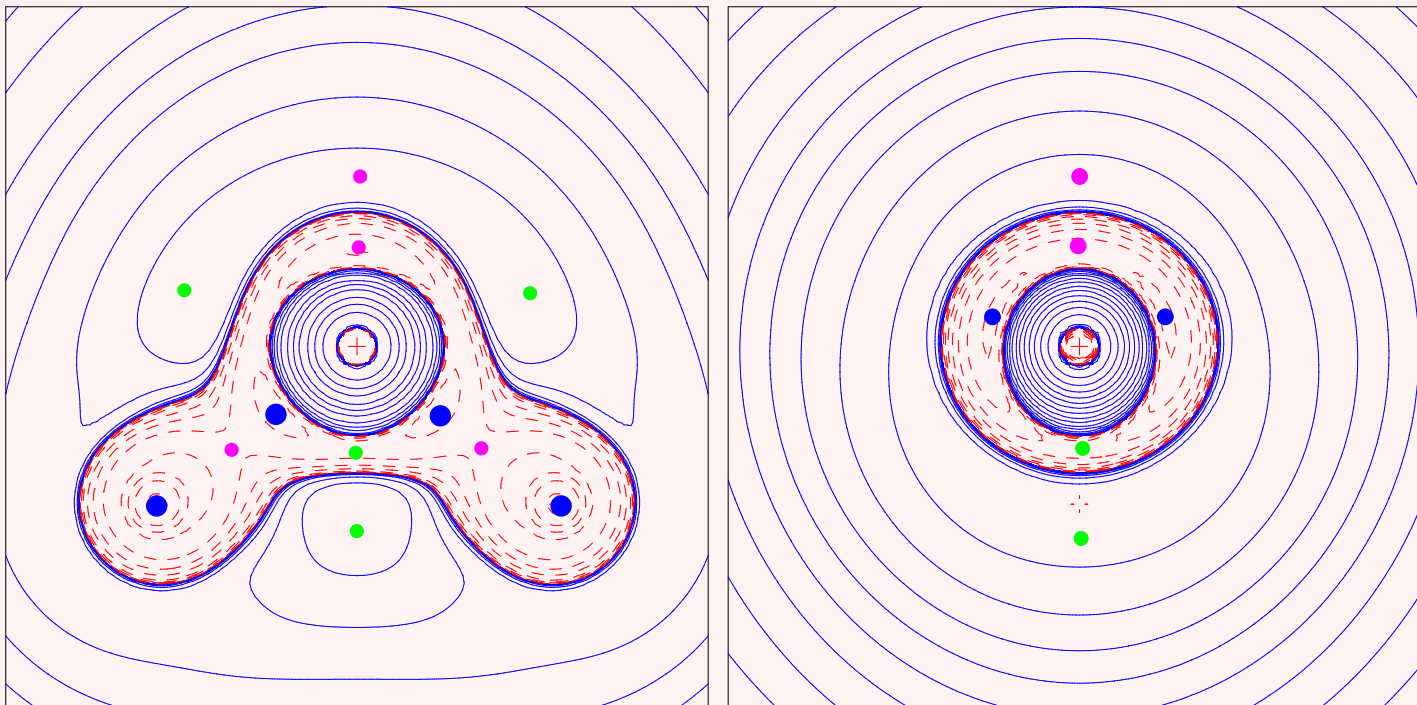
Radius	Li	Be	B	C	N	O	F	Ne
$r_2$	2.49	1.59	1.19	0.94	0.78	0.66	0.57	0.50
Radius	Na	Mg	Al	Si	P	S	Cl	Ar
$r_2$	0.44	0.40	0.36	0.33	0.30	0.28	0.26	0.24
$r_3$	3.44	2.55	2.08	1.76	1.52	1.34	1.20	1.08
Radius	K	Ca	Ga	Ge	As	Se	Br	Kr
$r_2$	0.23	0.21	0.13	0.12	0.12	0.12	0.11	0.11
$r_3$	0.98	0.90	0.49	0.47	0.45	0.43	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- $\zeta$  Clementi and Roetti basis set.

- $\nabla^2 \rho$  suffers a restructuration upon molecule formation:  $\text{Cl}_2$ , NaCl HF//6-311G\*\*



- $\nabla^2\rho$  changes more noticeably if symmetry breaks:  $\text{H}_2\text{O}:\text{HF}/6\text{-}311\text{G}^{**}$



- 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  $103.8^\circ$  and  $138.6^\circ$  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  $\hat{O}$  be the density associated to 1-electron operator  $\hat{O}$ :

$$\langle \hat{O} \rangle = \sum_{\Omega} \int_{\Omega} \hat{O} d\mathbf{r} = \sum_{\Omega} \hat{O}_{\Omega}, \quad (2)$$

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:

- $\mathcal{O} = 1 \Rightarrow V_{\Omega} = \int_{\Omega} dr$ . In isolated molecules  $V_{\Omega} \rightarrow \infty$  usually. It is common practice define an integration domain  $\Omega' = \Omega \cap I(\rho = 0.002)$  u.a. These atomic volumes are transferable.
- $\mathcal{O} = \rho \Rightarrow N_{\Omega} = \int_{\Omega} \rho dr$ . **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**,  $N_{\Omega}^{lm}$ , as

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

$N^{00}$  is the atomic population, the  $(N^{11}, N^{1\bar{1}}, N^{10})$  trio determines the **atomic dipolar moment** vector,  $\mu_{\Omega}$ , and the  $l = 2, 3, 4, \dots$  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  $N_{\Omega}^{lm}$  we may reconstruct the molecular  $N^{lm}$  moments. For  $l = 1$ , for instance,

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

## ■ Energetic components:

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

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

- Atomic energy: Using the virial Th.:  $E_\Omega = -T_\Omega$ . ! Equilibrium configurations only.
- Nucleus-electron potential energy:

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

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

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

## ■ Digression: Why the QTAIM?

- Only the atoms of the QTAIM have well defined energetic components:
  - Only if the separatrices are of  $\rho$  is the domain  $T$  quasi-unique.
- The QTAIM is a quantum theory of subsystems.
  - Open quantum regions

### 3. A world beyond $\rho(\mathbf{r})$ : IQA

- Chemically partitioning  $\rho_2$  introduces an energetic viewpoint in QTAIM.
- The energy depends only on the second-order reduced density matrix (2RDM):

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

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

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

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...

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

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

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

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

$$E_{int}^{AB} = V_{clas}^{AB} + V_{xc}^{AB}$$

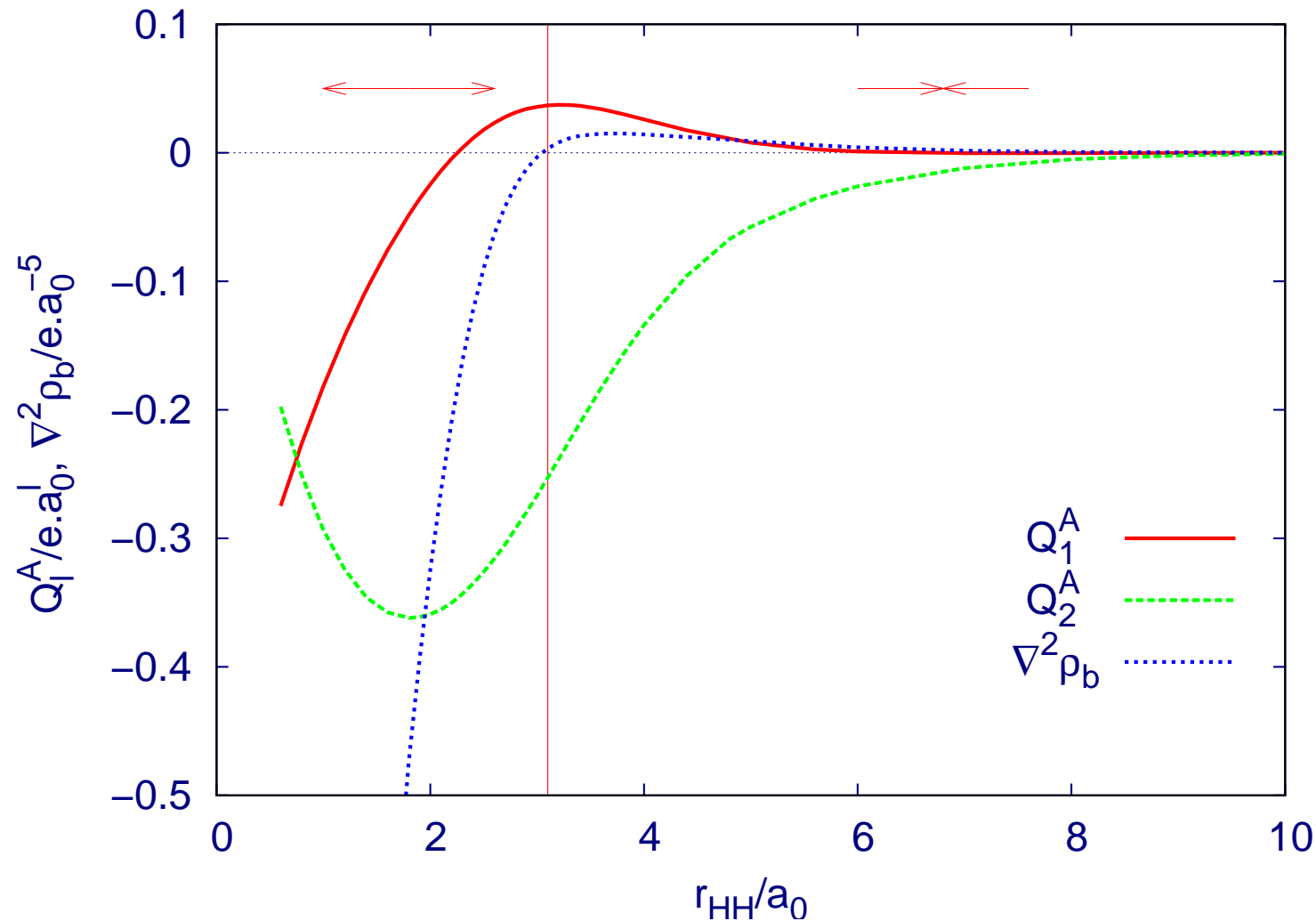
- If binding with respect to a reference is needed, then

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

- $\lambda^A = \int_{\Omega_A} d\mathbf{r}_1 \int_{\Omega_A} d\mathbf{r}_2 \rho_{xc}(\mathbf{r}_1, \mathbf{r}_2)$ ,  
 $\delta^{A,B} = 2 \int_{\Omega_A} d\mathbf{r}_1 \int_{\Omega_B} d\mathbf{r}_2 \rho_{xc}(\mathbf{r}_1, \mathbf{r}_2)$ , localization and delocalization indices. They measure the number of localized electrons, and the number of delocalized pairs ( $\approx$  covalent bond order)

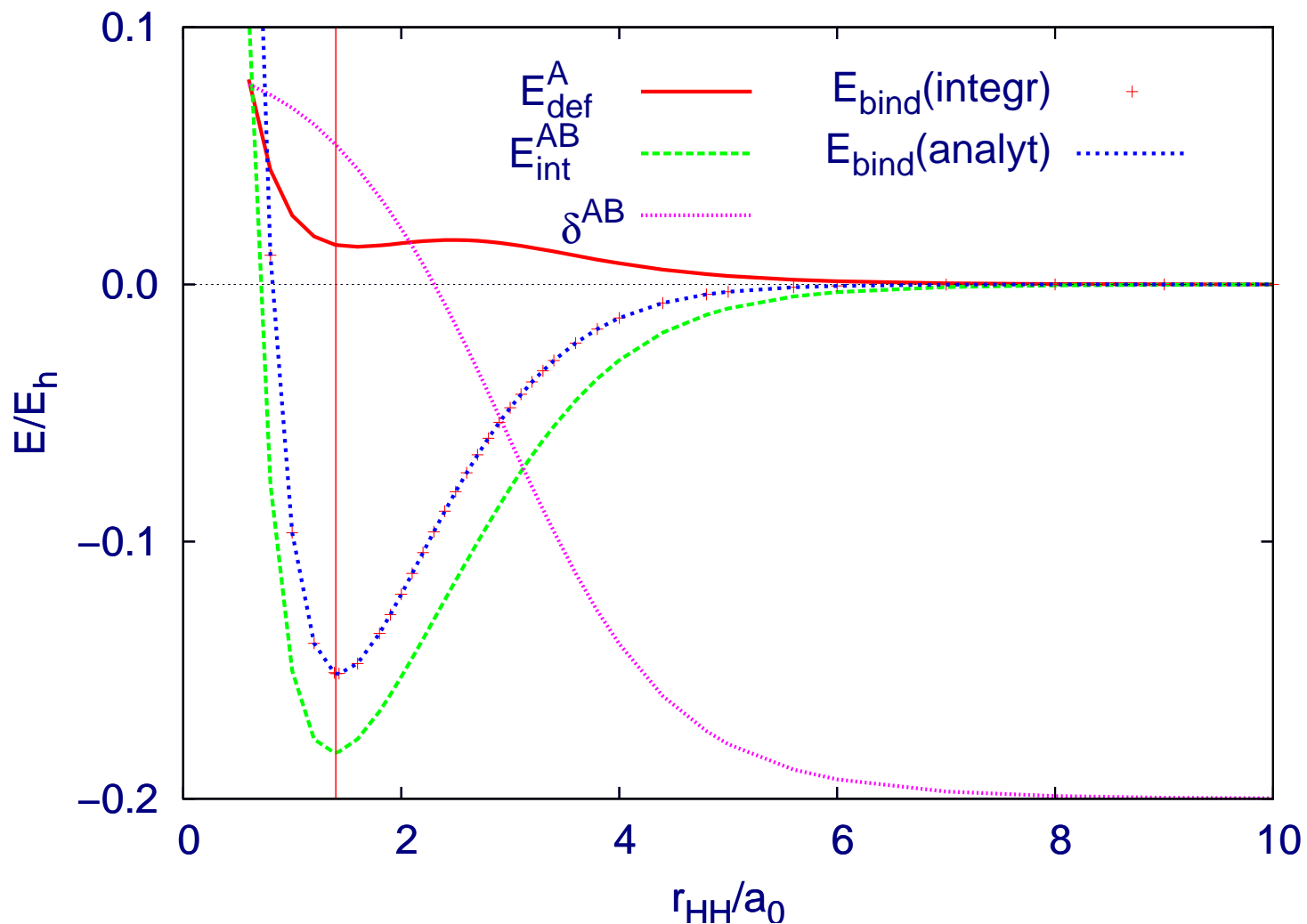
### 3. IQA in the $H_2$ molecule I. The $^1\Sigma_g^+$ state

- 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.

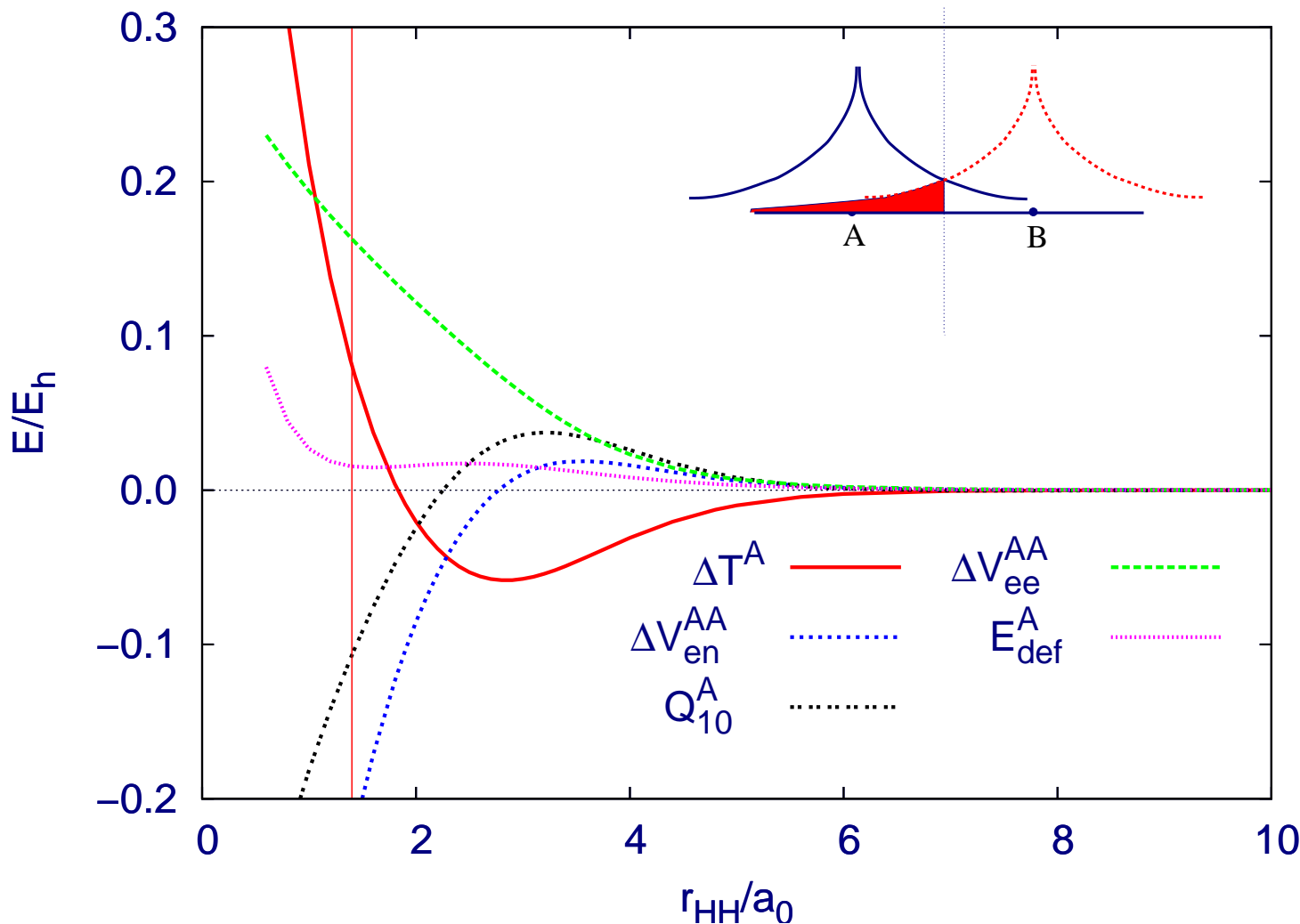
■ IQA analysis of  $E_{bind}$



- $\lim_{R \rightarrow \infty} E_{self} = E(H)$
- $E_{def}$  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.

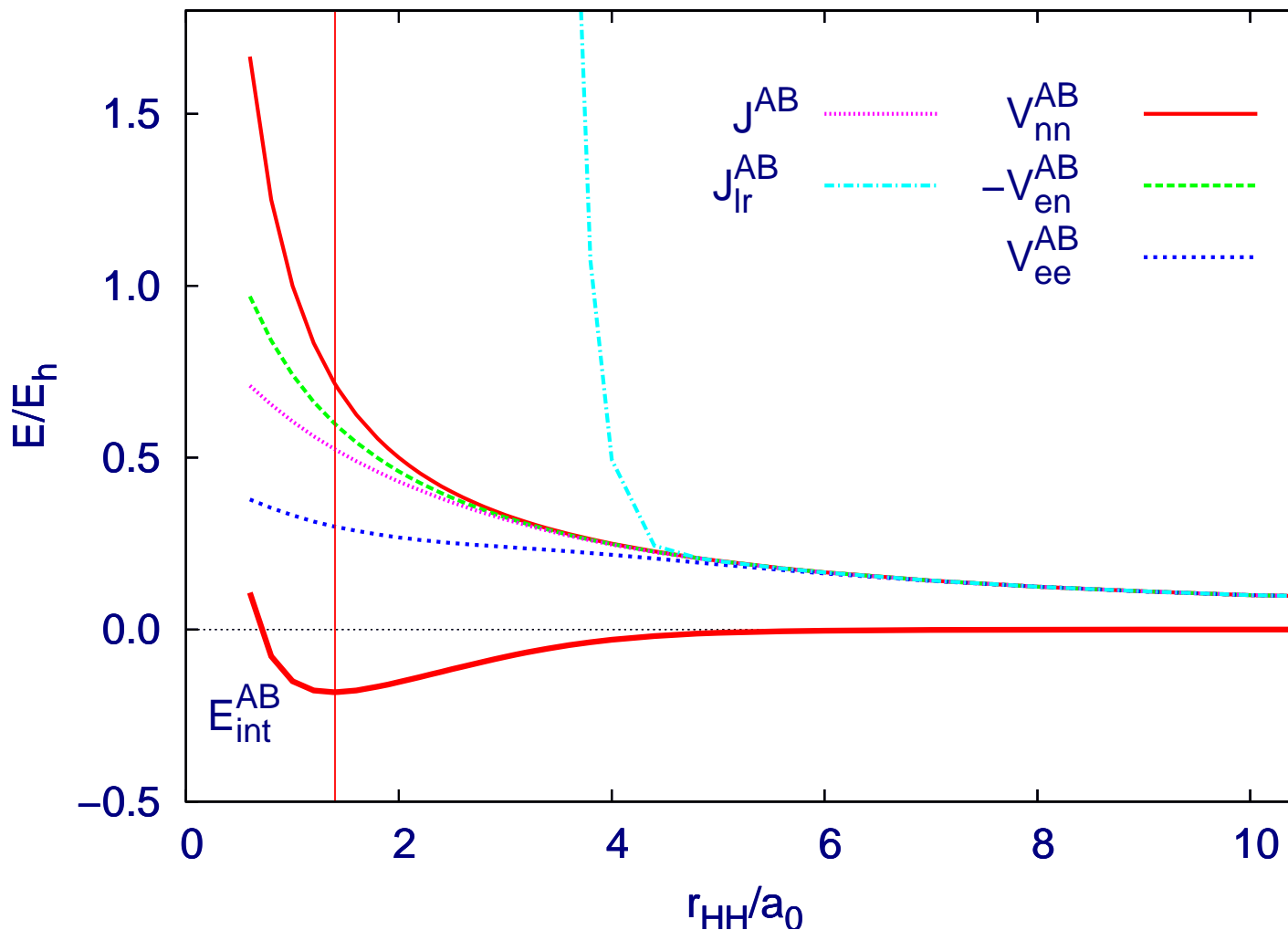


■ Self-Energy: A balance of large components.



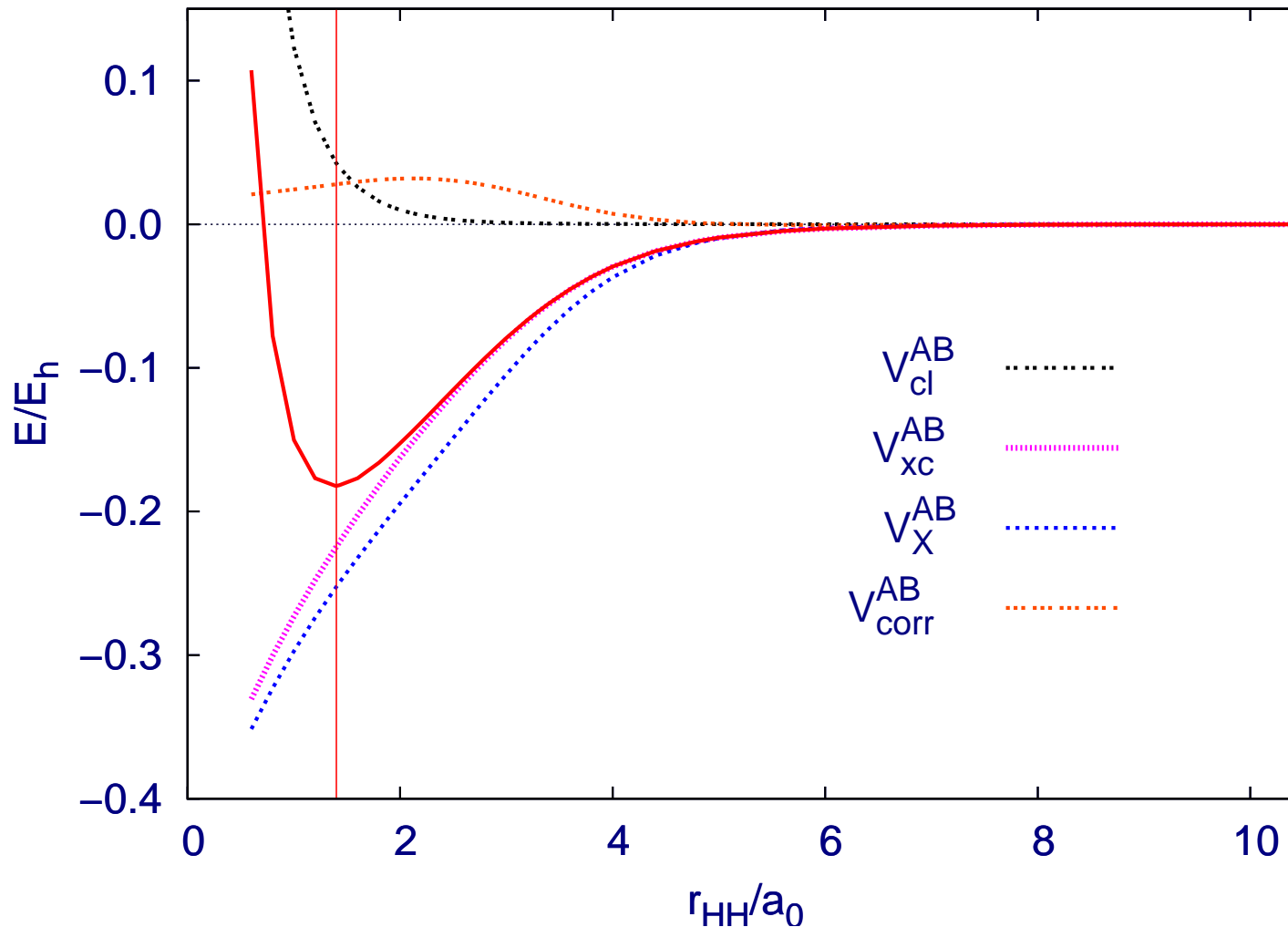
- $E_{def} > 0$ : from a restricted variational principle.
- $T^A$  follows  $Q_{10}$ , the atomic dipole.
- $V_{ne}$  has an important contribution from the delocalized electrons from atom  $B$
- $V_{ee}^{AA} \neq 0$ . A **direct** measure of electron delocalization
- Delocalization changes all energetic 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  $V_{corr}^{AB} \rightarrow V_X$ . **Cannot separate exchange from correlation.** Dissociation problem & Static correlation.

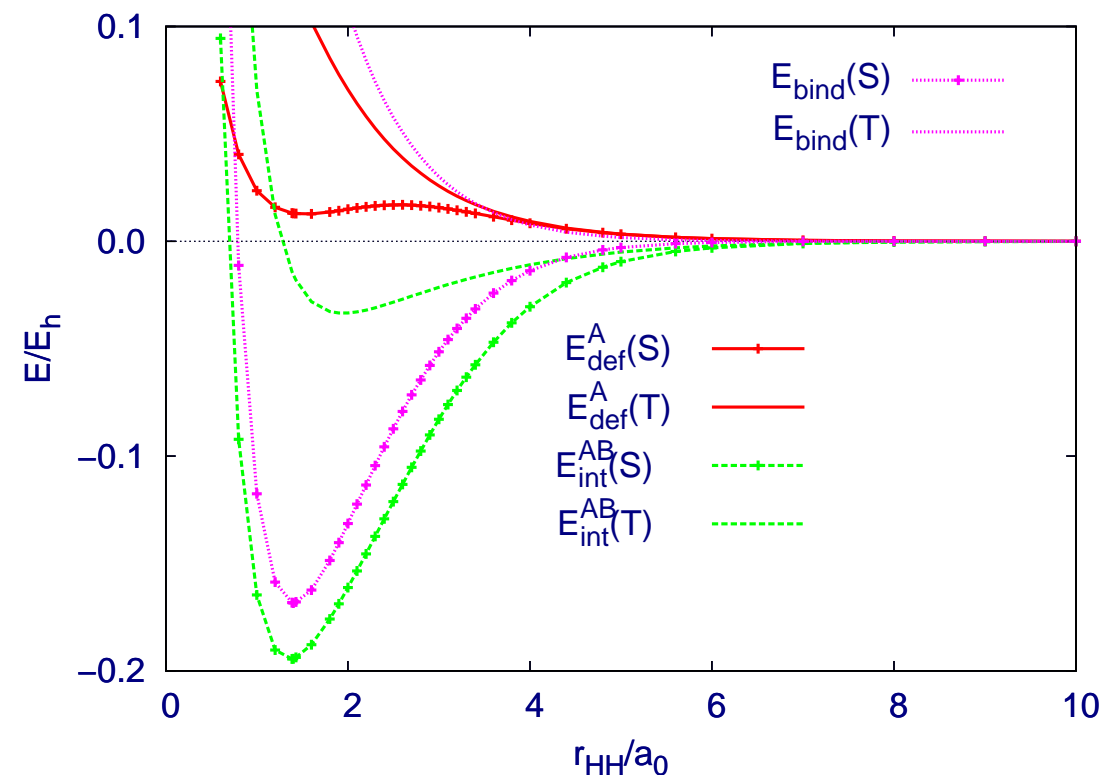
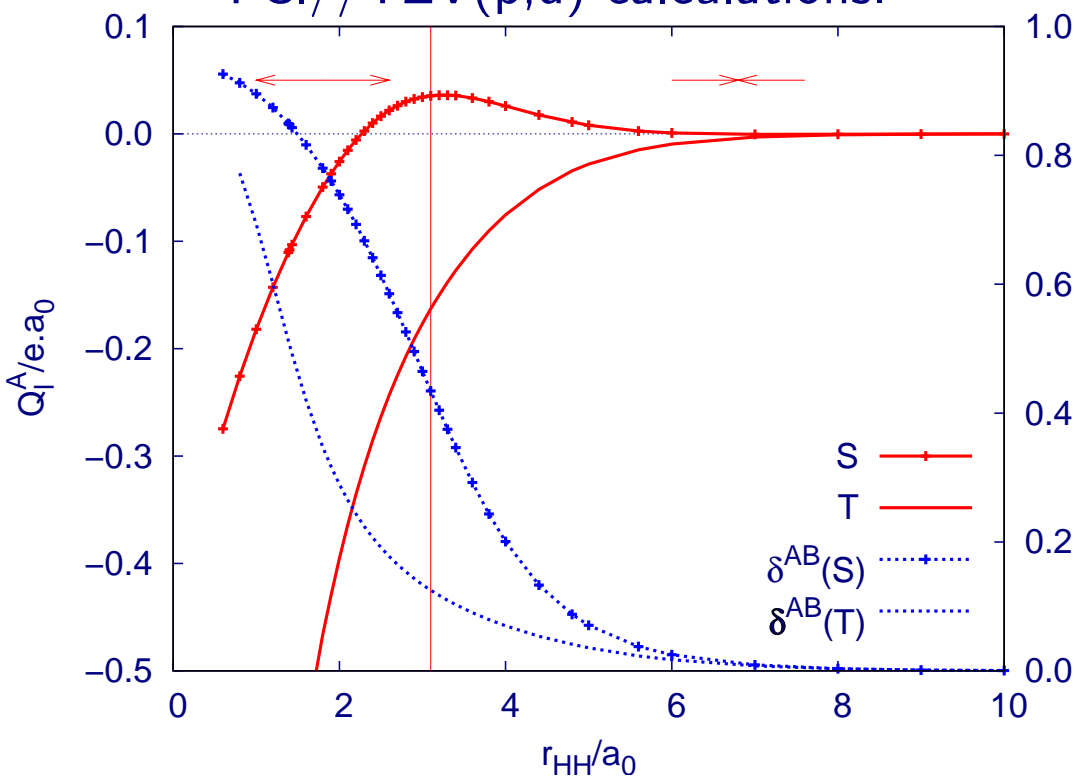
## Some numbers at the exp. geometry:

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<sub>2</sub> molecule II. The $^3\Sigma_u^+$ state

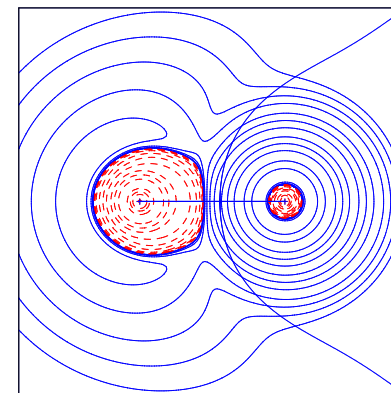
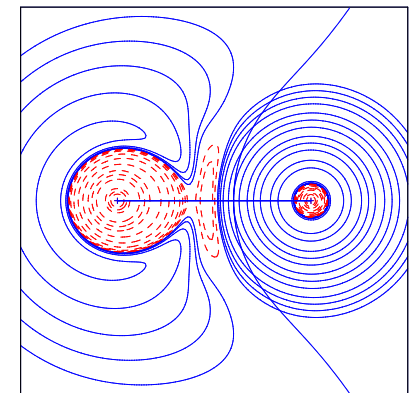
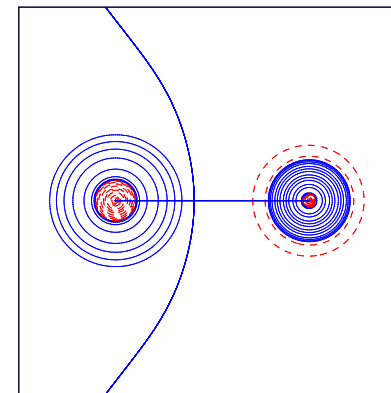
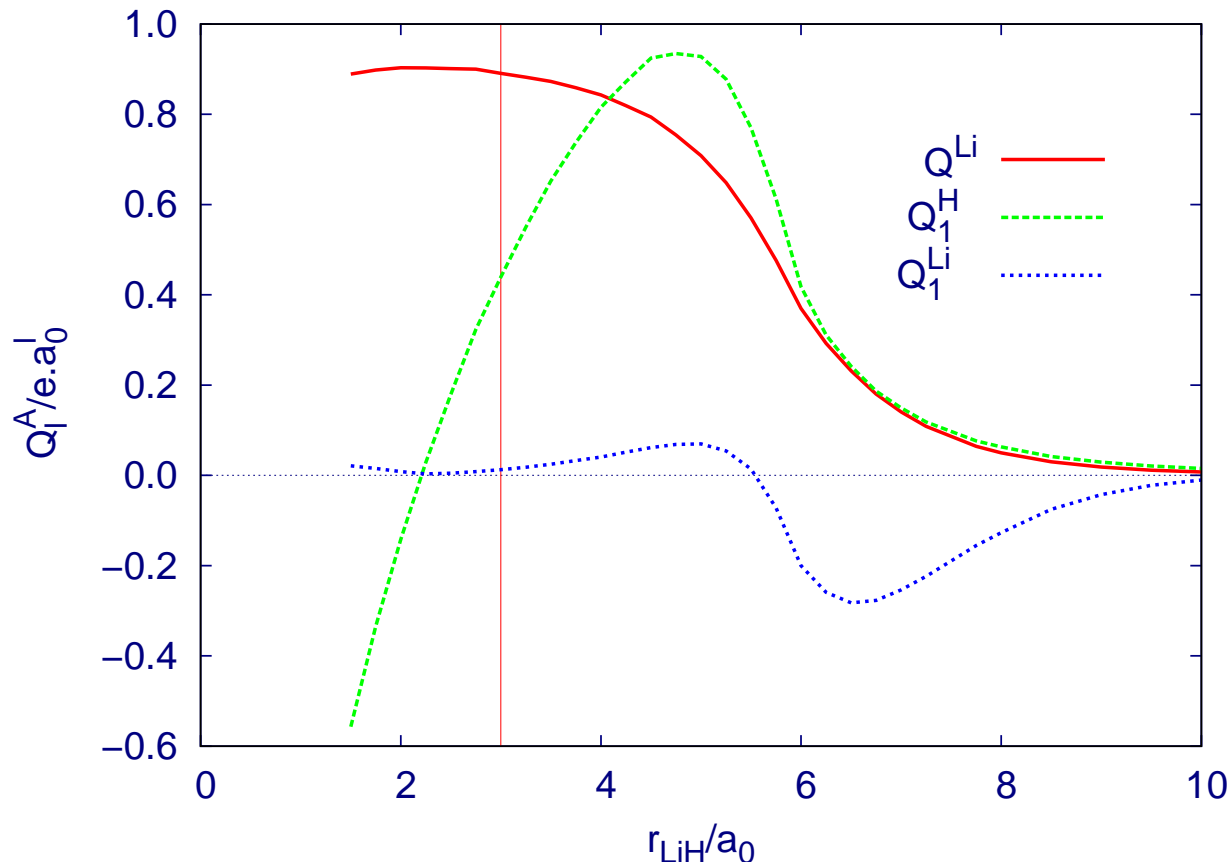
- FCI//TZV(p,d) calculations.



- The triplet does not accumulate bonding charge. Delocalization is smaller.
- A much smaller, but stabilizing,  $E_{int}$ . Why?
- The triplet has a much larger deformation energy. Why?

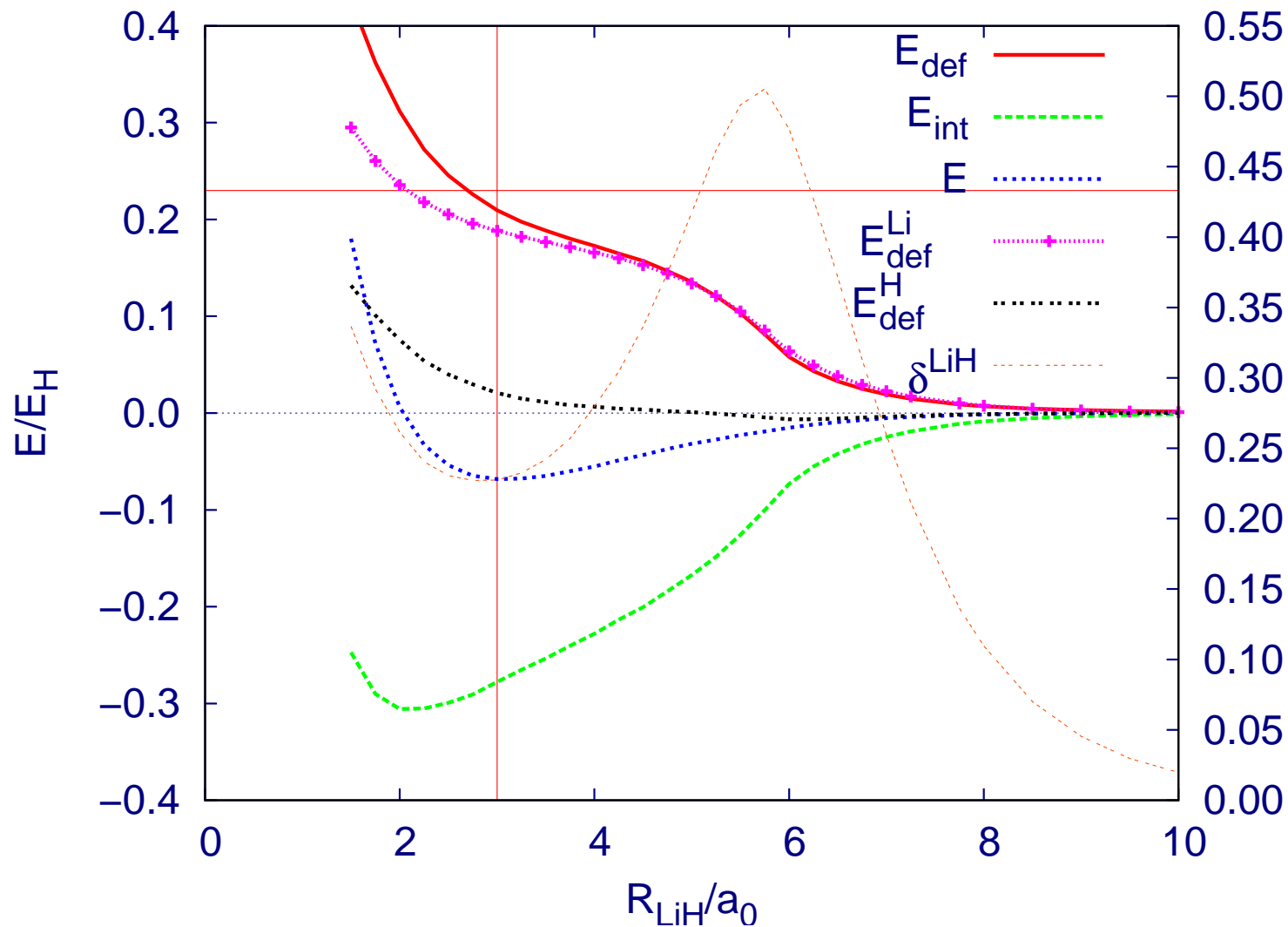
## Charge Transfer. The LiH molecule.

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



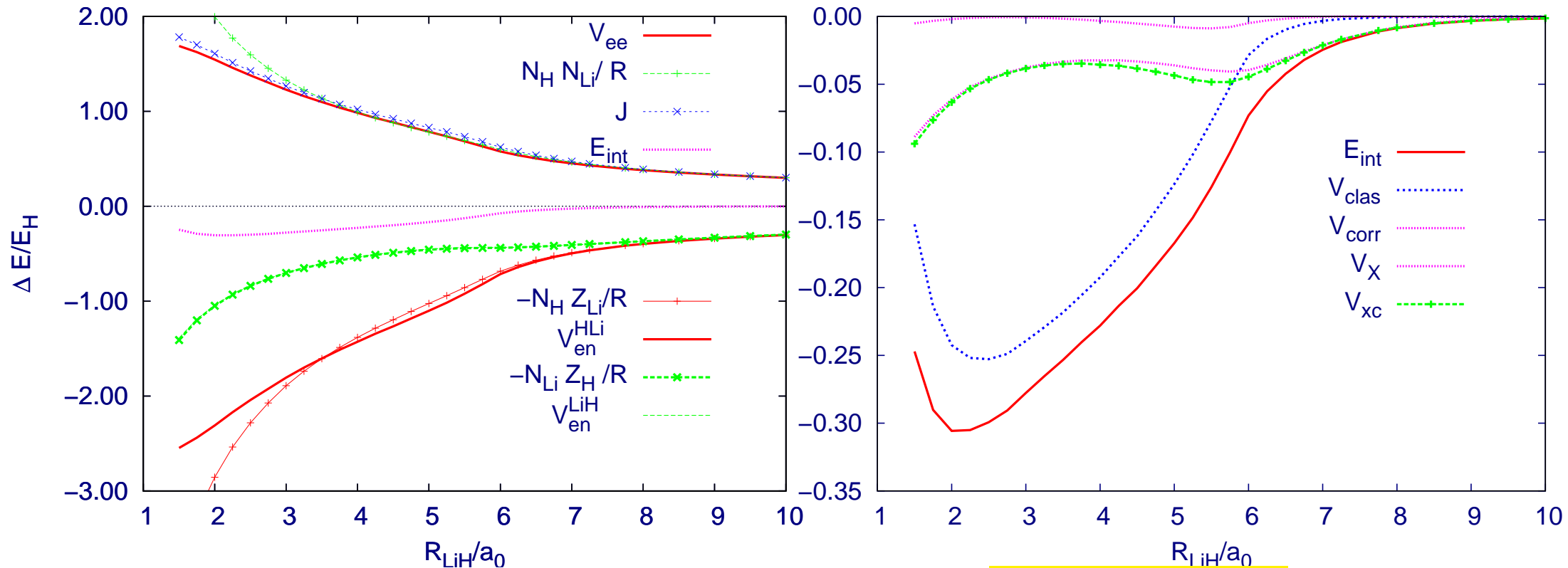
$R = 10, 5.5, 3$  bohr.  
 Hook Ionization.  
 Forward & backwards  
 polarization.

■ Binding energy Analysis: **The reference.**



- $E_{def}/\text{neutral atoms} \simeq 140$  kcal/mol.
- $E_{def}/\text{ions} \simeq -12$  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.
- $\delta^{LiH}$  describes beautifully the ionization.

## Interaction Energy. Classical Behavior

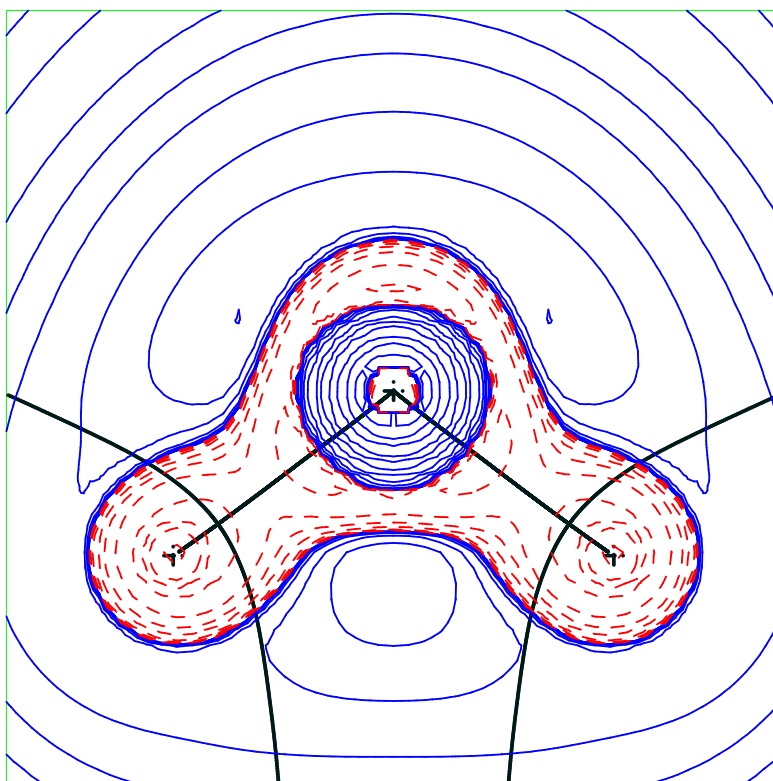


- All the interaction terms are very well represented by their **classical expressions**
- $V_{clas}$  is 86%  $E_{int}$  at  $R_e$ ! **Electrostatically binded** system.
- $V_{xc} \simeq$  resonance. Two regimes with a plateau. **Weakly correlated system.**



## Polar bonds: the $^1A_1$ H<sub>2</sub>O 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	
$\rho_b$	0.3896	○ Large density at BCP.
$\nabla^2 \rho_b$	-2.7361	○ Large negative Laplacian.
$G$	0.0897	○ Considerable CT.
$Q(H)$	0.5598	○ Shared interaction.
		○ Two non-bonded VCC's

## What do we expect on physical grounds?

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

- H–H interaction with important classical repulsion.

Property	O	H
$\Delta T^A$	0.6349	-0.1060
$\Delta V_{en}^{AA}$	-6.5823	0.1187
$\Delta V_{ee}^{AA}$	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
$\delta^{AB}$	0.6148	0.0404

- A reference is difficult to find.

- The H atom loses 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 classical/QM

- $V_{xc}$  for OH similar to the single bond in  $H_2$ .

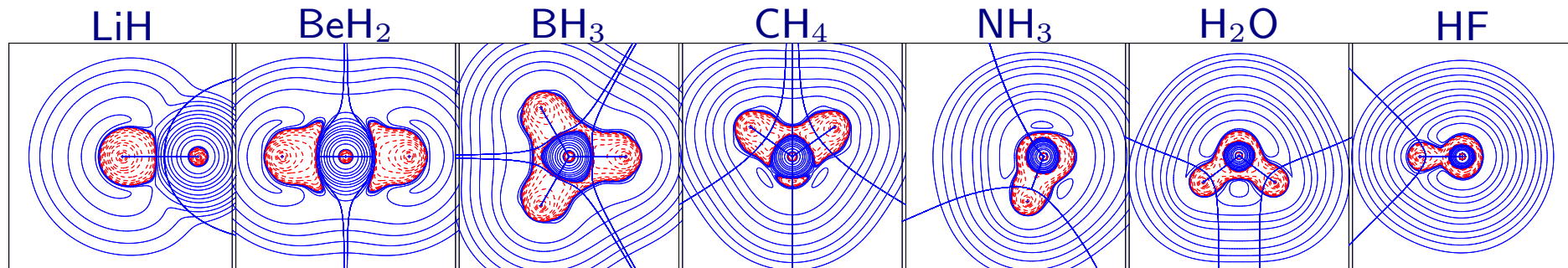
- HH interaction dominated by **classical, multipolar** repulsion.

- Negligible HH delocalization.

- Clear partition into bonded & non-bonded interactions.

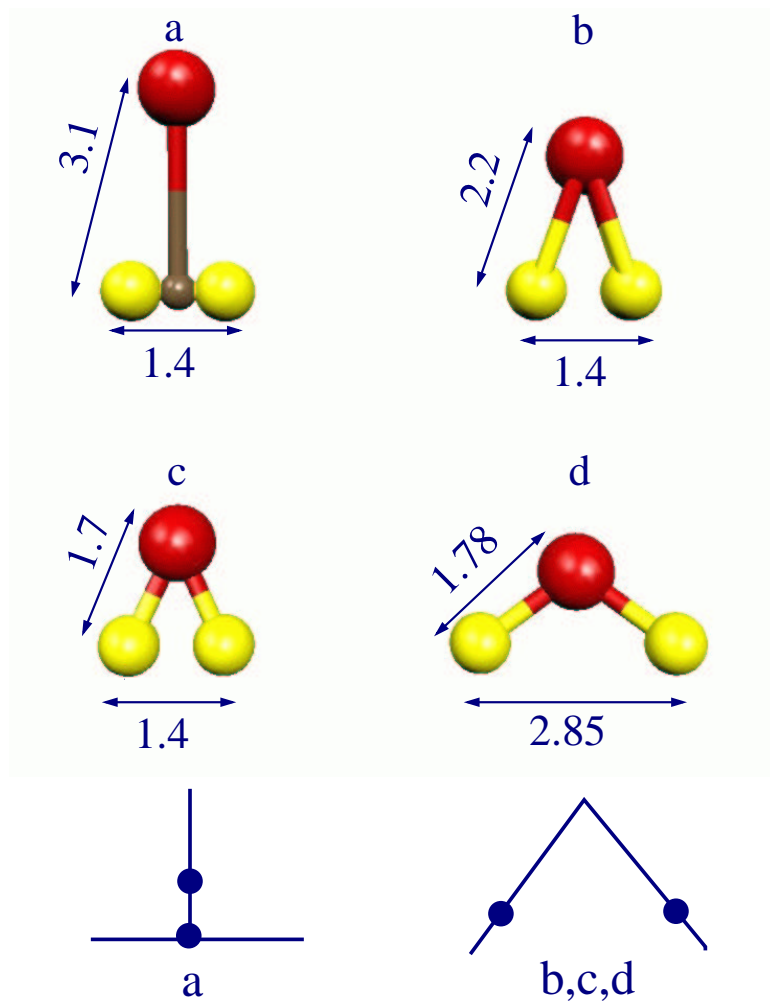
## 4. Other IQA examples.

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



	LiH	BeH <sub>2</sub>	BH <sub>3</sub>	CH <sub>4</sub>	NH <sub>3</sub>	H <sub>2</sub> O	HF
$Q(\text{H})$	-0.9111	-0.8684	-0.6973	-0.0394	0.3611	0.6035	0.5800
$\delta^{AH}$	0.2040	0.2651	0.5143	0.9835	0.8816	0.6450	0.6762
$\delta^{HH}$	-	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<sub>2</sub>O CAS[6,5]//6-311G\*\* calculation.



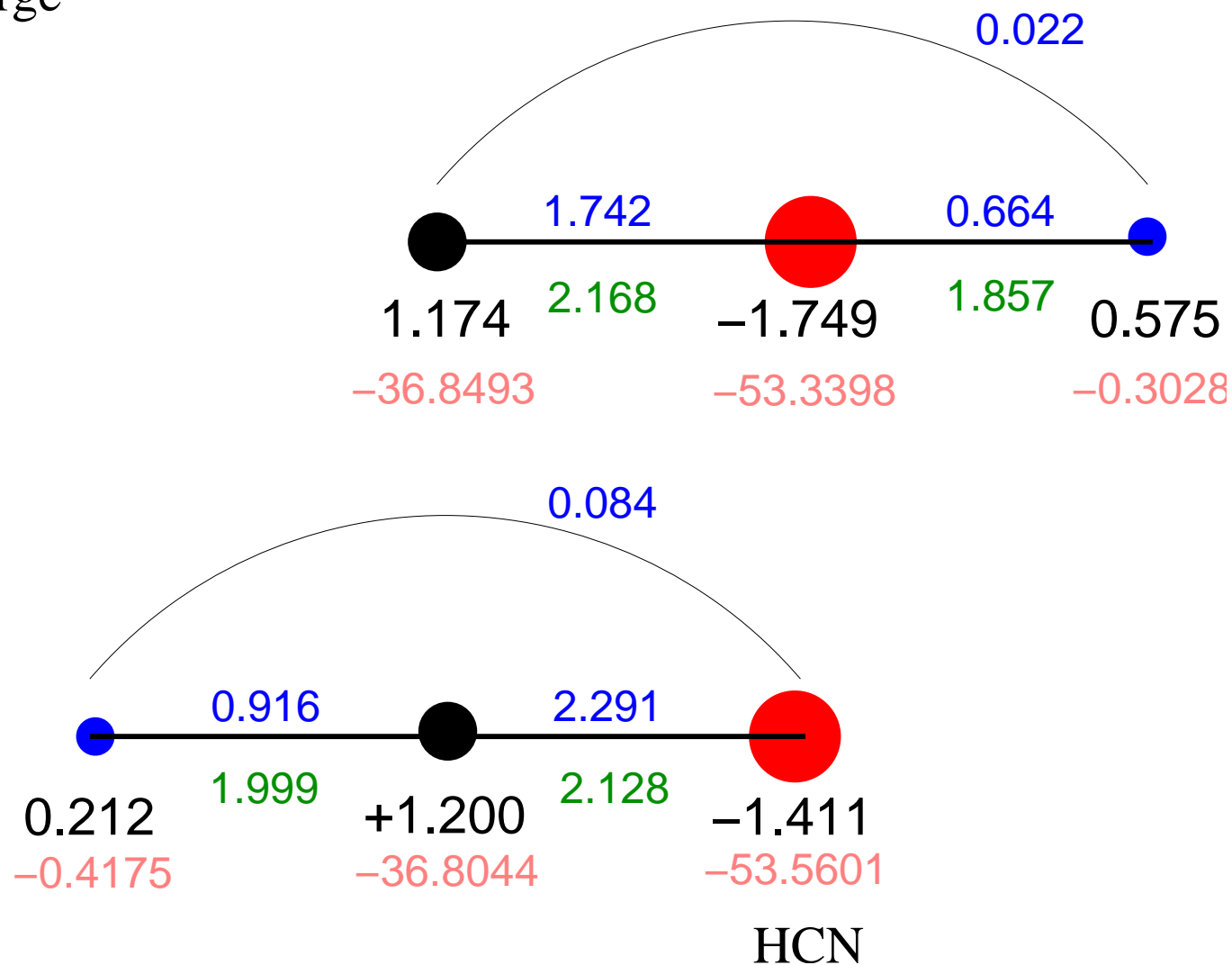
Property	a	b	c	d
$Q_H$	0.088	0.312	0.546	0.560
$E_{int}^{OH}$	-0.059	-0.227	-0.518	-0.490
$V_{clas}^{OH}$	0.001	-0.052	-0.304	-0.292
$V_{xc}^{OH}$	-0.060	-0.175	-0.214	-0.198
$E_{int}^{HH}$	-0.138	0.016	0.252	0.124
$V_{clas}^{HH}$	0.050	0.117	0.278	0.130
$V_{xc}^{HH}$	-0.188	-0.098	-0.026	-0.006
$E_{H_2}$	-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) ]

Net charge

 $\delta_{AB}$ 

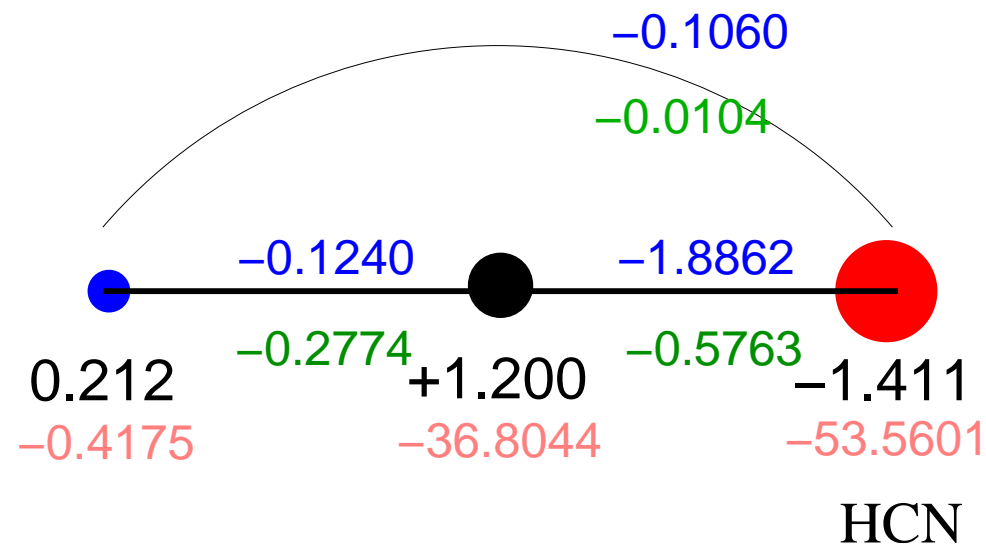
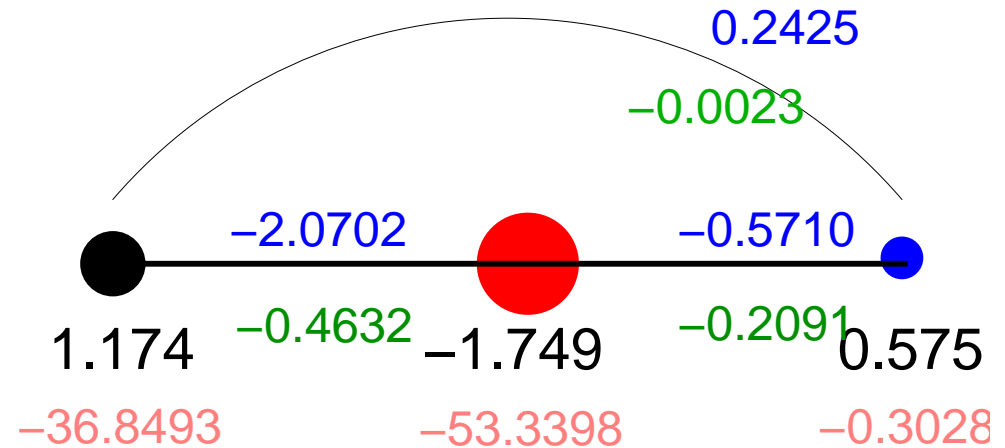
R(bohr)

 $E_{\text{self}}$ 

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Net charge

$E_{int}^{AB}$   
 $V_{xc}^{AB}$   
 $E_{self}$



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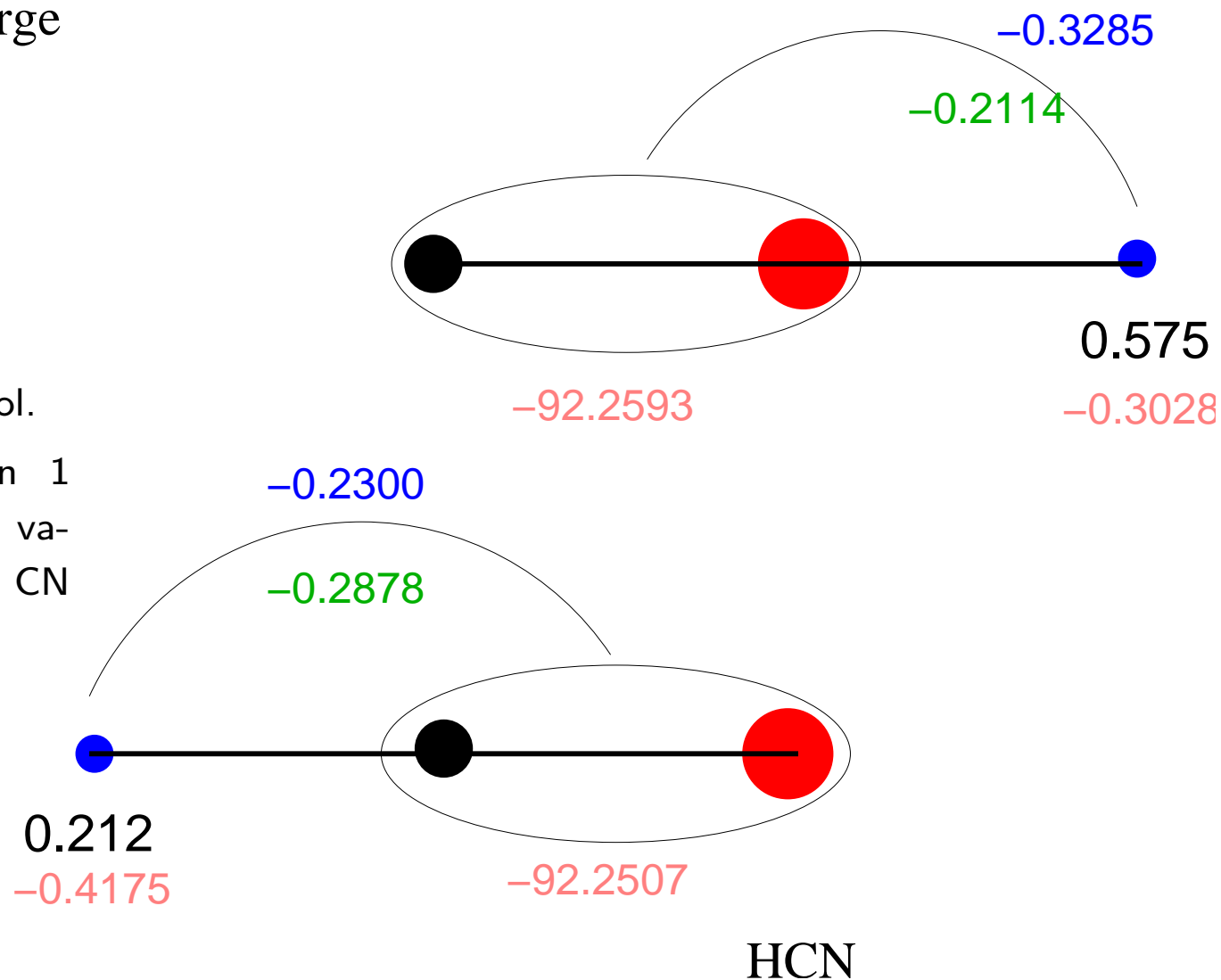
Net charge

$E_{int}^{AB}$

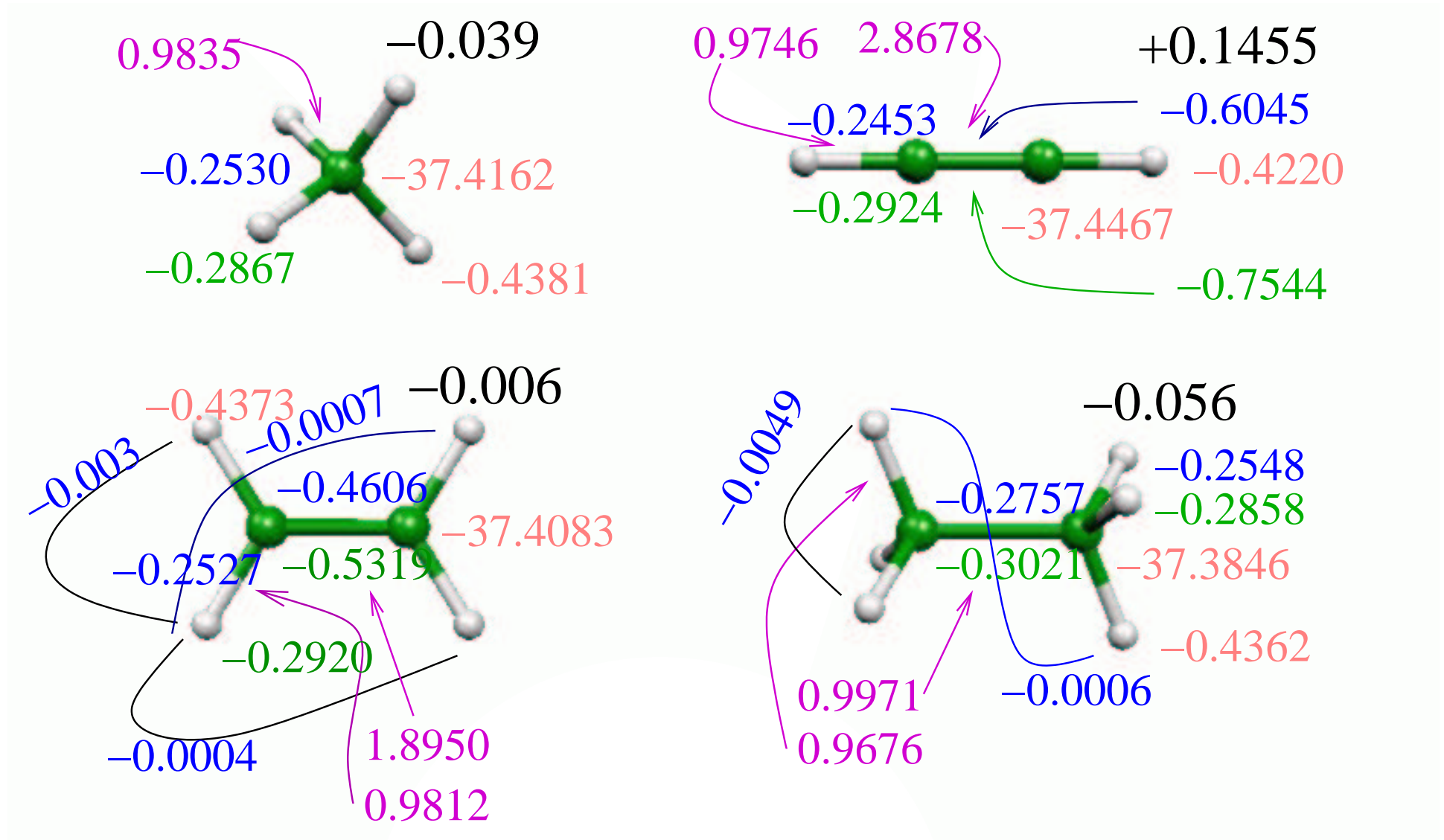
$V_{xc}^{AB}$

$E_{self}$

- $\Delta E \simeq 10$  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).

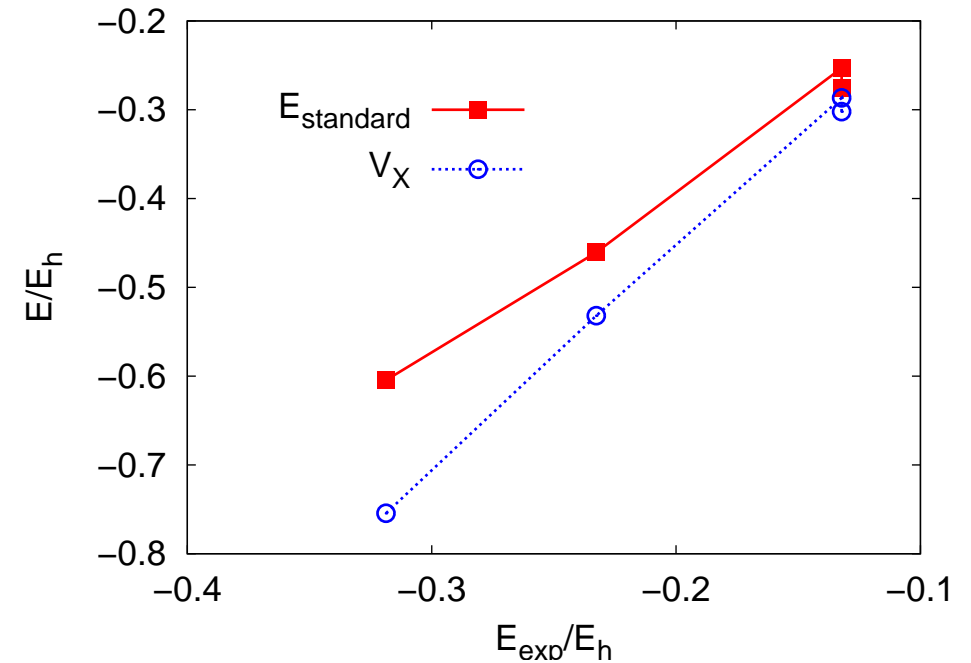
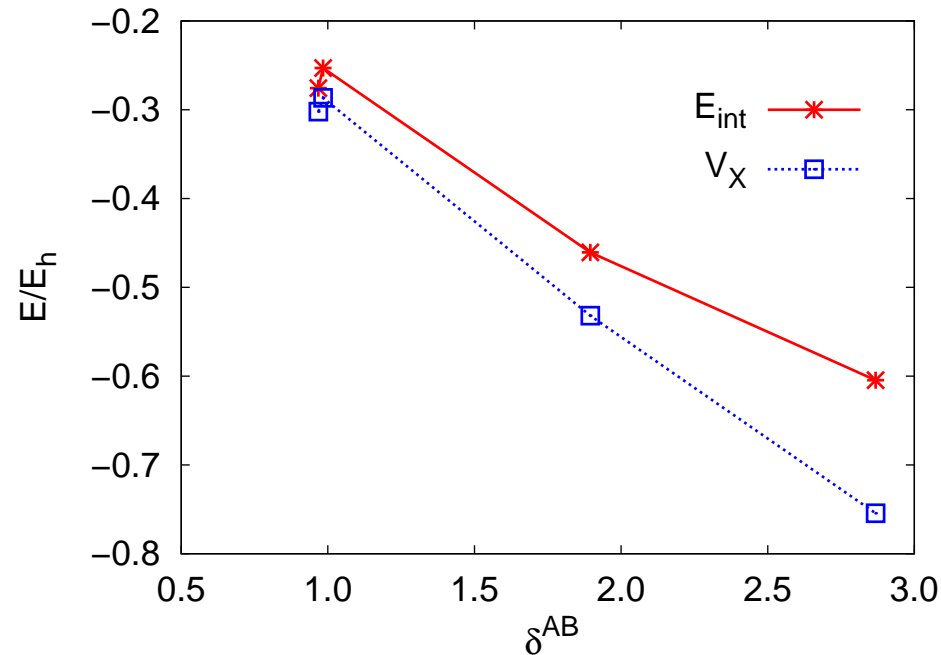


Multiple bonds. Ethane-Ethyne HF//TZV(p,d)





## ■ 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  $V_{xc}^{AB}$ .

## 4. Beyond IQA: Coarse-grained density matrices (CGDM)

- There is plenty of room at the bottom... CG may be introduced at any level.
  - $N$ -electron system,  $m$ -basins  $\Omega_1 \cup \dots \cup \Omega_m = R^3$ .
  - $\mathcal{N}$  CG (condensed),  $i = N - \mathcal{N}$  non-CG (free).
  - Structure:  $\mathbf{S} = (s_1, \dots, s_m)$ ,  $s_j = s^{\Omega_j}$
  - Condensation:  $\mathbf{C} = (c_1, \dots, c_m)$ ,  $c_j = c^{\Omega_j}$ ,  $\sum_j c_j \leq N$ .  
Thus  $i = N - \sum_j c_j$  free electrons.
  - The  $i$  free electrons at  $\mathbf{r}_1, \dots, \mathbf{r}_i$ .  $\mathbf{F} = (f_1, \dots, f_m)$ , with  $f_j = f^{\Omega_j}$ .
  - Structure  $\mathbf{S} = \mathbf{C} + \mathbf{F}$

$$\rho_i(\mathbf{r}_1, \dots, \mathbf{r}_i)[C] = \frac{N!}{i!c_1! \dots c_m!} \int_{D_C} d\mathbf{r}_{i+1} \dots d\mathbf{r}_N \rho_N$$

$$\rho_i(\mathbf{r}_1, \dots, \mathbf{r}_i) = \sum_{\{C\}} \rho_i(\mathbf{r}_1, \dots, \mathbf{r}_i)[C]$$

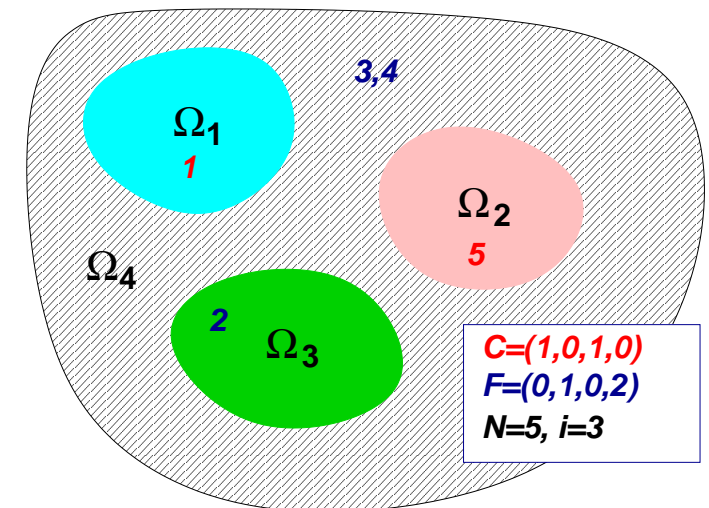
$$p(S) = \rho_0() [S \equiv C] = p(n_1, \dots, n_m)$$

$$\rho(\mathbf{r}_1^\alpha | S) = \rho(\mathbf{r}_1^\alpha)[C]/p(S)$$

$$E = \sum_S \tilde{E}(S)p(S)$$

$$\tilde{E}(S) = \sum_i^m \tilde{E}_{\text{self}}^i(S) + \sum_{i>j}^m \tilde{V}_{\text{int}}^{ij}(S)$$

IQA at the Structure level



## Electron number distribution functions (EDFs)

- $p(S) \equiv$  Weights of Resonance structures in real space
- Provide the full statistics of electron population

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- $\langle n_A n_B \rangle = \int_{\Omega_A} \int_{\Omega_B} \rho_2(\mathbf{r}_1, \mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2.$
- $\langle n_A n_B \rangle - \langle n_A \rangle \langle n_B \rangle = \text{cov}(n_A, n_B) = - \int_{\Omega_A} \int_{\Omega_B} \rho_{xc}(\mathbf{r}_1, \mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2$
- $\delta^{A,B} = -2\text{cov}(n_A, n_B)$

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 $\delta^{A,B} = -2 \sum_{n_A, n_B} \tilde{n}_A \tilde{n}_B p(n_A, n_B)$
- Similarly,  
 $\delta^{A,B,\dots,K} = \frac{(-2)^{K-1}}{(K-1)!} \left\langle \prod_{x=A}^K \tilde{n}_x \right\rangle$   
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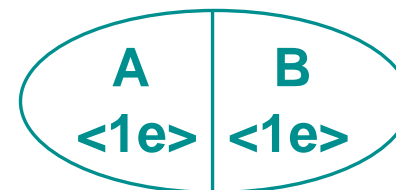
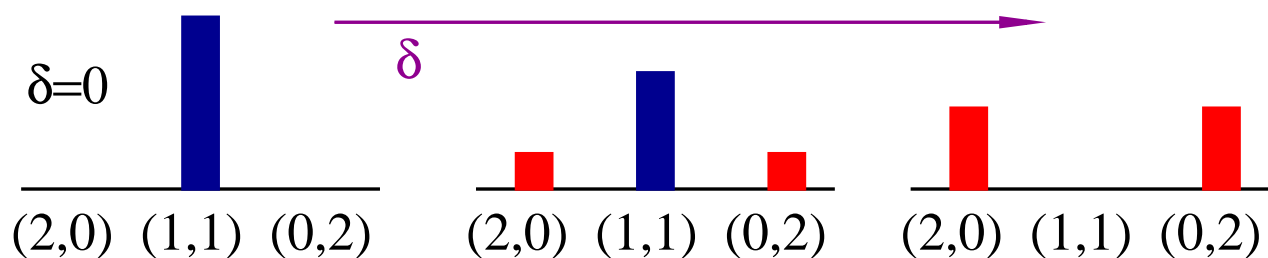
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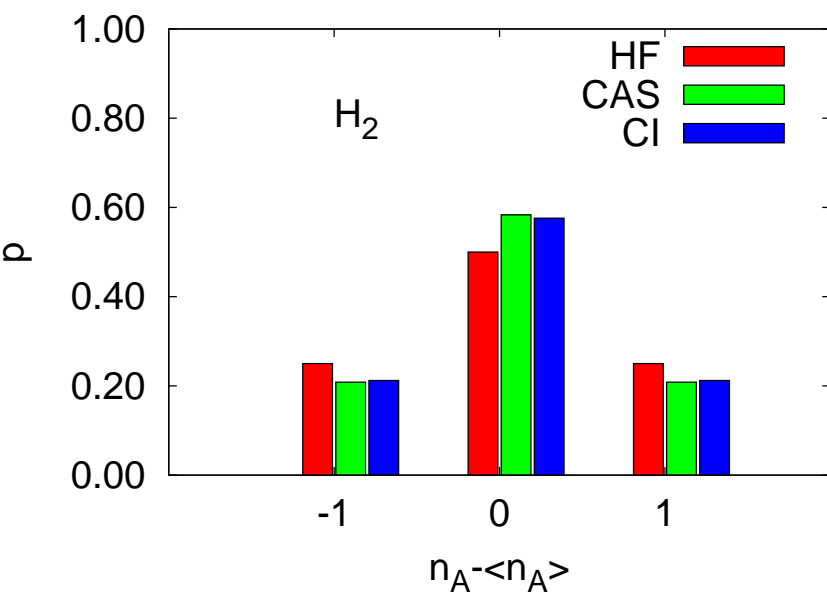
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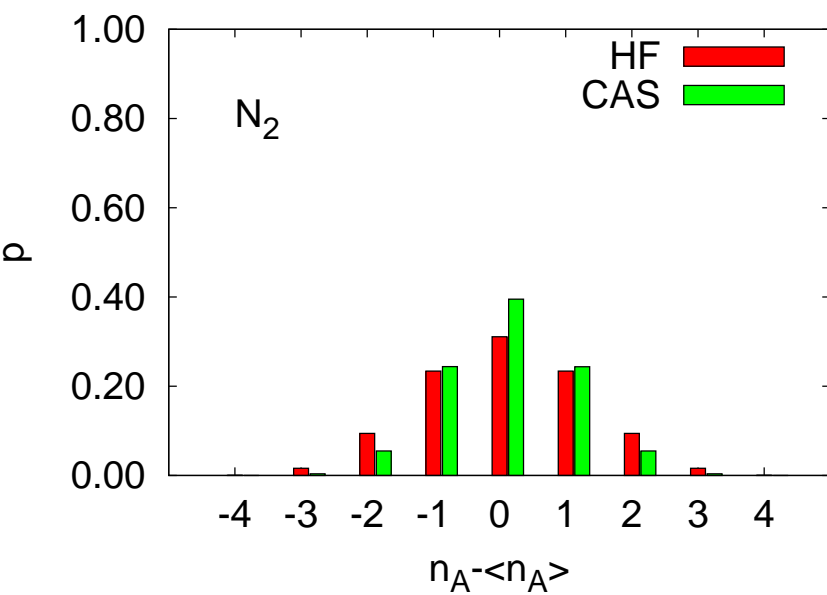
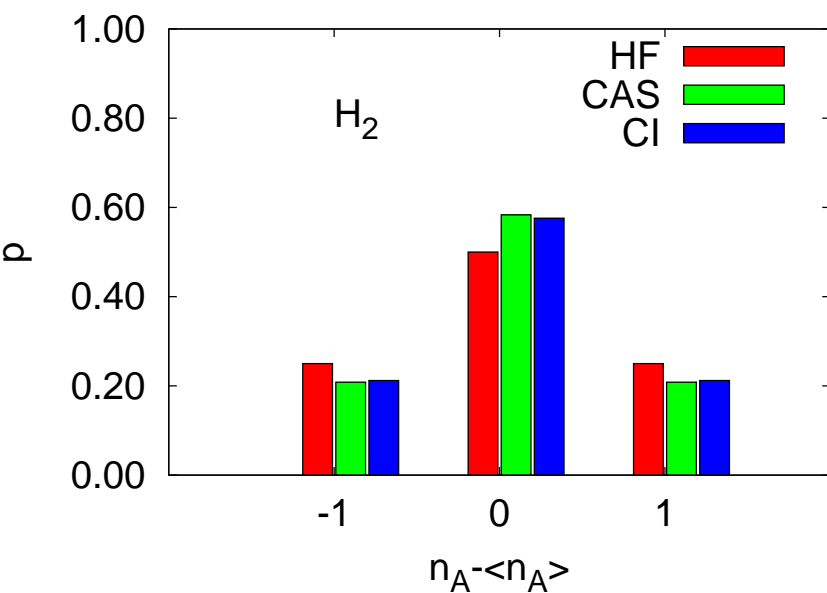
$\delta$  large  $\iff$  EDF broad. Example:  $2c - 2e$  case



## Examples

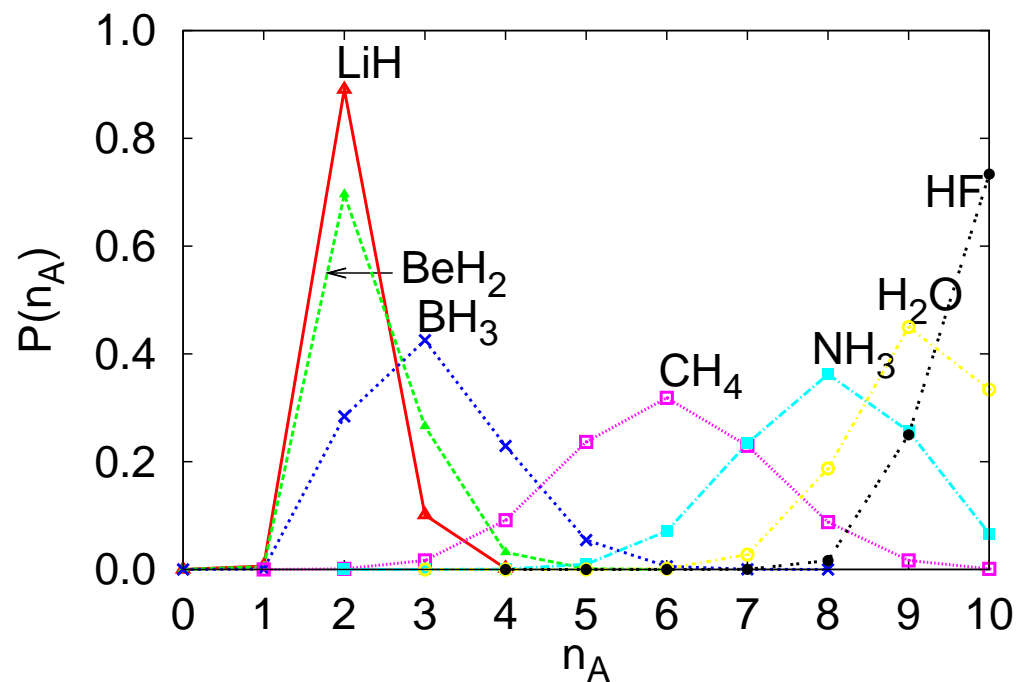
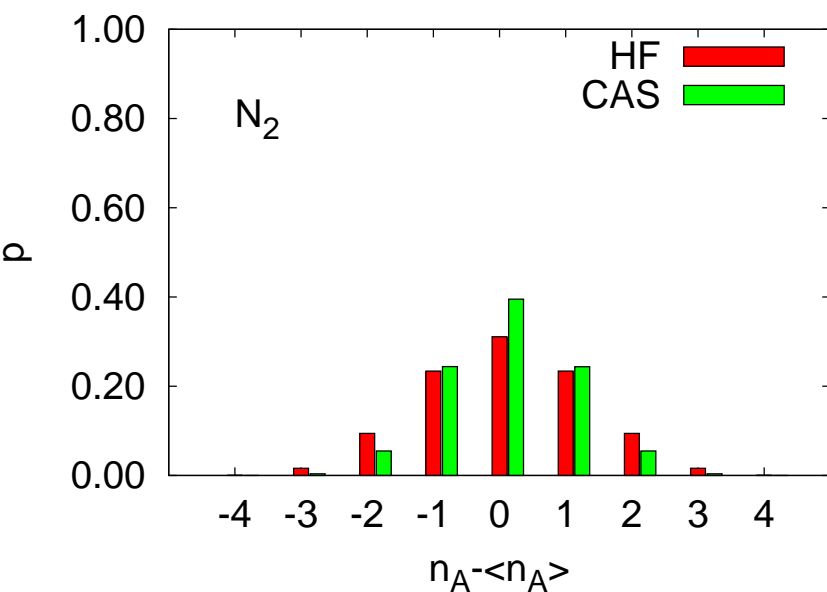
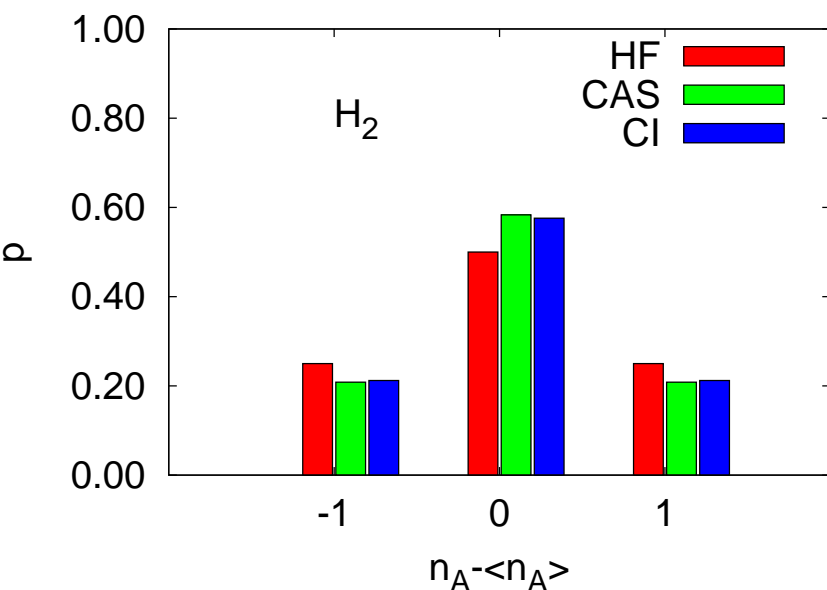


## Examples

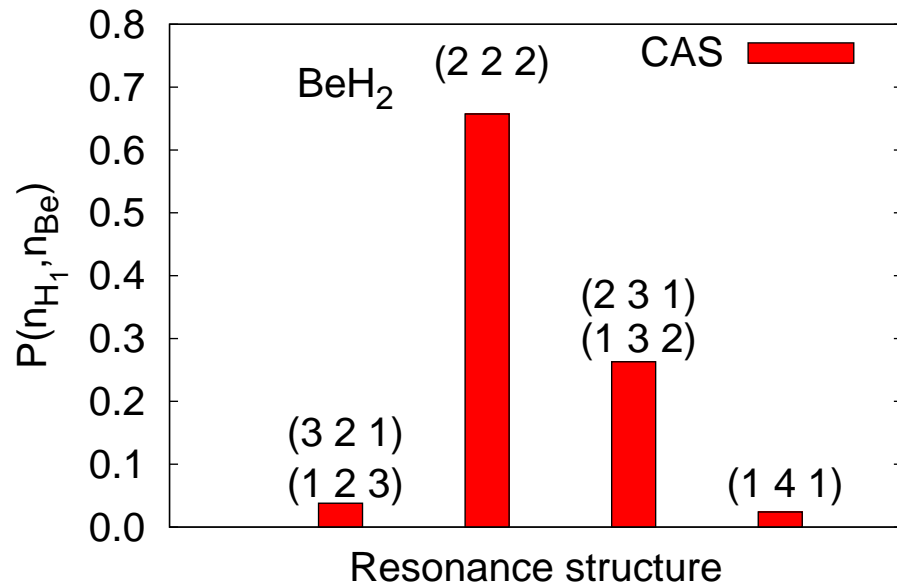




## Examples

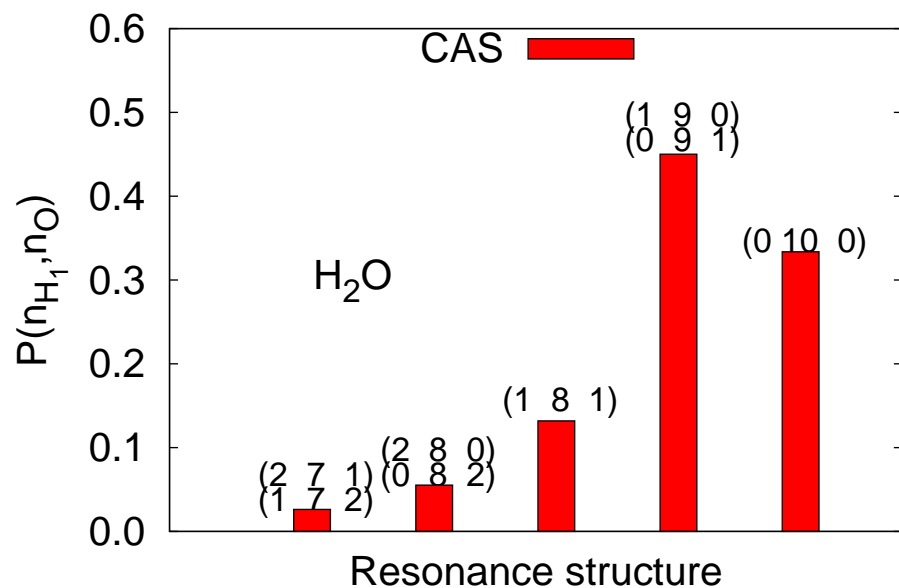
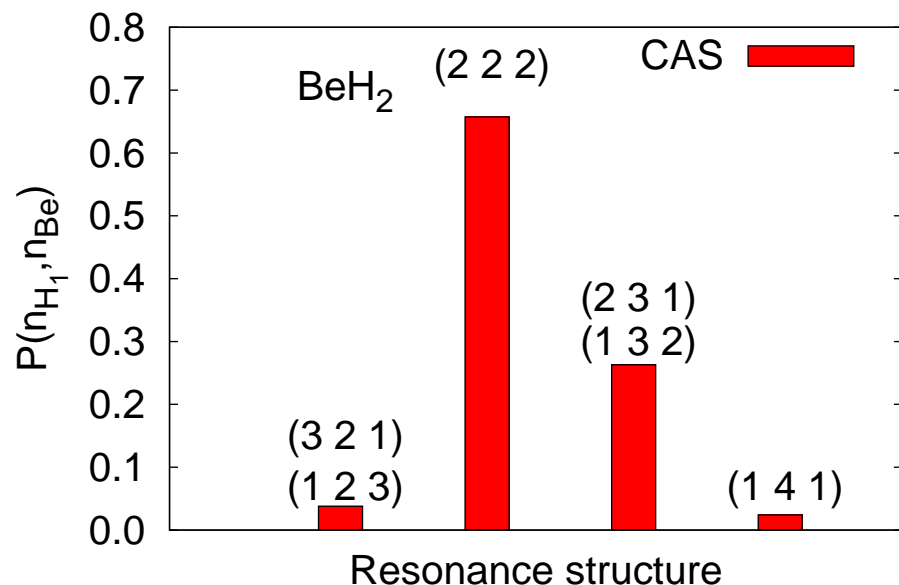


- $\max(n_A - \langle n_A \rangle)$  related to bond order...
- Correlation decreases the width of HF EDFs in  $A_2$ .
- In  $AH_n$ , a rather complex picture of Charge transfer appears.
  - only CH<sub>4</sub> shows  $n_A^{mp} = Z_A$ .
  - CT is asymmetric.



## BeH<sub>2</sub>

- 7:3 H<sup>-</sup>Be<sup>2+</sup>H<sup>-</sup> : H-Be<sup>+</sup>H<sup>-</sup> ↔ H<sup>-</sup>Be<sup>+</sup>-H
- (2 3 1) very different from (3 2 1): Chemistry
- Partial statistics available:
  - $\delta^{\text{Be,H}} = 0.302$ , but  $\delta_0^{\text{Be,H}} = 0.522$
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## H<sub>2</sub>O

- Less ionic than BeH<sub>2</sub>
- 1e transfers dominate..  $q(O) = -1.087$
- but the O<sup>2-</sup> contribution is important.
- Partial statistics
  - $\delta^{\text{O,H}} = 0.637$ , and  $\delta_0^{\text{O,H}} = 0.640$

## Spin resolved EDFs (SEDFs)

- There are just a handful of quantities to explore spin distribution in closed-shell systems.
  - Distribution of odd-electrons (Takatsuka).

- EDFs easily transformed into SEDFs:  $S \Rightarrow (S^\alpha, S^\beta)$

- One-electron properties split into  $(\alpha, \beta)$  pairs:

$$\langle n_A \rangle = \langle n_A^\alpha \rangle + \langle n_A^\beta \rangle$$

$$\langle M_s^A \rangle = \frac{1}{2}(\langle n_A^\alpha \rangle - \langle n_A^\beta \rangle)$$

- Two-electron properties into  $(\alpha\alpha, \alpha\beta, \beta\alpha, \beta\beta)$  components:

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- New two-electron indices may be defined: SCI (spin correlation index)

$$\text{SCI}^{A,B} = -8\langle M_s^A M_s^B \rangle = -2\langle (n_A^\alpha - n_A^\beta)(n_B^\alpha - n_B^\beta) \rangle$$

- If  $A, B$  is a bonded pair, we expect  $\text{SCI} > 0$  and large
- If  $A, B$  are paramagnetically coupled, we expect  $\text{SCI} < 0$  and large

- $\text{SCI}^{A,B} = \delta_{\alpha\alpha}^{A,B} + \delta_{\beta\beta}^{A,B} - \delta_{\alpha\beta}^{A,B} - \delta_{\beta\alpha}^{A,B}$

For HF wavefunctions,  $\text{SCI}^{A,B} = \delta^{A,B}$

New spin interpretation of  $\delta$ 's

## Examples

LiH Structure, $S$					
$n_{\text{Li}}^{\alpha}$	$n_{\text{H}}^{\alpha}$	$n_{\text{Li}}^{\beta}$	$n_{\text{H}}^{\beta}$	$p(S)$ (HF)	(CAS)
0	2	1	1	0.003	0.003
1	1	0	2	0.003	0.003
1	1	1	1	0.896	0.890
1	1	2	0	0.048	0.051
2	0	1	1	0.048	0.051
2	0	2	0	0.003	0.002

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- $\alpha$  and  $\beta$   $e$ 's statistically independent in HF.

- $p(S^{\alpha}, S^{\beta}) = p^{\alpha}(n_A^{\alpha}, n_B^{\alpha})p^{\beta}(n_A^{\beta}, n_B^{\beta})$

- In closed shells,  $p^{\alpha} \equiv p^{\beta}$

- In LiH,  $p^{\alpha}$  is a  $2e$  distribution.

$n_{\text{Li}}^{\alpha}$	$n_{\text{H}}^{\alpha}$	$p(S)$
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- Extremely correlated same-spin electrons.



## Examples

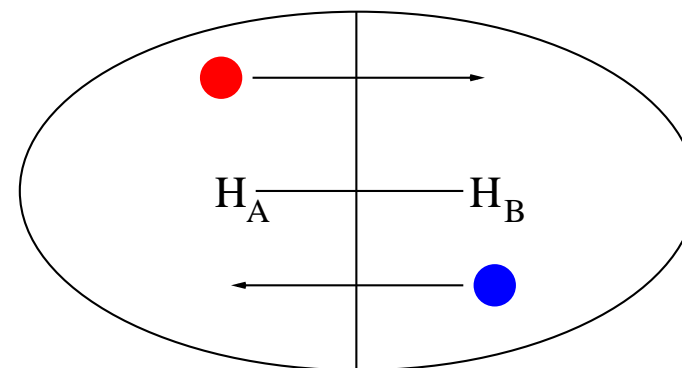
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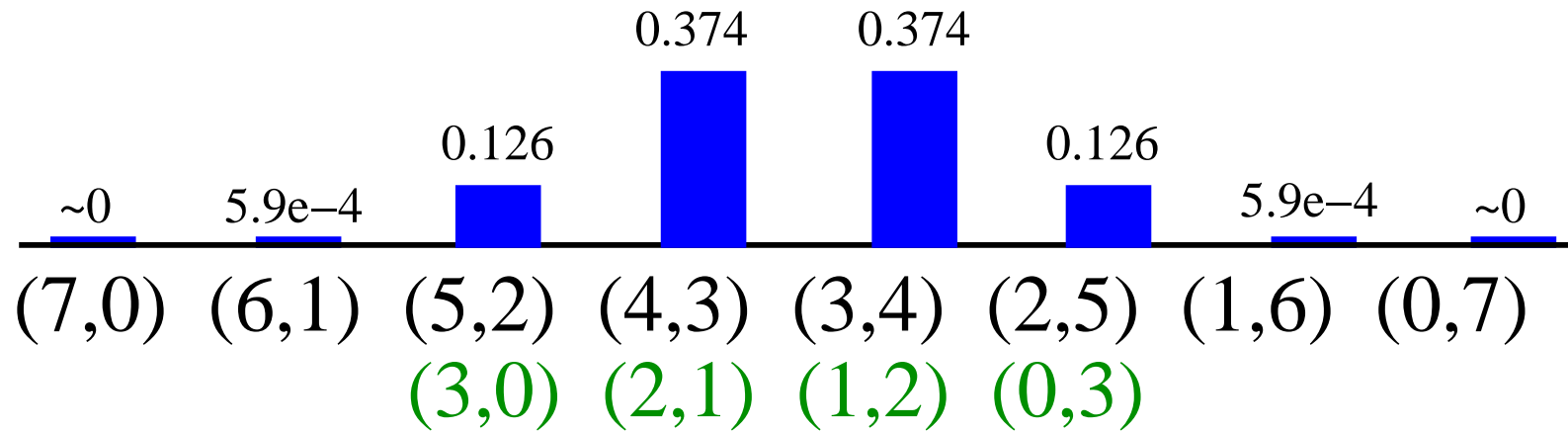
- Extremely correlated same-spin electrons.

- $\text{H}_2$  has only 1  $\alpha(\beta)$  electron not felt by the other:
- Two-equivalent basins  $\Rightarrow p^{\alpha}(0, 1) = p^{\alpha}(1, 0) = 1/2$
- $p^{\alpha} \otimes p^{\beta} = 1/4, 1/2, 1/4 [(2,0),(1,1),(0,2)] \Rightarrow \delta = 1.0$
- Interesting viewpoint of chemical bonds.
  - The electron pair  $\equiv$  Result of  $\alpha, \beta$  independence
  - $\alpha, \beta$  correlation (repulsion) changes  $p$  to  $(0.212, 0.576, 0.212)$



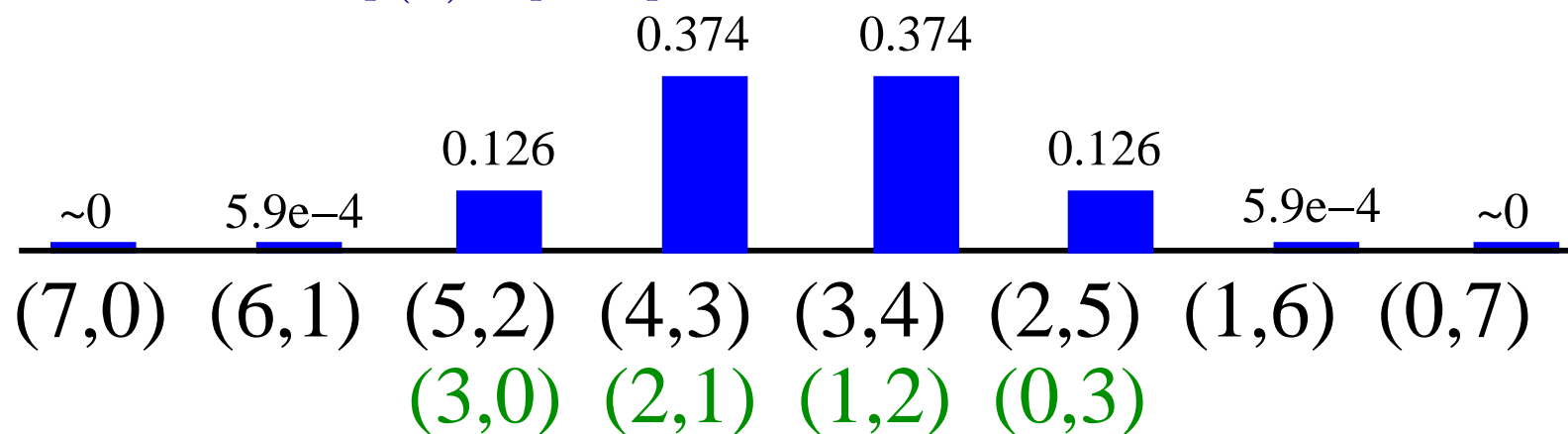
${}^1\Sigma_g^+ \mathbf{N}_2$ 

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

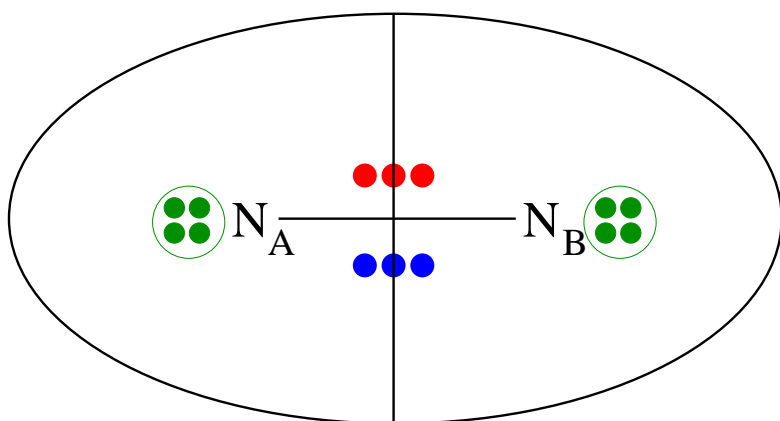


${}^1\Sigma_g^+$   $\text{N}_2$ 

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- 3 independent  $1e$   $p$ 's ( $p_1(0,1) = p_1(1,0) = 0.5$ ) provide:  $p_3 = p_1 \otimes p_1 \otimes p_1$   
 $p(3,0) = p(0,3) = 0.125$ ,  $p(2,1) = p(1,2) = 0.375$

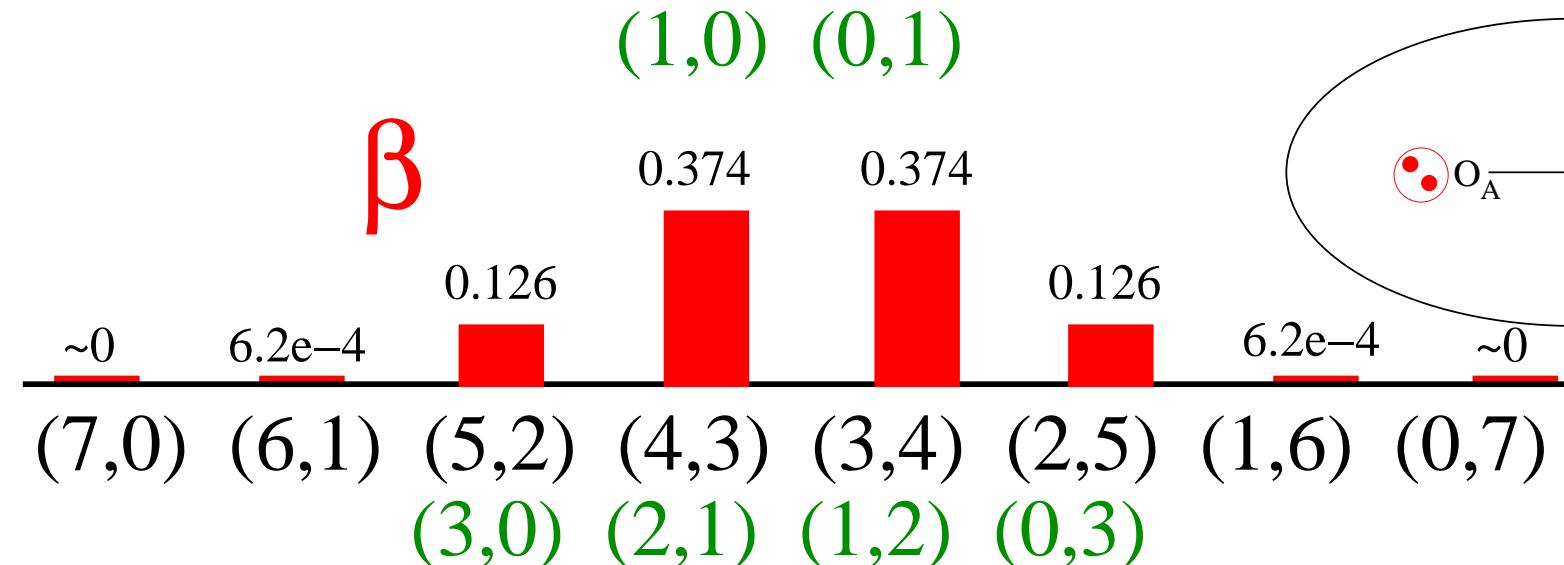
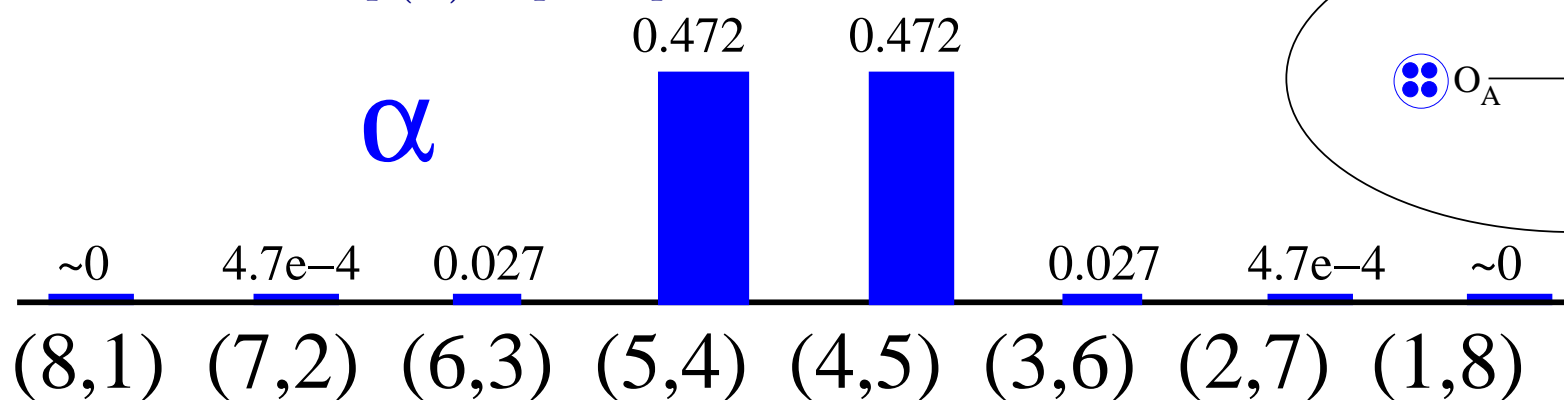


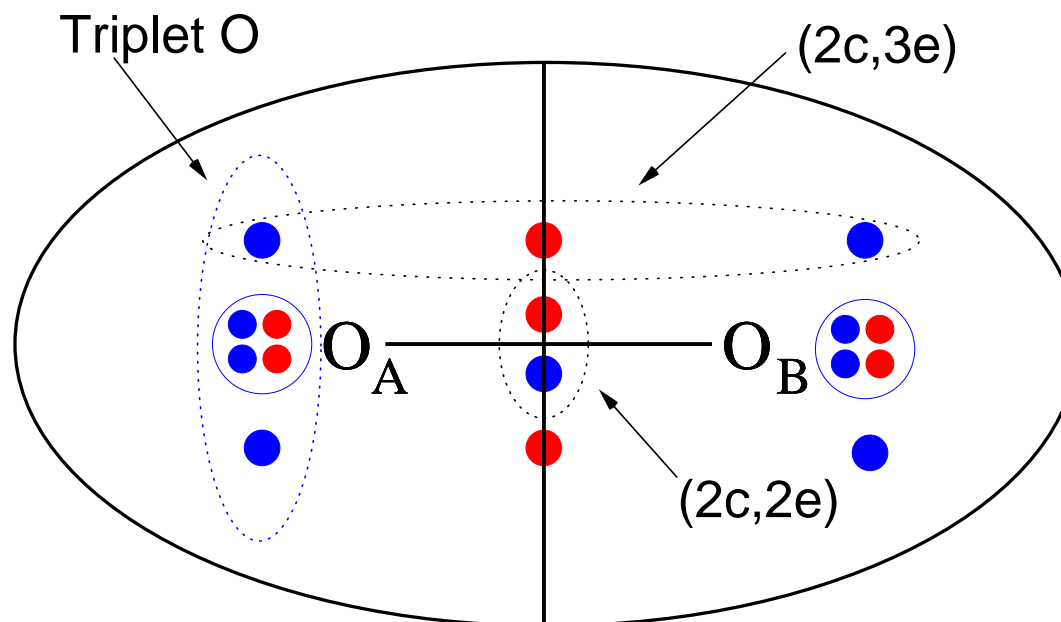
- 4 extremely localized electrons in each basin.
- 3  $\alpha$ , 3  $\beta$  fully delocalized electrons.
- Thus... 3 bonding pairs:  $\delta^{\alpha\alpha} = 1.519$ ,  $\delta = 3.038$
- Correlation (CAS[10,10]) hinders delocalization :

$$\delta^{\alpha\alpha} = 1.418, \delta^{\alpha\beta} = -0.424, \delta = 1.987$$

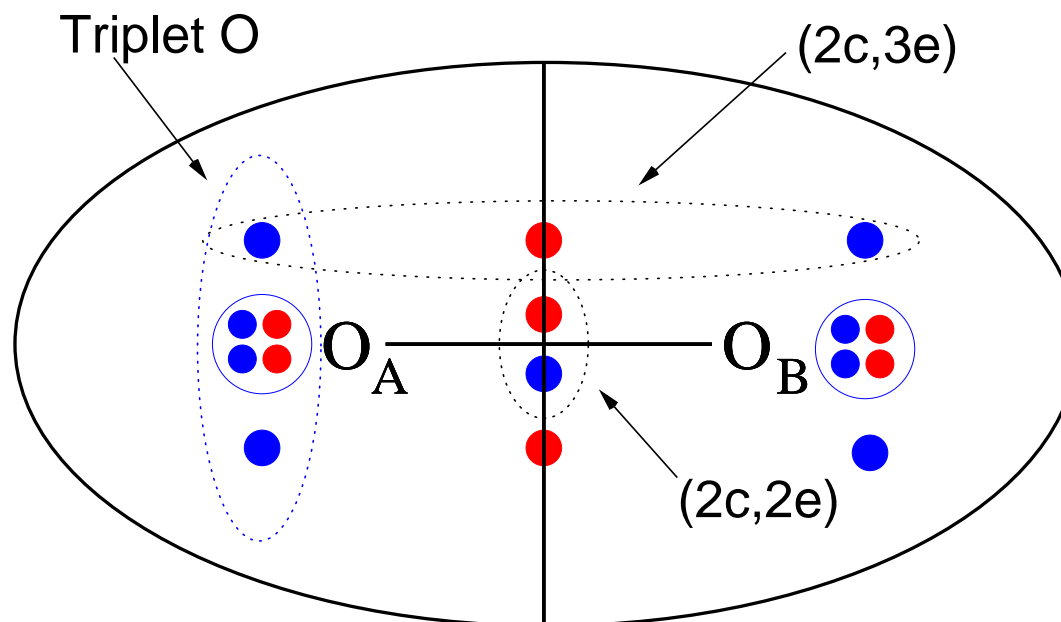
${}^3\Sigma_g^- \text{O}_2$ 

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





- Each O atom bears a localized core of 2  $\alpha\beta$  pairs, plus 2 localized  $\alpha$  electrons.
- Thus, each O bears a localized **triplet state**.
- 1 delocalized  $\alpha\beta$  pair contributes  $\delta \approx 1.0$
- 2 independent fully delocalized  $\beta$  electrons, each contributing  $\delta \approx 0.5$ : Two (2c,3e) bonds: Pauling's or modern VB calculations



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- $\delta^{\alpha\alpha} = 0.731, \delta^{\beta\beta} = 1.520, \delta = 2.251, \text{SCI} = 0.251.$
- $\delta^{\alpha\alpha} = 0.732, \delta^{\beta\beta} = 1.190, \delta^{\alpha\beta} = -0.192, \delta = 1.539, \text{SCI} = 0.307.$  Correlated

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