ICG Montpellier

Institut Charles Gerhardt CTMM

UMR 5253 - Institut de Chimie Moléculaire et des Matériaux de Montpellier

Insight into Chemical Bonding from Analysis of the Wavefunction

Eric CLOT

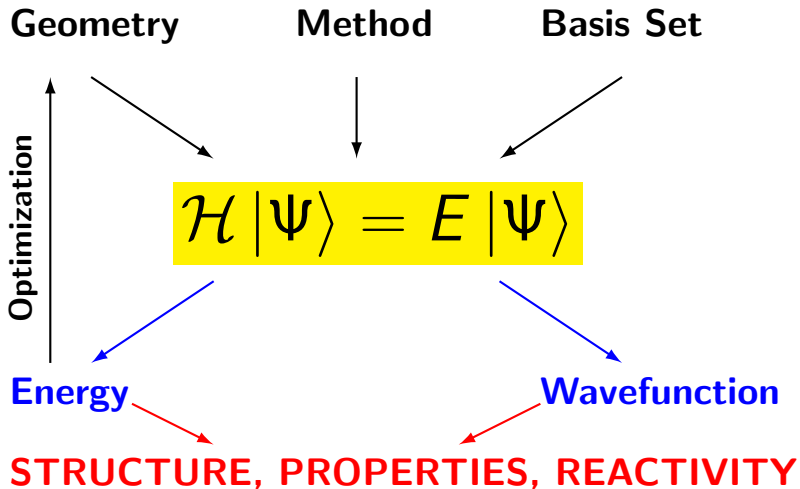UMR 5253 - CNRS, UM2, ENSCM, UM1

Experimental Chemists have Questions

- Where are the Nucleophilic and Electrophilic Sites in a Molecule ?
- How Strong are the Bonds within a Molecule ?
- What is the Nature of the Bonds between the Atoms ?
- Why is this Molecule more Stable than this Other ?
- How can we Describe the Interaction between two Reacting Molecules ?

They use Concepts to Rationalize the Results

- Lewis structure, Resonance, Hyperconjugation
- Electonegativity, Hybridation

Computational Chemists determine Wavefunctions

Wavefunction : Access to Density

$$\rho = \Psi^*(\vec{r})\Psi(\vec{r}) \longrightarrow \int \rho d\vec{r} = N$$

How Calculations can Answer the Experimentalists' Questions ?

- Is it possible to Evaluate the Charge of an Atom in a Molecule ?
- Is it possible to Cast the Information contained in the Wavefunction as a Localized Lewis Structure ?
- Is it possible to Describe the Deviation from the Strictly Localized Lewis Structure ?

Molecular Orbital Theory

MO as Linear Combination of AO : $\psi_i = \sum_k c_{ik} \chi_k$

	HOMO	LUMO
C(1s)	0.00000	0.00000
C(2s)	0.00000	0.00000
C(2p$_x$)	0.00000	0.82121
C(2p$_y$)	-0.18207	0.00000
C(2p$_z$)	0.00000	0.00000
O(1s)	0.00000	0.00000
O(2s)	0.00000	0.00000
O(2p$_x$)	0.00000	-0.76719
O(2p$_y$)	0.86995	0.00000
O(2p$_z$)	0.00000	0.00000
H1(1s)	-0.35917	0.00000
H2(1s)	0.35917	0.00000

H_2CO : HF/STO-3G

LUMO : $2b_1$

$3a_1$ $1b_1$ HOMO : $2b_2$

$1a_1$ $2a_1$ $1b_2$
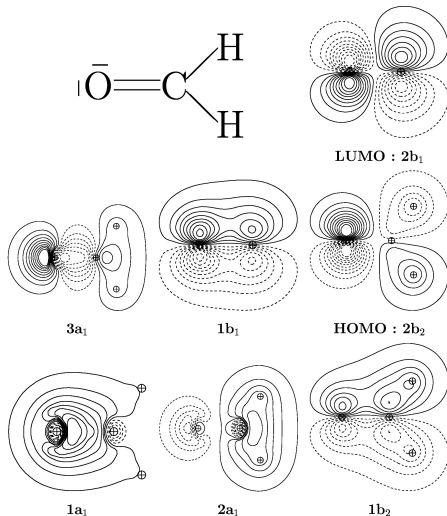
Molecular Symmetry : Delocalized Description

Mulliken Population Analysis

Density expressed with the MO

$$\rho = \sum_i^{occ} 2\psi_i^* \psi_i \text{ with 2 electrons in occupied MO } \psi_i$$

Density expressed with the AO

$$\rho = \sum_i^{occ} 2 \left(\sum_k \sum_\ell c_{ik}^* c_{i\ell} \chi_k^* \chi_\ell \right) = \sum_k \sum_\ell \left(\sum_i^{occ} 2 c_{ik}^* c_{i\ell} \right) \chi_k^* \chi_\ell$$

Number of Electrons

$$N = \sum_k \sum_\ell \left(\sum_i^{occ} 2 c_{ik}^* c_{i\ell} \right) S_{k\ell} = \sum_k \sum_\ell D_{k\ell} S_{k\ell}$$

D : Density Matrix
S : Overlap Matrix

Mulliken Population Analysis

Partitioning of the Electrons between atoms A and B.

$$N = \sum_{k}^{A}\sum_{\ell}^{A}D_{k\ell}S_{k\ell} + \sum_{k}^{B}\sum_{\ell}^{B}D_{k\ell}S_{k\ell} + \sum_{k}^{A}\sum_{\ell}^{B}D_{k\ell}S_{k\ell} + \sum_{k}^{B}\sum_{\ell}^{A}D_{k\ell}S_{k\ell}$$

Gross Populations on Atoms A and B

$$P_A = \sum_{k}^{A}\sum_{\ell}^{A}D_{k\ell}S_{k\ell} + \sum_{k}^{A}\sum_{\ell}^{B}D_{k\ell}S_{k\ell}$$

$$P_B = \sum_{k}^{B}\sum_{\ell}^{B}D_{k\ell}S_{k\ell} + \sum_{k}^{B}\sum_{\ell}^{A}D_{k\ell}S_{k\ell}$$

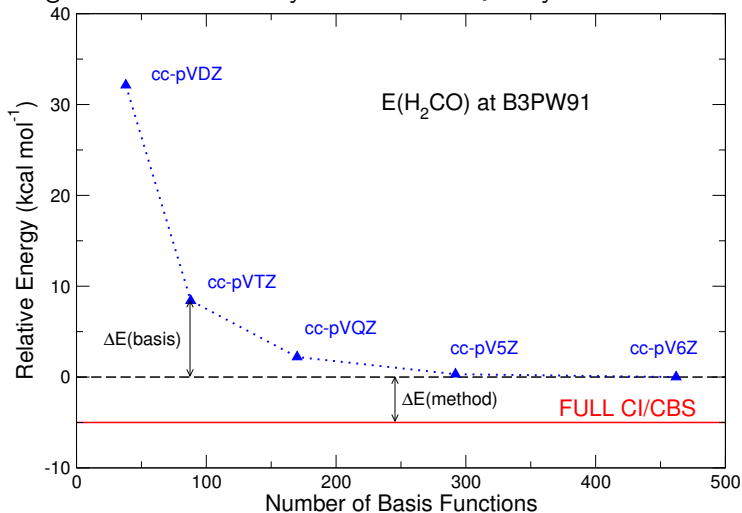Charges on Atoms A and B

$$Q_A = Z_A - P_A$$
$$Q_B = Z_B - P_B$$
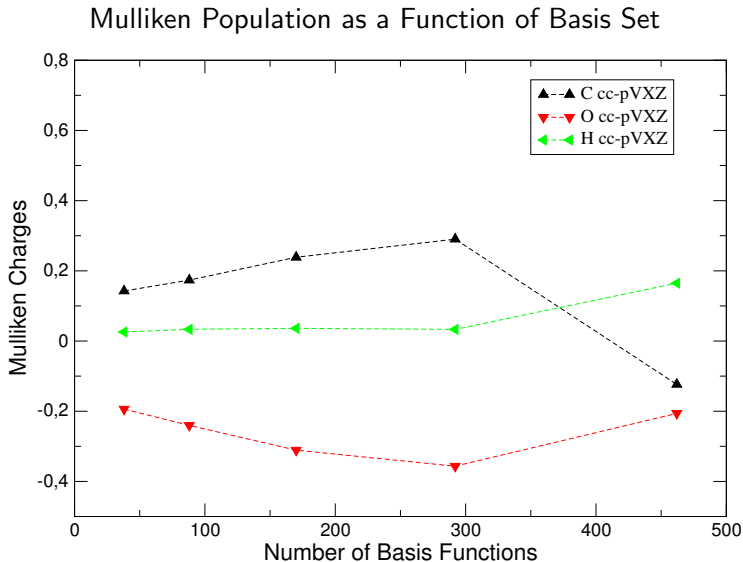
Errors in Calculations

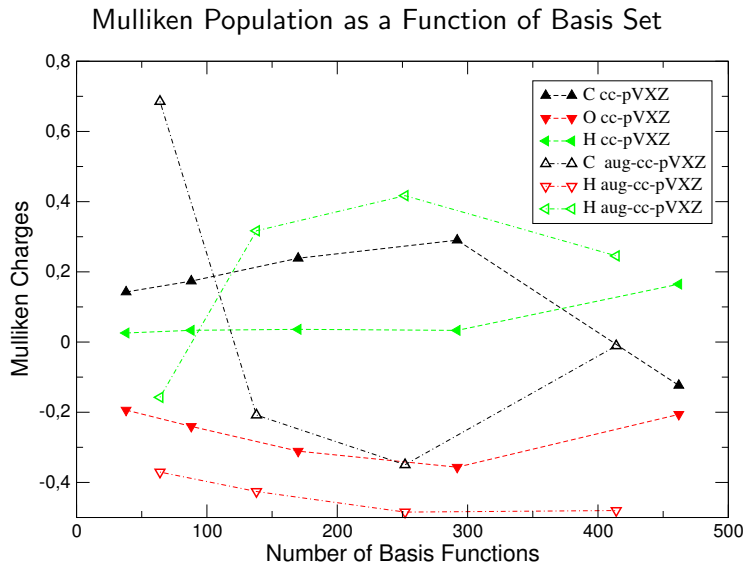Large Basis Sets Usually Increase the Quality of the Results.

Two Potential Sources of Errors

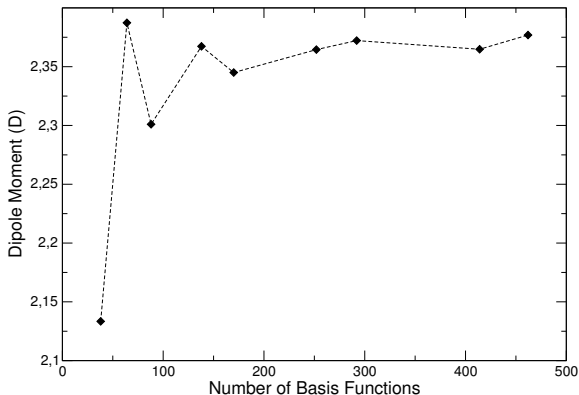Thom. H. Dunning Jr., *J. Phys. Chem. A.* **2000**, *104*, 9062

Mulliken Population as a Function of Basis Set

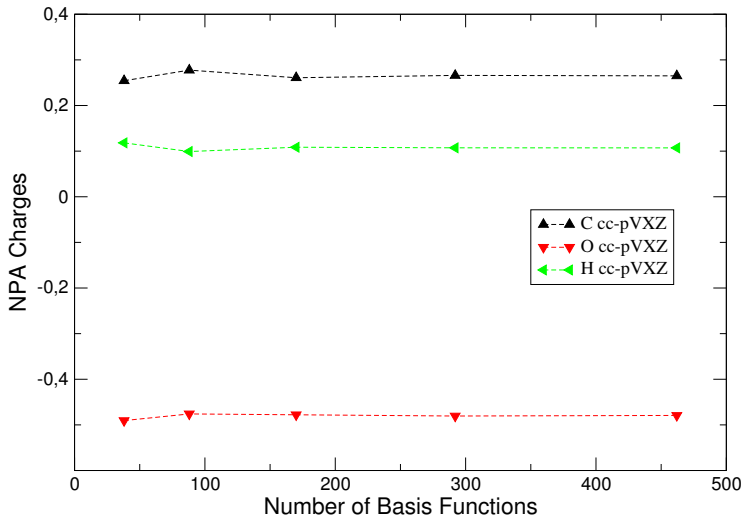Mulliken Population as a Function of Basis Set

Influence on Dipole Moment ?

Does the Lack of Accuracy in the Charges Affect the Value of the Dipole Moment ?

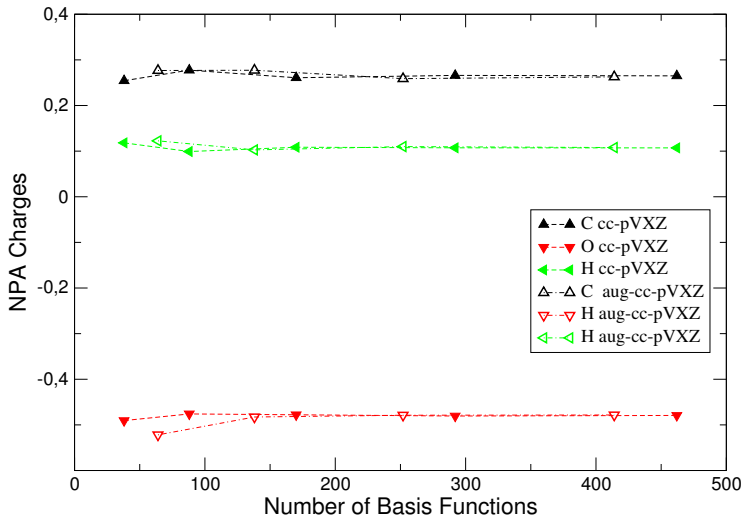$$\mu_e = \langle \Psi | - e\vec{r} | \Psi \rangle$$

NPA Charges as a Function of Basis Set

NPA Charges as a Function of Basis Set

Use Information in Wavefunction to Build a Lewis Structure

- Electronic Configuration for the Atoms in the Molecule :

  Natural Atomic Orbitals (NAO)

- Mixing of Natural Atomic Orbitals to Build Hybrids :

  Natural Hybrid Orbitals (NHO)

- Covalent Bond as Overlap between Hybrids :
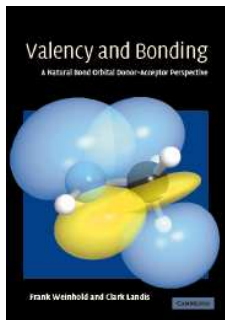
  Natural Bond Orbitals (NBO)

- Departure From Stricktly Localized Lewis Structure :

  Natural Localized Molecular Orbitals (NLMO)

NBO Web Site : **http://www.chem.wisc.edu/~nbo5/**

Valency and Bonding

A Natural Bond Orbital Donor-Acceptor Perspective

Frank Weinhold
University of Wisconsin, Madison
Clark R. Landis
University of Wisconsin, Madison

Density Matrix and MO

Molecular Orbitals Afford Compact Expression for Density Matrix

$$\rho = \sum_i^{occ} 2\psi_i^* \psi_i$$

Density Matrix H$_2$CO HF/STO-3G

MO	1	2	3	4	5	6	7	8	9	10	11	12
1	2	0	0	0	0	0	0	0	0	0	0	0
2	0	2	0	0	0	0	0	0	0	0	0	0
3	0	0	2	0	0	0	0	0	0	0	0	0
4	0	0	0	2	0	0	0	0	0	0	0	0
5	0	0	0	0	2	0	0	0	0	0	0	0
6	0	0	0	0	0	2	0	0	0	0	0	0
7	0	0	0	0	0	0	2	0	0	0	0	0
8	0	0	0	0	0	0	0	0	0	0	0	0
9	0	0	0	0	0	0	0	0	0	0	0	0
10	0	0	0	0	0	0	0	0	0	0	0	0
11	0	0	0	0	0	0	0	0	0	0	0	0
12	0	0	0	0	0	0	0	0	0	0	0	0

MO are Natural Orbitals for the HF Density Matrix

Density Matrix and AO

Density Matrix Easily Expressed with AO :

$$D_{k\ell} = \sum_{i}^{occ} 2 c_{ik}^* c_{i\ell}$$

AO	C(s)	C(s)	C(px)	C(py)	C(pz)	O(s)	O(s)	O(px)
C(s)	1.9996	0.5050	0.0000	0.0000	0.0011	0.0001	0.0704	0.0000
C(s)	0.5050	1.8233	0.0000	0.0000	-0.0593	0.0696	0.7516	0.0000
C(px)	0.0000	0.0000	1.1259	0.0000	0.0000	0.0000	0.0000	1.2052
C(py)	0.0000	0.0000	0.0000	1.6349	0.0000	0.0000	0.0000	0.0000
C(pz)	0.0011	-0.0593	0.0000	0.0000	1.5834	0.1166	0.9404	0.0000
O(s)	0.0001	0.0696	0.0000	0.0000	0.1166	1.9999	0.4746	0.0000
O(s)	0.0704	0.7516	0.0000	0.0000	0.9404	0.4746	1.9890	0.0000
O(px)	0.0000	0.0000	1.2052	0.0000	0.0000	0.0000	0.0000	1.2900
O(py)	0.0000	0.0000	0.0000	0.5363	0.0000	0.0000	0.0000	0.0000
O(pz)	-0.1137	-0.7984	0.0000	0.0000	-0.8885	-0.0056	0.0522	0.0000
H1(s)	0.1137	1.1140	0.0000	1.0160	-0.6462	0.0095	0.1413	0.0000
H2(s)	0.1137	1.1140	0.0000	-1.0160	-0.6462	0.0095	0.1413	0.0000

AO	O(py)	O(pz)	H1(s)	H2(s)
C(s)	0.0000	-0.1137	0.1137	0.1137
C(s)	0.0000	-0.7984	1.1140	1.1140
C(px)	0.0000	0.0000	0.0000	0.0000
C(py)	0.5363	0.0000	1.0160	-1.0160
C(pz)	0.0000	-0.8885	-0.6462	-0.6462
O(s)	0.0000	-0.0056	0.0095	0.0095
O(s)	0.0000	0.0522	0.1413	0.1413
O(px)	0.0000	0.0000	0.0000	0.0000
O(py)	1.9613	0.0000	-0.0053	0.0053
O(pz)	0.0000	1.7492	-0.1121	-0.1121
H1(s)	-0.0053	-0.1121	1.6320	0.2407
H2(s)	0.0053	-0.1121	0.2407	1.6320

Why Switching to an Apparently More Complicated Description ?

Obtaining Natural Atomic Orbital

Natural Orbitals are Eigenvectors of the First Order Density Matrix with Associated Occupation Numbers (Lowdin).

HF/STO-3G Density Matrix for s Subshell

AO	C(s)	C(s)	O(s)	O(s)	H1(s)	H2(s)
C(s)	1.9996	0.5050	0.0001	0.0704	0.1137	0.1137
C(s)	0.5050	1.8233	0.0696	0.7516	1.1140	1.1140
O(s)	0.0001	0.0696	1.9999	0.4746	0.0095	0.0095
O(s)	0.0704	0.7516	0.4746	1.9890	0.1413	0.1413
H1(s)	0.1137	1.1140	0.0095	0.1413	1.6320	0.2407
H2(s)	0.1137	1.1140	0.0095	0.1413	0.2407	1.6320

Natural Orbitals for Atomic Sub-Blocks: PNAO

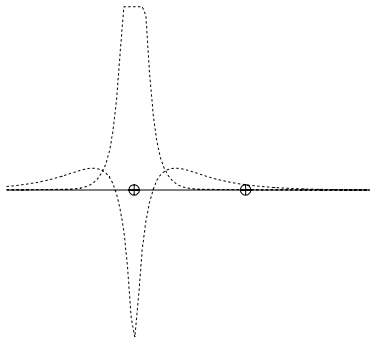| PNAO	C(s)	C(s)	O(s)	O(s)	H1(s)	H2(s)
C(s)	2.0000	0.0000	0.0140	0.1054	0.1635	0.1635
C(s)	0.0000	1.8069	0.1472	0.7476	1.1147	1.1147
O(s)	0.0140	0.1472	2.0000	0.0000	0.0238	0.0238
O(s)	0.1054	0.7476	0.0000	1.9876	0.1415	0.1415
H1(s)	0.1635	1.1147	0.0238	0.1415	1.6320	0.2407
H2(s)	0.1635	1.1147	0.0238	0.1415	0.2407	1.6320

PNAO Use Information to Build Free Atom-Like Orbitals

PNAO Introduce Orthogonality between AO on Each Atom

STO-3G Basis   **PNAO**

AO s on CarbonAO s on Oxygen
Overlap between PNAO on O and C

No Inter-Orthogonality Between Atoms

Shape of the PNAO

PNAO Introduce Orthogonality between AO on Each Atom
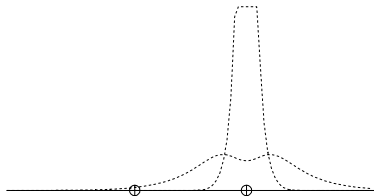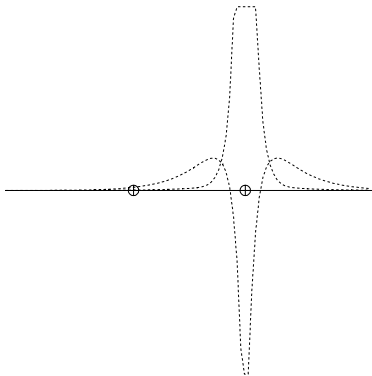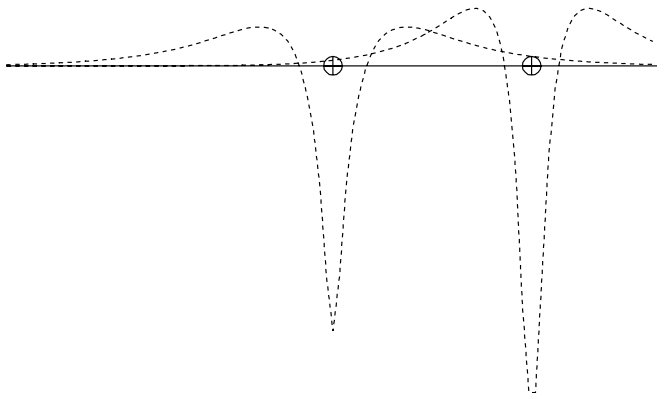
STO-3G Basis   **PNAO**

AO s on CarbonAO s on Oxygen
Overlap between PNAO on O and C

PNAO Introduce Orthogonality between AO on Each Atom

STO-3G Basis   **PNAO**

AO s on CarbonAO s on Oxygen
Overlap between PNAO on O and C

Natural **A**tomic **O**rbitals are Obtained by
Occupancy Weighted Symmetric Orthogonalization.

NAO	C(s)	C(s)	O(s)	O(s)	H1(s)	H2(s)
C(s)	2.0000	0.0000	0.0000	0.0005	-0.0006	-0.0006
C(s)	0.0000	1.0846	-0.0025	0.2565	0.5715	0.5715
O(s)	0.0000	-0.0025	2.0000	0.0000	0.0024	0.0024
O(s)	0.0005	0.2565	0.0000	1.7998	-0.0009	-0.0009
H1(s)	-0.0006	0.5715	0.0024	-0.0009	0.9898	-0.0986
H2(s)	-0.0006	0.5715	0.0024	-0.0009	-0.986	0.9898

Occupation Numbers

Carbon   Oxygen   Hydrogen

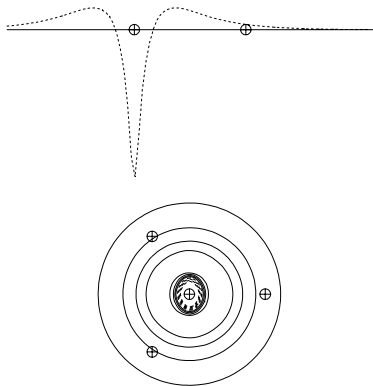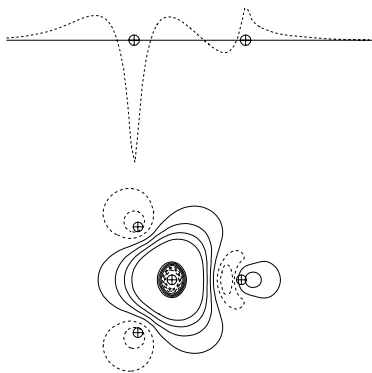$(1s)^2 (2s)^{1.0846}$ $(1s)^2 (2s)^{1.7998}$ $(1s)^{0.9898}$

Shape of NAO

The NAO have Orthogonalization Tails Because the Atom is not Free but in a Molecule.

PNAO 2s on Carbon

NAO 2s on Carbon

Procedure for Each ℓ Subshell Yields NAO

```
NATURAL POPULATIONS:  Natural atomic orbital occupancies
 NAO Atom No lang   Type(AO)    Occupancy      Energy
-----------------------------------------------------------
   1    C  1  s     Cor( 1s)     2.00000     -11.05961
   2    C  1  s     Val( 2s)     1.08465      -0.26151
   3    C  1  px    Val( 2p)     0.90133      -0.04488
   4    C  1  py    Val( 2p)     0.99303       0.07028
   5    C  1  pz    Val( 2p)     0.85395       0.14722

   6    O  2  s     Cor( 1s)     1.99999     -20.15600
   7    O  2  s     Val( 2s)     1.79984      -1.09032
   8    O  2  px    Val( 2p)     1.09867      -0.11643
   9    O  2  py    Val( 2p)     1.91859      -0.38125
  10    O  2  pz    Val( 2p)     1.37031      -0.15386

  11    H  3  s     Val( 1s)     0.98982       0.02246
  12    H  4  s     Val( 1s)     0.98982       0.02246
```

Effective Electron Configuration

The NPA Procedure Allows to Find the Linear Combinations of the Basis Set Functions that are Adapted to Describe the Core and Valence Electrons within a **Molecular Environment**.

- Atom: Core Valence Rydberg
- C: $(1s)^2$ $(2s)^2$ $(2p)^2$ $(3s)^0$ $(3p)^0$ $(3d)^0$
- O: $(1s)^2$ $(2s)^2$ $(2p)^4$ $(3s)^0$ $(3p)^0$ $(3d)^0$
- H: $(1s)^1$ $(2s)^0$ $(2p)^0$

Core + Valence = Minimal Basis Set

Natural Electron Configuration

```
Summary of Natural Population Analysis:

                                      Natural Population
                   Natural       ----------------------------------------------
  Atom No          Charge         Core       Valence     Rydberg      Total
----------------------------------------------------------------------------
   C  1           0.16705        2.00000     3.83295     0.00000      5.83295
   O  2          -0.18741        1.99999     6.18742     0.00000      8.18741
   H  3           0.01018        0.00000     0.98982     0.00000      0.98982
   H  4           0.01018        0.00000     0.98982     0.00000      0.98982
============================================================================
* Total *         0.00000        3.99999    12.00001     0.00000     16.00000

   Natural Population
--------------------------------------------------------
  Core                        3.99999 ( 99.9997% of   4)
  Valence                    12.00001 (100.0001% of  12)
  Natural Minimal Basis      16.00000 (100.0000% of  16)
  Natural Rydberg Basis       0.00000 (  0.0000% of  16)
--------------------------------------------------------

   Atom No          Natural Electron Configuration
----------------------------------------------------------------------------
   C  1          [core]2s( 1.08)2p( 2.75)
   O  2          [core]2s( 1.80)2p( 4.39)
   H  3                 1s( 0.99)
   H  4                 1s( 0.99)
```

Natural Charge : No Arbitrary Partioning

H₂CO B3PW91/6-31G**

Maximum of Density in Linear Combination of Basis Functions Most Adapted to Represent the Core and Valence Electrons : **Highly Transferable**

```
Summary of Natural Population Analysis:

                                    Natural Population
                    Natural    ---------------------------------------------
  Atom No           Charge      Core      Valence    Rydberg     Total
-----------------------------------------------------------------------
   C  1             0.21141    1.99960    3.76022    0.02876     5.78859
   O  2            -0.49216    1.99974    6.47229    0.02013     8.49216
   H  3             0.14038    0.00000    0.85538    0.00424     0.85962
   H  4             0.14038    0.00000    0.85538    0.00424     0.85962
=======================================================================
 * Total *         0.00000    3.99934   11.94328    0.05738    16.00000

                                 Natural Population
---------------------------------------------------------------
  Core                     3.99934 ( 99.9835% of    4)
  Valence                 11.94328 ( 99.5273% of   12)
  Natural Minimal Basis   15.94262 ( 99.6414% of   16)
  Natural Rydberg Basis    0.05738 (  0.3586% of   16)
---------------------------------------------------------------
```

Lewis Structure are Build with Valence Electrons

Constructing Natural Bond Orbitals

Off-Diagonal Elements of the Density Matrix in the NAO Basis Set Describe the Magnitude of the **Interaction** between NAOs Centered on **Different Atoms**.

```
      NAO        1       2       3       4       5
   ---------- ------- ------- ------- ------- -------
 1.  C 1( 1s )  2.0000  0.0000  0.0000  0.0000 -0.0013
 2.  C 1( 2s )  0.0000  1.0846  0.0000  0.0000 -0.1091
 3.  C 1( 2px)  0.0000  0.0000  0.9013  0.0000  0.0000
 4.  C 1( 2py)  0.0000  0.0000  0.0000  0.9930  0.0000
 5.  C 1( 2pz) -0.0013 -0.1091  0.0000  0.0000  0.8540
 6.  O 2( 1s )  0.0000 -0.0025  0.0000  0.0000  0.0017
 7.  O 2( 2s )  0.0005  0.2565  0.0000  0.0000  0.4119
 8.  O 2( 2px)  0.0000  0.0000  0.9951  0.0000  0.0000
 9.  O 2( 2py)  0.0000  0.0000  0.0000  0.2863  0.0000
10.  O 2( 2pz) -0.0007 -0.5117  0.0000  0.0000 -0.6850
11.  H 3( 1s ) -0.0006  0.5715  0.0000  0.6775 -0.4049
12.  H 4( 1s ) -0.0006  0.5715  0.0000 -0.6775 -0.4049
```

Coupling

{C(2s),C(2pz)}	{O(2s),O(2pz)}
	H(1s)
C(2px)	O(2px)
C(2py)	O(2py)
	H(1s)

Mixing NAOs: Hybrid Orbitals!

$$h_C = 0.5862s + 0.8101pz \text{ and } h_O = 0.4902s - 0.8716pz$$

How Are the Coefficients Determined ?

Lewis Structure

Driving Force : Cancellation of Off-Diagonal Terms
Consequences : Localization of Electron Pairs in Bonding
Orbitals (**BD**) or Lone Pairs (**LP**)

$$\sigma_{CO} = 0.6436 h_C + 0.7653 h_O$$
$$\pi_{CO} = 0.6714 px_C + 0.7412 px_O$$
$$\sigma_{CH} = 0.7180 h'_C + 0.6959 s_H$$
$$LP_O = 0.8716 s_O + 0.4902 pz_O$$
$$LP_O = py_O$$
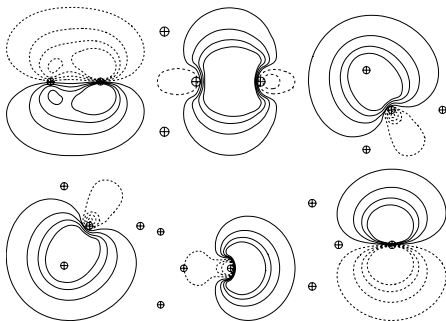
How Accurate is This Representation ?

Determining the NBO

The **NBO Procedure** Determines the **Connections** between Atoms that Maximize the Number of **Localized Orbitals** (BD or LP) with **Occupancy** as Close to **2** as Possible.

```
NATURAL BOND ORBITAL ANALYSIS:
                      Occupancies       Lewis Structure    Low   High
              Occ.    -------------------  ----------------  occ   occ
   Cycle   Thresh.  Lewis   Non-Lewis    CR  BD  3C  LP    (L)   (NL)   Dev
   ============================================================================
   1(1)     1.90   15.36324  0.63676      2   5   0   1     2     1     0.06
   2(2)     1.90   15.36324  0.63676      2   5   0   1     2     1     0.06
   3(1)     1.80   15.86241  0.13759      2   4   0   2     0     0     0.06
   ----------------------------------------------------------------------------

Structure accepted: No low occupancy Lewis orbitals

   --------------------------------------------------------
   Core                   3.99934 ( 99.984% of   4)
   Valence Lewis         11.86307 ( 98.859% of  12)
   ==================    ============================
   Total Lewis           15.86241 ( 99.140% of  16)
   --------------------------------------------------------
   Valence non-Lewis      0.11332 (  0.708% of  16)
   Rydberg non-Lewis      0.02426 (  0.152% of  16)
   ==================    ============================
   Total non-Lewis        0.13759 (  0.860% of  16)
   --------------------------------------------------------
```

B3PW91/6-31G**

Expression of the NBO

```
   (Occupancy)   Bond orbital/ Coefficients/ Hybrids
-------------------------------------------------------------------------------
 1. (1.99989) BD ( 1) C  1- O  2
            ( 35.49%)   0.5958* C  1 s(  0.00%)p 1.00( 99.77%)d 0.00(  0.23%)
                                       0.0000  0.0000  0.0000  0.9981 -0.0387
                                       0.0000  0.0000  0.0000  0.0000  0.0000
                                       0.0480  0.0000  0.0000  0.0000
            ( 64.51%)   0.8032* O  2 s(  0.00%)p 1.00( 99.69%)d 0.00(  0.31%)
                                       0.0000  0.0000  0.0000  0.9984 -0.0104
                                       0.0000  0.0000  0.0000  0.0000  0.0000
                                      -0.0555  0.0000  0.0000  0.0000
 2. (1.99980) BD ( 2) C  1- O  2
            ( 33.74%)   0.5808* C  1 s( 32.17%)p 2.10( 67.60%)d 0.01(  0.23%)
                                       0.0001  0.5622  0.0755  0.0000  0.0000
                                       0.0000  0.0000  0.8169  0.0931  0.0000
                                       0.0000  0.0000  0.0045  0.0477
            ( 66.26%)   0.8140* O  2 s( 41.03%)p 1.43( 58.58%)d 0.01(  0.39%)
                                       0.0000  0.6400  0.0272  0.0000  0.0000
                                       0.0000  0.0000 -0.7653  0.0131  0.0000
                                       0.0000  0.0000  0.0033  0.0620
 3. (1.99515) BD ( 1) C  1- H  3
            ( 58.78%)   0.7667* C  1 s( 34.03%)p 1.94( 65.88%)d 0.00(  0.10%)
                                       0.0001  0.5830 -0.0203  0.0000  0.0000
                                       0.7065 -0.0120 -0.3993  0.0031  0.0000
                                       0.0000 -0.0256 -0.0172 -0.0051
            ( 41.22%)   0.6420* H  3 s( 99.94%)p 0.00(  0.06%)
                                       0.9996  0.0132  0.0000 -0.0207  0.0112
```

Hybridation Follows Bent's Rule

atomic s character tends to concentrate in orbitals that are directed
toward electropositive groups

Description of Lone Pairs

When No Covalent Interaction between Atoms can be Found, Lone Pairs are Created to Accomodate Electron Density on a Single Atoms.

```
7. (1.98872) LP ( 1) O  2          s( 59.01%)p 0.69( 40.93%)d 0.00(  0.06%)
                                  -0.0004  0.7680 -0.0151  0.0000  0.0000
                                   0.0000  0.0000  0.6398 -0.0003  0.0000
                                   0.0000  0.0000  0.0030 -0.0248
8. (1.88435) LP ( 2) O  2          s(  0.00%)p 1.00( 99.81%)d 0.00(  0.19%)
                                   0.0000  0.0000  0.0000  0.0000  0.0000
                                   0.9990  0.0144  0.0000  0.0000  0.0000
                                   0.0000 -0.0431  0.0000  0.0000
```
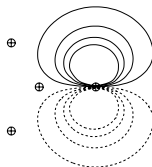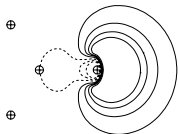

Lone Pairs Do Not Follow VSEPR

Description of AntiBond

The Overlap between two Hybrids to Create a Bonding Orbital Automatically Generates an Antibonding Orbital.

σ^*_{CO}

$$\sigma^* = 0.8140 h_C - 0.5808 h_O$$

$$\sigma = 0.5808 h_C + 0.8140 h_O$$

σ_{CO}
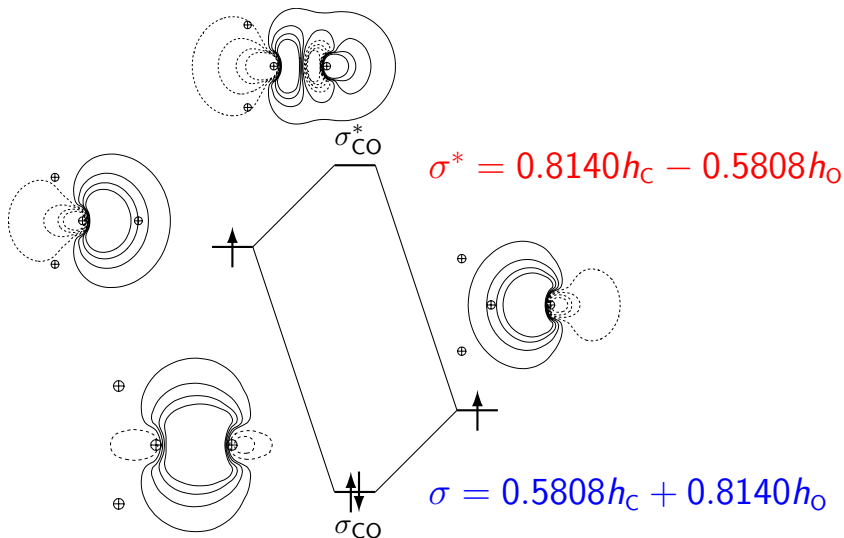
Hyperconjugation Interactions

The Empty AntiBonds can Accept Electron Density from the Occupied Bonds : **Departure from Lewis Structure**
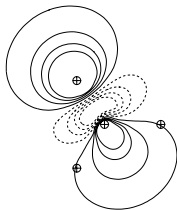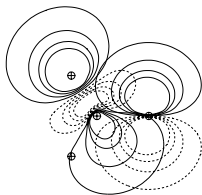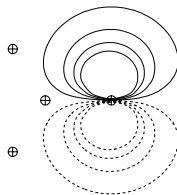
σ^*_{CH}　　　　Overlap : 0.2126　　　　LP_O

Resonance Forms :
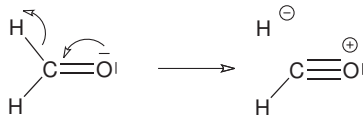
How Stabilizing is this Resonance ?

Donor-Acceptor Interactions

The Departure from the Lewis Structure is Due to Donor-Acceptor Electron Transfers between Occupied and Vacant NBOs.
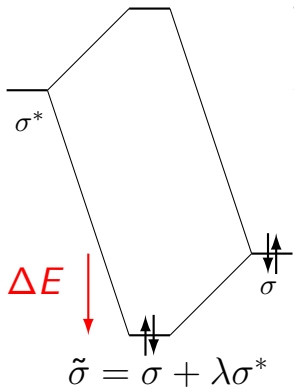
2$^{\text{nd}}$ Order Perturbation Theory

$$\Delta E = -2 \frac{\langle \sigma | \, \mathcal{F} \, | \sigma^* \rangle^2}{\varepsilon_{\sigma^*} - \varepsilon_{\sigma}}$$

$LP_0 \longrightarrow \sigma^*_{\text{CH}} = 20.1 \text{ kcal mol}^{-1}$

The Perturbed NBO Gives Access to **N**atural **L**ocalized **M**olecular **O**rbitals which Are Occupied stricktly by 2 Electrons

$\tilde{LP}_0 = 0.9706 LP_0 + 0.1631 \sigma^*_{\text{CH}} - 0.1631 \sigma'^*_{\text{CH}}$

σ^*

ΔE

σ

$\tilde{\sigma} = \sigma + \lambda \sigma^*$

MO **NLMO**
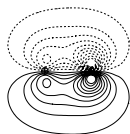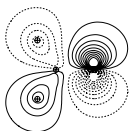
-11 eV -7.3 eV -11 eV -8.7
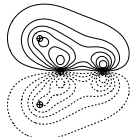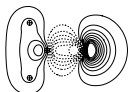
-13.5 eV -12.3 eV -15.5 eV -15.5
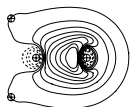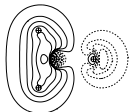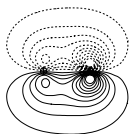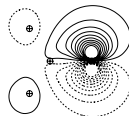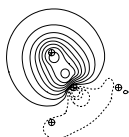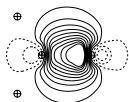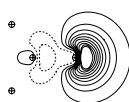
-29.0 eV -17.4 eV -29.7 eV -19.8

NBO Procedure: Summary

MO

AO
A   B

PNAO
A   B

INTRA-ATOMIC DIAGONALIZATION
WITHIN EACH SUBSHELL

OCCUPANCY WEIGHTED
ORTHOGONALIZATION

CR BP/LP BD* RY

CR   VAL   RY

**NATURAL
CHARGES**

NLMO

NBO

NAO

2ND ORDER PERTURBATION
DONOR-ACCEPTOR
INTERACTIONS TO CANCEL
OFF-DIAGONAL RED TERMS
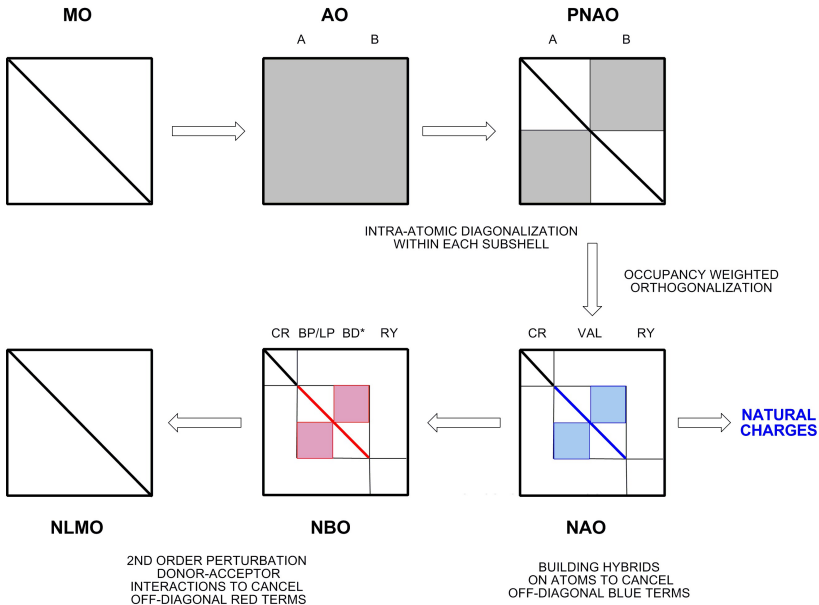
BUILDING HYBRIDS
ON ATOMS TO CANCEL
OFF-DIAGONAL BLUE TERMS
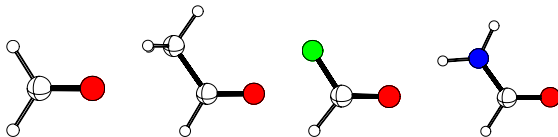
Natural Charges

C	0.211	0.403	0.727	0.497
O	-0.492	-0.520	-0.526	-0.604
H	0.140	0.145	0.150	0.144
X	0.140	-0.028	-0.351	-0.037

Natural Electron Configuration

C	$s^{1.05}p^{2.71}$	$s^{0.94}p^{2.62}$	$s^{0.90}p^{2.33}$	$s^{0.87}p^{2.60}$
O	$s^{1.72}p^{4.76}$	$s^{1.72}p^{4.80}$	$s^{1.72}p^{4.79}$	$s^{1.71}p^{4.88}$

Is it Possible to Rationalize the Trends ?

Donor-Acceptor Interactions

The Magnitude of the Donor-Acceptor Interactions Depends on the Nature of the Substituent.

	$LP_O \longrightarrow \sigma^*_{CH}$	$LP_O \longrightarrow \sigma^*_{CX}$	$LP_X \longrightarrow \pi^*_{C0}$
X = H	20.1	20.1	
X = CH$_3$	21.6	19.6	5.0
X = F	17.9	45.1	33.8
X = NH$_2$	21.1	24.4	62.6

Inductive Effect -I

F > NH> > H > CH$_3$
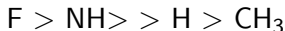
Mesomeric Effect +M

NH$_2$ > F > CH$_3$ > H

Resonance Forms

Within NBO it is Possible to Determine the Relative Weights of the Different Resonance Forms.
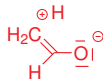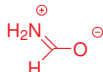
The Relative Weights of the Resonance Forms Allow to Explain the
Values of the Structural Parameters and some Properties

	C–O	C–H	∠ H-C-O	$\nu(CO)$
X = H	1.205	1.110	122.4	1862.8
X = CH_3	1.209	1.115	114.8	1857.9
X = F	1.185	1.098	127.5	1930.5
X = NH_2	1.215	1.109	112.0	1855.5

**NBO can also be Used to Analyze Chemical Shielding Tensor
and NMR Coupling Constants**

Bent Bonds in Cyclopropane

Expression of Natural Hybrid allows to Determine Orientation with Respect to Line Centers
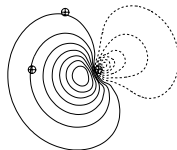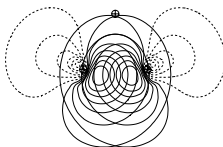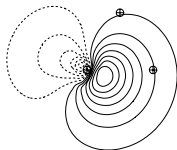
Angle : 23.4°
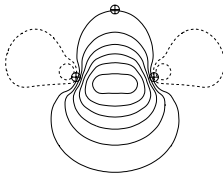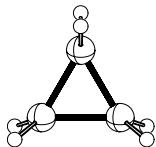
Deviation from Lineariy Relates to Strain

3 Centers 2 Electrons Bond

For B_2H_6 NBO Analysis Leaves 14.5% of the Density as Non-Lewis

Need to Consider Simultaneously Hybrids on 3 Atoms
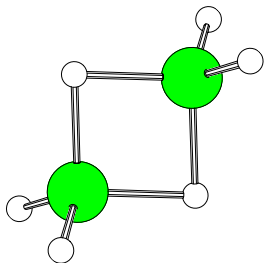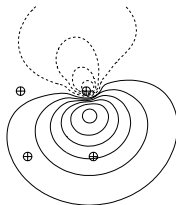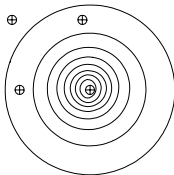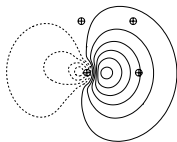
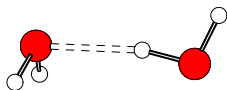

$$\tau = 0.53h_b + 0.65h_h + 0.53h_b'$$
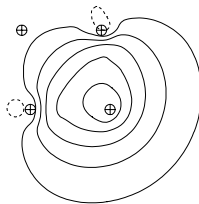
For Adducts between Molecules, NBO Offers an Interpretation of
the Interaction Energy

Water Dimer

$$LP_O \longrightarrow \sigma^*_{OH}$$

$$\Delta E_{pert} = 13.2 \text{ kcal mol}^{-1}$$

$$\Delta E = -7 \text{ kcal mol}^{-1}$$
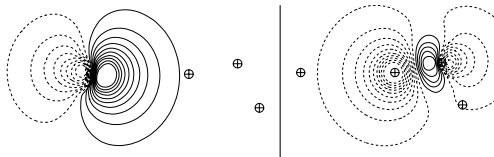
**Description of Hydrogen Bond as a Charge Transfer
Interaction**

What About Transition Metal Complexes ?

The Lewis **Octet** Rule Becomes a **Dodectet** Rule for Transition Metal Complexes.

$$|G_M - 6| + nV_L + e_u = 6$$

G_M : Group Number of the Metal
n : Stoichiometric ML_n Formula Ratio
V_L : Valency of the Ligand
e_u : Number of Unpaired Electron

	3	4	5	6	8	9	10
chlorides	$ScCl_3$	$TiCl_5$	$NbCl_5$	WCl_5	$RuCl_3$	$RhCl_3$	$PdCl_2$
oxides	Sc_2O_3	TiO_2	Nb_2O_5	WO_3	RuO_2	Rh_2O_3	PdO
alkyls		$ZrMe_4$	$NbMe_5$	WMe_6	$Ru(Mes)_4$	$Rh(Mes)_3$	

sd Hybridation

Geometry Dictated by Hybridation between s and d Orbitals

Two Geometries for OsH$_4$

	α_{accute}	α_{obtuse}
sd^2	90.0	90.0
sd^3	70.53	109.47
sd^4	65.91	114.09
sd^5	63.43	116.57
sd^{10}	58.91	121.09
d	54.74	125.26
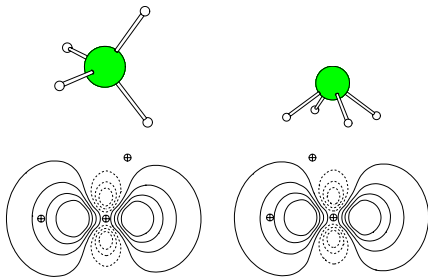
$\Delta E = 1.7$ kcal mol^{-1}

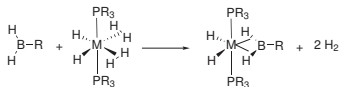**Angle Lower than 90° !**

For Trans Ligand : 3 centers 4 electrons Bond !

Boranes are Important Reagents in H_2 Storage and Catalysis

What are the Factors Leading to Stable Adducts ?
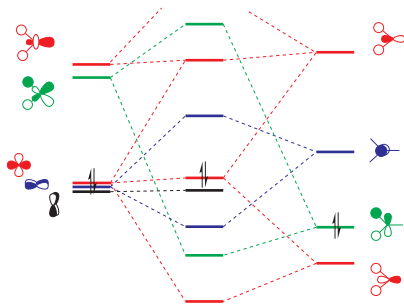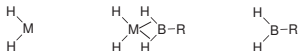
Competition Between
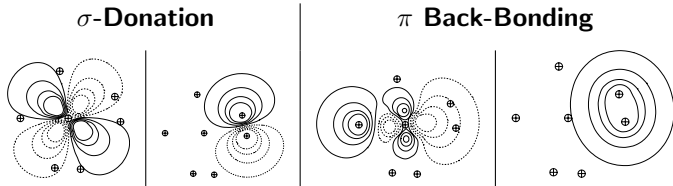Coordination of 2 σ(H–H)
and 2 σ(B–H) Bonds.

	Me	Ph	NMe$_2$
Ru	-5.8	-4.0	7.9
Rh$^+$	-8.4	-10.3	-6.2
Ir$^+$	-10.2	-11.2	-5.3

**Vacant Orbital on Boron
Crucial for Back-Bonding**

Coordination of H–H

The Coordination of H_2 is Described as Resulting from a Balance between σ-Donation and π Back-Bonding.
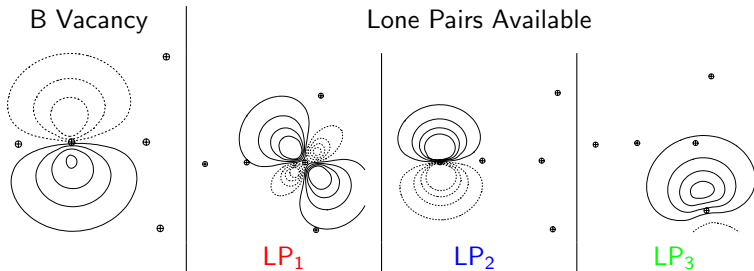
| | σ-**Donation** | | | π **Back-Bonding** | |

	$\sigma(H_2) \to \sigma^*(MH)$	occ.	$LP(M) \to \sigma^*(H_2)$	occ
M = Ru	150	1.717	24	0.117
M = Rh$^+$	92	1.794	11	0.054
M = Ir$^+$	205	1.733	19	0.082

Back-Donation to H_2 From Same d Orbital on M

Coordination of H_2BNMe_2

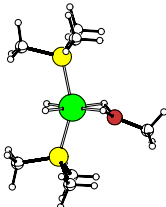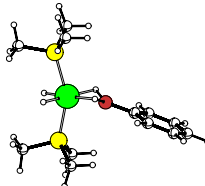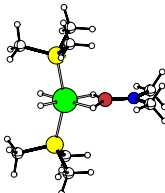The π-Acidity at Boron offers an Alternative for π Back-Bonding.

B Vacancy

Lone Pairs Available

LP_1 LP_2 LP_3

	$\sigma(BH) \to \sigma^*(MH)$	occ	$LP(M) \to \sigma^*(BH)$	occ	$LP \to LP^*(B)$	occ
M = Ru	140	1.757	21	0.046	10/81/17	0.518
M = Rh$^+$	82	1.827	2	0.017	12/108/11	0.494
M = Ir$^+$	247	1.766	4	0.034	/107/	0.528

Cationic Fragments are More Electrophilic

Consequences on Geometry

The Competition Between the Charge Transfer Dictates the Final
Structure.

	H_2BMe	H_2BPh	H_2BNMe_2
Ru–B	1.933	1.942	1.969
Rh–B	2.032	2.061	2.118
Ir–B	1.990	2.011	2.056