Chemical Materials Department

Atoms in Molecules. The problem of atomic charges and electronic structure of molecules

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GAMESS + AMALL

Electronic Characteristics of molecules

- Electron Densities Distribution,
- Atomic Charges,
- Dipole Moments,
- Quadrupole moments,
- Polarizabilities,
- Hyperpolarizabilities,

……

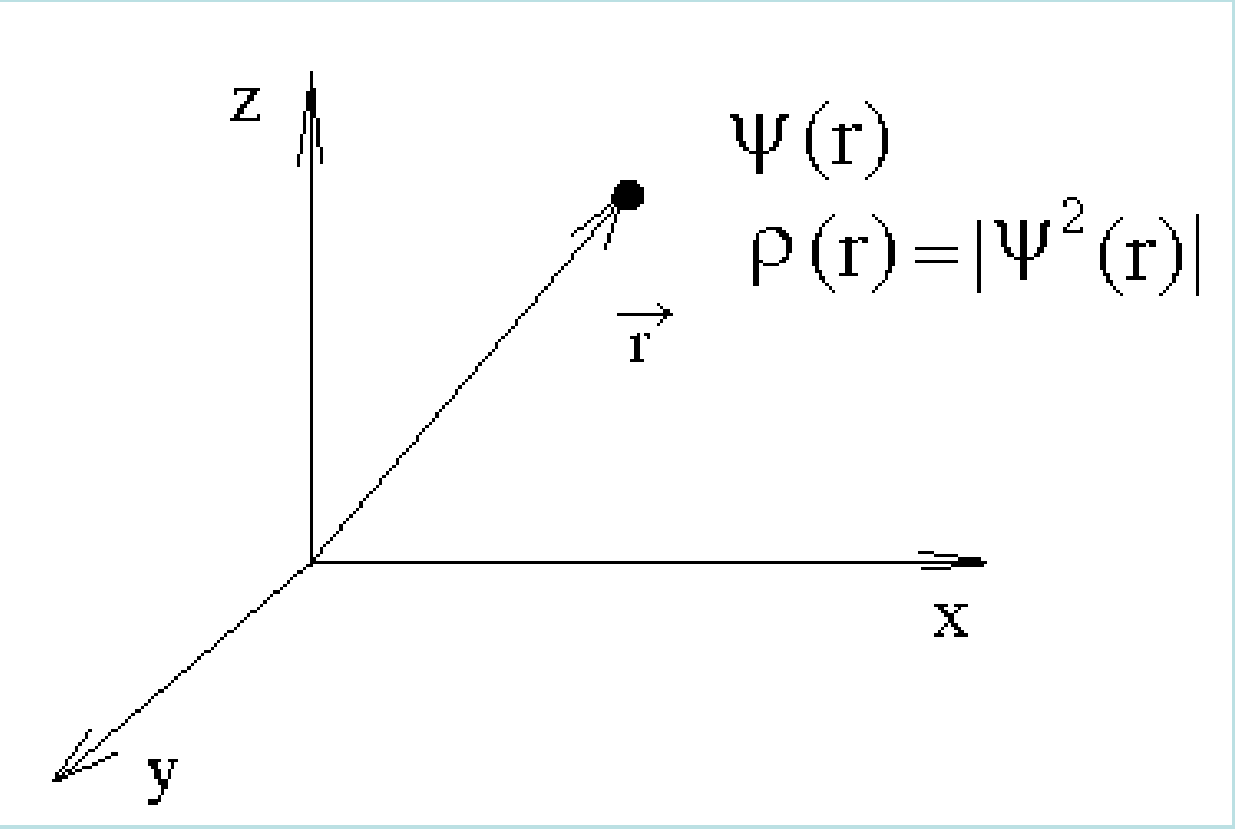
Chemist would like to consider a molecule as a collection of atoms

Classical Chemistry:
Molecules = atoms + *Chemical bonds*

Quantum Chemistry:
Molecules = nucleus + *electrons*

No Atoms in molecules !

The wave function and electron density



ATOM in molecule

$$H\Psi_A(1...N) = E\Psi_A(1...N)$$

$$\Psi_A = \Psi_A(1...N)$$

$$\rho_e(N) = -\Psi_A^*\Psi_A$$

$$\rho_e = -\int \Psi_A^*\Psi_A d\tau_2 d\tau_3 ... d\tau_N$$ RDM-1

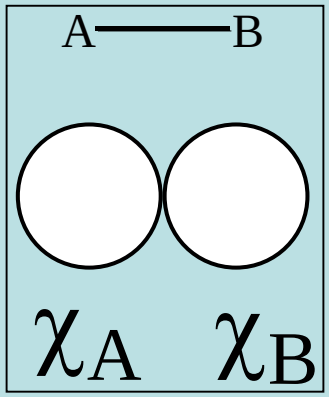
$$\rho_A = \int_{V_A} \rho_e dV$$ At the border of V: $\rho_e \approx 0$

$$V_A = \frac{4}{3}\pi r_A^3$$

Atomic charge: $q_A = Z_A - \rho_A$

Electron Densities in π-electron theory

ZDO $\quad \chi_\mu(\vec{r})\chi_\nu(\vec{r})dr = 0$



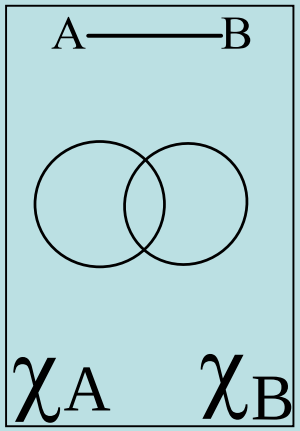
$$\left|\varphi_i\right\rangle = c_{A(i)}\left|\chi_A\right\rangle + c_{B(i)}\left|\chi_B\right\rangle$$

$$\left\langle\varphi_i\middle|\varphi_i\right\rangle = c^2_{A(i)} + c^2_{B(i)} = 1$$

$$\rho_A = 2\sum_i^{\text{occ.MO}} c^2_{A(i)}$$

$$q_A = Z_A - \rho_A$$

Electron densities in *ab initio* approaches (Mulliken)



$$\chi_\mu(\vec{r})\chi_\nu(\vec{r})dr \neq 0$$

$$\int \chi_\mu(\vec{r})\chi_\nu(\vec{r})dr \neq 0$$

$$|\phi_i\rangle = c_{A(i)}|\chi_A\rangle + c_{B(i)}|\chi_B\rangle$$

$$\langle\phi_i|\phi_i\rangle = c_{A(i)}^2 s_{AA} + c_{B(i)}^2 s_{BB} + 2c_{A(i)}c_{B(i)}s_{AB} = 1$$

$$\sum_i \langle\phi_i|\phi_i\rangle = N$$

$$s_{AA} = \langle\chi_A|\chi_A\rangle = 1 \qquad s_{BB} = \langle\chi_B|\chi_B\rangle = 1 \qquad s_{AB} = \langle\chi_A|\chi_B\rangle$$

$$P_A = \sum_i c_{A(i)}^2 + c_{A(i)}c_{B(i)}S_{AB}$$

$$P_B = \sum_i c_{B(i)}^2 + c_{A(i)}c_{B(i)}S_{AB}$$

$$N = P_A + P_B$$

Atomic populations according to Mulliken

(1896-1986)

(Nobel prize 1966)

Electron density at atom

$$P_A = \sum_{a \in A} \rho_a + \frac{1}{2} \sum_{r \in A,\, s \notin A} \rho_{rs} s_{rs}$$

$$P_{AB} = \sum_{a \in A} \sum_{b \in B} \rho_{ab} s_{ab}$$ - Bond order

$$W_{AB} = \sum_{a \in A} \sum_{a \in A} \left(\rho_{ab} s_{ab}\right)^2$$ - Wiberg Indices

Mulliken charges too sensitive to basis set choice

Hartree-Fock O(H_2O)

3-21G	-0.74
6-31G(d,p)	-0.67
6-311G(2d,2p)	-0.52
cc-pVDZ	-0.26
cc-pVTZ	-0.48
cc-pVQZ	-0.51
aug-cc-pVDZ	-0.26
aug-cc-pVTZ	-0.41

Electron Densities by P.- O. Löwdin

Orthogonalization by P.- O. Löwdin

$$s_{ab} = \langle \chi_a | \chi_b \rangle \neq 0 \qquad s^{-1/2} \rightarrow \langle \tilde{\chi}_a | \tilde{\chi}_b \rangle = \delta_{ab}$$

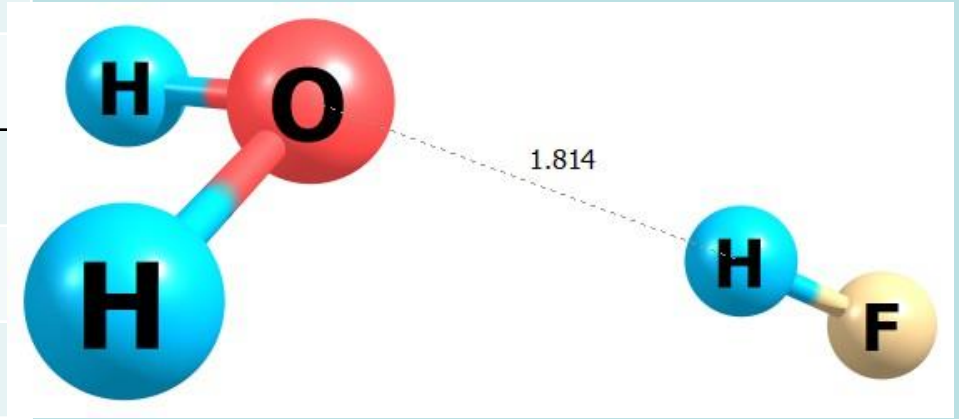
Water, 6-311+G(2d,p)

	By Mulliken	By Löwdin
ρ(O)	8.5941	8.3908
ρ(H)	0.7029	0.8062
charge O	-0.5941	-0.3908
charge H	+0.2971	+0.1970

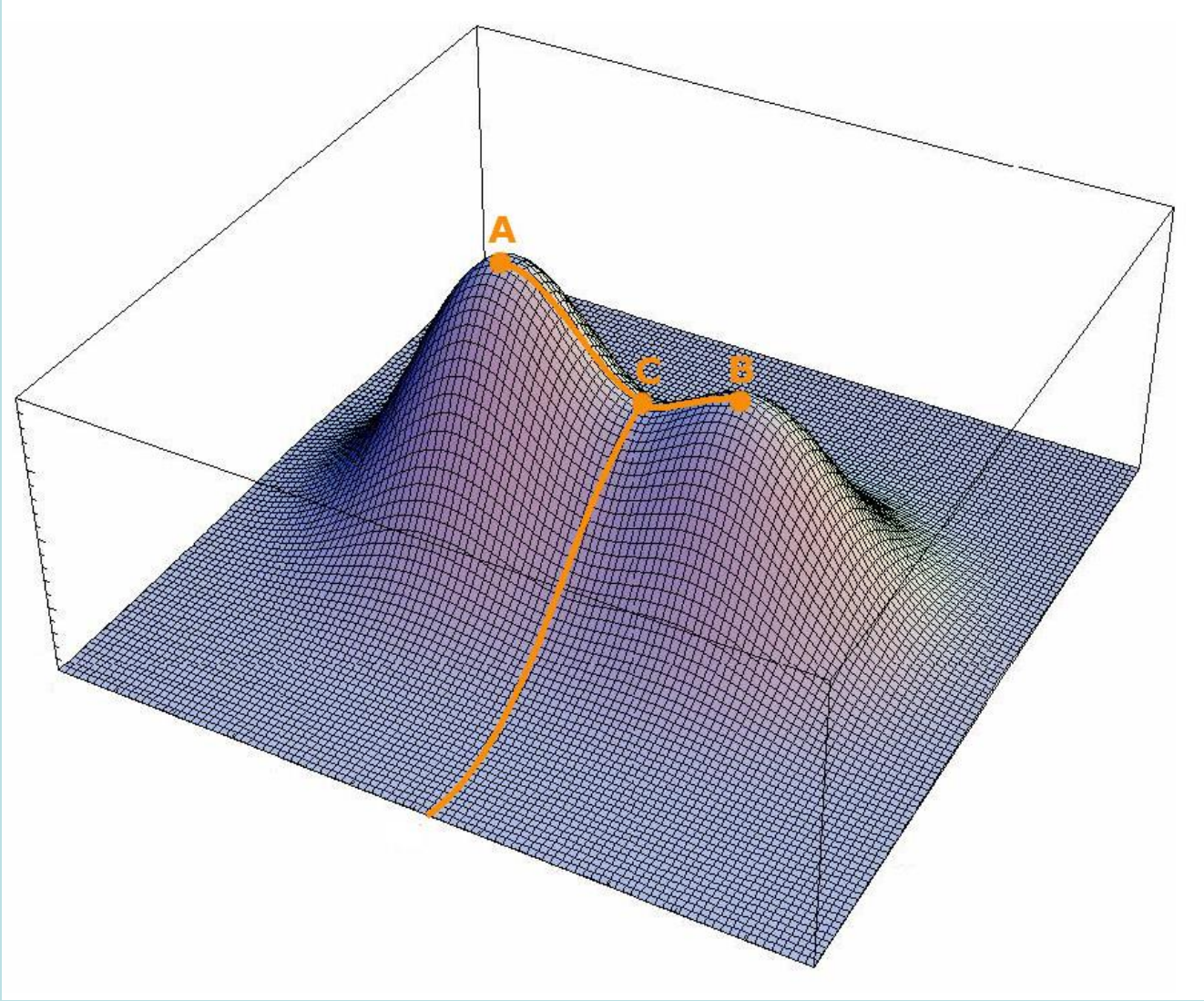
Hydrogen bond in $FH\ldots H_2O$ complex

Atomic charges HF / 6-311+G(2d,p)

	By Mulliken	By Löwdin
F	-0.3575	-0.2319
H	+0.3575	0.2319
O	-0.5941	-0.3909
H	+0.2971	+0.194
H	+0.2971	+0.194



Bader's Theory

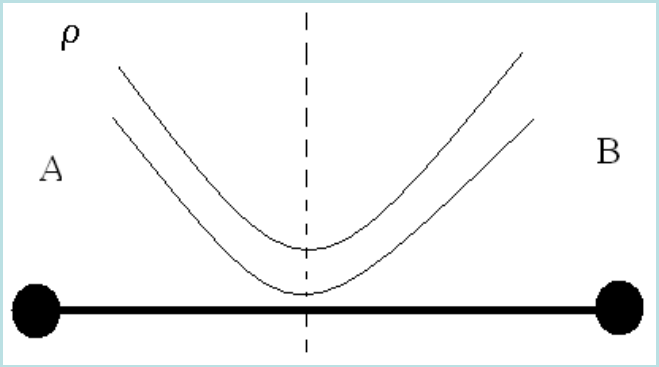


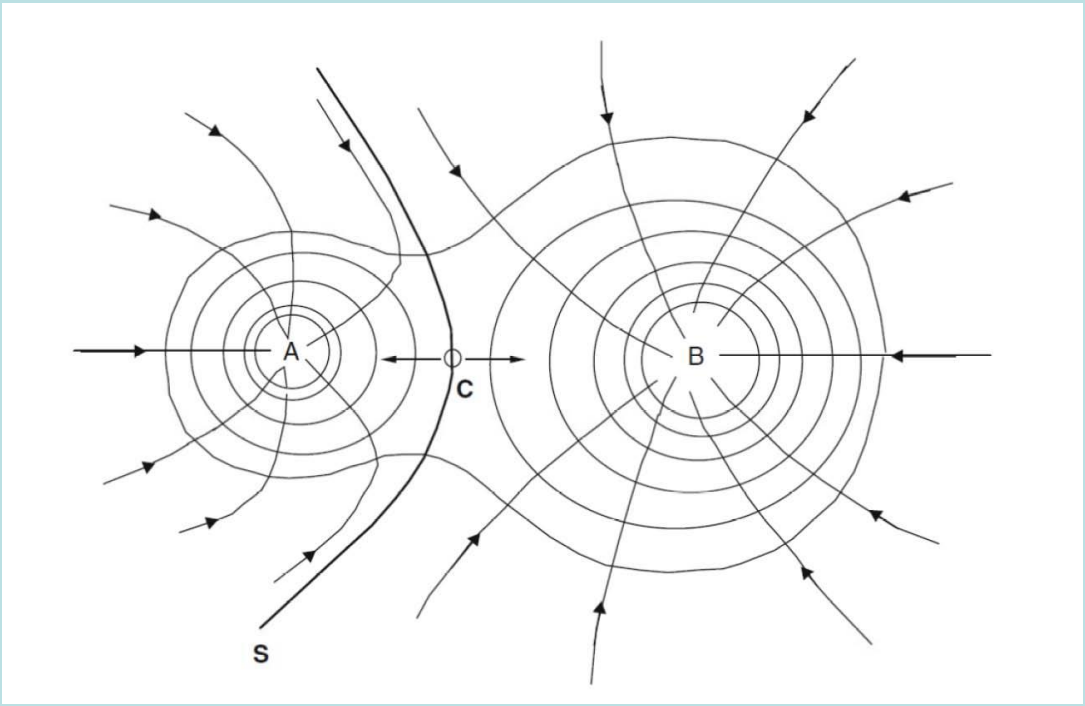
Bader's Theory

$$\rho(\vec{r}) \rightarrow \nabla\rho(\vec{r}) \rightarrow \nabla\rho(\vec{r})\cdot n(\vec{r}) = 0$$

Richard F. W. Bader

(1931-2012)

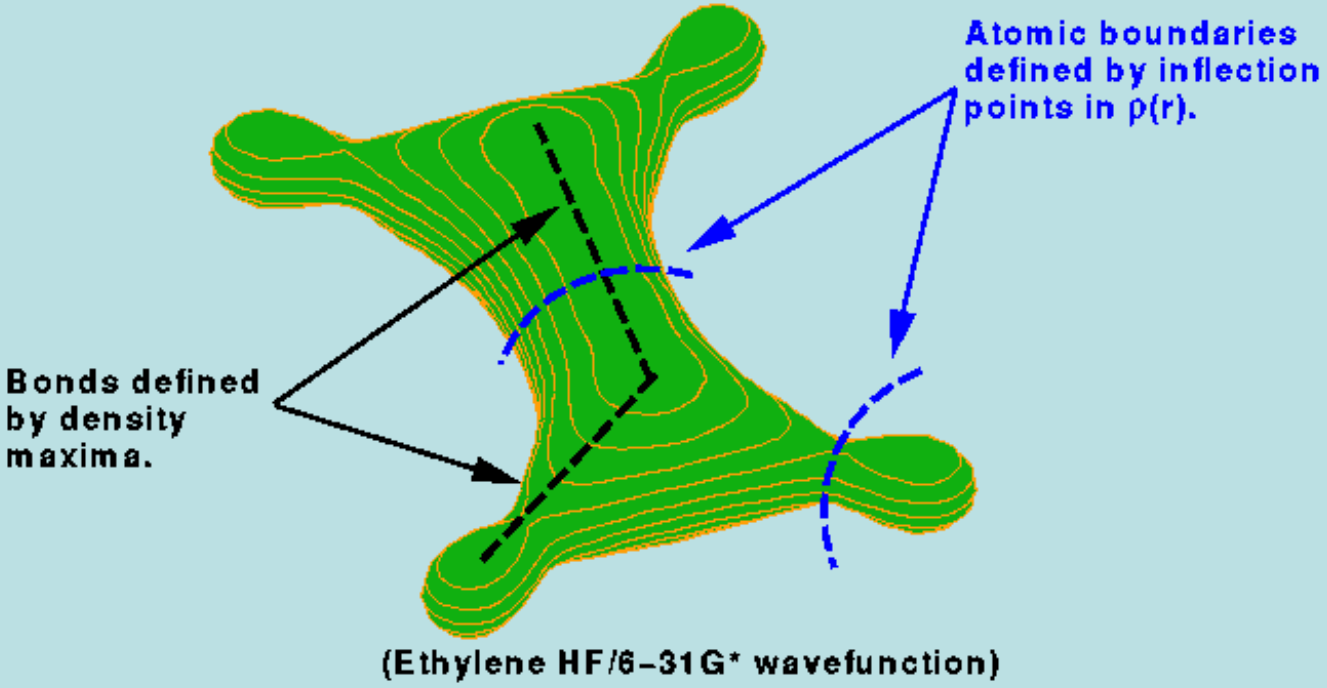




Bader's Atoms in Molecules Analysis

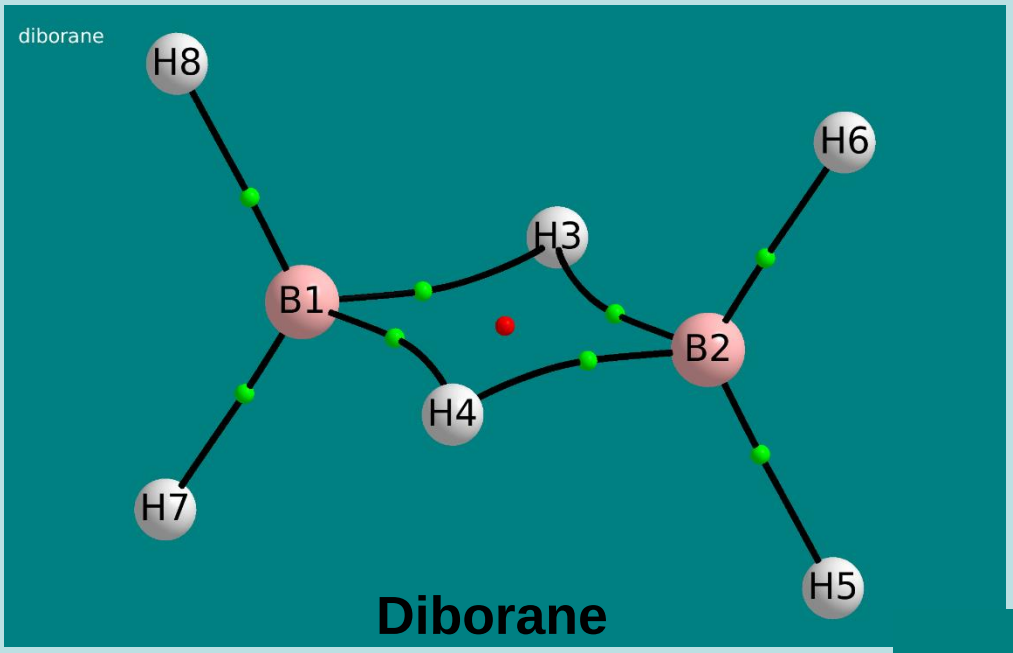
(see R.F. Bader, *Chem. Rev.* 91, pp. 893–928, (1991))

Topology of electron density used to define atomic "basins" and bonds.



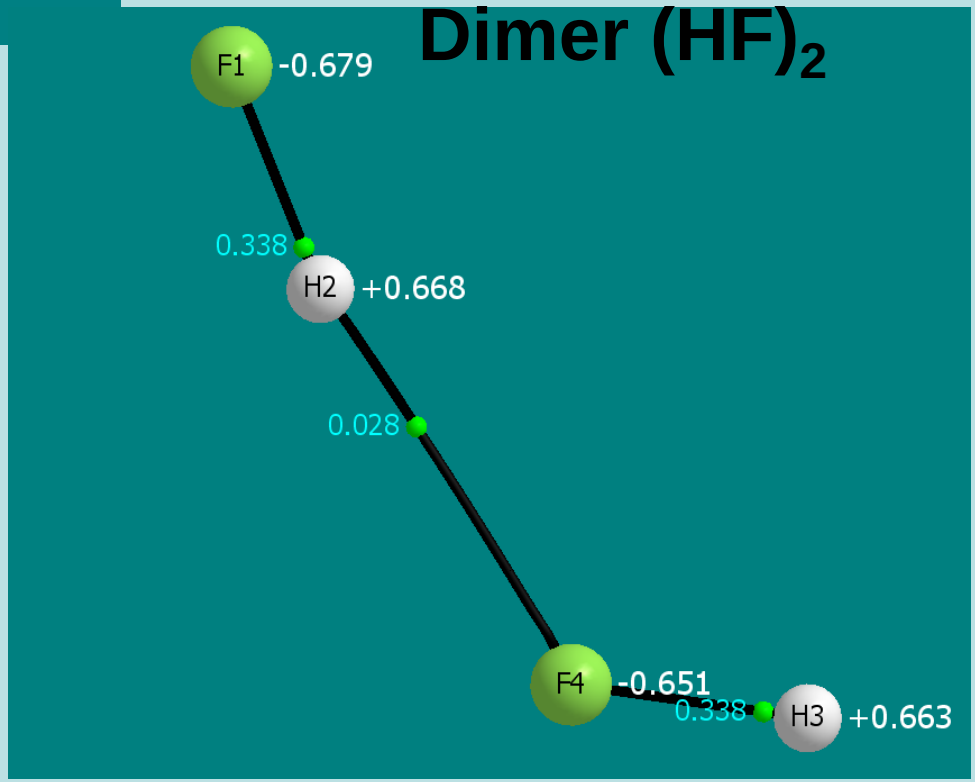
Критичні точки (КТ) електронної густини та їх характери

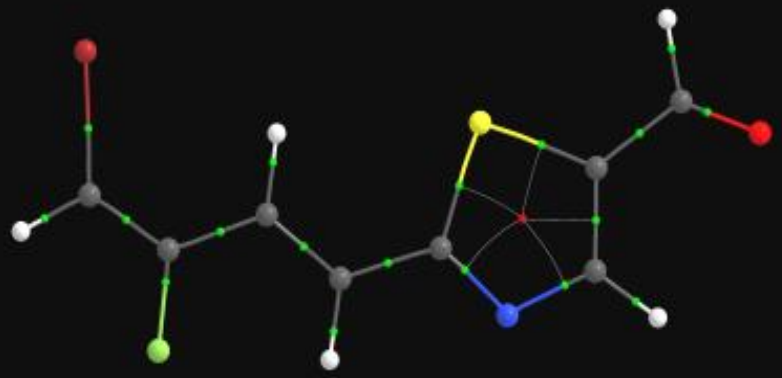
Параметр КТ	**Характери КТ**	**Локалізація КТ**
(3,-3)	Локальний максимум, (*Nuclear Attractor*, NA)	ядро
(3,-1)	Мінімум на лінії зв’язку, (*Bond Critical Point*, BCP)	зв’язок
(3,+1)	Мінімум в «центрі» циклу, (*Ring Critical Point*, RCP)	цикл
(3,+3)	Мінімум в «центрі» клітини, (*Cage Critical Point*, CCP)	клітина (каскад циклів)

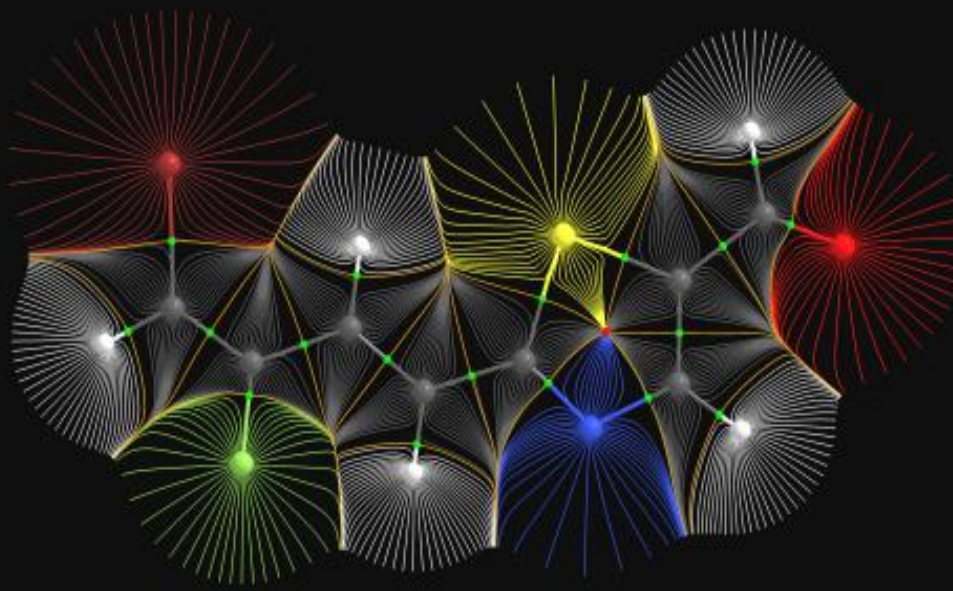


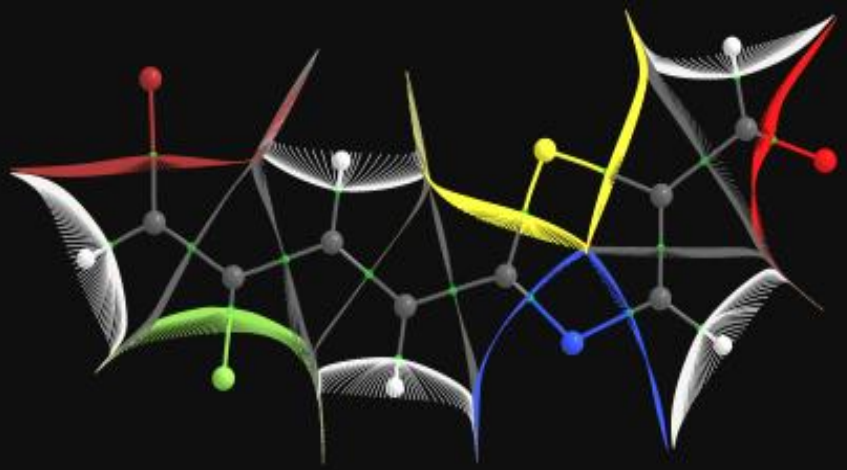
Diborane

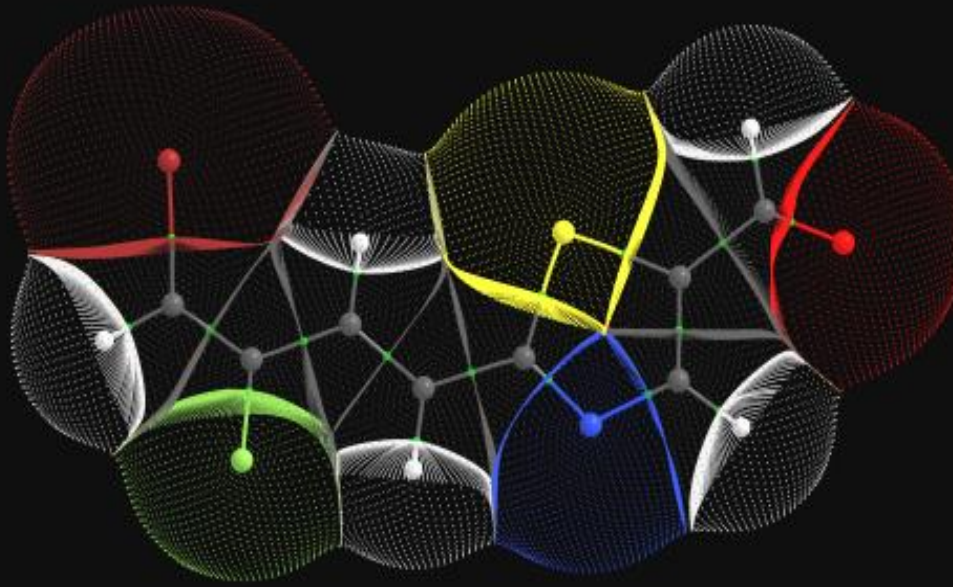
Dimer $(HF)_2$

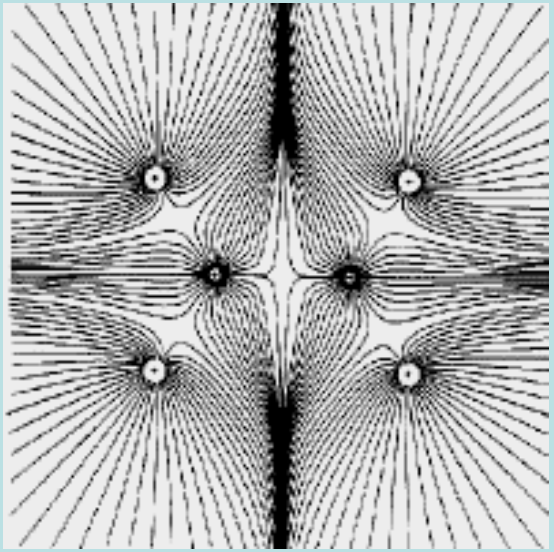


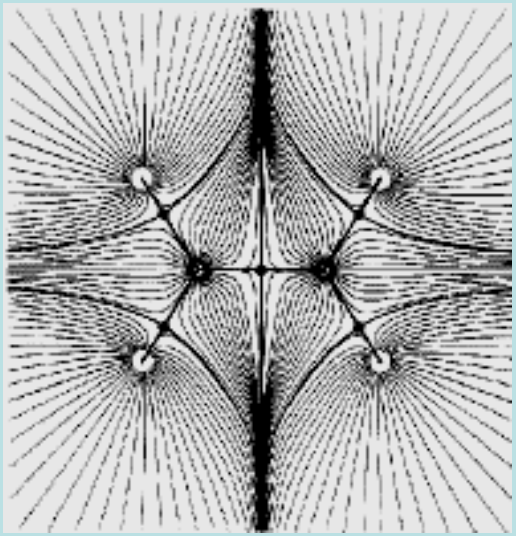




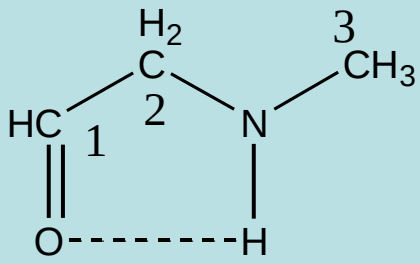




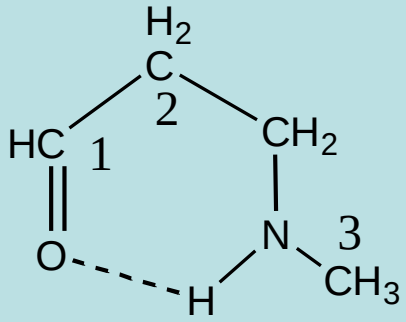




Intramolecular Hydrogen Bond



A

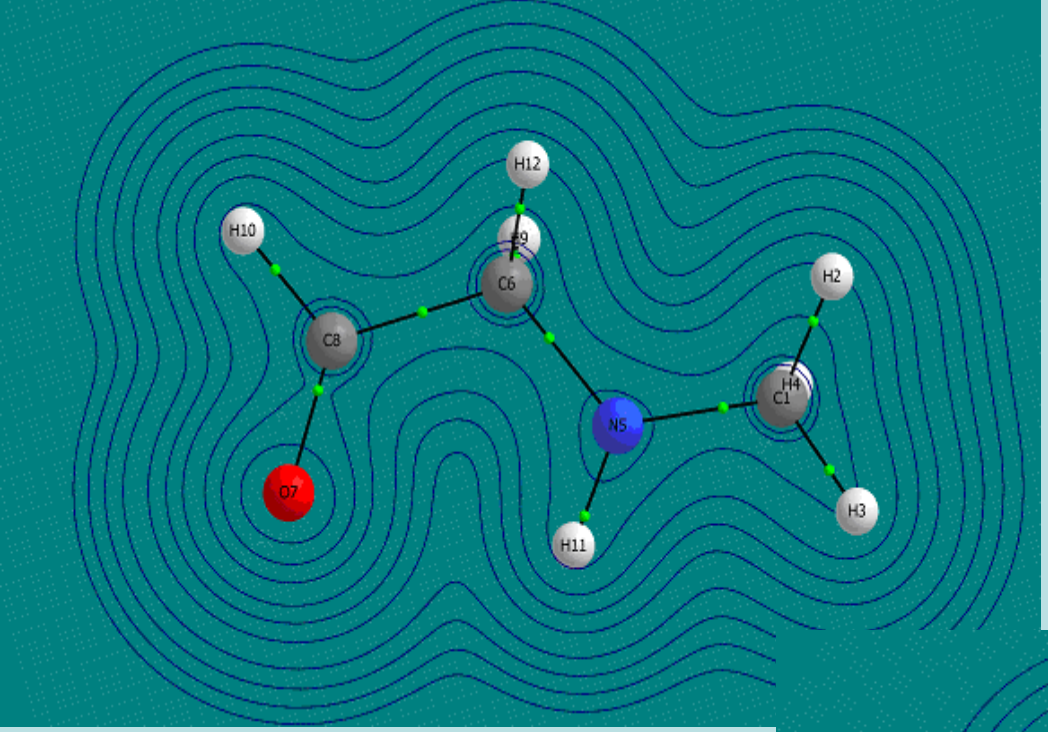


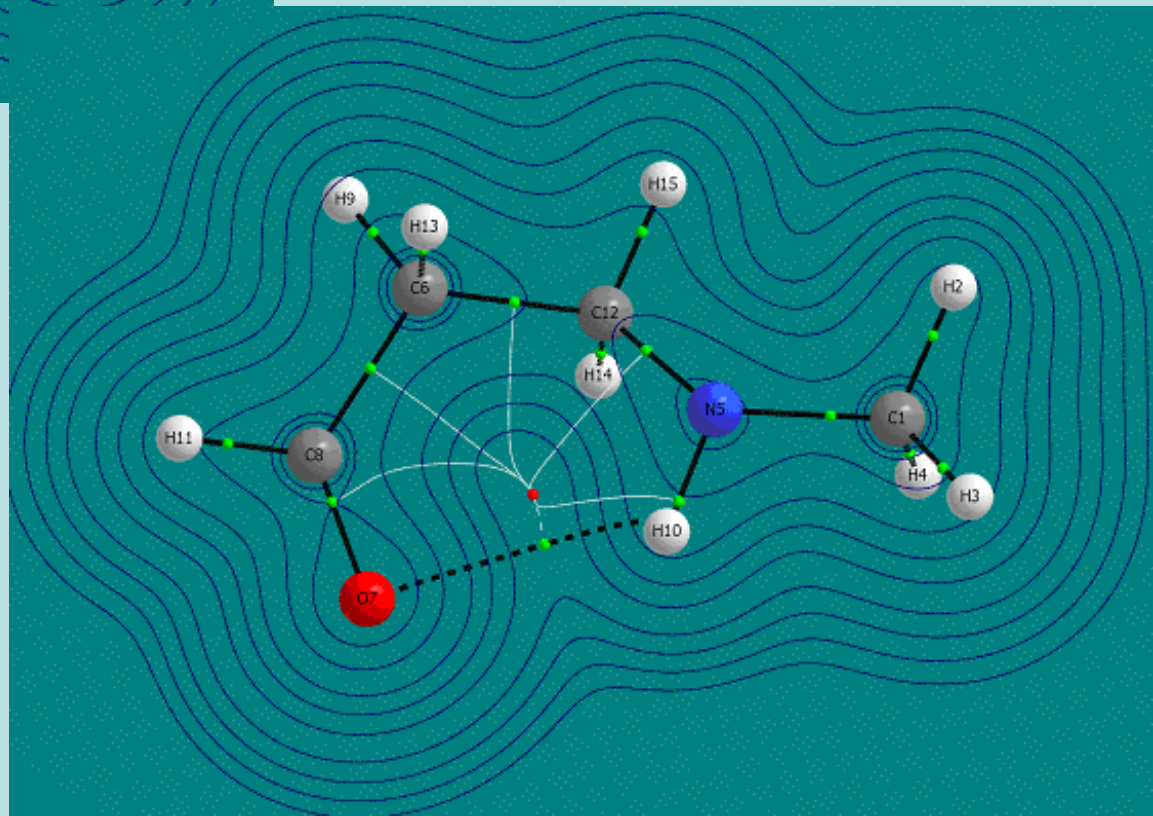
B

Atomic Charges

	Mulliken	Lowdin	Bader
C1	0.324	0.105	1.233
C2	-0.201	-0.218	0.506
C3	-0.290	-0.335	0.540
N	-0.693	-0.404	-1.280
O	-0.476	-0.271	-1.329
H	0.367	0.278	0.402

	Mulliken	Lowdin	Bader
C1	0.331	0.114	1.213
C2	-0.429	-0.319	0.043
C3	-0.288	-0.335	0.526
N	-0.708	-0.416	-1.274
O	-0.487	-0.286	-1.340
H	0.366	0.272	0.392


H12
H10
H9
C6
H2
C8
H4
C1
N5
O7
H3
H11


H9
H15
H13
C6
C12
H2
H14
N5
C1
H11
C8
H4
H3
H10
O7

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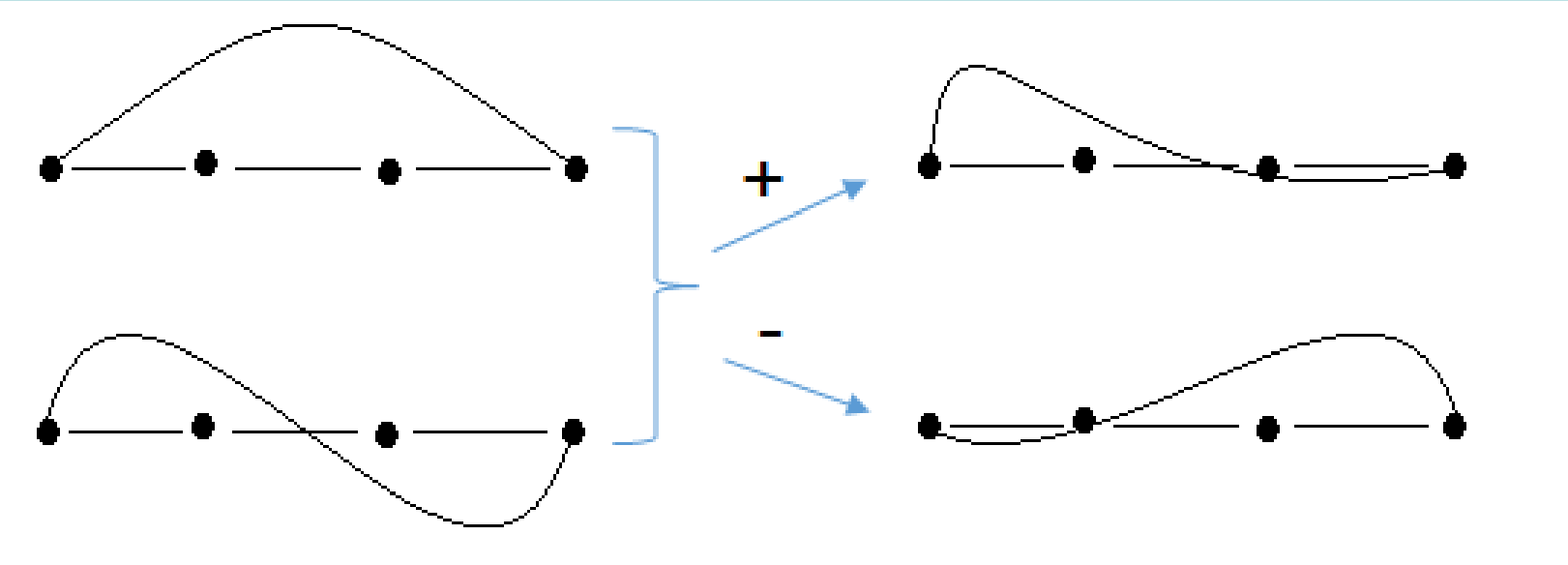
Molecular Orbitals Localization



Unitary Transformation

$$U = \begin{vmatrix} \cos\theta & \sin\theta \\ -\sin\theta & \cos\theta \end{vmatrix}$$

Edmiston-Ruedenberg

$$\max \left\langle ii \left| \frac{1}{r_{12}} \right| ii \right\rangle$$

Pipek-Mezey

$$\min \left\langle i \left| \bar{N} \right| i \right\rangle$$