18-Electron Rule: Myth or Reality?
An NBO Perspective

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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
- Electronegativity, Hybridation
Computational Chemistry

\[ \mathcal{H} |\psi\rangle = E |\psi\rangle \]

- Geometry
- Method
- Basis Set

Optimization

Energy

Wavefunction

STRUCTURE, PROPERTIES, REACTIVITY
Complex with octahedral geometry

3 non bonding orbitals: up to 6 d electrons possible.

18 electrons rule!
Complex with square planar geometry

3 non bonding orbitals:
up to 6 electrons possible.

1 quasi non bonding orbital:
up to 2 electrons possible.

stable with 16 electrons!
Natural Bonding Orbitals: Concept

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 Strictly 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

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NBO Procedure: Summary

MO → AO → PNAO

1. Intra-atomic diagonalization within each subshell
2. Occupancy weighted orthogonalization
3. Natural charges

MO → NLMO

2nd order perturbation donor-acceptor interactions to cancel off-diagonal red terms

NBO → NAO

Building hybrids on atoms to cancel off-diagonal blue terms
Description of an NBO

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

\[ \sigma^* = 0.8140h_C - 0.5808h_O \]

\[ \sigma = 0.5808h_C + 0.8140h_O \]
Hyperconjugation Interactions

The Empty AntiBonds can Accept Electron Density from the Occupied Bonds: **Departure from Lewis Structure**

- $\sigma^*_{CH}$
- Overlap: 0.2126
- LP$_O$

**Resonance Forms:**

How Stabilizing is this Resonance?
The Departure from the Lewis Structure is Due to Donor-Acceptor Electron Transfers between Occupied and Vacant NBOs.

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

\[ \tilde{\sigma} = \sigma + \lambda \sigma^* \]

The Perturbed NBO Gives Access to Natural Localized Molecular Orbitals which Are Occupied strictly by 2 Electrons

\[ \tilde{\mathcal{P}}_0 = 0.9706\mathcal{P}_0 + 0.1631\sigma^*_{CH} + 0.1631\sigma'^*_{CH} \]
Group 3-12 binary oxides, chlorides and alkyl compounds that are available most cheaply and in largest quantities follow a simple relation.

\[ |G_M - 6| + n_X V_X + e_u = 6 \]

- \( G_M \): Group Number of the Metal
- \( n_X \): Number of X Ligands
- \( V_X \): Valency of the X Ligand
- \( e_u \): Number of Unpaired Electron

chlorides

<table>
<thead>
<tr>
<th>Clusters</th>
<th>ScCl3</th>
<th>TiCl4</th>
<th>NbCl5</th>
<th>WCl5</th>
<th>RuCl3</th>
<th>RhCl3</th>
<th>PdCl2</th>
</tr>
</thead>
<tbody>
<tr>
<td>oxides</td>
<td>Sc2O3</td>
<td>TiO2</td>
<td>Nb2O5</td>
<td>WO3</td>
<td>RuO2</td>
<td>Rh2O3</td>
<td>PdO</td>
</tr>
<tr>
<td>alkyls</td>
<td>ZrMe4</td>
<td>NbMe5</td>
<td>Me6</td>
<td>Me6</td>
<td>Me6</td>
<td>Me6</td>
<td></td>
</tr>
</tbody>
</table>
Each bond linkage to a **monovalent ligand X** is associated with a shared pair of electrons:

\[ e_{bp} = 2n_X V_X \]

Each bond linkage to a **Lewis base L** is associated with a dative pair of electrons:

\[ e_{dp} = 2n_L \]

For a closed shell compound with \( G_M \geq 6 \), the empirical rule gives:

\[ G_M - n_X V_X + e_{bp} + 2n_L = 12 \]

with the non-bonded lone pair electrons

\[ e_{lp} = G_M - n_X V_X \]

The dodectet rule holds:

\[ e_{bp} + e_{lp} + e_{dp} = 12 \]
In each case, NBO gives a Lewis structure that obeys the dodectet rule.

Only one s and five d orbitals are necessary to build the hybrids on the metal able to accommodate 6 pairs of electrons.
sd Hybridation

Geometry Dictated by Hybridation between s and d Orbitals

<table>
<thead>
<tr>
<th></th>
<th>$\alpha_{\text{acute}}$</th>
<th>$\alpha_{\text{obtuse}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>sd</td>
<td>90.0</td>
<td>90.0</td>
</tr>
<tr>
<td>sd$^2$</td>
<td>90.0</td>
<td>90.0</td>
</tr>
<tr>
<td>sd$^3$</td>
<td>70.53</td>
<td>109.47</td>
</tr>
<tr>
<td>sd$^4$</td>
<td>65.91</td>
<td>114.09</td>
</tr>
<tr>
<td>sd$^5$</td>
<td>63.43</td>
<td>116.57</td>
</tr>
<tr>
<td>sd$^{10}$</td>
<td>58.91</td>
<td>121.09</td>
</tr>
<tr>
<td>d</td>
<td>54.74</td>
<td>125.26</td>
</tr>
</tbody>
</table>

$\angle H - W - H = 62.4^\circ \ 67.0^\circ \ 114.6^\circ$
Influence of a $\pi$-Accepting Ligand

The $\pi$-back-donation from a lone pair on the metal to a $\pi$-accepting orbital on the ligand induces changes in the preferred geometries.
sd$^4$ Hybridation

$65.9^\circ$ and $114.1^\circ$

NLMO: $\tilde{\sigma}_{WH} = 0.92\sigma_{WH} - 0.33\pi^*_CO$

%NRT

\begin{align*}
\text{H}_3\text{W} &= 37.9 \\
\text{H}_3\text{W} &= 37.0 \\
\text{H}_3\text{W} &= 6.2 \\
\text{H}_3\text{W} &= 5.9
\end{align*}
$\text{W(CO)}_3$ and $\text{W(CO)}_6$

$\text{W(CO)}_3$ : Three Lone Pairs Involved in Back-Bonding

$\text{W(CO)}_6$ is Hypervalent (18-e) with 3-Centers 4-Electrons Bonds

\[
\begin{align*}
\sigma (\text{W-C}) & \quad \text{LP(W)} & \quad \text{LP(C)} \\
\text{NBO} & -0.527 & -0.178 & -0.204 \\
\text{NLMO} & -0.638 & -0.272 & -0.600
\end{align*}
\]
The vast majority of transition metal complexes are either octahedral or square planar with 18- or 16-electrons, respectively. The mechanism to override the 12-electron rule and to add extra ligands involves a particular type of bonding, the 3c-4e \( \omega \)-bond introduce by Pimentel to describe bonding in hypervalent main group compounds.
Kubas’ Complex

The first dihydrogen complex $W(CO)_3(PR_3)_2(H_2)$ is a typical octahedral complex following the 18-electron rule.

The Lewis structure proposed by NBO contains a $W(CO)_2(PR_3)$ 12-electron fragment and three entities (CO, PR$_3$, H$_2$) in interaction through 3-center 4-electron $\omega$-bonds to reach an 18-electron configuration.

$sd^2$ Hybridation: three M-L bonds at 90°.
Analyzing Electron Transfer Upon Coordination

The composition of the NLMO allows to estimate the strength of $\sigma$-donation from the ligands.

$$\tilde{\sigma}(H_2) = 0.92\sigma(H_2) + 0.37\sigma^*(WC)$$
$$\tilde{LP}(P) = 0.86LP(P) + 0.46\sigma^*(WP)$$
$$\tilde{LP}(C) = 0.87LP(C) + 0.46\sigma^*(WC)$$
The composition of the NLMO allows to estimate the strength of $\pi$-back-donation from the metal.

\[ \tilde{LP}(W) = 0.90LP(W) + 0.3\pi^*(CO) + 0.2\sigma^*(H_2) \]
\[ \tilde{LP}(W) = 0.87LP(W) + 0.3\pi^*(CO) + 0.3\pi'^*(CO) \]
\[ \tilde{LP}(W) = 0.85LP(W) + 0.32\pi^*(CO) + 0.28(\pi'^*(CO) + \pi''^*(CO)) \]
Analyzing Trans Influence

The composition of the $\tilde{\sigma}(H_2)$ and $\tilde{LP}(W)$ NLMOs allows to estimate the strength of $\sigma$-donation and $\pi$-back-donation.

<table>
<thead>
<tr>
<th></th>
<th>H–H (Å)</th>
<th>$\tilde{\sigma}(H_2)$</th>
<th>$\tilde{LP}(W)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO</td>
<td>0.853</td>
<td>$0.92\sigma(H_2) + 0.37\sigma^*(WC)$</td>
<td>$0.90LP(W) + 0.3\pi^<em>(CO) + 0.2\sigma^</em>(H_2)$</td>
</tr>
<tr>
<td>NHC</td>
<td>0.930</td>
<td>$0.895\sigma(H_2) + 0.418\sigma^*(WC)$</td>
<td>$0.86LP(W) + 0.18\pi^<em>(CN) + 0.28\sigma^</em>(H_2)$</td>
</tr>
<tr>
<td>PH$_3$</td>
<td>0.943</td>
<td>$0.886\sigma(H_2) + 0.432\sigma^*(WC)$</td>
<td>$0.91LP(W) + 0.29\sigma^*(H_2)$</td>
</tr>
</tbody>
</table>

Observed H–H bond distance results from both $\sigma$-donation and $\pi$-back-donation.
Guidelines

- In general, an octahedral ML$_6$ d$^6$ complex will have a structure where the strong $\sigma$-donors are creating a $C_{3v}$ like ML$_3$ 12-electron fragment with mutual 90° angles.
- The three remaining ligands are engaged in non-symmetric $\omega$-bonds and the composition of the NLMOs gives access to the extent of charge transfers from the ligand to the metal and from the metal to the ligand.
- The best situation for the structure is obtained when the weakest ligand is trans to the strongest one.
- The same situation holds for ML$_4$ d$^8$ complexes with a $C_{2v}$-like 12-electron building block.
- Again the same pattern is valid for ML$_2$ d$^{10}$ systems with a 12-electron M-L unit as the Lewis structure.
Many catalytic cycles are drawn with particular emphasis on the number of electrons but not on the relative positions of the various ligands with different stereoelectronic properties.
Wilkinson’s catalyst is hypervalent with 16-electron and upon phosphine dissociation another hypervalent complex is formed (14-electron).

The ML$_3$ intermediate has a T-geometry and not a Y-shape.

**The phosphine engaged in an $\omega$-bond dissociates.**
Dihydrogen Activation

The vacant site trans to P does not allow too strong ethylene coordination and affords an easy pathway for $\text{H}_2$ oxidative addition.

The ML$_5$ intermediate is not a trigonal bipyramid.

The oxidative addition is easy because the nature of the M-P bond trans to H can change smoothly.
The catalyst needs to adapt the relative position of the ligands to open a low energy pathway.

Best to avoid situations with two strong donor ligands mutually trans.
The easiest pathway preserves a situation where the three strongest ligands in each step are creating a pseudo $C_{3v}$ $ML_3$ fragment with the three remaining ligands engaged in $\omega$-bonds.
Muraï’s Reaction

Selective C–C coupling in ortho of the carbonyl group. Ru(H₂)₂(H)₂(PR₃)₂ allows to work in mild conditions, contrary to the catalyst developped by Muraï, Ru(CO)(H)₂(PPh₃)₃.

Substituting the carbonyl with pyridine impedes the C-C coupling but leads to the characterization of the C–H activation product.
Ortho C-H activation with chelation

Formation of the agostic interaction more difficult than actual C–H cleavage.

$\sigma$-CAM mechanism preserves the optimal relative position of the ligands
Ethylene Insertion into Ru–H or Ru–C?
Ethylene Insertion

Coordination cis to aromatic ring is mandatory to achieve low barrier for insertion into Ru-H.

Insertion is associated with H transfer from H₂ to H.

Here again the typical ML₃ fragment of strong donors is maintained.
C-C Coupling

Isomerization to cis phosphines is necessary to achieve a geometry adapted to C-C coupling.

H–H cleavage is necessary to keep the cis phosphine complex at low energy
Catalytic Cycle

1. Oxidative cleavage of C-H
2. Reductive coupling of H-H
3. Insertion of CH2=CH2 into Ru-H
4. Coordination of O=C
5. Reductive coupling of C-C
6. Oxidative cleavage of H-H
7. Product release
8. Coordination of CH2=CH2
9. Isomerization to cis P

decoordination O=C
coordination CH2=CH2
Transition metals use essentially s and d orbitals to create bonds with the ligands: **sd\(^n\) hybridation**

A stable configuration is reached when 6 pairs of electrons surround the metal: **dodectet rule**

Hypervalency is easily obtained through donation from a lone pair into a M-X antibond: **ω-bond**.

18-electron or 16-electron complexes are hypervalent and the relative positions of the strong donor ligands follow the dodectet rule: **sd\(^2\) or sd hybridation**.

Dodectet rule also explains the mutual position of the ligands along a catalytic cycle.