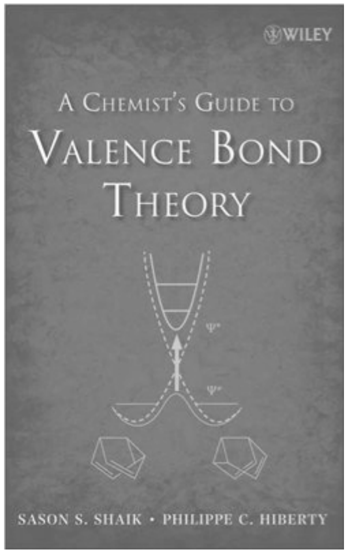
Densities, NBOs, and Lewis Structures

Robustness of Lewis-like Concepts in the Computational Age

Clark R. Landis & Frank Weinhold

2012 Ab Initio VB
Paris



WILEY

A CHEMIST'S GUIDE TO

VALENCE BOND

THEORY

SASON S. SHAIK • PHILIPPE C. HIBERTY

Motivations

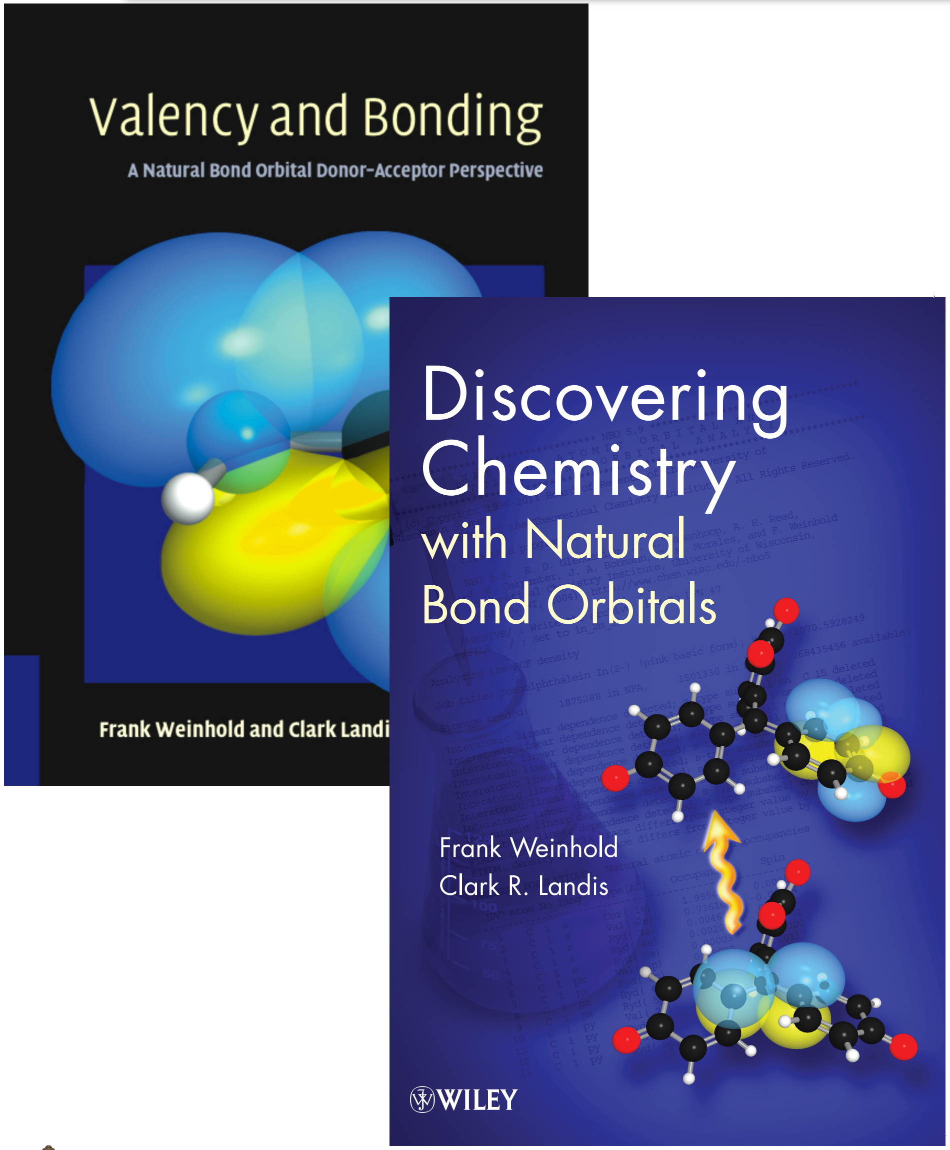
"The nature of the chemical bond is the problem at the heart of all chemistry" *Bryce Crawford, Jr. (1953)*

"The more accurate the computations become, the more the concepts tend to vanish into thin air" *R. S. Mulliken, J. Chem. Phys. 43, S2 (1965).*

"It is at least arguable that, from the point of view of quantum chemistry as usually practiced, the supercomputer has dissolved the bond" *B. T. Sutcliffe, Int. J. Quantum Chem. 58, 645 (1996)*

"It is nice to know that the computer understands the problem. But I would like to understand it too." *E. P. Wigner as quoted in E. J. Heller and S. Tomsovic, Physics Today (July 1993, p. 38)*

Discovering Chemistry with NBOs



NBO Translates Accurate Calculations into Chemical Insights

- Charges
- Lewis Structures
- Bond Types
- Hybrid Descriptors
- Bond Orders
- Charge Transfer
- Resonance Weights
- NMR Descriptors
- Steric Analysis
- (Natural) Energy Decomposition Analysis
- Bond Critical Points

A Common Scenario

How to describe the complex of an N-Heterocyclic carbene bonded to AuCl?

You run a quick Gaussian (or Jaguar, GAMESS, Orca, ADF, etc.) calculation with geometry optimization and quickly verify that the computation reproduces experiment. But what about the bonding?

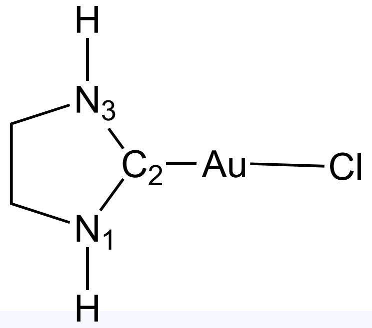
One approach is to analyze canonical molecular orbital (CMO) coefficients and Mulliken populations and perhaps visualize the orbital shapes.

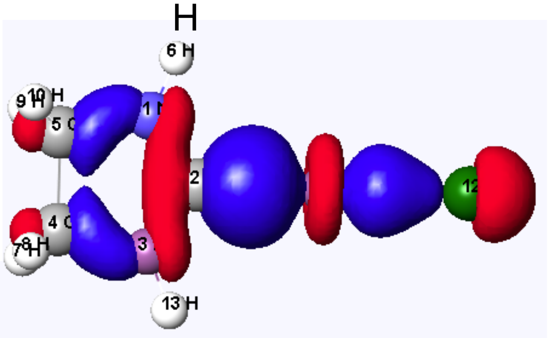
The NBO approach is to :

- create effective atomic orbitals for each atom in the molecular environment
- examine the bonding from a Lewis-like perspective
- quantify the primary donor-acceptor interactions using perturbation theory
- describe delocalizations through resonance configurations
- visualize interactions of localized lone pair, hybrid, bond, and antibond orbitals
- and so on…

(NHC)AuCl Canonical MOs

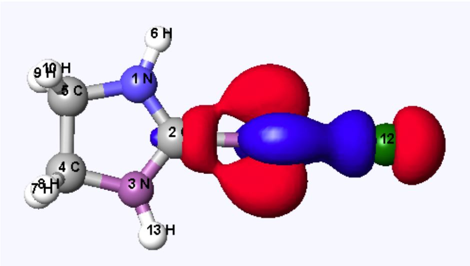
```
HOMO energy:     -0.23593
LUMO energy:     -0.04045

 Orbital energies:
-101.46464  -14.38676  -14.38656  -10.29210  -10.26306  -10.26286
  -9.37784   -7.13949   -7.13433   -7.13421   -4.16373   -2.31225
  -2.28786   -2.28672   -1.05212   -0.93173   -0.81437   -0.72825
  -0.68674   -0.68130   -0.58647   -0.54378   -0.52834   -0.49192
  -0.44770   -0.43812   -0.43567   -0.41755   -0.32862   -0.32549
  -0.29784   -0.29614   -0.29434   -0.28681   -0.26195   -0.23631
  -0.23593   -0.04045   -0.03908   -0.01938   -0.00909   -0.00481
   0.00183    0.01508    0.02385    0.02989    0.03162
```



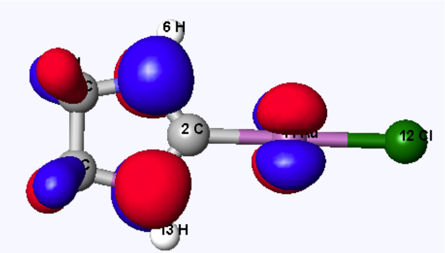


C-Au-Cl bond

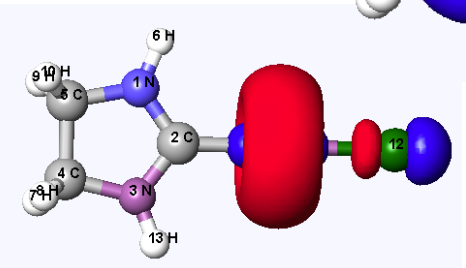
HOMO-10



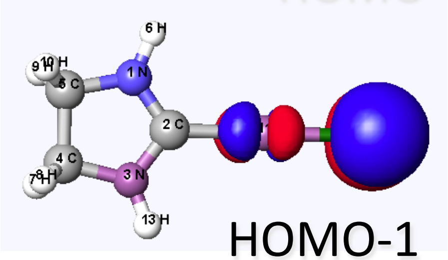
HOMO-4



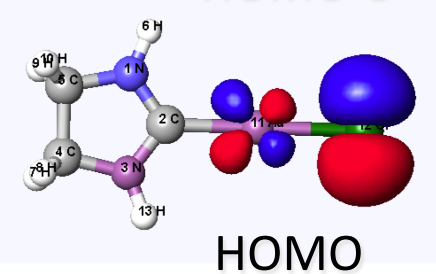
HOMO-3



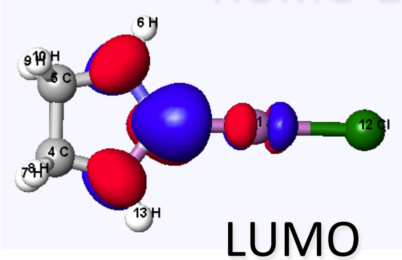
HOMO-2



HOMO-1



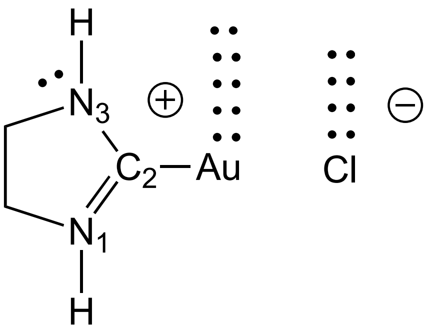
HOMO

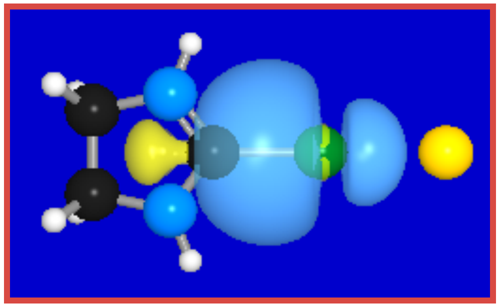


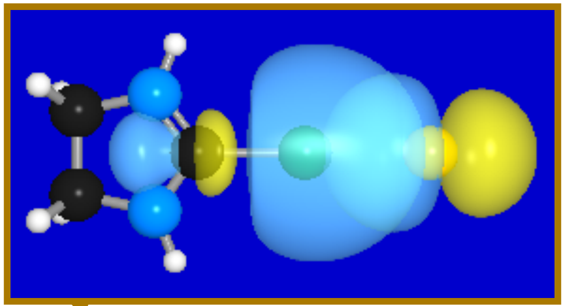
LUMO

(NHC)AuCl NBO Analysis

```
Summary of Natural Population Analysis:
                                        Natural Population
                Natural    ---------------------------------------------
   Atom No      Charge        Core      Valence    Rydberg      Total
 --------------------------------------------------------------------
     C  2      0.22582      1.99941     3.71769    0.05708      5.77418
     N  3     -0.60891      1.99940     5.59195    0.01756      7.60891
    Au 11      0.36956     67.99429    10.60876    0.02738     78.63044
    Cl 12     -0.63292      9.99994     7.62286    0.01012     17.63292

      Atom No          Natural Electron Configuration
 ----------------------------------------------------------------
      Au 11      [core]6s( 0.97)5d( 9.63)6p( 0.01)7p( 0.01)
      Cl 12      [core]3s( 1.96)3p( 5.67)3d( 0.01)

 (Occupancy)   Bond orbital/ Coefficients/ Hybrids
 -----------------------------------------------------------------
1. (1.99010) BD ( 1) N  1- C  2
               ( 63.32%)   0.7958* N  1 s( 38.53%)p 1.59( 61.35%)
               ( 36.68%)   0.6056* C  2 s( 31.59%)p 2.16( 68.29%)
2. (1.97386) BD ( 2) N  1- C  2
               ( 80.87%)   0.8993* N  1 s(  0.00%)p 1.00( 99.97%)
               ( 19.13%)   0.4374* C  2 s(  0.00%)p 1.00( 99.59%)
5. (1.99010) BD ( 1) C  2- N  3
               ( 36.67%)   0.6056* C  2 s( 31.59%)p 2.16( 68.29%)
               ( 63.33%)   0.7958* N  3 s( 38.54%)p 1.59( 61.35%)
6. (1.95643) BD ( 1) C  2-Au 11
               ( 75.03%)   0.8662* C  2 s( 37.14%)p 1.69( 62.85%)
               ( 24.97%)   0.4997*Au 11 s( 80.71%)d 0.24( 19.07%)

SECOND ORDER PERTURBATION THEORY ANALYSIS OF FOCK MATRIX IN NBO BASIS
                                                          E(2)  E(j)-E(i) F(i,j)
     Donor NBO (i)              Acceptor NBO (j)        kcal/mol   a.u.    a.u.
 ================================================================================
  37. LP ( 4)Cl12            221. BD*( 1) C 2-Au11       134.79     0.42    0.214
```







General NBO Procedure

- Find orbitals and electron configurations for *atoms* in molecules

  Natural Atomic Orbitals (NAOs) and Natural Population Analysis (NPA)

- Find Lewis structure, bonds and bond-forming orbitals

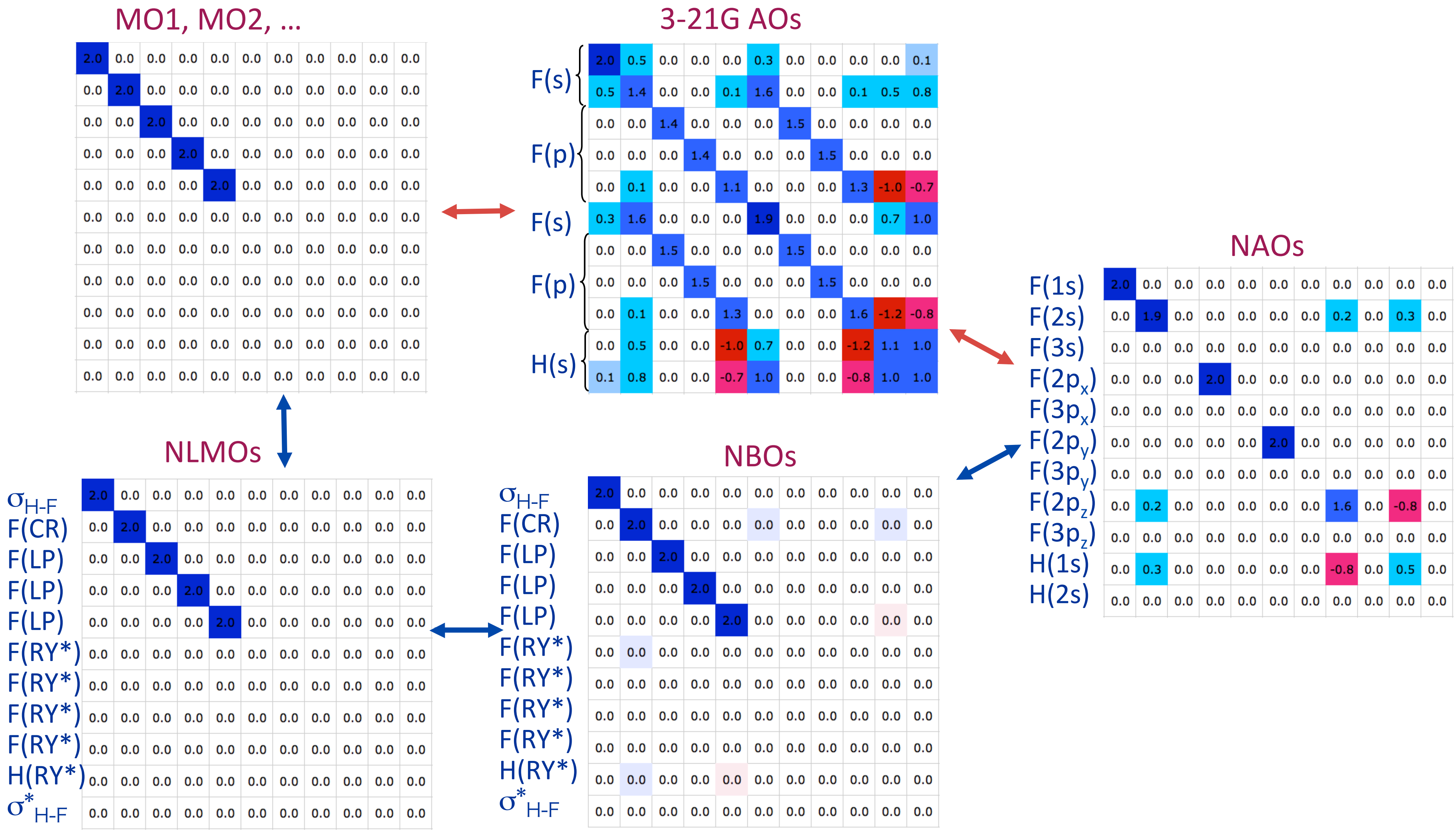
  Natural Bond Orbitals (NBOs) and Natural Hybrid Orbitals (NHOs) and Natural Lewis Structures

- Describe departures from idealized Lewis structures

  Natural Resonance Theory (NRT) and Natural Localized Molecular Orbitals (NLMOs)

Transformation Summary

Density Matrices of HF in different basis sets.



MO1, MO2, …

2.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
0.0	2.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
0.0	0.0	2.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
0.0	0.0	0.0	2.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
0.0	0.0	0.0	0.0	2.0	0.0	0.0	0.0	0.0	0.0	0.0
0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0

3-21G AOs

F(s)	2.0	0.5	0.0	0.0	0.0	0.3	0.0	0.0	0.0	0.0	0.1
	0.5	1.4	0.0	0.0	0.1	1.6	0.0	0.0	0.1	0.5	0.8
F(p)	0.0	0.0	1.4	0.0	0.0	0.0	1.5	0.0	0.0	0.0	0.0
	0.0	0.0	0.0	1.4	0.0	0.0	0.0	1.5	0.0	0.0	0.0
	0.0	0.1	0.0	0.0	1.1	0.0	0.0	0.0	1.3	-1.0	-0.7
F(s)	0.3	1.6	0.0	0.0	0.0	1.9	0.0	0.0	0.0	0.7	1.0
F(p)	0.0	0.0	1.5	0.0	0.0	0.0	1.5	0.0	0.0	0.0	0.0
	0.0	0.0	0.0	1.5	0.0	0.0	0.0	1.5	0.0	0.0	0.0
	0.0	0.1	0.0	0.0	1.3	0.0	0.0	0.0	1.6	-1.2	-0.8
H(s)	0.0	0.5	0.0	0.0	-1.0	0.7	0.0	0.0	-1.2	1.1	1.0
	0.1	0.8	0.0	0.0	-0.7	1.0	0.0	0.0	-0.8	1.0	1.0

NAOs

F(1s)	2.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
F(2s)	0.0	1.9	0.0	0.0	0.0	0.0	0.0	0.2	0.0	0.3	0.0
F(3s)	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
F($2p_x$)	0.0	0.0	0.0	2.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
F($3p_x$)	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
F($2p_y$)	0.0	0.0	0.0	0.0	0.0	2.0	0.0	0.0	0.0	0.0	0.0
F($3p_y$)	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
F($2p_z$)	0.0	0.2	0.0	0.0	0.0	0.0	0.0	1.6	0.0	-0.8	0.0
F($3p_z$)	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
H(1s)	0.0	0.3	0.0	0.0	0.0	0.0	0.0	-0.8	0.0	0.5	0.0
H(2s)	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0

NLMOs

$\sigma_{H\text{-}F}$	2.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
F(CR)	0.0	2.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
F(LP)	0.0	0.0	2.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
F(LP)	0.0	0.0	0.0	2.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
F(LP)	0.0	0.0	0.0	0.0	2.0	0.0	0.0	0.0	0.0	0.0	0.0
F(RY*)	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
F(RY*)	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
F(RY*)	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
F(RY*)	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
H(RY*)	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
$\sigma^*_{H\text{-}F}$	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0

NBOs

$\sigma_{H\text{-}F}$	2.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
F(CR)	0.0	2.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
F(LP)	0.0	0.0	2.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
F(LP)	0.0	0.0	0.0	2.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
F(LP)	0.0	0.0	0.0	0.0	2.0	0.0	0.0	0.0	0.0	0.0	0.0
F(RY*)	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
F(RY*)	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
F(RY*)	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
F(RY*)	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
H(RY*)	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
$\sigma^*_{H\text{-}F}$	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0

Natural Population Analysis: HF

```
Summary of Natural Population Analysis:

                                         Natural Population
            Natural    ---------------------------------------------
 Atom No    Charge          Core      Valence    Rydberg      Total
--------------------------------------------------------------------
   F  1    -0.54846      1.99995      7.54234    0.00617     9.54846
   H  2     0.54846      0.00000      0.44626    0.00528     0.45154
====================================================================
* Total *   0.00000      1.99995      7.98860    0.01145    10.00000

                                     Natural Population
--------------------------------------------------------
  Core                         1.99995 ( 99.9973% of   2)
  Valence                      7.98860 ( 99.8575% of   8)
  Natural Minimal Basis        9.98855 ( 99.8855% of  10)
  Natural Rydberg Basis        0.01145 (  0.1145% of  10)
--------------------------------------------------------

   Atom No          Natural Electron Configuration
-------------------------------------------------------------
     F  1      [core]2s( 1.91)2p( 5.63)
     H  2            1s( 0.45)
```

Contraction from 22 AO basis functions to 6 NAOs describes 99.89% of electron density (this number comes from the trace of the Cor and Val blocks of the density matrix in the NAO basis, divided by the total e count)

Natural Charges:
- weak dependence on basis set
- rigorous treatment of overlaps avoids many problems that plague other population analyses

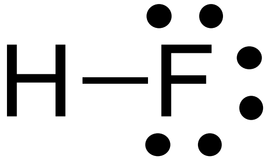
Natural Lewis Structures - HF

```
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    9.99523   0.00477       1   1   0   3     0      0    0.00
-----------------------------------------------------------------------------

 Structure accepted: No low occupancy Lewis orbitals

 --------------------------------------------------------
   Core                      1.99995 ( 99.997% of   2)
   Valence Lewis             7.99528 ( 99.941% of   8)
  ==================       ============================
   Total Lewis               9.99523 ( 99.952% of  10)
  -----------------------------------------------------
   Valence non-Lewis         0.00000 (  0.000% of  10)
   Rydberg non-Lewis         0.00477 (  0.048% of  10)
  ==================       ============================
   Total non-Lewis           0.00477 (  0.048% of  10)
 --------------------------------------------------------
```

Is HF well-described as a single bond with 3 lone pairs on F?

The NAO → NBO transformation locates 1 core (CR) pair of electrons, 1 H-F bond (BD), and 3 lone pairs (LP).

These natural bond orbitals account for 99.95% of the total electron density.



Nature of Lone Pairs in HF

```
 (Occupancy)   Bond orbital/ Coefficients/ Hybrids
 -------------------------------------------------------------------------------
   1. (2.00000) BD ( 1) F  1- H  2
               ( 77.66%)   0.8813* F  1 s( 20.39%)p 3.90( 79.49%)d 0.01(  0.12%)
                                         0.0000 -0.4506  0.0287  0.0000  0.0000
                                         0.0000  0.0000  0.0000  0.0000  0.0000
                                         0.0000  0.0000  0.0000  0.8912 -0.0274
                                        -0.0019  0.0000  0.0000  0.0000  0.0000
                                         0.0000 -0.0342
               ( 22.34%)   0.4726* H  2 s( 99.88%)p 0.00(  0.12%)
                                        -0.9994  0.0000  0.0000  0.0000  0.0000
                                         0.0000 -0.0341
   3. (1.99939) LP ( 1) F  1             s( 79.68%)p 0.25( 20.31%)d 0.00(  0.00%)
                                         0.0000  0.8926  0.0112  0.0000  0.0000
                                         0.0000  0.0000  0.0000  0.0000  0.0000
                                         0.0000  0.0000  0.0000  0.4506 -0.0074
                                         0.0045  0.0000  0.0000  0.0000  0.0000
                                         0.0000 -0.0041
   4. (1.99795) LP ( 2) F  1             s(  0.00%)p 1.00( 99.98%)d 0.00(  0.02%)
                                         0.0000  0.0000  0.0000  0.0000  0.0000
                                         0.9998  0.0112 -0.0003  0.0000  0.0000
                                         0.0000  0.0000  0.0000  0.0000  0.0000
                                         0.0000  0.0000  0.0000 -0.0156  0.0000
                                         0.0000  0.0000
   5. (1.99795) LP ( 3) F  1             s(  0.00%)p 1.00( 99.98%)d 0.00(  0.02%)
                                         0.0000  0.0000  0.0000  0.0000  0.0000
                                         0.0000  0.0000  0.0000  0.0000  0.9998
                                         0.0112 -0.0003  0.0000  0.0000  0.0000
                                         0.0000  0.0000  0.0000  0.0000 -0.0156
                                         0.0000  0.0000
```

$sp^{3.9}$ hybrid

$sp^{0.25}$ hybrid

p_x

p_y

Useful relations

$$h_A = \frac{1}{\sqrt{1+\lambda}}\left[s_A + \sqrt{\lambda}\, p_A\right]$$

sp^{λ} hybrid orbitals

$$\%p = 100\% \frac{\lambda}{1+\lambda}$$

$$\%s = 100\% \frac{1}{1+\lambda}$$

HF

Polarity and Ionicity

For a 2c/2e bond between atoms A and B, the form of the NBO is:

$$\sigma_{AB} = c_A h_A + c_B h_B$$

where c_A and c_B are *polarization coefficients*

The polarity of the NBO is succinctly described by the *natural ionicity* parameter, i_{AB}

$$i_{AB} = \frac{c_A^2 - c_B^2}{c_A^2 + c_B^2}$$

This parameter smoothly varies from i_{AB}= -1 (c_A=0, pure ionic hybrid on atom B) to i_{AB}= -0 (purely covalent) to i_{AB}= +1 (c_B=0, pure ionic hybrid on atom A)

```
     (Occupancy)   Bond orbital/ Coefficients/ Hybrids
 ---------------------------------------------------------------------------------
   1. (2.00000) BD ( 1) F  1- H  2
                ( 77.66%)   0.8813* F  1 s( 20.39%)p 3.90( 79.49%)d 0.01(  0.12%)
                ( 22.34%)   0.4726* H  2 s( 99.88%)p 0.00(  0.12%)
```

$100\% \times c_A^2$

$100\% \times c_B^2$

For HF: i_{AB}=0.554 polar but far removed from the ionic limit

In NBO searches, natural ionicities of $|i_{AB}|$>0.95 result in an ionic Lewis structure

Bent’s Rule and Natural Electronegativity

Henry Bent formulated a remarkable rule correlating electronegativity with orbital hybridizations:

A central atom tends to direct hybrids of higher p-character (greater λ) toward more electronegative substituents.
or equivalently,
Atomic s-character (lower λ) tends to accumulate in hybrids directed toward the least electronegative substituents

Least electronegative substituent = vacuum => lone pairs tend to high s-character

Bent’s rule suggests that
electronegativities can be determined from NBO polarizations.

Two useful equations:

$$i_{AH} = 1 - \exp[-0.45(\Xi_A - \Xi_H)]$$

$$\Xi_A = \Xi_H - \frac{\ln(1 - i_{AH})}{0.45}$$

For HF, $\Xi_F - \Xi_H =$
$-\ln(1-0.556)/0.45 = 1.80$
(Pauling $\Xi_F - \Xi_H = 3.98-2.2 = 1.78$)

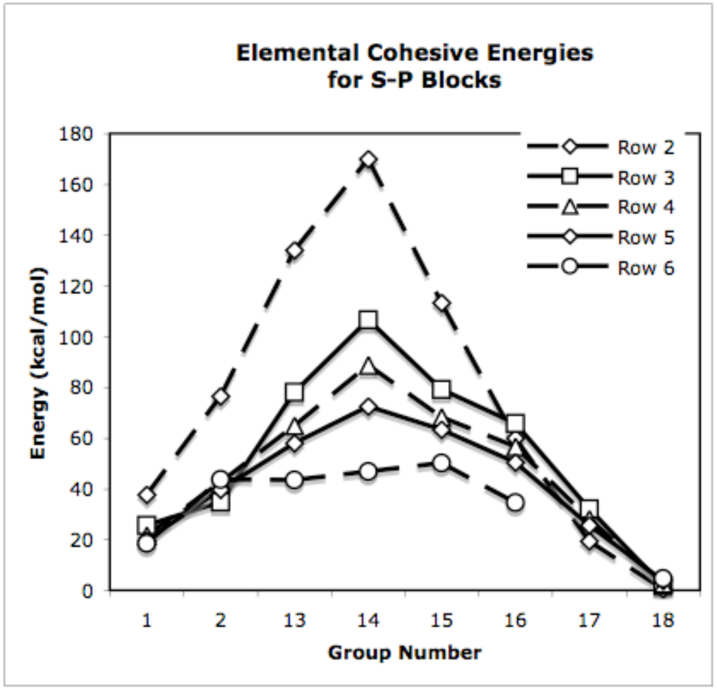
P- and D-Block Parallels

Symmetry about Group 14 → 8e rule

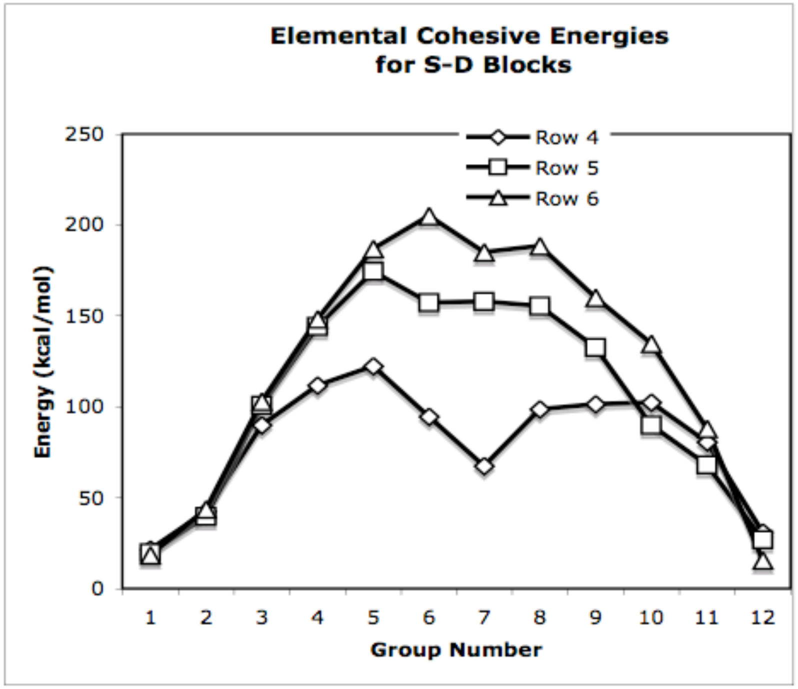
LiH	BeH_2	B_2H_6	CH_4	NH_3	OH_2	FH
Li_2O	BeO	B_2O_3	CO_2	N_2O	O_2	F_2O
LiF	BeF_2	BF_3	CF_4	NF_3	OF_2	F_2

Symmetry about Group 6 → 12e rule

CsH	BaH_2	LaR_3	$HfMe_4$	$TaMe_5$	WMe_6	$ReMe_6$	OsR_4	IrR_3	?	AuR
Cs_2O	BaO	La_2O_3	HfO_2	Ta_2O_5	WO_3	Re_2O_7	OsO_2	Ir_2O_3	PtO	Au_2O_3
CsCl	$BaCl_2$	$LaCl_3$	$HfCl_4$	$TaCl_5$	WCl_6	$ReCl_5$	$OsCl_3$	$IrCl_3$	$PtCl_2$	AuCl



(a)



(b)

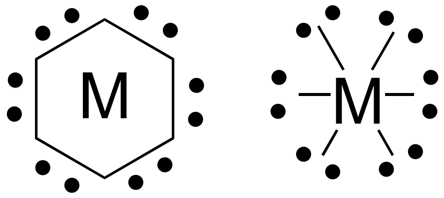
Transition Metal Complexes

Common ML_n stoichiometries (chem. supply catalog, \$, quantity)

Compositional Symmetry about Group 6 → 12e rule

CsH	BaH_2	LaR_3	$HfMe_4$	$TaMe_5$	WMe_6	$ReMe_6$	OsR_4	IrR_3	?	AuR
Cs_2O	BaO	La_2O_3	HfO_2	Ta_2O_5	WO_3	Re_2O_7	OsO_2	Ir_2O_3	PtO	Au_2O_3
CsCl	$BaCl_2$	$LaCl_3$	$HfCl_4$	$TaCl_5$	WCl_6	$ReCl_5$	$OsCl_3$	$IrCl_3$	$PtCl_2$	AuCl

Duodectet Rule (Rule of 12)



Lewis-like structures using one s + five d orbitals for valence

sd^{μ} hybrid orbitals

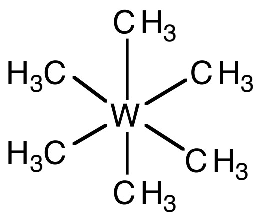
negligible p-character
In metal bonding

$$\boxed{h_M = \frac{1}{\sqrt{1+\mu}}\left[s_M + \sqrt{\mu}\, d_M\right]}$$

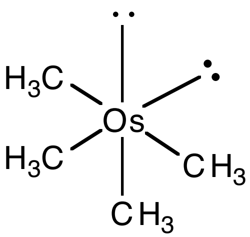
Lewis Structures for the D-Block

- Begin with a Lewis Structure

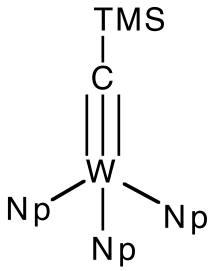
  s and d orbitals dominate bonding: *12 e^- rule*



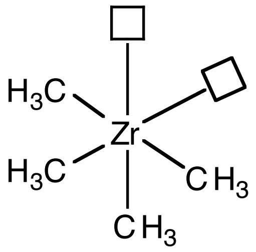
sd^5 hybrids



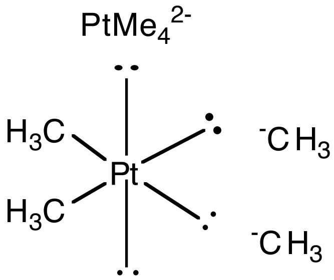
sd^3 hybrids



sd^3 hybrids



hypovalent



hypervalent

- Determine Hybridizations

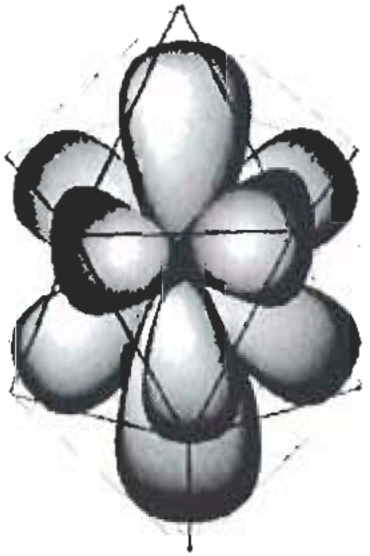
  Lone pairs: pure d

  σ bonds: sd^{n-1} where n= # of sigma bonds

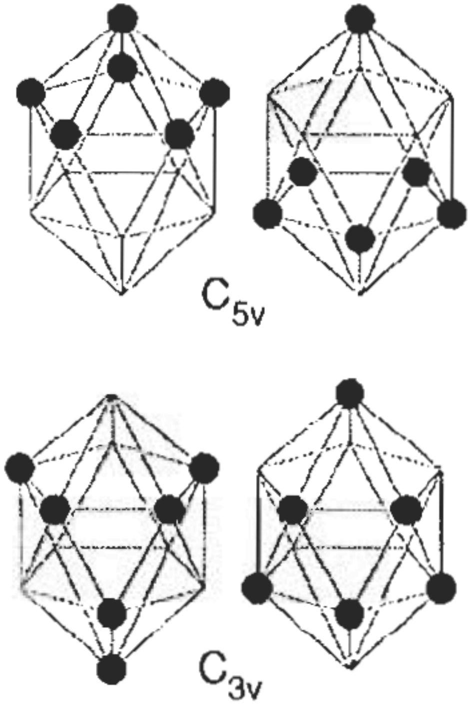
  π bonds: pure d

- Structure: The best geometry is that which minimizes overlap of bonding orbitals (lone pairs only occupy d-orbitals)

Origin of 4 Minima for WH_6



sd^5 hybridization

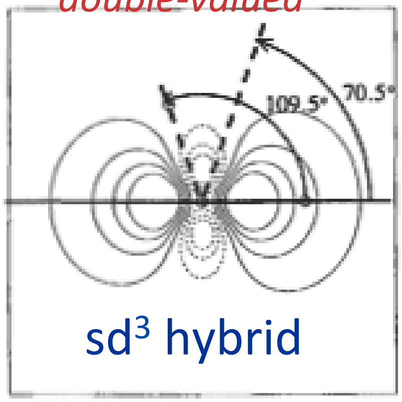


Only four arrangements of 6H’s on the vertices of an icosahedron avoid trans arrangements

For sd$^\mu$ hybrids, orthonormality condition

$$\cos\omega = \pm\sqrt{\frac{\bar{\mu}-2}{3\,\bar{\mu}}} \qquad \bar{\mu} = \sqrt{\mu_1\mu_2}$$

double-valued



sd^3 hybrid

sd^5	63°,117°
sd^4	66°,114°
sd^3	71°,109°
sd^2	90°
sd^1	*90°*

sd^5 hybridization: ω = 63° & 117°

natural bond angles

Icosahedron has vertex-centroid-vertex angles of 63° & 117°

Due to centrosymmetric nature of sd^n hybrids, trans arrangements are strongly disfavored

How “true” are sd$^\mu$ hybrids? 12 e MH$_n$

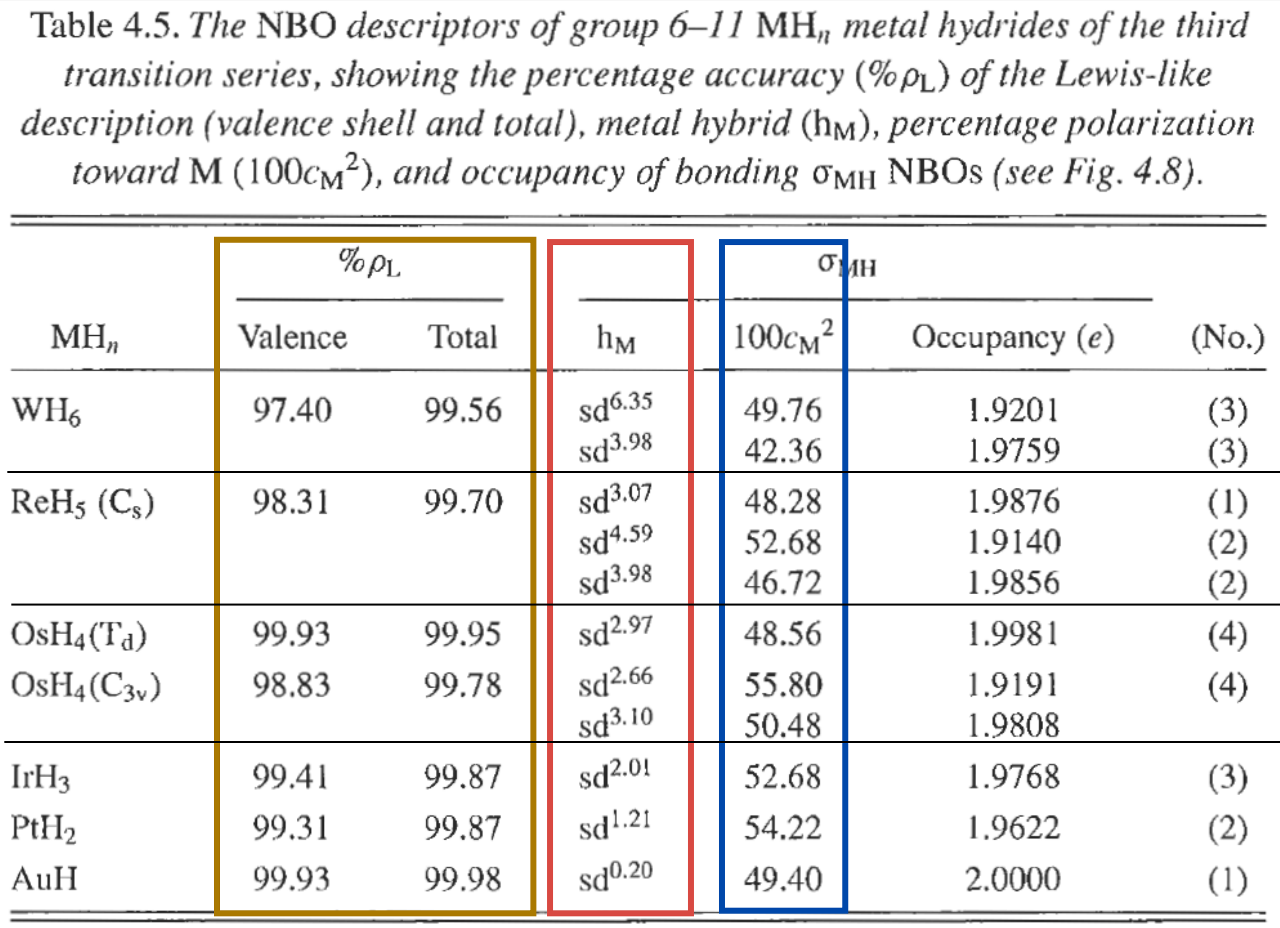


Table 4.5. *The* NBO *descriptors of group 6–11* MH$_n$ *metal hydrides of the third transition series, showing the percentage accuracy (*%ρ_L*) of the Lewis-like description (valence shell and total), metal hybrid (*h_M*), percentage polarization toward* M (100c_M^2)*, and occupancy of bonding* σ_{MH} NBOs *(see Fig. 4.8).*

	%ρ_L		σ_{MH}				
MH$_n$	Valence	Total	h_M	100c_M^2	Occupancy (e)	(No.)	
WH$_6$	97.40	99.56	sd$^{6.35}$	49.76	1.9201	(3)	sd^5
			sd$^{3.98}$	42.36	1.9759	(3)	
ReH$_5$ (C$_s$)	98.31	99.70	sd$^{3.07}$	48.28	1.9876	(1)	
			sd$^{4.59}$	52.68	1.9140	(2)	sd^4
			sd$^{3.98}$	46.72	1.9856	(2)	
OsH$_4$(T$_d$)	99.93	99.95	sd$^{2.97}$	48.56	1.9981	(4)	sd^3
OsH$_4$(C$_{3v}$)	98.83	99.78	sd$^{2.66}$	55.80	1.9191	(4)	
			sd$^{3.10}$	50.48	1.9808		
IrH$_3$	99.41	99.87	sd$^{2.01}$	52.68	1.9768	(3)	sd^2
PtH$_2$	99.31	99.87	sd$^{1.21}$	54.22	1.9622	(2)	sd^1
AuH	99.93	99.98	sd$^{0.20}$	49.40	2.0000	(1)	s

high accuracy

high covalency

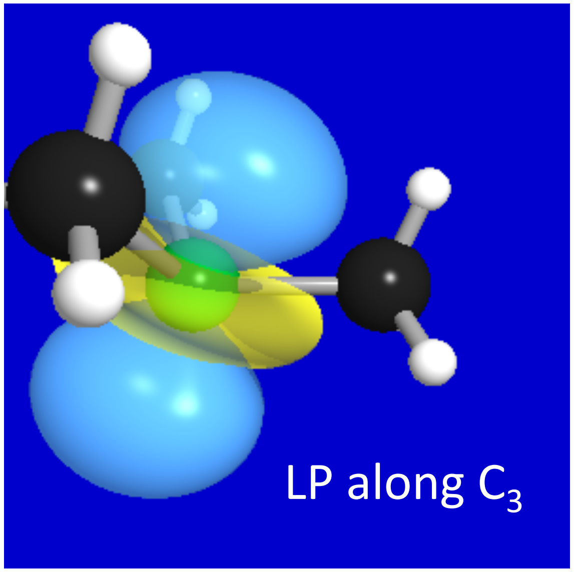
(i_{MH} ≈0 apolar)

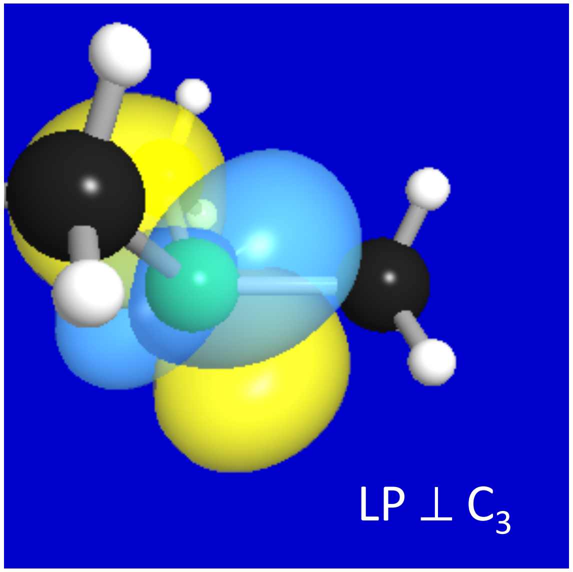
near-ideal hybridization

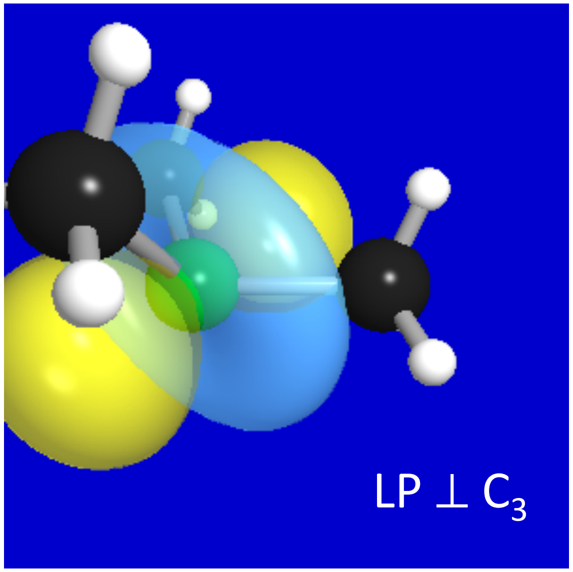
Where are the lone pairs on $IrMe_3$?

```
 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   103.69240   0.30760      7  12   0   3     0      0   0.04
 -----------------------------------------------------------------------------

 -------------------------------------------------------
   Effective Core          60.00000
   Core                    13.96311 ( 99.736% of  14)
   Valence Lewis           29.72929 ( 99.098% of  30)
  ==================      ============================
   Total Lewis            103.69240 ( 99.704% of 104)
```

Rapid convergence to single Lewis structure With 3 Ir LPs and 3 Ir-C σ bonds ($sd^{2.20}$)

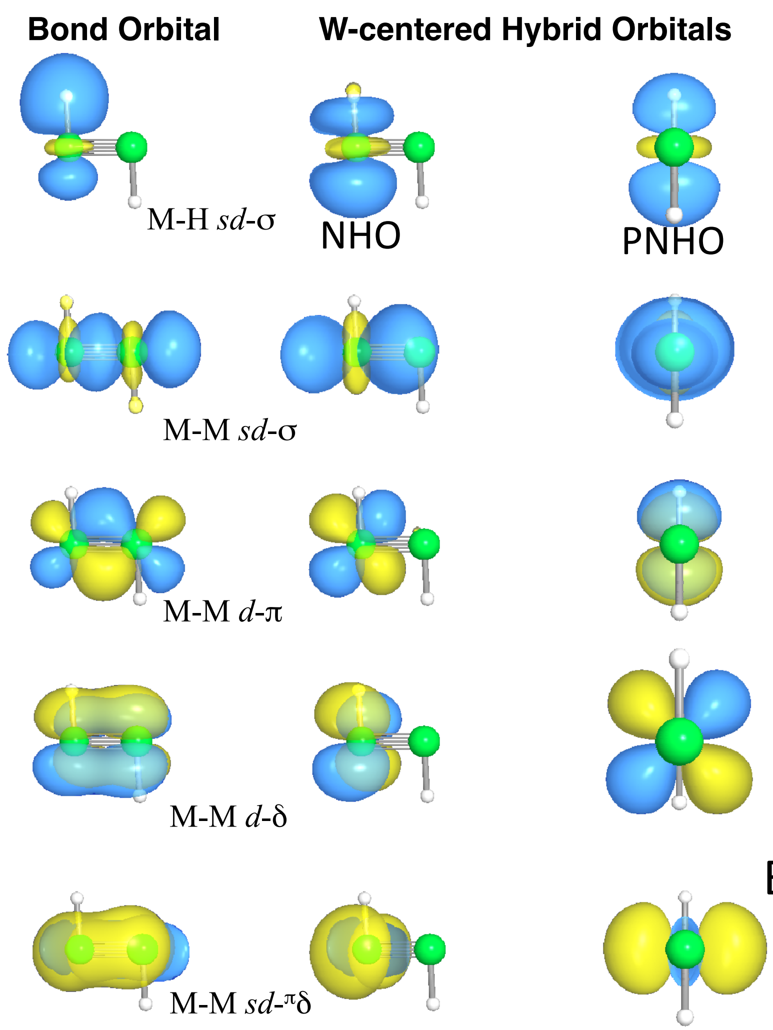

LP along C_3


LP $\perp$ C_3


LP $\perp$ C_3

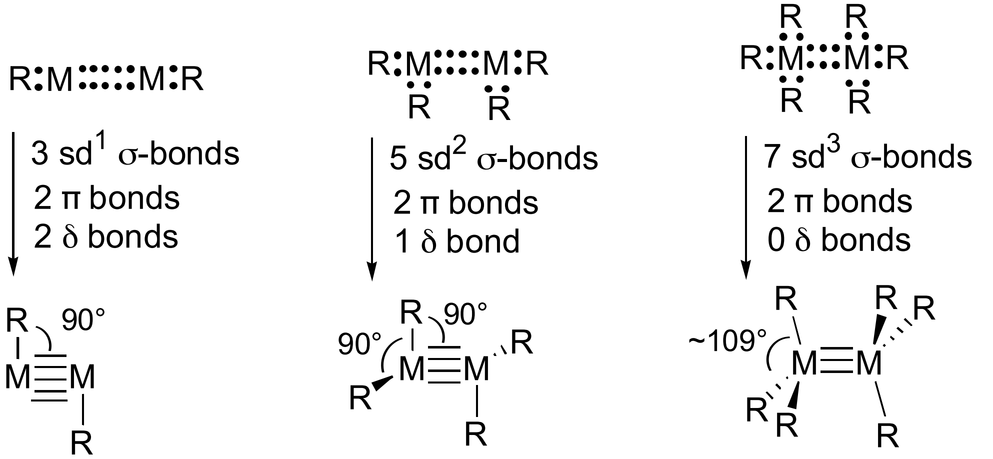
W_2H_2

HW-WH Multiple bonds in abundance !



Plan view

End view



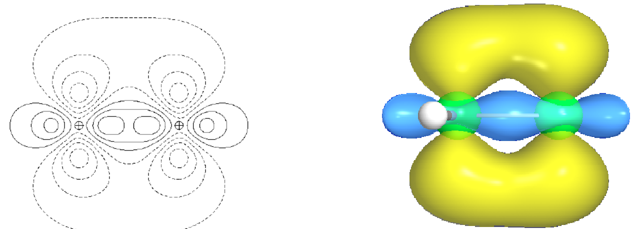
3 sd^1 σ-bonds
2 π bonds
2 δ bonds

5 sd^2 σ-bonds
2 π bonds
1 δ bond

7 sd^3 σ-bonds
2 π bonds
0 δ bonds

```
Cycle    Thresh.    Lewis     Non-Lewis      CR   BD   3C   LP
=================================================================
   1(1)     1.90    149.80114    0.19886       8    7    0    0       0
 -----------------------------------------------------------------
 -------------------------------------------------------------

   Effective Core            120.00000
   Core                       15.92675 ( 99.542% of  16)
   Valence Lewis              13.87439 ( 99.103% of  14)
  ==================         ============================
   Total Lewis               149.80114 ( 99.867% of 150)
```

Better view

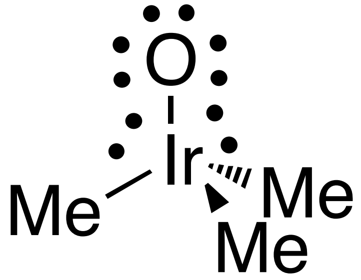


Weird-looking δ orbital

OIrMe$_3$: Single, Double, or Triple Ir-O?

```
 -------------------------------------------------------
   Effective Core          60.00000
   Core                    15.96480 ( 99.780% of  16)
   Valence Lewis           35.12384 ( 97.566% of  36)
  ==================       ============================
   Total Lewis            111.08864 ( 99.186% of 112)
  -----------------------------------------------------
   Valence non-Lewis        0.85035 (  0.759% of 112)
   Rydberg non-Lewis        0.06101 (  0.054% of 112)
  ==================       ============================
   Total non-Lewis          0.91136 (  0.814% of 112)
 -------------------------------------------------------
     (Occupancy)   Bond orbital/ Coefficients/ Hybrids
 -------------------------------------------------------------------------------
   1. (1.97623) BD ( 1)Ir  1- O  2
               ( 40.20%)   0.6341*Ir  1 s( 14.19%)p 0.02(  0.24%)d 6.03( 85.58%)
               ( 59.80%)   0.7733* O  2 s(  9.77%)p 9.22( 90.11%)d 0.01(  0.12%)
   2. (1.96204) BD ( 1)Ir  1- C  3
               ( 46.37%)   0.6810*Ir  1 s( 28.66%)p 0.00(  0.09%)d 2.49( 71.24%)
               ( 53.63%)   0.7323* C  3 s( 18.49%)p 4.40( 81.41%)d 0.01(  0.10%)

  24. (1.97183) LP ( 1) O  2             s( 90.23%)p 0.11(  9.77%)d 0.00(  0.00%)

  25. (1.73076) LP ( 2) O  2             s(  0.00%)p 1.00( 99.96%)d 0.00(  0.04%)

  26. (1.72995) LP ( 3) O  2             s(  0.00%)p 1.00( 99.96%)d 0.00(  0.04%)

  22. (1.96962) LP ( 1)Ir  1             s(  0.00%)p 1.00(  0.04%)d99.99( 99.96%)

  23. (1.96957) LP ( 2)Ir  1             s(  0.00%)p 1.00(  0.04%)d99.99( 99.96%)
```

NBO converges on a Lewis structure with Ir-O *single* bond but notice the low occupancy of the O pπ lp's and the 0.82 e deficiency of the Valence Lewis density.

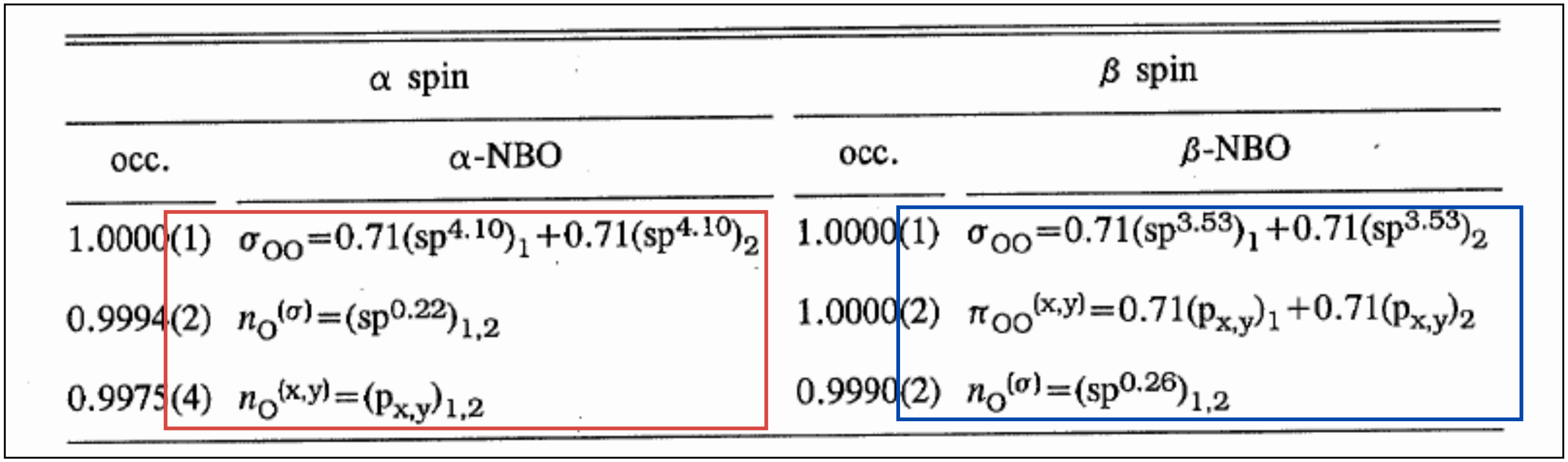


Ir-O bonds have more d-character than Ir-C bonds.

Open Shell Lewis Structures - O_2

Just as UHF calculations have DODS - Different Orbitals for Different Spins
NBO analysis of α- and β-densities yields

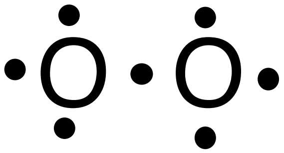
DLDS - Different Lewis Structures for Different Spins



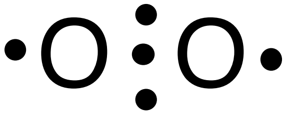
α spin		β spin	
occ.	α-NBO	occ.	β-NBO
1.0000(1)	$\sigma_{OO}=0.71(sp^{4.10})_1+0.71(sp^{4.10})_2$	1.0000(1)	$\sigma_{OO}=0.71(sp^{3.53})_1+0.71(sp^{3.53})_2$
0.9994(2)	$n_O^{(\sigma)}=(sp^{0.22})_{1,2}$	1.0000(2)	$\pi_{OO}^{(x,y)}=0.71(p_{x,y})_1+0.71(p_{x,y})_2$
0.9975(4)	$n_O^{(x,y)}=(p_{x,y})_{1,2}$	0.9990(2)	$n_O^{(\sigma)}=(sp^{0.26})_{1,2}$

1 σ-bond, 2 σ-LPs, 4 π-LPs
(N.B., n_O indicates an LP)

1 σ-bond, 2 π-bonds, 2 σ-LPs)



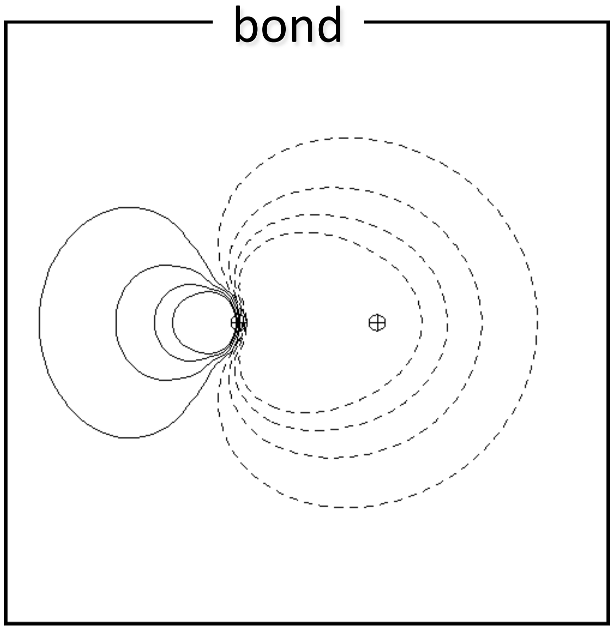
In UHF world, filled NBOs
and LPs have 1e



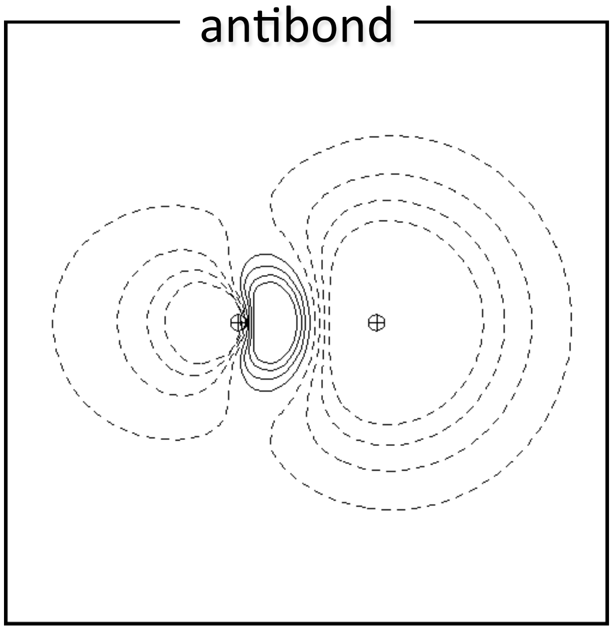
HF

For Every Bond an Antibond

```
 (Occupancy)   Bond orbital/ Coefficients/ Hybrids
 ---------------------------------------------------------------------------------
 1. (2.00000) BD ( 1) F   1 - H   2
                ( 77.61%)   0.8810* F   1 s( 20.31%)p 3.92( 79.58%)d 0.01(  0.11%)

                ( 22.39%)   0.4731* H   2 s( 99.85%)p 0.00(  0.15%)

29. (0.00000) BD*( 1) F   1 - H   2
                ( 22.39%)   0.4731* F   1 s( 20.31%)p 3.92( 79.58%)d 0.01(  0.11%)
                ( 77.61%)  -0.8810* H   2 s( 99.85%)p 0.00(  0.15%)
```



bond

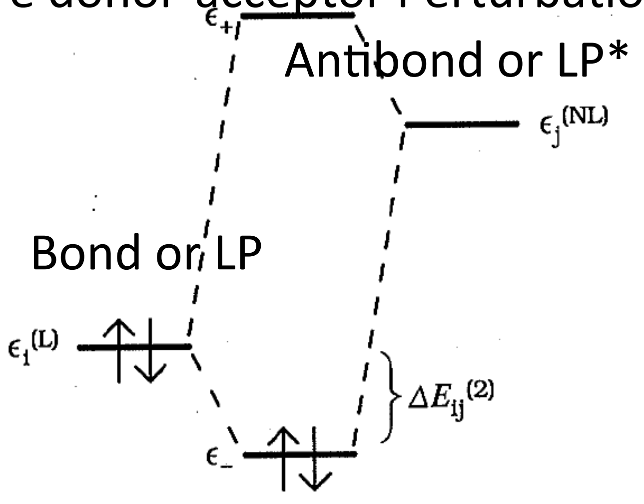


antibond

Analysis of Delocalization: Formamide

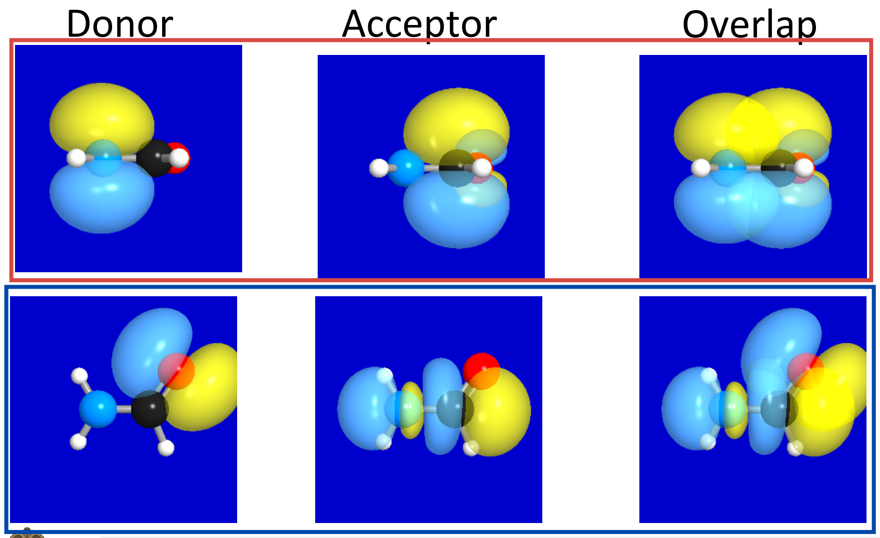
```
SECOND ORDER PERTURBATION THEORY ANALYSIS OF FOCK MATRIX IN NBO BASIS
    Threshold for printing:   0.50 kcal/mol
                                                 E(2)  E(j)-E(i) F(i,j)
     Donor NBO (i)        Acceptor NBO (j)     kcal/mol   a.u.    a.u.
====================================================================

 10. LP ( 1) N 1     85. BD*( 1) C 2- O 3       59.58    0.29    0.117
 11. LP ( 1) O 3     30. RY*( 1) C 2            13.32    1.83    0.139
 11. LP ( 1) O 3     31. RY*( 2) C 2             1.32    1.88    0.044
 11. LP ( 1) O 3     45. RY*(16) C 2             1.34    2.75    0.054
 11. LP ( 1) O 3     50. RY*( 4) O 3             0.53    1.84    0.028
 11. LP ( 1) O 3     53. RY*( 7) O 3             0.50    1.80    0.027
 11. LP ( 1) O 3     82. BD*( 1) N 1- C 2        1.29    1.14    0.035
 11. LP ( 1) O 3     87. BD*( 1) C 2- H 6        0.99    1.04    0.029
 12. LP ( 2) O 3     31. RY*( 2) C 2             3.65    1.44    0.067
 12. LP ( 2) O 3     34. RY*( 5) C 2             0.54    2.56    0.035
 12. LP ( 2) O 3     82. BD*( 1) N 1- C 2       23.52    0.71    0.117
 12. LP ( 2) O 3     87. BD*( 1) C 2- H 6       22.03    0.60    0.105
```

2 e donor-acceptor Perturbation



$$\Delta E_{ij}^{(2)} = \boxed{-2}|F_{ij}|^2/(\epsilon_j^{(NL)} - \epsilon_i^{(L)})$$

More generally, the occupancy (q_i) of the NBO

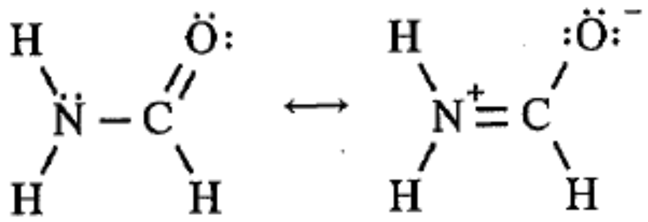


Estimate donor-acceptor matrix element by PNBO overlap

N.B. The $E^{(2)}$ values appear large because they do not include steric terms

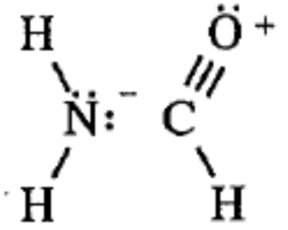
formamide

Resonance and Arrow Pushing



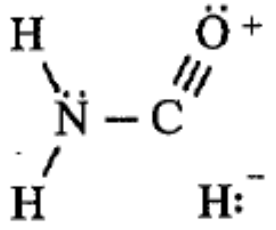
```
LP ( 1) N 1   BD*( 1) C 2- O 3  59.58 kcal/mol
```

$n_O^{(y)} \rightarrow \sigma^*_{CN}$:



```
LP ( 2) O 3  BD*( 1) N 1- C 2  23.52 kcal/mol
```

$n_O^{(y)} \rightarrow \sigma^*_{CH}$:

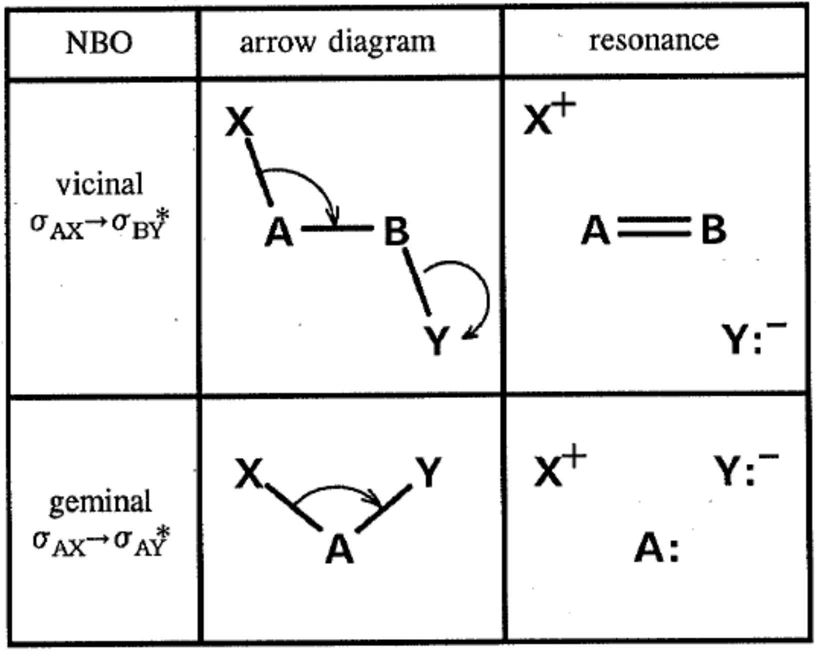


```
LP ( 2) O 3   BD*( 1) C 2- H 6   22.03 kcal/mol
```

Strong delocalizations imply significant contributions from other resonance structures

π delocalizations - conjugation

σ Delocalizations - hyperconjugation



NBO	arrow diagram	resonance
vicinal $\sigma_{AX}\rightarrow\sigma^*_{BY}$	X A—B Y	X^+ A=B $Y:^-$
geminal $\sigma_{AX}\rightarrow\sigma^*_{AY}$	X Y A	X^+ $Y:^-$ A:

$IrOMe_3$

Delocalizations and Occupancy Shifts

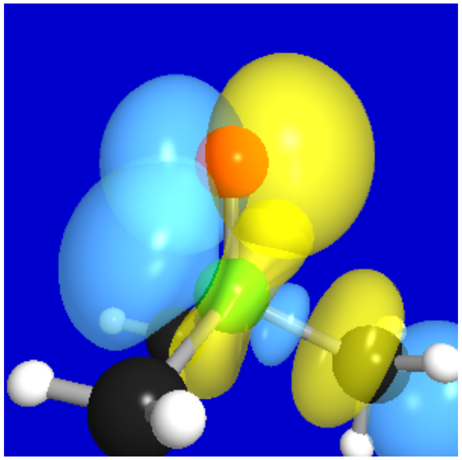
```
(Occupancy)   Bond orbital/ Coefficients/ Hybrids
 ------------------------------------------------------------------------------
  25. (1.73076) LP ( 2) O  2              s(  0.00%)p 1.00( 99.96%)d 0.00(  0.04%)
  26. (1.72995) LP ( 3) O  2              s(  0.00%)p 1.00( 99.96%)d 0.00(  0.04%)

 184. (0.22732) BD*( 1)Ir  1- C  3
                ( 53.63%)   0.7323*Ir  1 s( 28.66%)p 0.00(  0.09%)d 2.49( 71.24%)
                ( 46.37%)  -0.6810* C  3 s( 18.49%)p 4.40( 81.41%)d 0.01(  0.10%)
 185. (0.22732) BD*( 1)Ir  1- C  7
                ( 53.63%)   0.7323*Ir  1 s( 28.66%)p 0.00(  0.09%)d 2.49( 71.24%)
                ( 46.37%)  -0.6810* C  7 s( 18.49%)p 4.40( 81.41%)d 0.01(  0.10%)
 186. (0.22737) BD*( 1)Ir  1- C 11
                ( 53.63%)   0.7323*Ir  1 s( 28.66%)p 0.00(  0.09%)d 2.49( 71.25%)
                ( 46.37%)  -0.6810* C 11 s( 18.48%)p 4.41( 81.42%)d 0.01(  0.10%)
```

Low Occupancy
O LPs

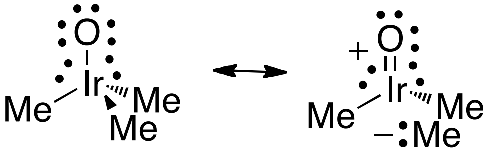
↓

High Occupancy
Ir-C antibonds

```
 SECOND ORDER PERTURBATION THEORY ANALYSIS OF FOCK MATRIX IN NBO BASIS
                                                          E(2)  E(j)-E(i) F(i,j)
     Donor NBO (i)              Acceptor NBO (j)        kcal/mol   a.u.    a.u.
 ===============================================================================
  25. LP ( 2) O 2            184. BD*( 1)Ir 1- C 3        18.36     0.32    0.069
  25. LP ( 2) O 2            185. BD*( 1)Ir 1- C 7        18.36     0.32    0.069
```



```
 NATURAL BOND ORBITALS (Summary):
                                                      Principal Delocalizations
          NBO                Occupancy     Energy    (geminal,vicinal,remote)
 ===============================================================================
  25. LP ( 2) O  2            1.73076    -0.28198   184(v),185(v),28(v),49(v)
  26. LP ( 3) O  2            1.72995    -0.28196   186(v),184(v),185(v),27(v)
                                                   43(v)
```



Natural Localized MOs (`NLMO`)

The delocalization of Lewis NBOs into non-Lewis NBOs creates symmetric and antisymmetric combinations with a small mixing coefficient (t_{ij})

$$\tilde{\Omega}_i^{(L)} = (1 - t_{ij}^2)^2 \Omega_i^{(L)} + t_{ij}\Omega_j^{(NL)}$$

$$\tilde{\Omega}_j^{(NL)} = (1 - t_{ij}^2)^2 \Omega_j^{(NL)} - t_{ij}\Omega_i^{(L)}$$

Or more generally over many delocalizations as

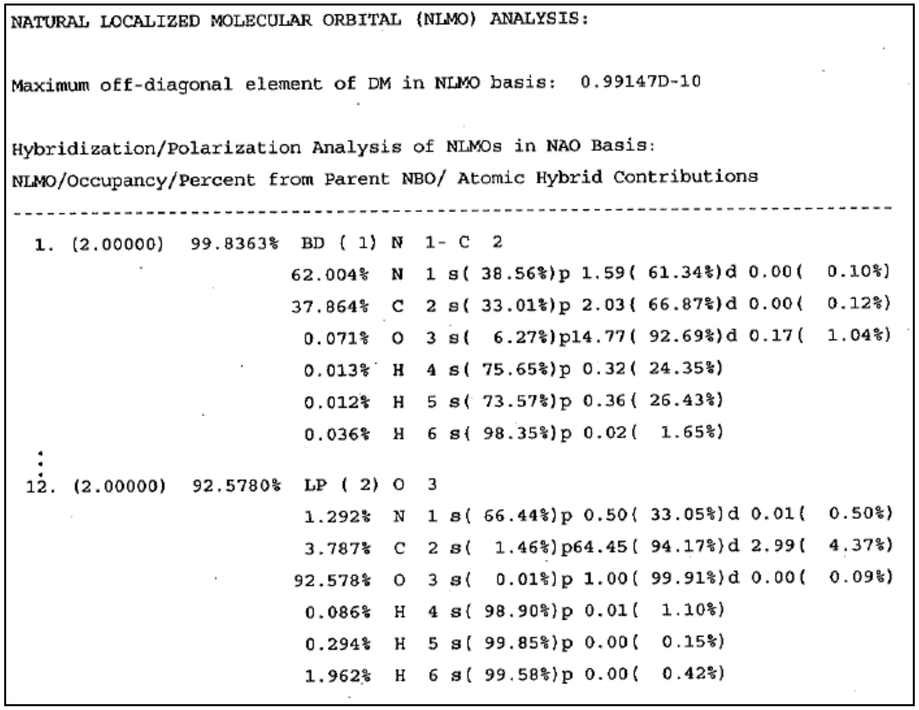
$$\tilde{\Omega}_i^{(L)} = t_{ii}\Omega_i^{(L)} + \sum_j^{NL} t_{ij}\Omega_j^{(NL)}\ , \ i = 1,2,\ldots,N/2$$

$$\tilde{\Omega}_j^{(NL)} = t_{jj}\Omega_j^{(NL)} + \sum_i^{L} t_{ji}\Omega_i^{(L)}\ , \ j = N/2+1,\ldots$$

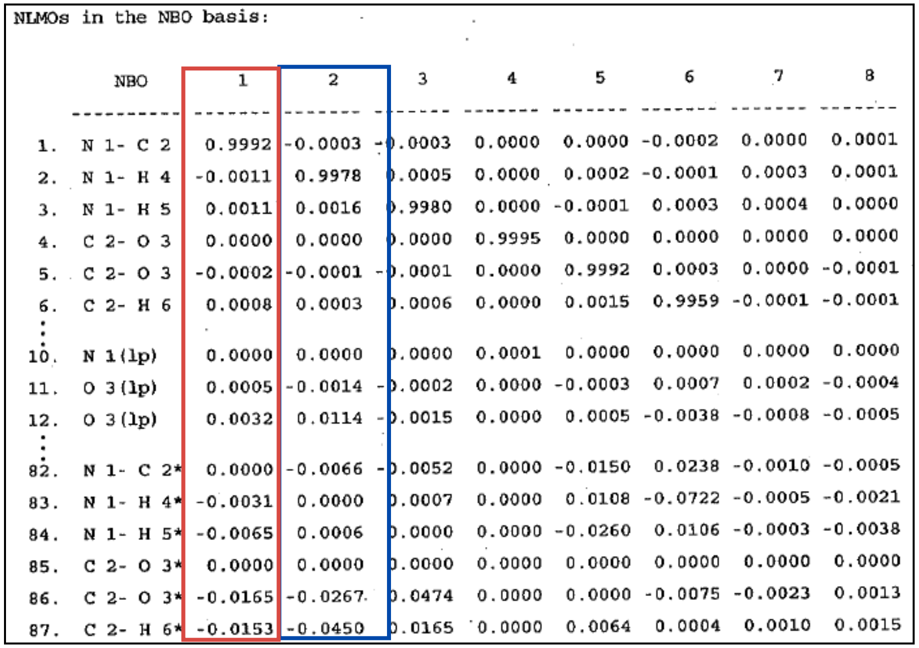
This mixing produces exactly doubly occupied Natural Localized Molecular Orbitals (NLMOs) that are *unitarily equivalent* to Canonical Molecular Orbitals (CMOs). NLMOs are equaly valid to CMOs as descriptors of the density and, thus, all computed observable properties.

NLMOs are the *least delocalized* orbitals that are unitarily equivalent to CMOs.

NLMOs of formamide



```
NATURAL LOCALIZED MOLECULAR ORBITAL (NLMO) ANALYSIS:

Maximum off-diagonal element of DM in NLMO basis:  0.99147D-10

Hybridization/Polarization Analysis of NLMOs in NAO Basis:
NLMO/Occupancy/Percent from Parent NBO/ Atomic Hybrid Contributions
-------------------------------------------------------------------------------
  1. (2.00000)   99.8363%  BD ( 1) N  1- C  2
                        62.004%  N  1 s( 38.56%)p 1.59( 61.34%)d 0.00(  0.10%)
                        37.864%  C  2 s( 33.01%)p 2.03( 66.87%)d 0.00(  0.12%)
                         0.071%  O  3 s(  6.27%)p14.77( 92.69%)d 0.17(  1.04%)
                         0.013%  H  4 s( 75.65%)p 0.32( 24.35%)
                         0.012%  H  5 s( 73.57%)p 0.36( 26.43%)
                         0.036%  H  6 s( 98.35%)p 0.02(  1.65%)
  :
 12. (2.00000)   92.5780%  LP ( 2) O  3
                         1.292%  N  1 s( 66.44%)p 0.50( 33.05%)d 0.01(  0.50%)
                         3.787%  C  2 s(  1.46%)p64.45( 94.17%)d 2.99(  4.37%)
                        92.578%  O  3 s(  0.01%)p 1.00( 99.91%)d 0.00(  0.09%)
                         0.086%  H  4 s( 98.90%)p 0.01(  1.10%)
                         0.294%  H  5 s( 99.85%)p 0.00(  0.15%)
                         1.962%  H  6 s( 99.58%)p 0.00(  0.42%)
```

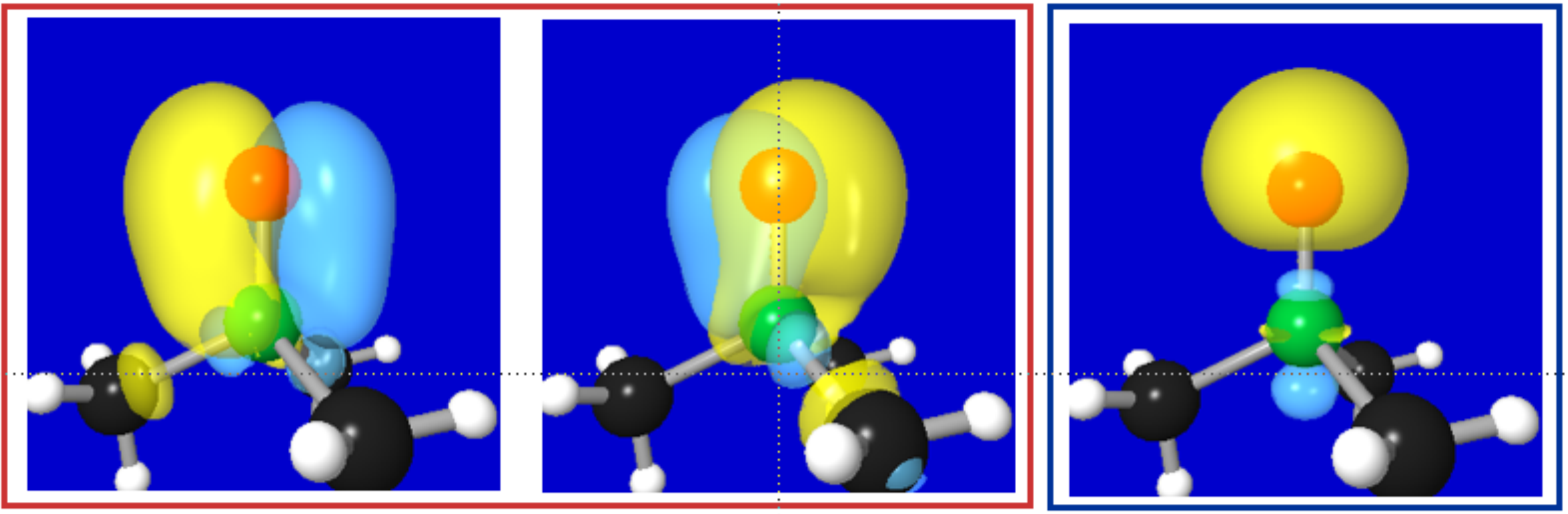


```
NLMOs in the NBO basis:

        NBO        1       2       3       4       5       6       7       8
    ---------- ------- ------- ------- ------- ------- ------- ------- -------
  1.  N 1- C 2   0.9992 -0.0003 -.0003  0.0000  0.0000 -0.0002  0.0000  0.0001
  2.  N 1- H 4  -0.0011  0.9978  .0005  0.0000  0.0002 -0.0001  0.0003  0.0001
  3.  N 1- H 5   0.0011  0.0016  .9980  0.0000 -0.0001  0.0003  0.0004  0.0000
  4.  C 2- O 3   0.0000  0.0000  .0000  0.9995  0.0000  0.0000  0.0000  0.0000
  5.  C 2- O 3  -0.0002 -0.0001 -.0001  0.0000  0.9992  0.0003  0.0000 -0.0001
  6.  C 2- H 6   0.0008  0.0003  .0006  0.0000  0.0015  0.9959 -0.0001 -0.0001
  :
 10.  N 1(lp)    0.0000  0.0000  .0000  0.0001  0.0000  0.0000  0.0000  0.0000
 11.  O 3(lp)    0.0005 -0.0014 -.0002  0.0000 -0.0003  0.0007  0.0002 -0.0004
 12.  O 3(lp)    0.0032  0.0114 -.0015  0.0000  0.0005 -0.0038 -0.0008 -0.0005
  :
 82.  N 1- C 2*  0.0000 -0.0066 -.0052  0.0000 -0.0150  0.0238 -0.0010 -0.0005
 83.  N 1- H 4* -0.0031  0.0000  .0007  0.0000  0.0108 -0.0722 -0.0005 -0.0021
 84.  N 1- H 5* -0.0065  0.0006  .0000  0.0000 -0.0260  0.0106 -0.0003 -0.0038
 85.  C 2- O 3*  0.0000  0.0000  .0000  0.0000  0.0000  0.0000  0.0000  0.0000
 86.  C 2- O 3* -0.0165 -0.0267  .0474  0.0000  0.0000 -0.0075 -0.0023  0.0013
 87.  C 2- H 6* -0.0153 -0.0450  .0165  0.0000  0.0064  0.0004  0.0010  0.0015
```

$$\text{NLMO 1: } \tilde{\sigma}_{CN} = 0.9992\,\sigma_{CN} - 0.0165\,\sigma^*_{CO} - 0.0153\,\sigma^*_{CH} - \ldots$$

$$\text{NLMO 2: } \tilde{\sigma}_{NH(s)} = 0.9978\,\sigma_{NH(s)} - 0.0450\,\sigma^*_{CH} - 0.0267\,\sigma^*_{CO} - \ldots$$

NLMOs of $IrOMe_3$



```
25. (2.00000)  86.3110%  LP ( 2) O  2
  7.220% Ir  1 s(  0.00%)p 1.00(  0.87%)d99.99( 99.13%)
 86.311%  O  2 s(  0.00%)p 1.00( 99.95%)d 0.00(  0.05%)
  3.113%  C  3 s( 19.33%)p 4.17( 80.55%)d 0.01(  0.12%)
  3.115%  C  7 s( 19.32%)p 4.17( 80.55%)d 0.01(  0.12%)
```

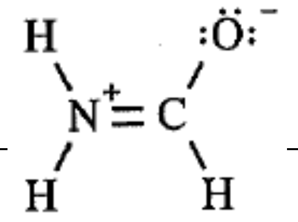
```
24. (2.00000)  98.5637%  LP ( 1) O  2
 0.983% Ir  1 s( 92.00%)p 0.00(  0.45%)d 0.08(  7.55%)
98.570%  O  2 s( 89.75%)p 0.11( 10.25%)d 0.00(  0.00%)
```

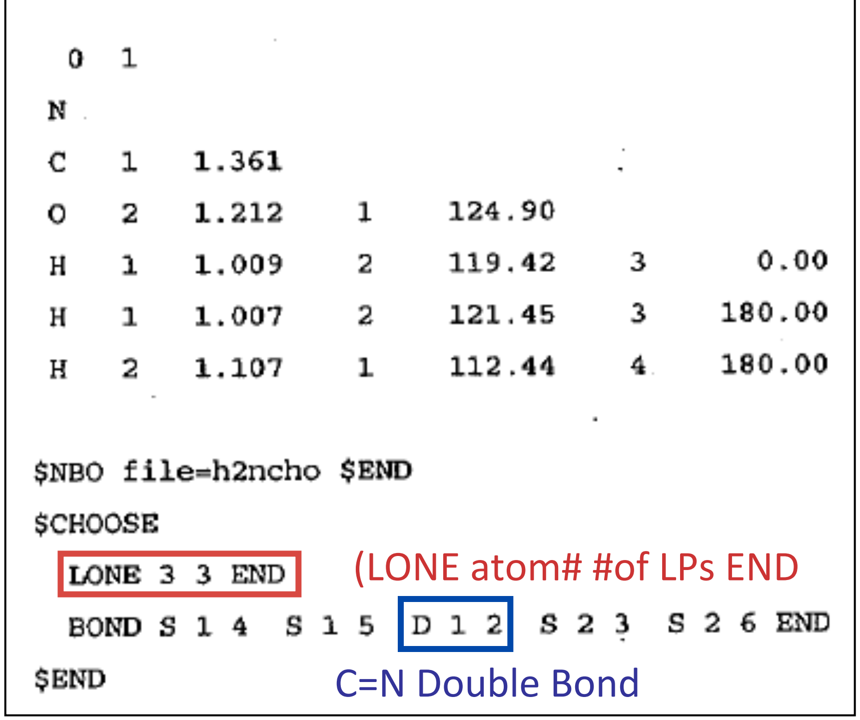
Partial multiple Ir-O bond character arise from O LP to Ir-C σ^* delocalizations
This means that the C_3 symmetry of $IrMe_3$ is retained.

`$CHOOSE` an Alternate Lewis Structure

General Format of `$CHOOSE` section:

```
$CHOOSE
   LONE     (1c list)   END
   BOND     (2c list)   END
   3CBOND   (3c list)   END
$END
```

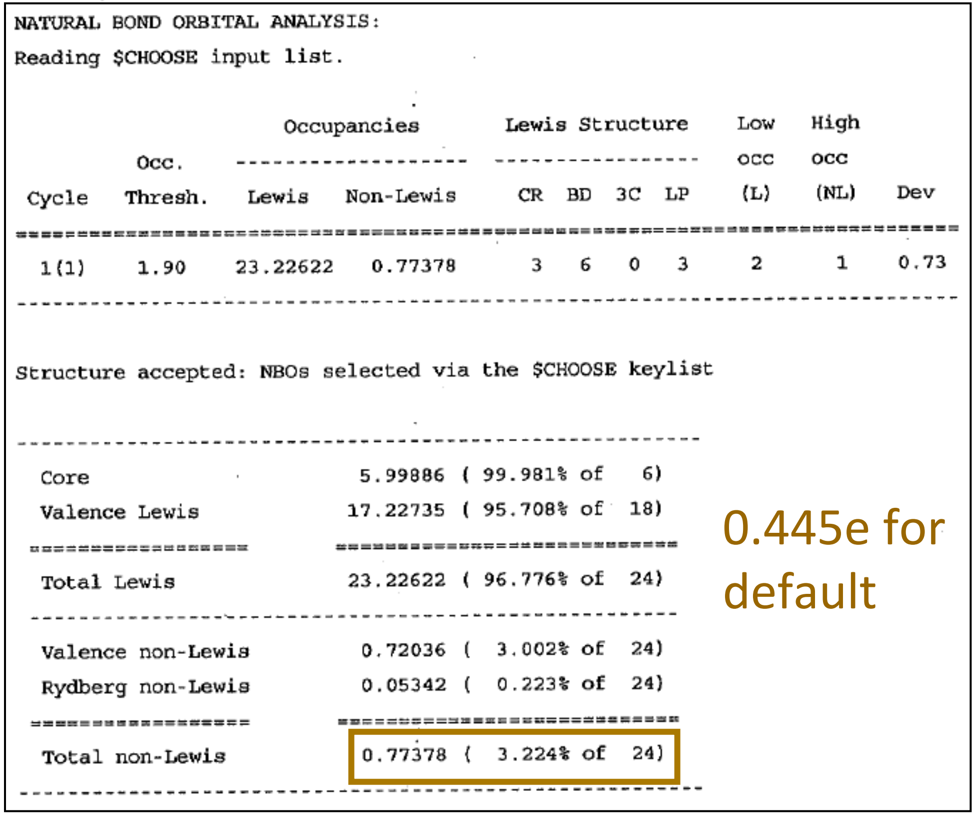




```
H2NCHO

 0  1
 N
 C   1   1.361
 O   2   1.212    1    124.90
 H   1   1.009    2    119.42    3      0.00
 H   1   1.007    2    121.45    3    180.00
 H   2   1.107    1    112.44    4    180.00

$NBO file=h2ncho $END
$CHOOSE
  LONE 3 3 END
  BOND S 1 4  S 1 5  D 1 2  S 2 3  S 2 6 END
$END
```

(LONE atom# #of LPs END

C=N Double Bond



```
NATURAL BOND ORBITAL ANALYSIS:
Reading $CHOOSE input list.

                         Occupancies        Lewis Structure    Low   High
          Occ.      -------------------   -----------------    occ   occ
 Cycle   Thresh.    Lewis     Non-Lewis     CR  BD  3C  LP     (L)   (NL)   Dev
================================================================================
  1(1)    1.90    23.22622    0.77378        3   6   0   3      2      1    0.73
--------------------------------------------------------------------------------

Structure accepted: NBOs selected via the $CHOOSE keylist

------------------------------------------------------------
  Core                      5.99886 ( 99.981% of   6)
  Valence Lewis            17.22735 ( 95.708% of  18)
 ==================       ============================
  Total Lewis              23.22622 ( 96.776% of  24)
 -----------------------------------------------------
  Valence non-Lewis         0.72036 (  3.002% of  24)
  Rydberg non-Lewis         0.05342 (  0.223% of  24)
 ==================       ============================
  Total non-Lewis           0.77378 (  3.224% of  24)
 -------------------------------------------------------------
```

0.445e for default

$DELete Density

formamide

```
#N b3lyp/6-311++g** NoSymm POP=NBODel IOP(5/48=10000)

H2NCHO deletion

 0 1
N
C 1 1.361
O 2 1.212 1 124.90
H 1 1.009 2 119.42 3   0.00
H 1 1.007 2 121.45 3 180.00
H 2 1.107 1 112.44 4 180.00

$NBO file=h2ncho $END
$DEL
 delete 1 element 10 85
$END
```

In this example we delete the $F_{10,85}$ element of the Fock matrix in the NBO basis. This element is:
N LP → C-O π^*

Would formamide be planar if the N LP to π^* C=O delocalization were eliminated?

A unique feature of the NBO program Is the ability to *selectively delete elements of the Fock matrix (F_{ij}) and perform reoptimizations* with this deletion.

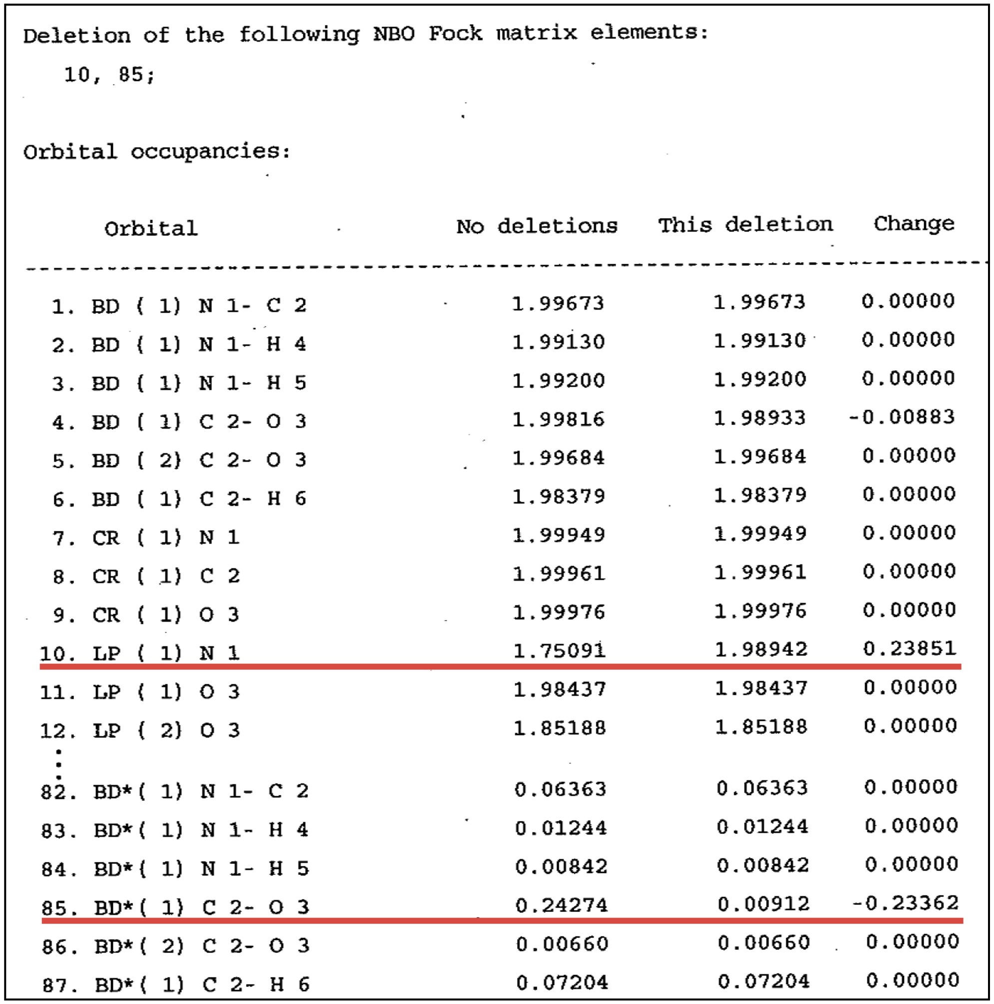
Here is an input file for deleting the matrix element using Gaussian 03.

Special Features of `$DELete`

- Requires intimate linking (NBO linked to ESS) with ab initio program
- POP=NBODel is required
- Turn off symmetry (NoSymm)
- IOP only needed for initial release of G03

formamide

$DELete N LP → C-O π*: Occupancy



```
Deletion of the following NBO Fock matrix elements:
   10, 85;


Orbital occupancies:


      Orbital                          No deletions   This deletion   Change
------------------------------------------------------------------------------
  1. BD ( 1) N 1- C 2                    1.99673        1.99673      0.00000
  2. BD ( 1) N 1- H 4                    1.99130        1.99130      0.00000
  3. BD ( 1) N 1- H 5                    1.99200        1.99200      0.00000
  4. BD ( 1) C 2- O 3                    1.99816        1.98933     -0.00883
  5. BD ( 2) C 2- O 3                    1.99684        1.99684      0.00000
  6. BD ( 1) C 2- H 6                    1.98379        1.98379      0.00000
  7. CR ( 1) N 1                         1.99949        1.99949      0.00000
  8. CR ( 1) C 2                         1.99961        1.99961      0.00000
  9. CR ( 1) O 3                         1.99976        1.99976      0.00000
 10. LP ( 1) N 1                         1.75091        1.98942      0.23851
 11. LP ( 1) O 3                         1.98437        1.98437      0.00000
 12. LP ( 2) O 3                         1.85188        1.85188      0.00000
  :
 82. BD*( 1) N 1- C 2                    0.06363        0.06363      0.00000
 83. BD*( 1) N 1- H 4                    0.01244        0.01244      0.00000
 84. BD*( 1) N 1- H 5                    0.00842        0.00842      0.00000
 85. BD*( 1) C 2- O 3                    0.24274        0.00912     -0.23362
 86. BD*( 2) C 2- O 3                    0.00660        0.00660      0.00000
 87. BD*( 1) C 2- H 6                    0.07204        0.07204      0.00000
```

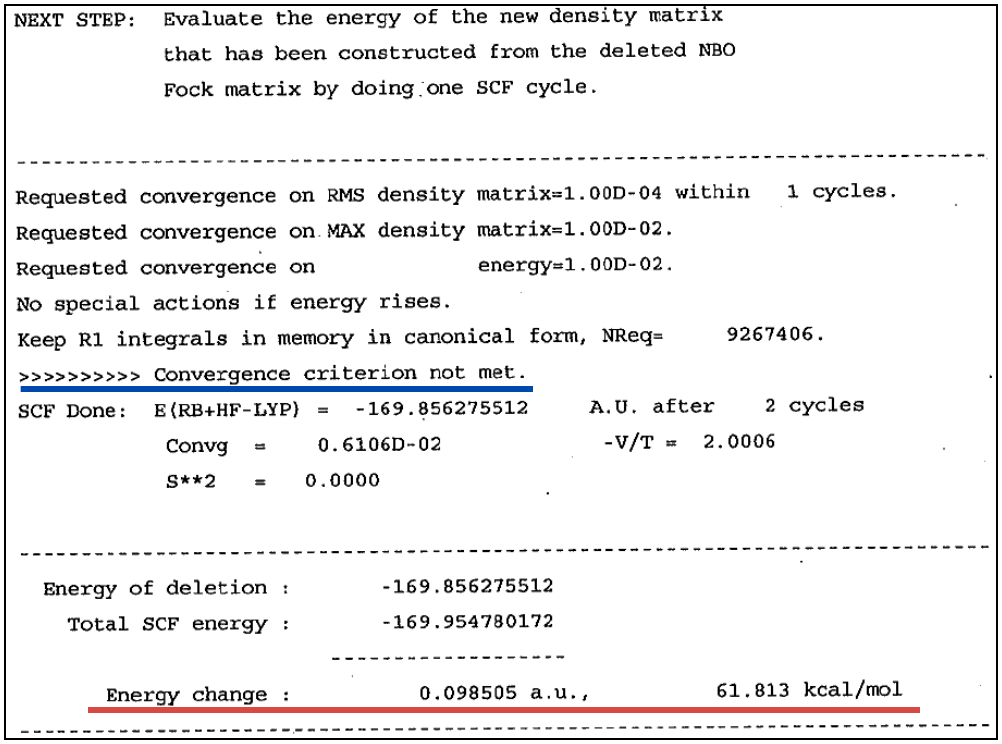
Gaussian has rediagonalized the modified Fock matrix and obtained a new density matrix. NBO analysis of the density (pre- and post-deletion) is shown to the left as NBO occupancies .

What is the result of our deletion?

To transfer, density out of C-Oπ* and back to N LP!

formamide

$DELete N LP → C-O π^*: Energy



```
NEXT STEP:  Evaluate the energy of the new density matrix
            that has been constructed from the deleted NBO
            Fock matrix by doing one SCF cycle.

------------------------------------------------------------------------------
Requested convergence on RMS density matrix=1.00D-04 within   1 cycles.
Requested convergence on MAX density matrix=1.00D-02.
Requested convergence on             energy=1.00D-02.
No special actions if energy rises.
Keep R1 integrals in memory in canonical form, NReq=      9267406.
>>>>>>>>>> Convergence criterion not met.
SCF Done:  E(RB+HF-LYP) =  -169.856275512     A.U. after    2 cycles
            Convg  =    0.6106D-02              -V/T =  2.0006
            S**2   =   0.0000

------------------------------------------------------------------------------
  Energy of deletion :        -169.856275512
    Total SCF energy :        -169.954780172
                           -------------------
       Energy change :           0.098505 a.u.,          61.813 kcal/mol
------------------------------------------------------------------------------
```

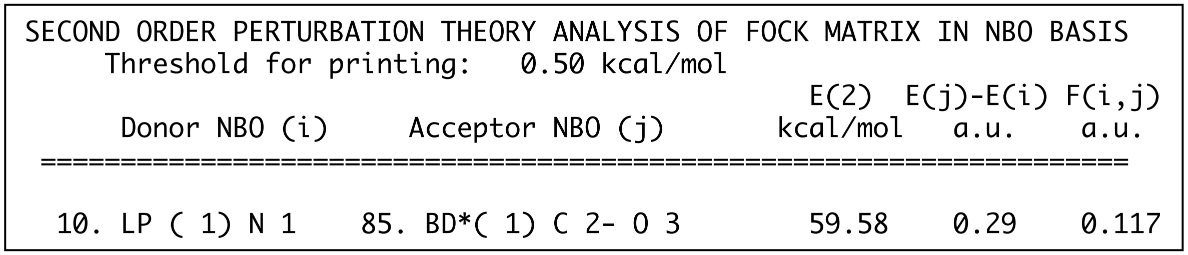
Gaussian has rediagonalized the modified Fock matrix in one cycle (so we don’t revert to original density)

Ignore the Convergence warning!

What is the result of our deletion?

An *increase* in energy (we deleted a stabilizing interaction) by 61.8 kcal/mol

Does this make sense? Recall previous perturbative estimate:



```
SECOND ORDER PERTURBATION THEORY ANALYSIS OF FOCK MATRIX IN NBO BASIS
     Threshold for printing:   0.50 kcal/mol
                                                       E(2)  E(j)-E(i) F(i,j)
      Donor NBO (i)       Acceptor NBO (j)           kcal/mol   a.u.    a.u.
 ===================================================================
  10. LP ( 1) N 1      85. BD*( 1) C 2- O 3          59.58     0.29    0.117
```

Will the perturbative estimates always be close to the deletion results?

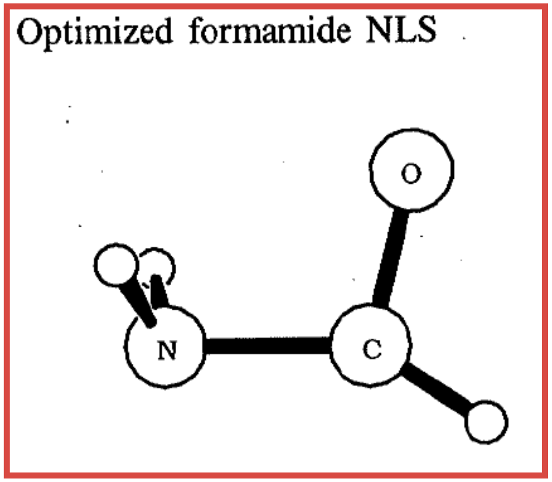
formamide

Reoptimize with ALL $F_{(NBO,*)}$ `$DELeted`

```
#b3lyp/6-311++G** pop=nbodel nosymm opt

$delete/nostar optimization of formamide

0 1
n
c 1 cn
o 2 co 1 nco
h 1 nh 2 cnh 3 ocnh
h 1 nhp 2 cnhp 3 ocnhp
h 2 ch 1 nch 4 hnch

 cn 1.26
 co 1.11
 nco 134.
 nh 1.09
 cnh 129.
 ocnh 10.
 nhp 1.01
 cnhp 121.
 ocnhp 158.
 ch 1.10
 nch 112.
 hnch 160.

$NBO PRINT=0 $END
$DEL
 NOSTAR
$END
```

Required elements for this job:

- pop=nbodel, nosymm, opt
- Z-matrix with symbolic names (no more than 50 variables)
- `$DEL` and `$END` bracketing the requested delentions)
- Patience! All derivatives are computed numerically


Optimized formamide NLS

The result is dramatic!

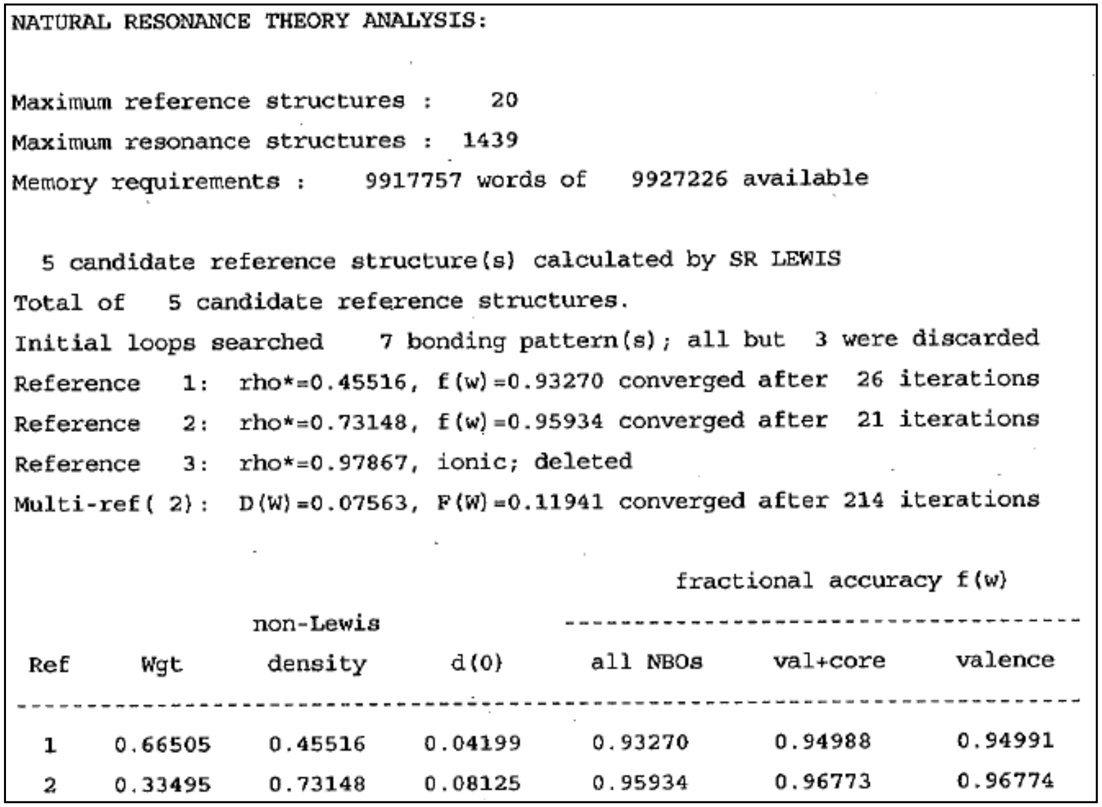
C-N 1.57(1.26)Å
C-O 1.35(1.11)Å
C-H 1.04(1.10)Å
C-N-H 102(129)°
C-N-O 104(134)°
N-C-H 146(112)°

formamide

Natural Resonance Theory (`NRT`)

The foregoing suggests that multiple resonance structures contribute to the full description of formamide and $IrOMe_3$. In the spirit of NBO analysis, optimal resonance structures are those that, in combination, best account for the true density ($\mathbf{D}^{(\text{true})}$).

$$\mathbf{D}^{(\text{true})} = \sum_{\alpha} w_{\alpha} \mathbf{D}_{\alpha}^{(\text{L})}$$



```
NATURAL RESONANCE THEORY ANALYSIS:

Maximum reference structures :    20
Maximum resonance structures :  1439
Memory requirements :     9917757 words of    9927226 available

  5 candidate reference structure(s) calculated by SR LEWIS
Total of    5 candidate reference structures.
Initial loops searched     7 bonding pattern(s); all but  3 were discarded
Reference   1:  rho*=0.45516, f(w)=0.93270 converged after  26 iterations
Reference   2:  rho*=0.73148, f(w)=0.95934 converged after  21 iterations
Reference   3:  rho*=0.97867, ionic; deleted
Multi-ref( 2):  D(W)=0.07563, F(W)=0.11941 converged after 214 iterations

                                         fractional accuracy f(w)
                  non-Lewis           ---------------------------------
 Ref      Wgt      density      d(0)      all NBOs     val+core     valence
-----------------------------------------------------------------------------
  1     0.66505    0.45516    0.04199    0.93270     0.94988     0.94991
  2     0.33495    0.73148    0.08125    0.95934     0.96773     0.96774
```

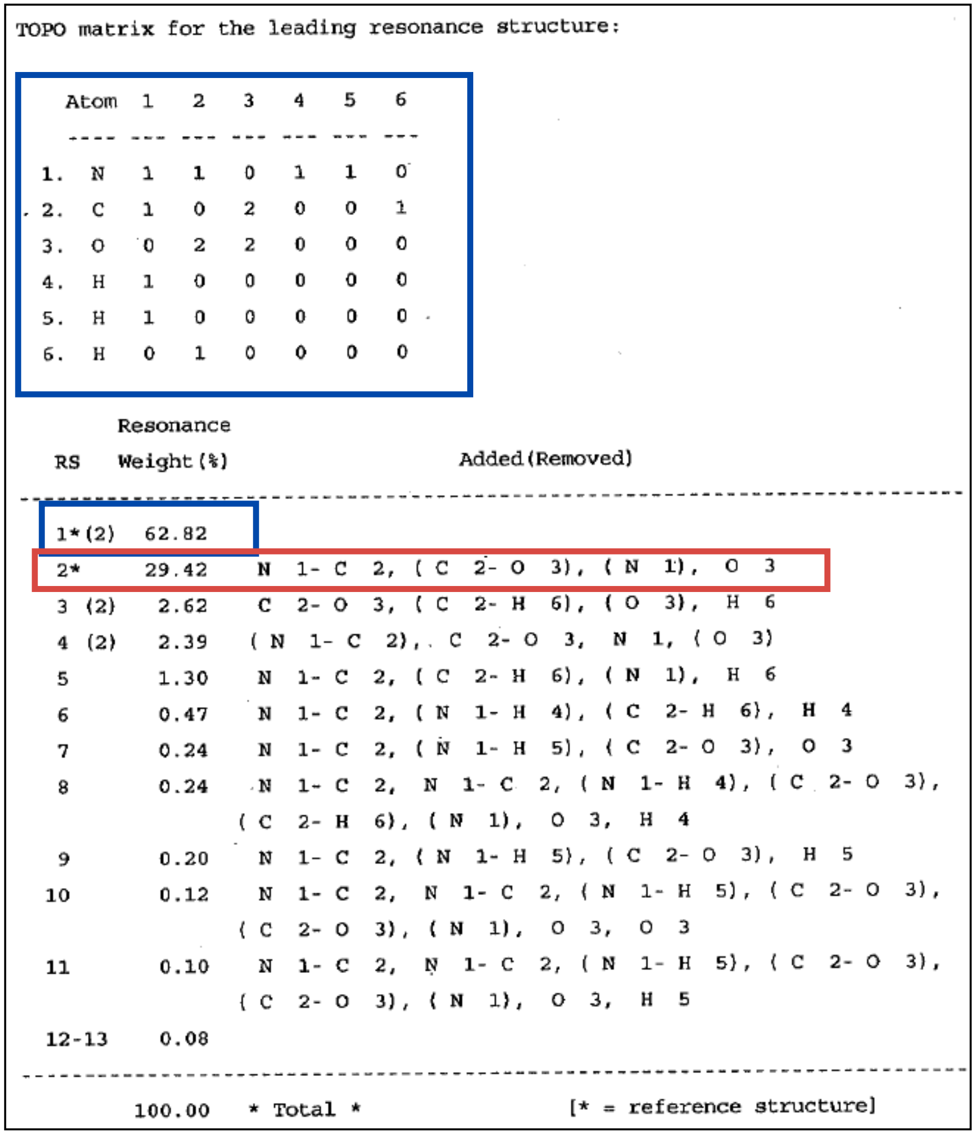
Use the keyword `NRT` to request this analysis. Initial output for formamide shows:

5 initial candidates, settling on 2

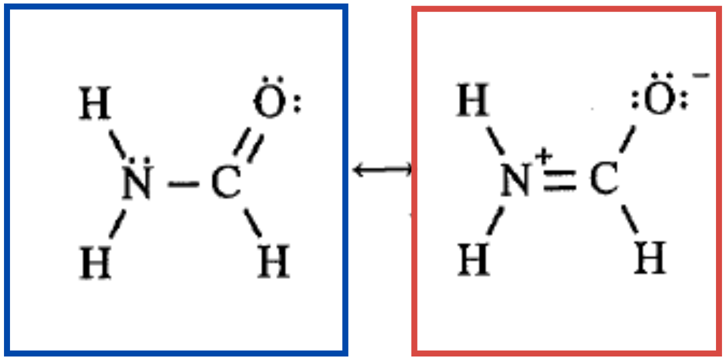
F(w) is the fractional improvement: 0 = no improvement
0.5 = error halved
1 = infinitely better

NRT - Weights

formamide



```
TOPO matrix for the leading resonance structure:

   Atom  1   2   3   4   5   6
   ---- --- --- --- --- --- ---
 1.  N   1   1   0   1   1   0
 2.  C   1   0   2   0   0   1
 3.  O   0   2   2   0   0   0
 4.  H   1   0   0   0   0   0
 5.  H   1   0   0   0   0   0
 6.  H   0   1   0   0   0   0

        Resonance
  RS    Weight(%)                  Added(Removed)
---------------------------------------------------------------------------
  1*(2)   62.82
  2*      29.42   N  1- C  2, ( C  2- O  3), ( N  1),  O  3
  3 (2)    2.62   C  2- O  3, ( C  2- H  6), ( O  3),  H  6
  4 (2)    2.39  ( N  1- C  2), C  2- O  3,  N  1, ( O  3)
  5        1.30   N  1- C  2, ( C  2- H  6), ( N  1),  H  6
  6        0.47   N  1- C  2, ( N  1- H  4), ( C  2- H  6),  H  4
  7        0.24   N  1- C  2, ( N  1- H  5), ( C  2- O  3),  O  3
  8        0.24   N  1- C  2,  N  1- C  2, ( N  1- H  4), ( C  2- O  3),
                 ( C  2- H  6), ( N  1),  O  3,  H  4
  9        0.20   N  1- C  2, ( N  1- H  5), ( C  2- O  3),  H  5
 10        0.12   N  1- C  2,  N  1- C  2, ( N  1- H  5), ( C  2- O  3),
                 ( C  2- O  3), ( N  1),  O  3,  O  3
 11        0.10   N  1- C  2,  N  1- C  2, ( N  1- H  5), ( C  2- O  3),
                 ( C  2- O  3), ( N  1),  O  3,  H  5
 12-13     0.08
---------------------------------------------------------------------------
         100.00   * Total *                [* = reference structure]
```



Primary (62.92%)

Secondary (29.42%)

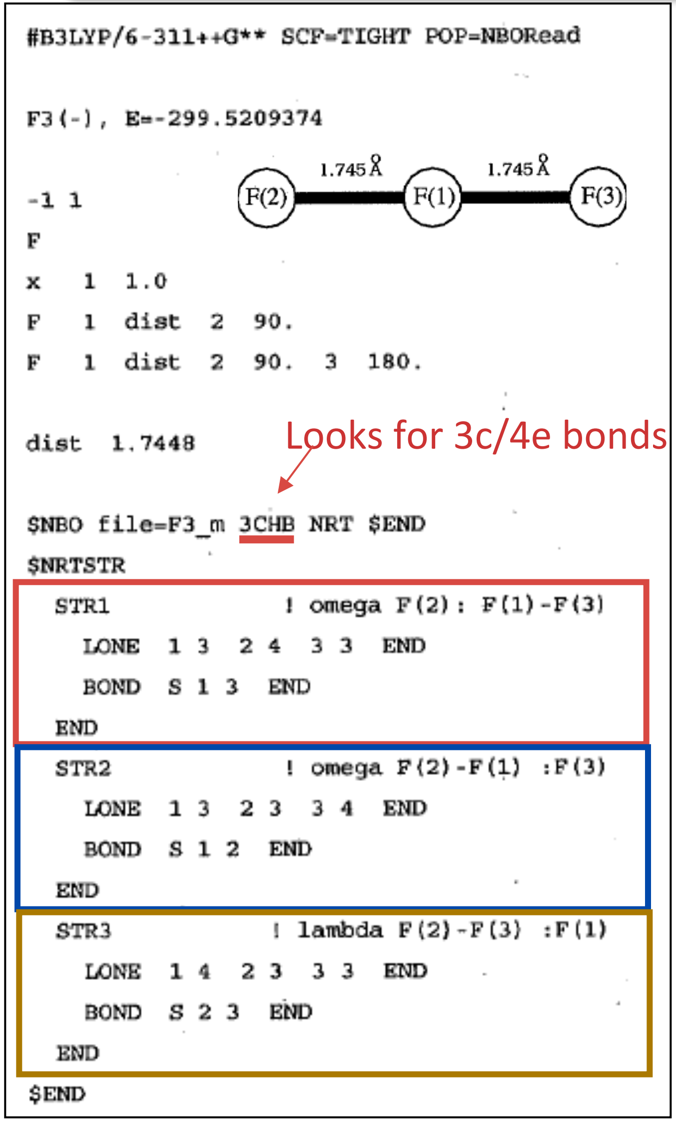
Add C-N bond

Remove C-O bond

Remove N LP

Add O LP

Multicenter 3c/4e "Hyperbonding" (3CHB)

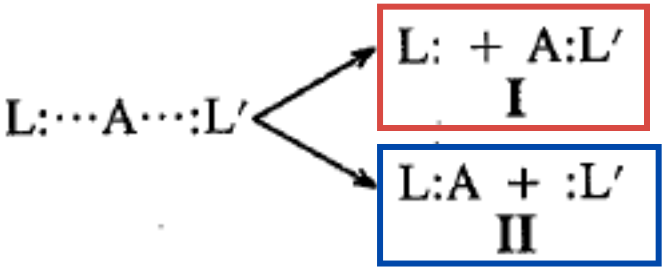


```
#B3LYP/6-311++G** SCF=TIGHT POP=NBORead

F3(-), E=-299.5209374

-1 1
F
x   1  1.0
F   1  dist  2  90.
F   1  dist  2  90.  3  180.

dist  1.7448

$NBO file=F3_m 3CHB NRT $END
$NRTSTR
  STR1                ! omega F(2): F(1)-F(3)
    LONE  1 3  2 4  3 3  END
    BOND  S 1 3  END
  END
  STR2                ! omega F(2)-F(1) :F(3)
    LONE  1 3  2 3  3 4  END
    BOND  S 1 2  END
  END
  STR3               ! lambda F(2)-F(3) :F(1)
    LONE  1 4  2 3  3 3  END
    BOND  S 2 3  END
  END
$END
```

Looks for 3c/4e bonds

Too many electrons for normal Lewis valence space = Hypervalent

Where do they go? Coulson recognized that F_3^- does not exceed valence counts as fragments shown below in general form:



L:···A···:L′

L: + A:L′
I

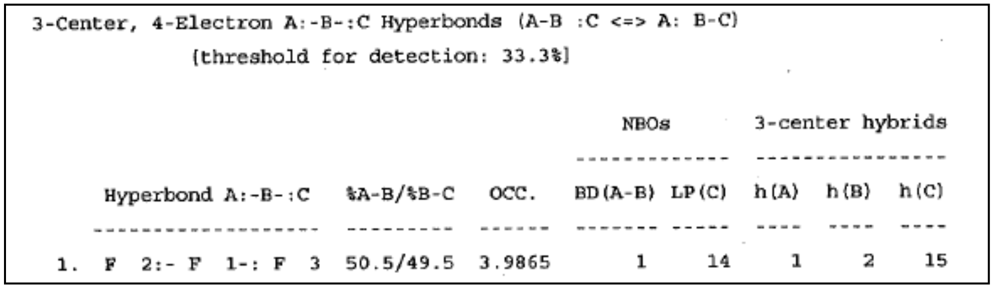
L:A + :L′
II

Resonance between structures I and II gives rise to an ω-bond

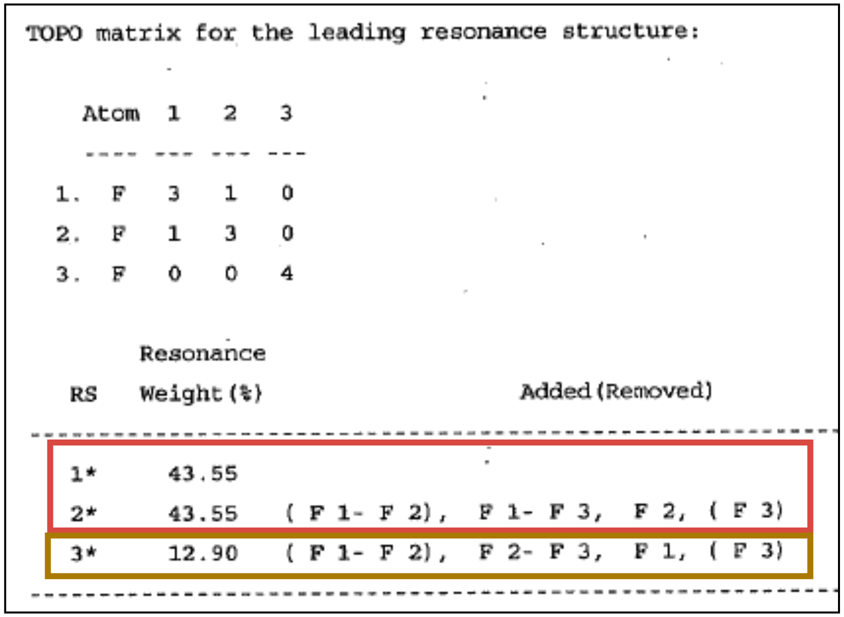
In principle, another resonance contributor is the Harcourt "Long-bond" or $\hat{\sigma}$-bond

F_3^-

3c/4e ω-Bond is a Donor-Acceptor Bond



```
 3-Center, 4-Electron A:-B-:C Hyperbonds (A-B :C <=> A: B-C)
             [threshold for detection: 33.3%]

                                                     NBOs        3-center hybrids
                                                  -------------  ----------------
      Hyperbond A:-B-:C     %A-B/%B-C    occ.    BD(A-B) LP(C)   h(A)  h(B)  h(C)
     -------------------    ---------   ------   ------- -----   ----  ----  ----
  1.  F  2:- F  1-: F  3    50.5/49.5   3.9865       1      14      1     2    15
```

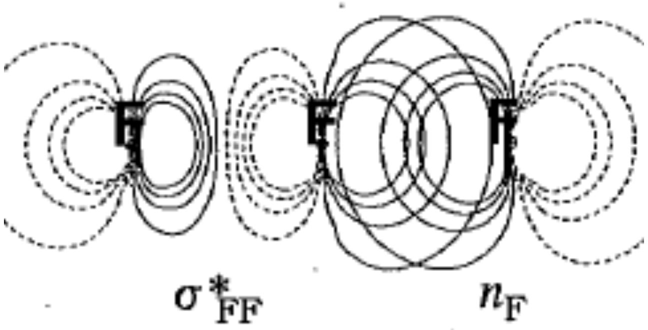


```
 TOPO matrix for the leading resonance structure:

    Atom  1   2   3
    ---- --- --- ---
  1.  F   3   1   0
  2.  F   1   3   0
  3.  F   0   0   4

        Resonance
  RS    Weight(%)                     Added(Removed)
 -------------------------------------------------------------
  1*     43.55
  2*     43.55    ( F 1- F 2),  F 1- F 3,  F 2,  ( F 3)
  3*     12.90    ( F 1- F 2),  F 2- F 3,  F 1,  ( F 3)
 -------------------------------------------------------------
```

3c/4e ω-Bond is a Donor-Acceptor Bond

The lone pair of an F^- donates into the F-F antibond

$n_F \rightarrow \sigma^*_{FF}$ (133.8 kcal/mol)

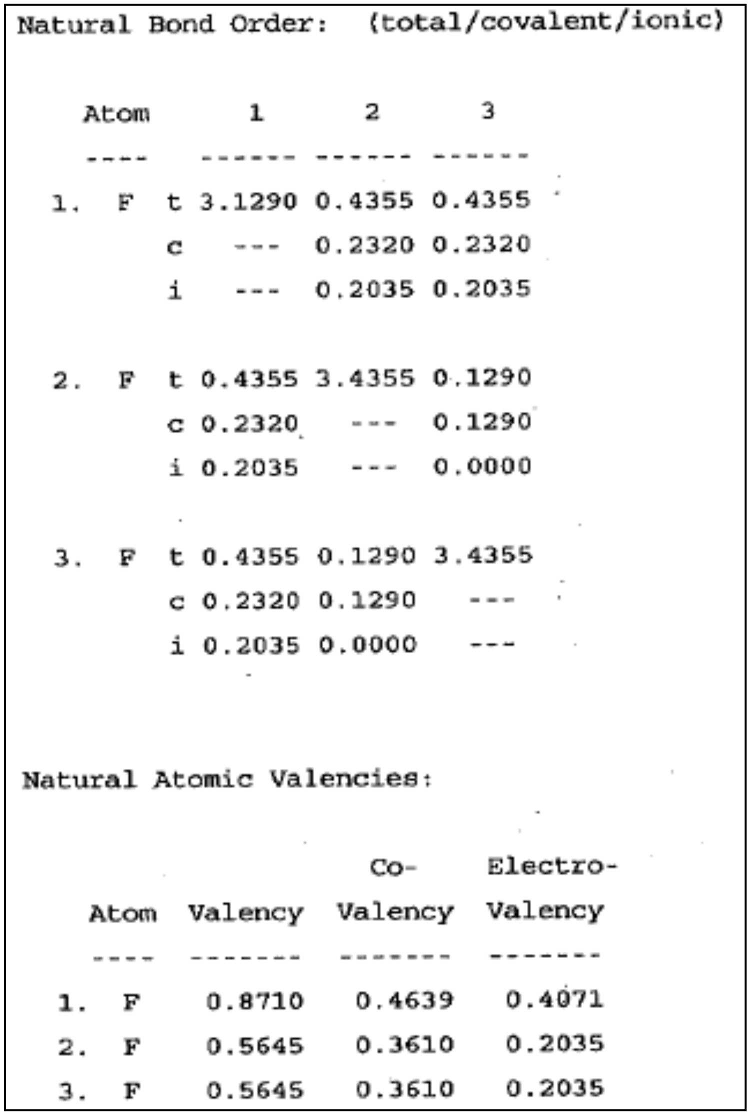


ω-bond

“long”-bond

F_3^-

Summary `NRT` Output: 3c/4e Bond



```
Natural Bond Order:   (total/covalent/ionic)

    Atom        1         2         3
    ----     ------    ------    ------
  1.  F   t 3.1290  0.4355  0.4355
          c   ---   0.2320  0.2320
          i   ---   0.2035  0.2035

  2.  F   t 0.4355  3.4355  0.1290
          c 0.2320    ---   0.1290
          i 0.2035    ---   0.0000

  3.  F   t 0.4355  0.1290  3.4355
          c 0.2320  0.1290    ---
          i 0.2035  0.0000    ---


Natural Atomic Valencies:

                          Co-      Electro-
    Atom   Valency    Valency    Valency
    ----   -------    -------    -------
  1.  F     0.8710     0.4639     0.4071
  2.  F     0.5645     0.3610     0.2035
  3.  F     0.5645     0.3610     0.2035
```

Main Points:
F1-F2 bond order ~ 0.5 (ca. 50% covalent)

F2-F3 bond order ~ 0.13 (100% covalent)

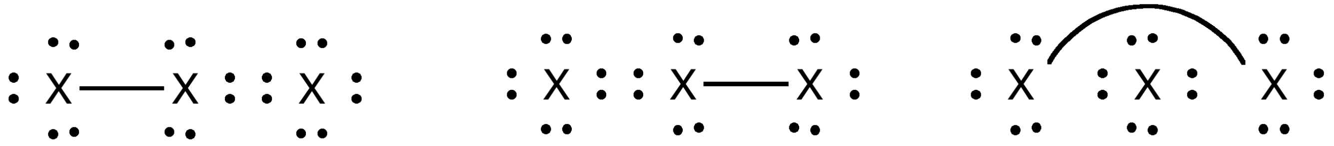
The standard chemical valency of F=1
is NOT exceeded

This is the resonance equivalent of
the Pimentel-Rundle 3c/4e bond.

Trihalides, NRT, and Ab Initio VB

F_3^-

Density-based resonance weights are similar to Ab Initio VB[‡]



X = F	43% (37%)	43% (37%)	13% (26%)
X = Cl	44% (42%)	44% (42%)	12% (15%)
X = Br	43% (41%)	43% (41%)	14% (15%)
X = I	43% (41%)	43% (41%)	14% (15%)

"long-bond" structures

[‡] Braïda & Hiberty *J. Phys. Chem. A* **2008**, *112*, 13045-13052.

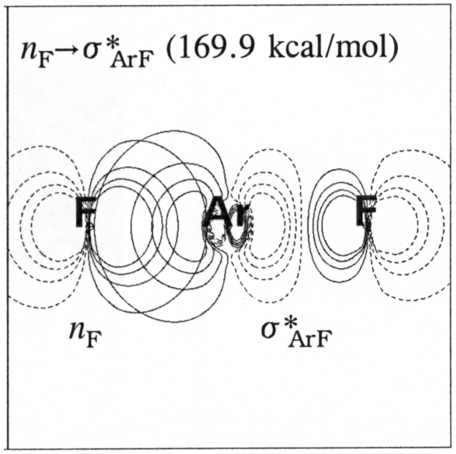
Long-Bonds ($\hat{\sigma}$) and Long-Antibonds ($\hat{\sigma}^*$)

ArF_2 vs. Metastable NeF_2 vs. Metastable HeF_2

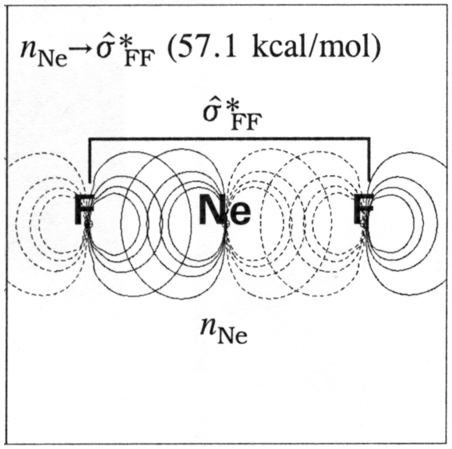
ArF_2	Metastable NeF_2	Metastable HeF_2
87% ω-bonded	26% ω-bonded	46% ω-bonded
13% $\hat{\sigma}$-bonded	74% $\hat{\sigma}$-bonded	53% $\hat{\sigma}^*$-bonded

The ω-, $\hat{\sigma}$-, and $\hat{\sigma}^*$-bonds are donor-acceptor interactions

(b) ArF_2 (ω-bonded)

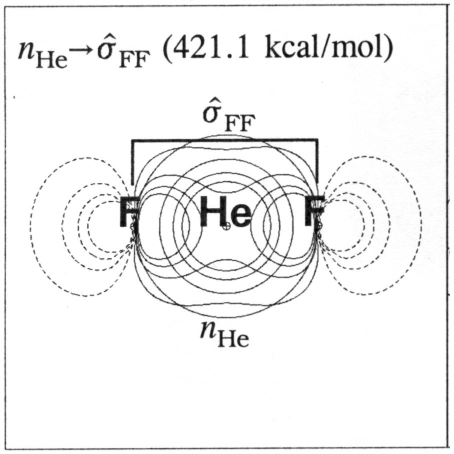


(b) NeF_2 ($\hat{\sigma}$-bonded)



F-F antibond acceptor for Ne *p*-lone pair

(a) HeF_2 ($\hat{\sigma}^*$-bonded)

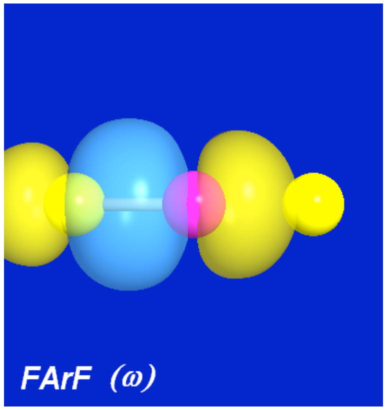


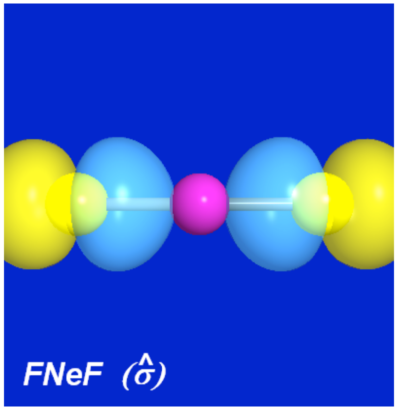
F-F bond acceptor for He *s*-lone pair

Long-Bonds ($\hat{\sigma}$) and Long-Antibonds ($\hat{\sigma}^*$)

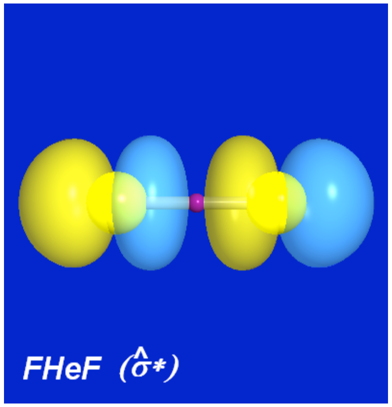
ArF_2 vs.	Metastable NeF_2 vs.	Metastable HeF_2
87% ω-bonded	26% ω-bonded	46% ω-bonded
13% $\hat{\sigma}$-bonded	74% $\hat{\sigma}$-bonded	53% $\hat{\sigma}^*$-bonded

The ω-, $\hat{\sigma}$-, and $\hat{\sigma}^*$-bonds are donor-acceptor interactions





F-F antibond acceptor for
Ne *p*-lone pair

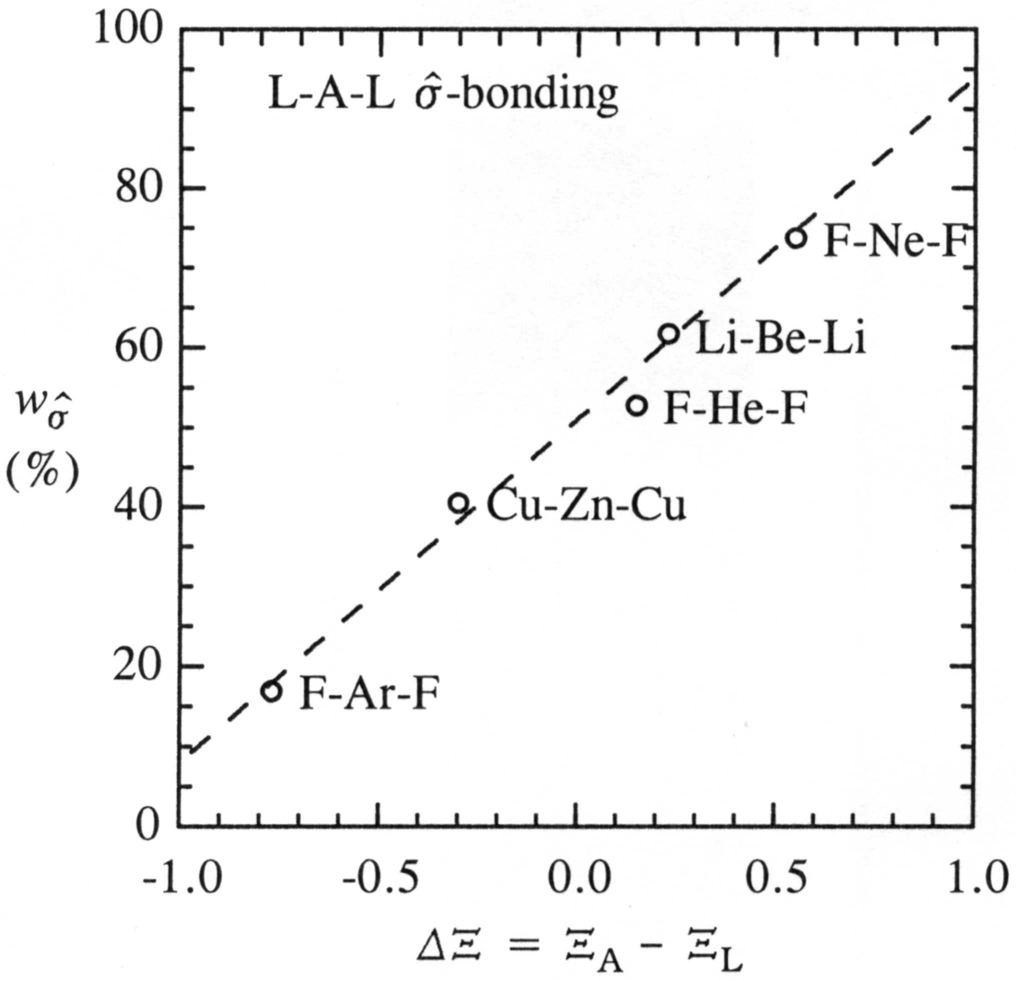


F-F bond acceptor for
He *s*-lone pair

Many Types of Hypervalency

L-A-L'	R_{AL}	Q_A	$w_{I/II}$	w_{III}	$\Delta E^{(2)}{}_{D \to A}$	type
$F\text{-}F\text{-}F^-$	1.745	−0.107	43.6	12.9	133.8	ω
F-Ne-F	1.874	+0.228	13.1	73.7	57.1	$\hat{\sigma}$
F-He-F	1.246	+0.515	23.6	52.8	421.1	$\hat{\sigma}$ *
F-Ar-F	1.878	+0.756	41.6	16.9	169.9	ω
$Li\text{-}Li\text{-}Li^-$	3.011	+0.026	43.2	13.6	27.0	ω
Li-Be-Li	2.504	−0.006	19.2	61.7	55.7	$\hat{\sigma}$ *
$Cu\text{-}Cu\text{-}Cu^-$	2.383	−0.014	41.7	16.7	81.9	ω
Cu-Zn-Cu	2.350	+0.228	29.8	40.5	114.7	$\hat{\sigma}$ *

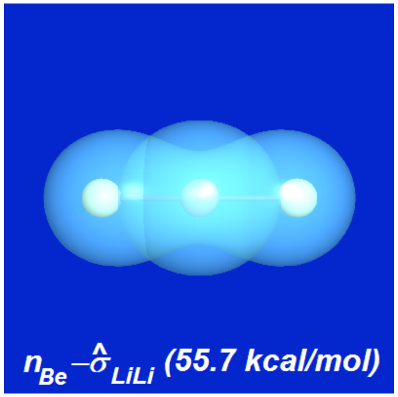
ΔEN and Long-Bond Contributions

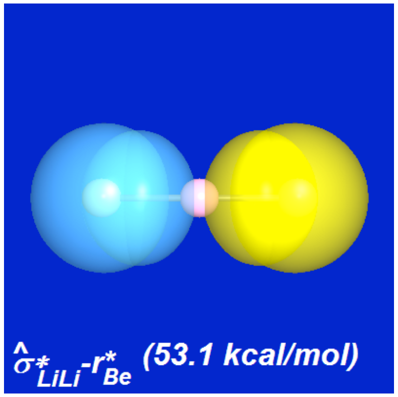


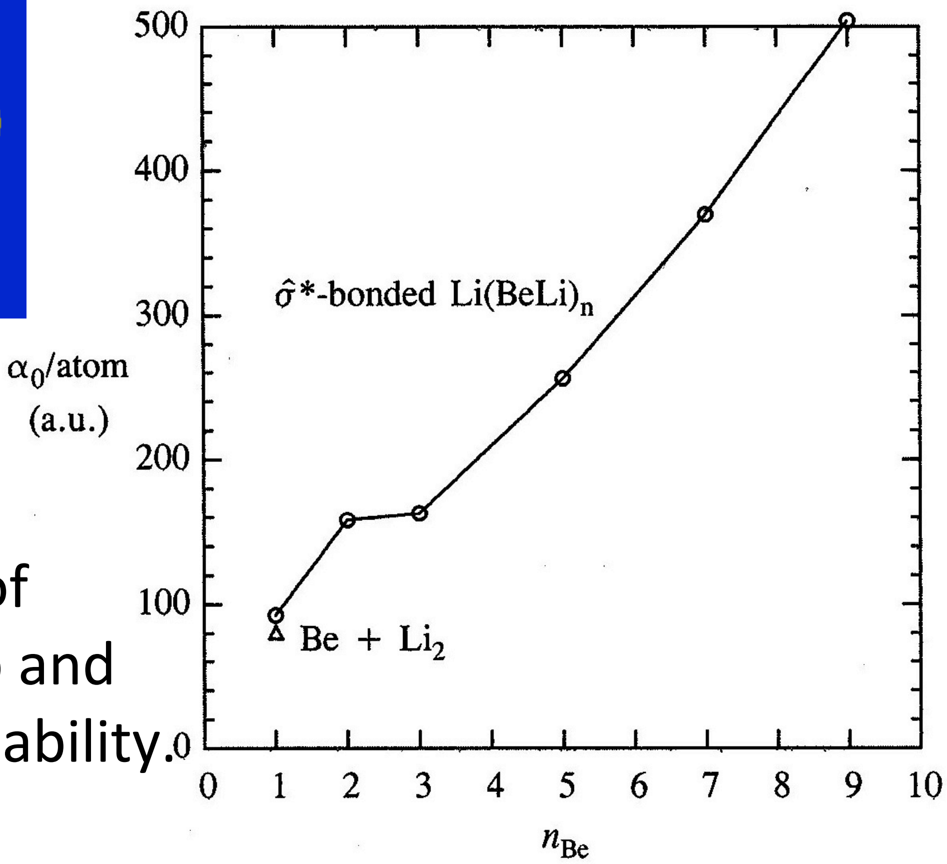
Long-bond resonance structures play a greater role with increasing EN of the termini relative to the central atom.

Li(BeLi)$_n$ Chains and Isotropic Polarizability

Be is both a Donor (Be 2s) to empty Li-Li “bond” and Acceptor (Be 2p) from filled Li-Li “antibond” : *Reciprocal D-A*







Reciprocal D-A interactions in linear chains of Li(BeLi)$_n$ give rise to *cooperative* reduction of atom-centered charge buildup and exponential increase in polarizability.

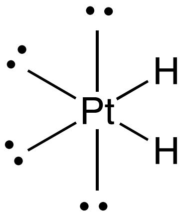
PtH_4^{2-}

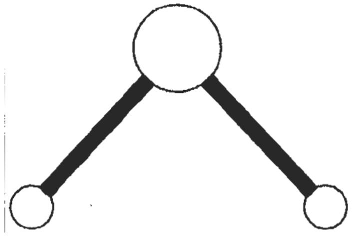
D-block Hypervalency and Buildup

```
 -----------------------------------------------------
   Effective Core              60.00000
   Core                         7.97869 ( 99.734% of   8)
   Valence Lewis               11.89032 ( 99.086% of  12)
  ==================          ============================
   Total Lewis                 79.86901 ( 99.836% of  80)
```

```
  (Occupancy)   Bond orbital/ Coefficients/ Hybrids
 --------------------------------------------------------------
    1. (1.94793) BD ( 1)Pt 1- H 2
( 47.40%)   0.6885*Pt 1 s( 46.74%)p 0.01(  0.48%)d 1.13( 52.78%)
( 52.60%)   0.7252* H 2 s( 99.76%)p 0.00(  0.24%)
```

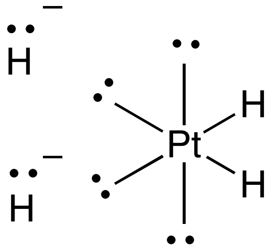
We will work our way from PtH_2 to PtH_4^{2-}




(e) PtH_2 (C_{2v})

2 “sd^1” Pt hybrids, 4 Pt LPs

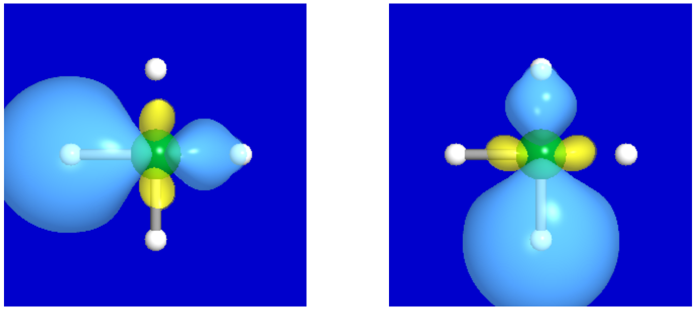
```
67. (0.59820) BD*( 1)Pt  1- H  4
 ( 61.65%)   0.7852*Pt  1 s( 48.36%)p 0.01(  0.29%)d 1.06( 51.36%)
 ( 38.35%)  -0.6193* H  4 s( 99.91%)p 0.00(  0.09%)
68. (0.59820) BD*( 1)Pt  1- H  5
 ( 61.65%)   0.7852*Pt  1 s( 48.36%)p 0.01(  0.29%)d 1.06( 51.36%)
 ( 38.35%)  -0.6193* H  5 s( 99.91%)p 0.00(  0.09%)
```



What acceptors are available?

Pt-H antibonds!

Strong 3c/4e delocalization is evident in the NLMOs

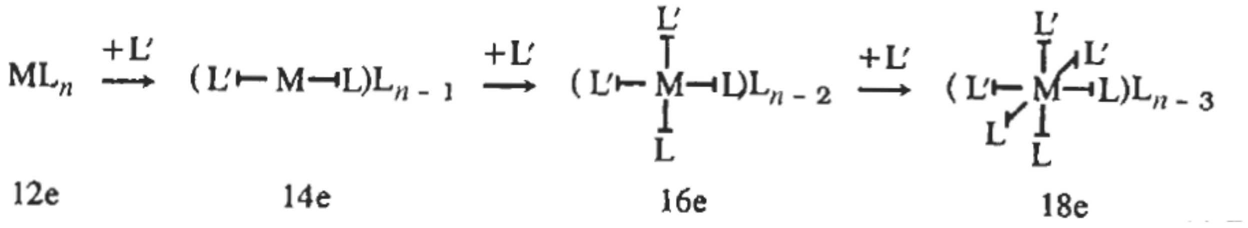


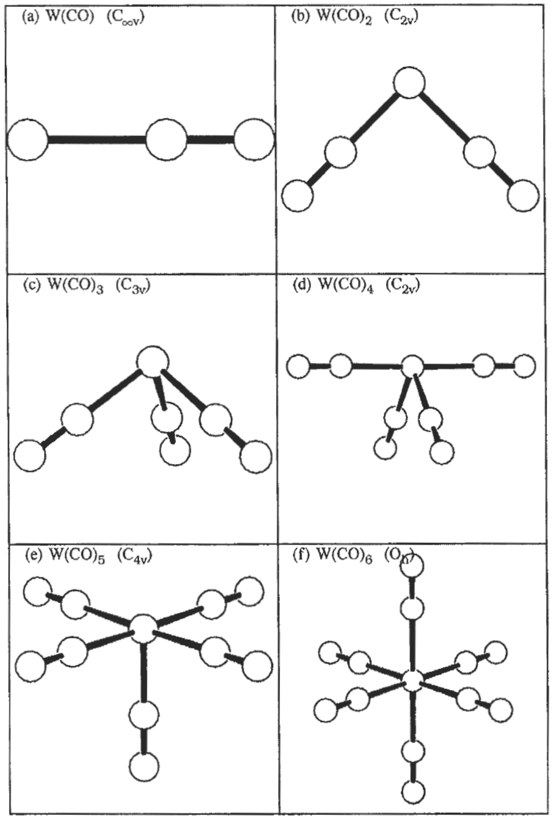
Hypervalency is the rule rather than the exception for TM’s

Strong 3c-4e interactions arise from centrosymmetry of sd^μ NHOs

Understanding “Real” D-Block Complexes

The transition from
12e to 18e complexes
Involves 3c/4e bonding





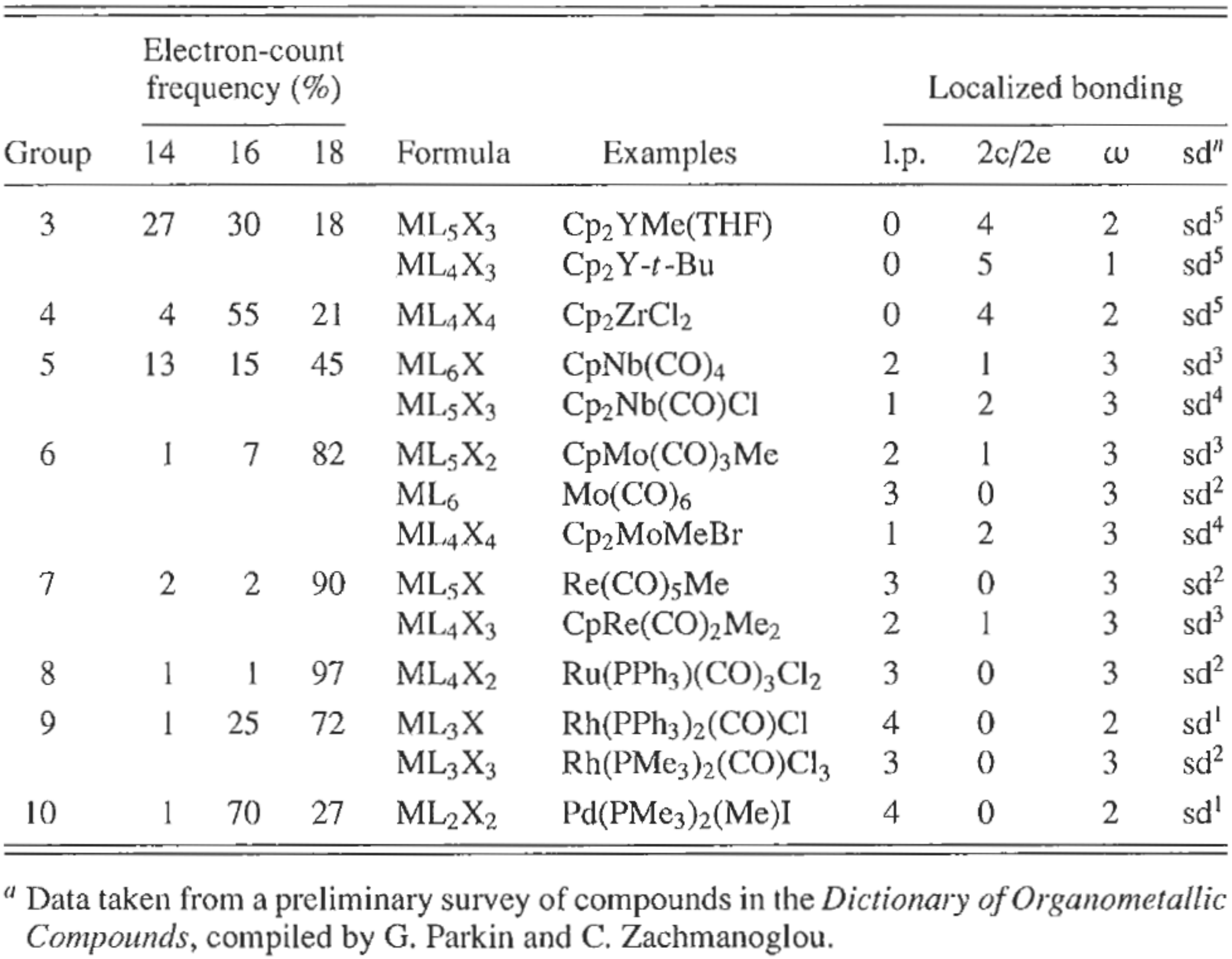
W(CO) - 8e, hypovalent, 1“sd^1” hybrid, 3 LPs, 2 LP*
$W(CO)_2$- 10e, hypovalent,2 “sd^1” hybrids, 3 LPs, 1 LP*

$W(CO)_3$- 12e, e-precise, 2 sd^2 hybrids, 3 LPs, 0 LP*
$W(CO)_4$- 14e, hypervalent, 3 sd^2 hybrids, 3 LPs, 1 ω-bond

$W(CO)_5$ - 16e, hypervalent, 2 sd^2 hybrids, 3 LPs, 2 ω-bonds
$W(CO)_6$ - 18e, hypervalent, 3 sd^2 hybrids, 3LPs, 3 ω-bonds

In all cases there is significant W LP → C=O π^* delocalization

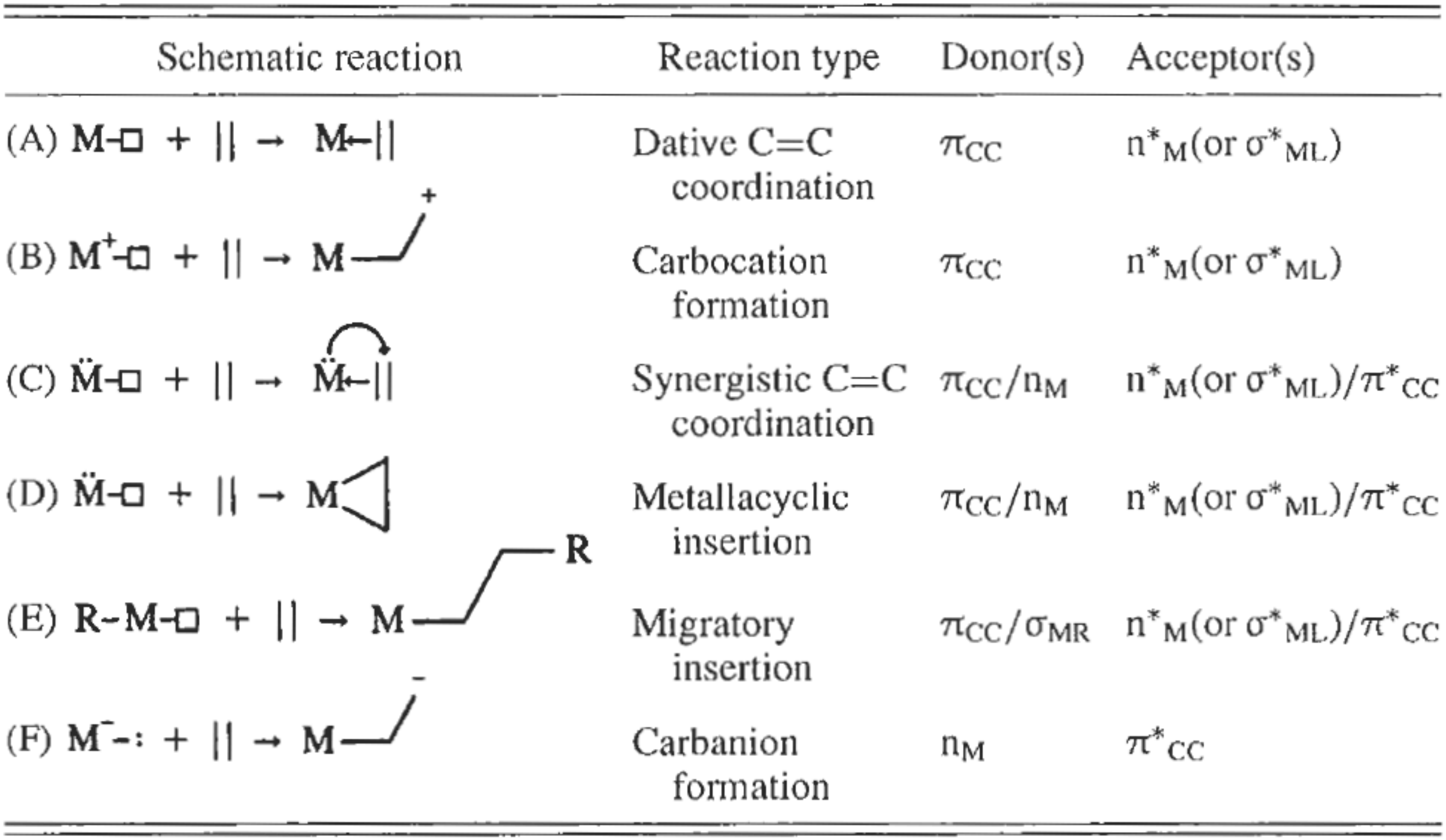
Some “Real” D-Block Complexes



	Electron-count frequency (%)					Localized bonding			
Group	14	16	18	Formula	Examples	l.p.	2c/2e	ω	sd^n
3	27	30	18	ML_5X_3	$Cp_2YMe(THF)$	0	4	2	sd^5
				ML_4X_3	Cp_2Y-*t*-Bu	0	5	1	sd^5
4	4	55	21	ML_4X_4	Cp_2ZrCl_2	0	4	2	sd^5
5	13	15	45	ML_6X	$CpNb(CO)_4$	2	1	3	sd^3
				ML_5X_3	$Cp_2Nb(CO)Cl$	1	2	3	sd^4
6	1	7	82	ML_5X_2	$CpMo(CO)_3Me$	2	1	3	sd^3
				ML_6	$Mo(CO)_6$	3	0	3	sd^2
				ML_4X_4	$Cp_2MoMeBr$	1	2	3	sd^4
7	2	2	90	ML_5X	$Re(CO)_5Me$	3	0	3	sd^2
				ML_4X_3	$CpRe(CO)_2Me_2$	2	1	3	sd^3
8	1	1	97	ML_4X_2	$Ru(PPh_3)(CO)_3Cl_2$	3	0	3	sd^2
9	1	25	72	ML_3X	$Rh(PPh_3)_2(CO)Cl$	4	0	2	sd^1
				ML_3X_3	$Rh(PMe_3)_2(CO)Cl_3$	3	0	3	sd^2
10	1	70	27	ML_2X_2	$Pd(PMe_3)_2(Me)I$	4	0	2	sd^1

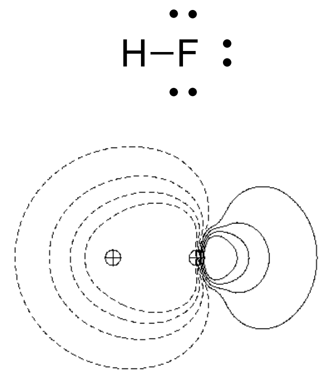
[a] Data taken from a preliminary survey of compounds in the *Dictionary of Organometallic Compounds*, compiled by G. Parkin and C. Zachmanoglou.

Some “Real” D-Block Transformations



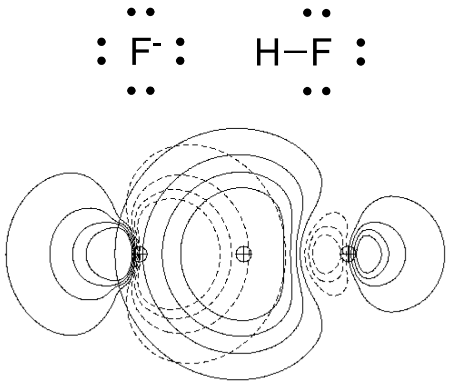
Schematic reaction	Reaction type	Donor(s)	Acceptor(s)
(A) $M{-}\square + \| \rightarrow M{\leftarrow}\|$	Dative C=C coordination	π_{CC}	$n^*_M(\text{or } \sigma^*_{ML})$
(B) $M^{+}{-}\square + \| \rightarrow M{-}\!/^{+}$	Carbocation formation	π_{CC}	$n^*_M(\text{or } \sigma^*_{ML})$
(C) $\ddot{M}{-}\square + \| \rightarrow \overset{\curvearrowright}{\ddot{M}{\leftarrow}\|}$	Synergistic C=C coordination	π_{CC}/n_M	$n^*_M(\text{or } \sigma^*_{ML})/\pi^*_{CC}$
(D) $\ddot{M}{-}\square + \| \rightarrow M\triangleleft$	Metallacyclic insertion	π_{CC}/n_M	$n^*_M(\text{or } \sigma^*_{ML})/\pi^*_{CC}$
(E) $R{-}M{-}\square + \| \rightarrow M{-}\!/{-}R$	Migratory insertion	π_{CC}/σ_{MR}	$n^*_M(\text{or } \sigma^*_{ML})/\pi^*_{CC}$
(F) $M^{-}{-}{:} + \| \rightarrow M{-}\!/^{-}$	Carbanion formation	n_M	π^*_{CC}

CuF & CuF_2^-: Analogs of HF & FHF$^-$

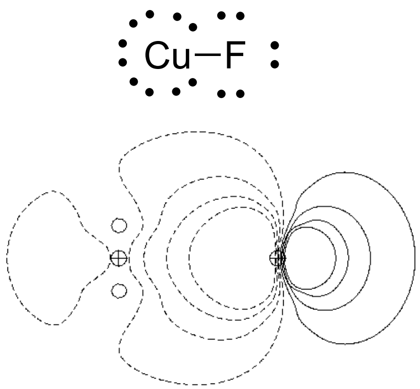


$\sigma_{H\text{-}F} = 0.47H_s + 0.88F_{sp^{3.98}}$

$Q_H = +0.54$

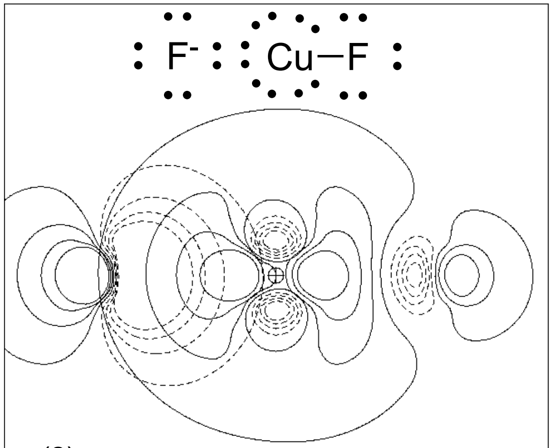


$E^{(2)}(LP_F \rightarrow \sigma^*_{H\text{-}F})$=169 kcal/mol



$\sigma_{H\text{-}F} = 0.34Cu_{sd^{0.13}} + 0.94F_{sp^{3.98}}$

$Q_{Cu} = +0.75$

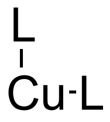


$E^{(2)}(LP_F \rightarrow \sigma^*_{Cu\text{-}F})$=67 kcal/mol

Idealized Geometries of CuL_n

$Cu^{(III)}$

CuL_2,12e
2 2c/2e



CuL_2

C_{2v}

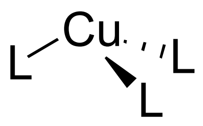
$Cu^{(I)}$

CuL_2,14e
1 3c/4e bonds

L-Cu-L

$D_{\infty h}$

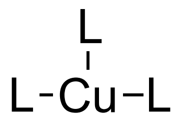
CuL_3, 12e
3 2c/2e



C_{3v}

$Cu^{(III)}$

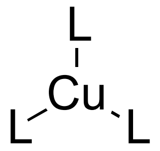
CuL_3, 14e
1 2c/2e & 1 3c/4e



$\overset{L}{L-Cu-L}$

C_{2v}

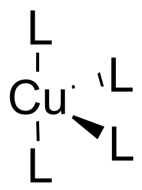
CuL_3, 16e
1 4c/6e bond



D_{3h}

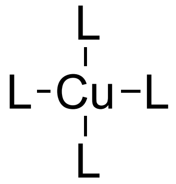
$Cu^{(I)}$

CuL_4, 14e
2 2c/2e, 1 3c/4e



C_{2v}

CuL_4, 16e
2 3c/4e bonds

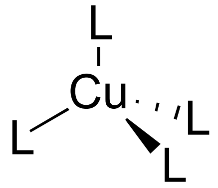


$\underset{L}{\overset{L}{L-Cu-L}}$

D_{4h}

$Cu^{(III)}$

CuL_4, 18e
1 5c/8e bond



T_d

$Cu^{(I)}$

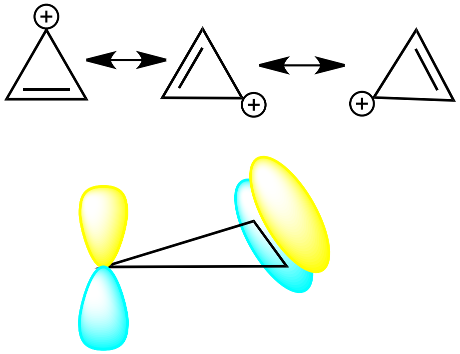
A Localized Perspective on JT Effects

Any non-linear molecule with a spatially degenerate electronic ground state will undergo a geometrical distortion that removes that degeneracy
… but which motion and by how much?

Example: Cyclopropenyl radical

Start at the D_{3h} geometry, closed-shell cations and anions.

$C_3H_3^+$

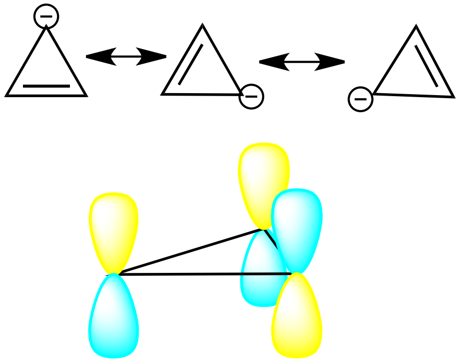


$\pi \rightarrow n_{Cp}$ 270 kcal/mol

C_3H_3

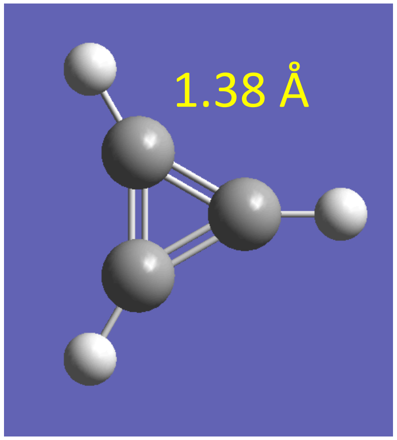
In the radical, the α-spin system emulates the anion whereas the β-spin system emulates the cation.

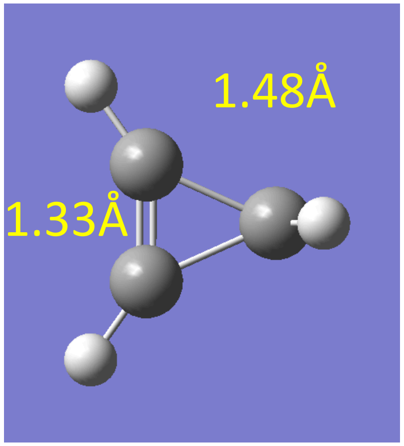
$C_3H_3^-$

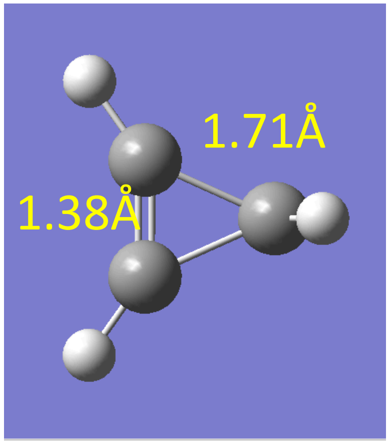


No $n \rightarrow \pi^*$ possible

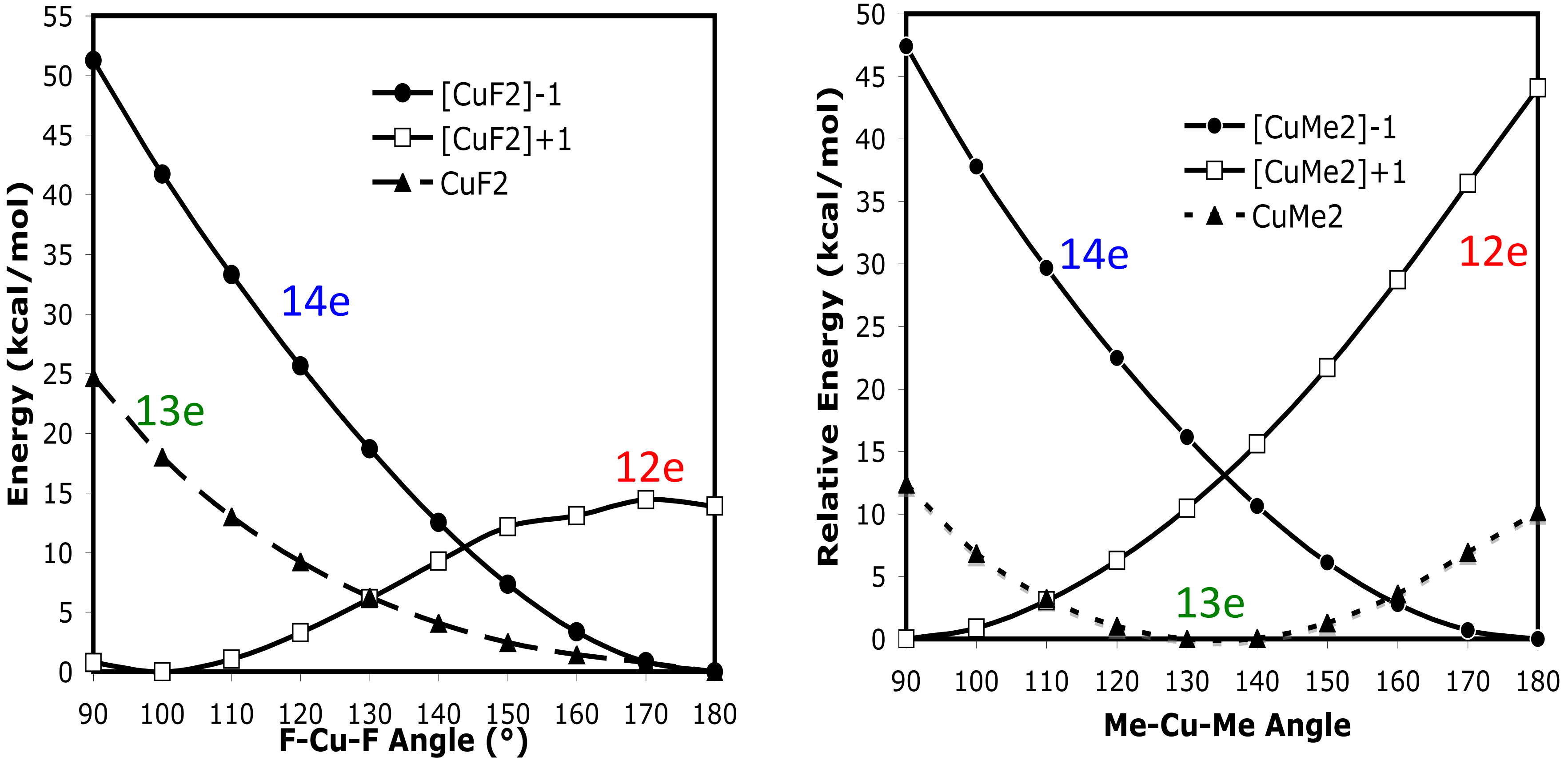
C_3H_3 Radical = Avg. of Anion and Cation







PES for 13e CuL_2 = Mean of 12e & 14e



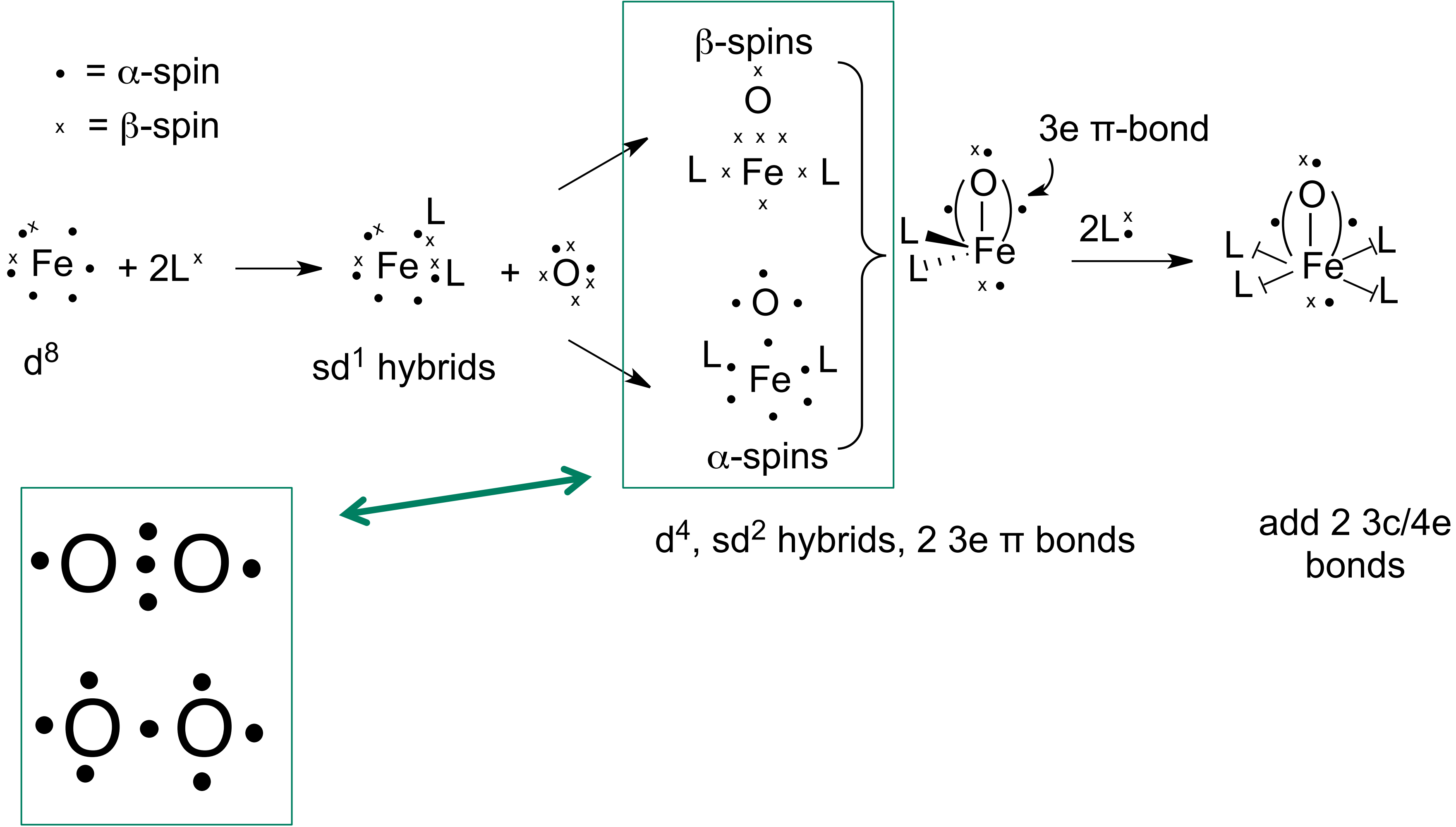
Lewis Structure of FeO(porphyrin)

Starting point: Neutral Fe, O, Porphyrin

Porphyrin = 2 N: and 2 N·

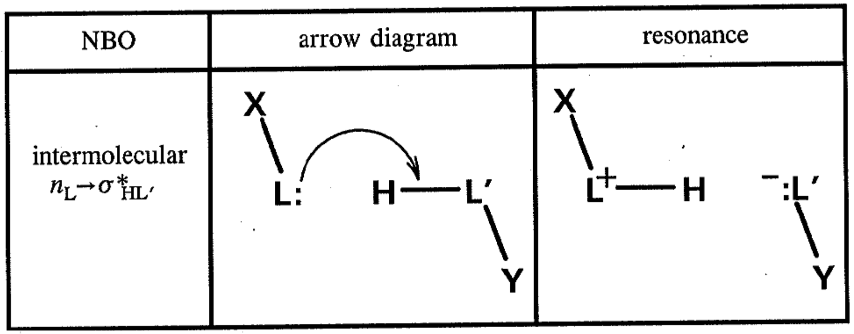
• = α-spin

x = β-spin

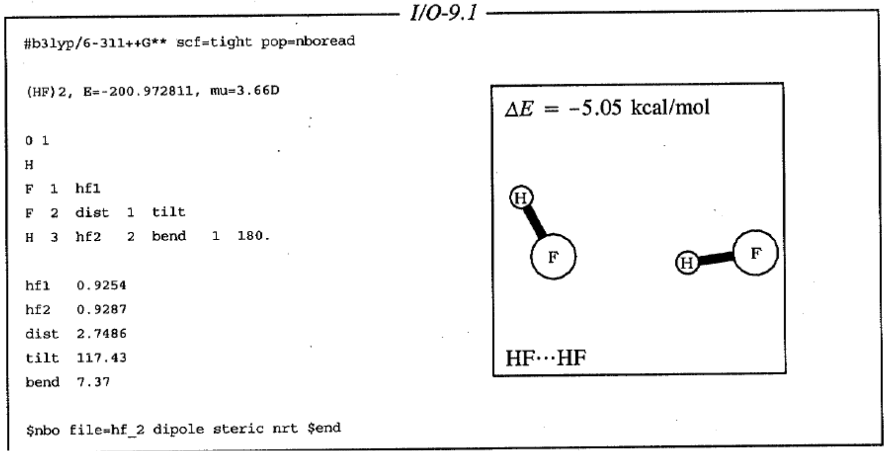


HF•••HF

The Nature of Hydrogen Bonding



NBO	arrow diagram	resonance
intermolecular $n_L \to \sigma^*_{HL'}$		

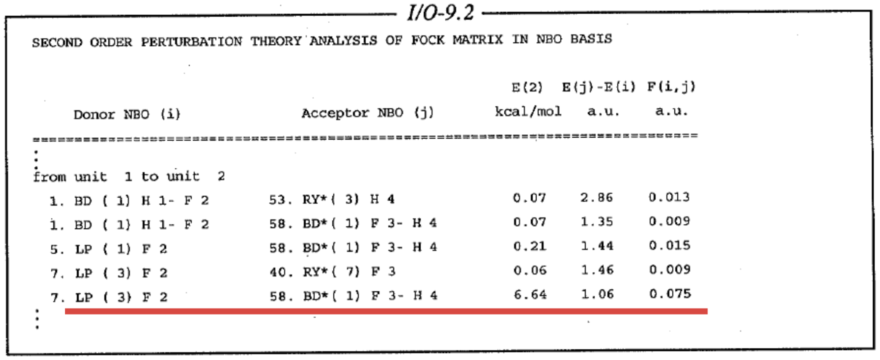


I/O-9.1

```
#b3lyp/6-311++G** scf=tight pop=nboread

(HF)2, E=-200.972811, mu=3.66D

0 1
H
F  1  hf1
F  2  dist  1  tilt
H  3  hf2   2  bend   1  180.

hf1   0.9254
hf2   0.9287
dist  2.7486
tilt  117.43
bend  7.37

$nbo file=hf_2 dipole steric nrt $end
```

$\Delta E = -5.05$ kcal/mol

HF···HF



I/O-9.2

```
SECOND ORDER PERTURBATION THEORY ANALYSIS OF FOCK MATRIX IN NBO BASIS

                                                     E(2)  E(j)-E(i) F(i,j)
    Donor NBO (i)              Acceptor NBO (j)    kcal/mol   a.u.    a.u.
===============================================================================
:
from unit  1 to unit  2
  1. BD ( 1) H 1- F 2        53. RY*( 3) H 4          0.07    2.86    0.013
  1. BD ( 1) H 1- F 2        58. BD*( 1) F 3- H 4     0.07    1.35    0.009
  5. LP ( 1) F 2             58. BD*( 1) F 3- H 4     0.21    1.44    0.015
  7. LP ( 3) F 2             40. RY*( 7) F 3          0.06    1.46    0.009
  7. LP ( 3) F 2             58. BD*( 1) F 3- H 4     6.64    1.06    0.075
:
```

The structure of HF•••FH is not the linear structure expected if the H-bond were electrostatic in nature.

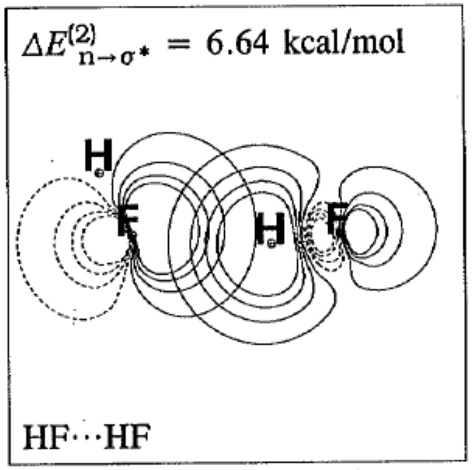
At the B3LYP level the dimer is stabilized by -5 kcal/mol.

How do we characterize this weak but ubiquitous interaction?

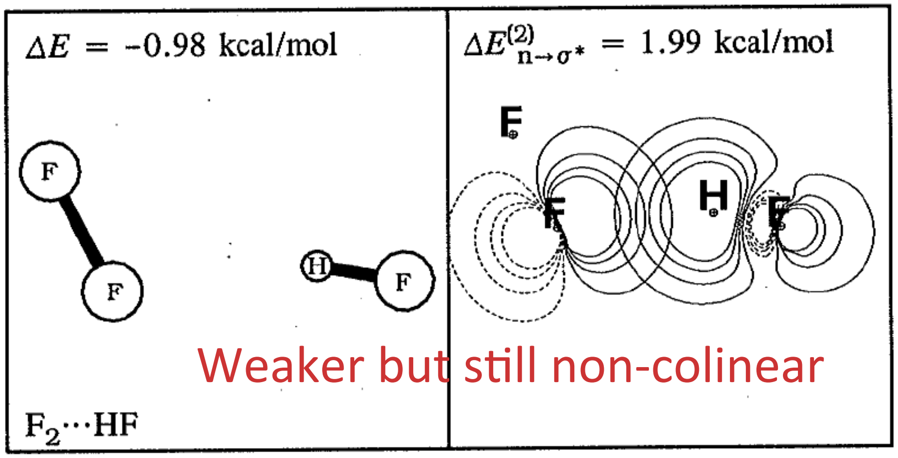
NBO analysis shows strong delocalization involving the F$^{\pi}$LP (off-axis) donating into the H-F σ^* antibond.

$$n_{F(2)} \to \sigma^*_{H(4)F(3)}:\ \Delta E^{(2)}_{D\to A} = 6.64\ \text{kcal/mol}$$

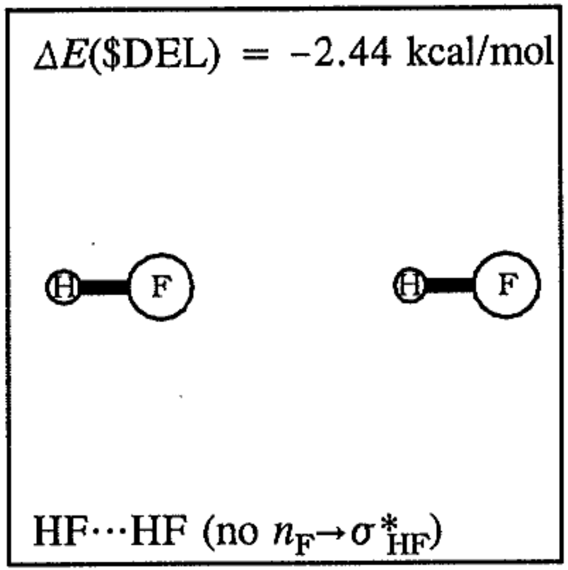
HF•••HF: A Donor-Acceptor Complex



Zero dipole-dipole by replacing one HF with F_2 →



Weaker but still non-colinear



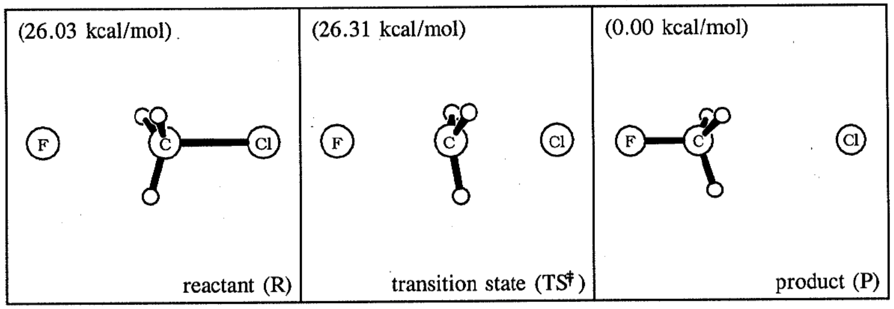
`$DELETE` all delocalizations from Lewis to non-Lewis orbitals (`NOSTAR`) and reoptimize:

- Collinear HF•••HF !
- Dimerization Energy reduced by 1/2
- F-F distance increases by 0.6Å
- After deletion, best described as dipole-dipole complex.

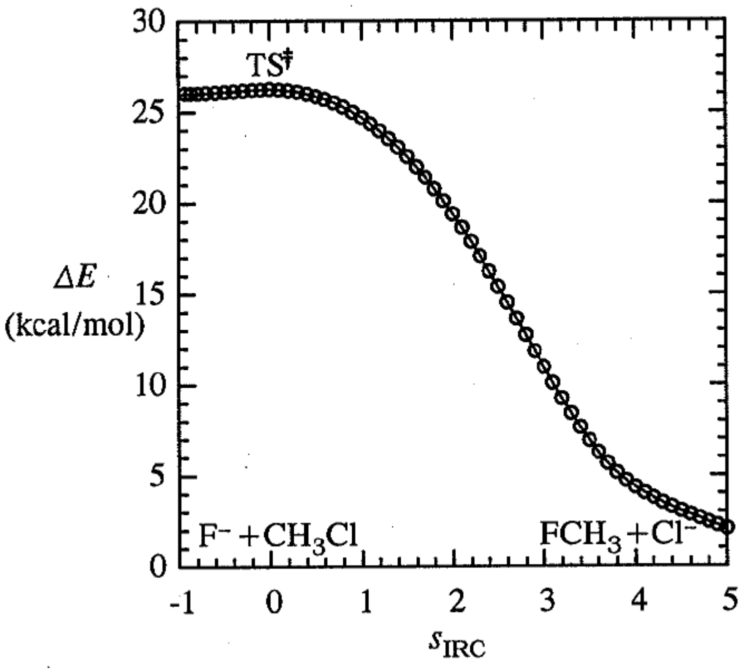
$F^- + ClCH_3$

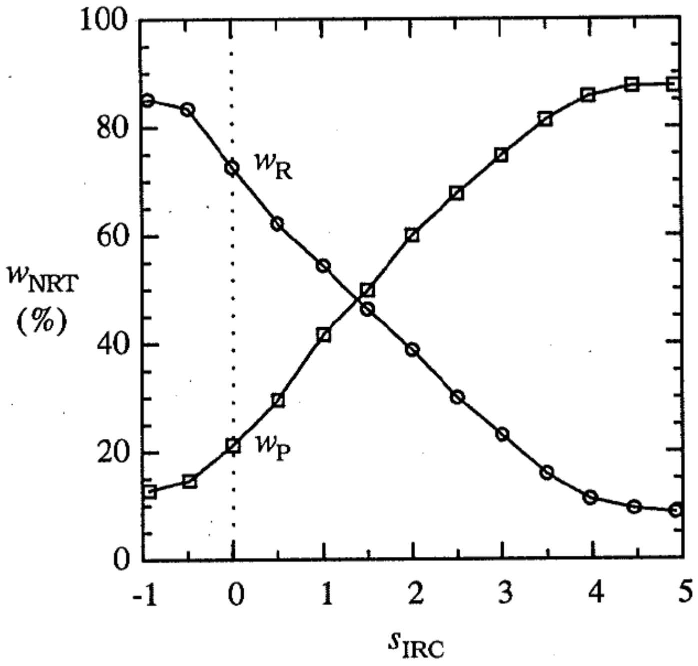
NRT Analysis of S_N2 Reaction

$F^- + CH_3Cl \rightarrow FCH_3 + Cl^-$



- In proceeding through TS‡, strong F^- LP → σ* C-Cl delocalization (3c/4e)
- NRT characterizes TS‡ as "reactant-like" in terms of Hammond Postulate





Summary

- NBO Methods generate localized bond descriptions from Densities
- Localized bond descriptions strongly support Lewis and Lewis-like bonding descriptions across the periodic table
- Lewis-like structures, hybridization, and 3c/4e bonding and other resonance motifs describe the majority of bonding situations
- For unrestricted calculations, “Different Lewis Structures for Different Spins”
- Interpolation between Lewis-like tendencies of α and β spins provides the localized bond alternative to Jahn-Teller rationalizations