Gaussian Calculations of Simple Organometallic Molecules: technical aspects

“Practical theoretical chemistry”

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Presentation

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Gaussian Calculations of Simple Organometallic Molecules: technical aspects

- Introduction

- Practical theoretical chemistry
  - Gaussian program
  - Input file
  - Running the calculation
  - Information from output

- Types of complexes to be analyzed
  - Metal carbonyls
  - Metal olefin complexes

- Theoretical chemistry “on paper”
Selected Bibliography:


Some useful links:

Glossary of Common Terms and Abbreviations in Quantum Chemistry
http://cccbdb.nist.gov/glossary.asp

The Absolute Beginners Guide to Gaussian (David Young)
http://www.ccl.net/cca/documents/dyoung/topics-orig/gaussian.html

Background Reading for Basis Sets
http://www.shodor.org/chemviz/basis/teachers/background.html

UNIX Tutorial for Beginners
http://www.ee.surrey.ac.uk/Teaching/Unix/

vi Editor Commands
http://www.cs.rit.edu/~cslab/vi.html

Etc.
Introduction

BACK
“Every attempt to employ mathematical methods in the study of chemical questions must be considered profoundly irrational and contrary to the spirit of chemistry.”
Auguste Compte, French philosopher, 1830

TODAY
Computational chemistry is a standard tool of science. For example, there are now >20 journals devoted to the subject.

Chemometrics and Intelligent Laboratory Systems
Computational and Theoretical Polymer Science
Electronic Journal of Theoretical Chemistry
International Journal of Quantum Chemistry
Journal of Chemical Information and Computer Sciences
Journal of Chemical Theory and Computation
Journal of Chemometrics
Journal of Computational Chemistry
Journal of Computer Aided Chemistry
Journal of Mathematical Chemistry
Theoretical Chemistry Accounts (Theoretical Chimica Acta)

Journal of Molecular Graphics and Modelling
Journal of Molecular Modeling
Journal of Molecular Structure: THEOCHEM
Journal of the Chemical Computing Group
Journal of Theoretical and Computational Chemistry
Macromolecular Theory and Simulations
Perspectives in Drug Discovery and Design
Proteins Structure, Function, and Genetics
Structural Chemistry
At one time, computational chemistry techniques were used only by experts extremely experienced in using tools that were for the most part difficult to understand and apply. Today, advances in software have produced programs that are easily used by any chemist…”

TODAY

I am… any chemist
You are… any chemists
What type of calculations?

DFT (Density Functional Theory)

• DFT is an exact re-formulation of quantum mechanics in terms of probability density instead of wave function.

• The ground state energy was obtained from a minimization of the $E[\rho]$ functional (this functional exists, but is unknown). The Kohn-Sham method is the employed methodology.
The Nobel Prize in Chemistry 1998

"for his development of the density-functional theory"

Walter Kohn
1/2 of the prize
USA
University of California
Santa Barbara, CA, USA
b. 1923
(in Vienna, Austria)

"for his development of computational methods in quantum chemistry"

John A. Pople
1/2 of the prize
United Kingdom
Northwestern University
Evanston, IL, USA
b. 1925
d. 2004
Introduction

References from SciFinder® database for “Quantum Chemistry” and “Density Functional Theory” (last 10 years).
Publications on *Web of Science* for the years 1994–2008 with the topics density functional theory (DFT) and B3LYP.

Percentage share of papers with the topic density functional theory or DFT in the more general areas of organometallic and homogeneous catalysis (1996–2008, *Web of Science*).

Deviation between calculated and experimental bond lengths for several families of compounds as a function of the calculation type.
What type of program?

Gaussian

http://www.gaussian.com/

An electronic structure package capable of predicting many properties of atoms, molecules, reactive systems, (e.g.; molecular energies, structures, vibrational frequencies, electron densities, ...) utilizing *ab initio*, density functional theory, semi-empirical, molecular mechanics, and various hybrid methods.
Gaussview

http://www.gaussian.com/gv_plat.htm

Graphical interface for Gaussian

• build molecules or reactive systems
• setup Gaussian input files
• graphically examine results

Additional information about

• Overview of Capabilities and Features
See: http://www.gaussian.com/g_prod/gv5b.htm
Where?

Centro Informático Científico de Andalucía
Where?

Camerino
PC room

SSH protocol

CICA
pool.cica.es
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- Types of complexes to be analyzed
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  - Metal olefin complexes

- Theoretical chemistry “on paper”
Login:

- From your terminal, open the SSH program
Login:

- In the SSH window open Quick Connect
Login:
- In the SSH window open Quick Connect
Login:

- Write:

  Host name: pool.cica.es
  User Name: eucheme# (where # is 01-25)

Click eucheme01
Login:

- Write your password: acaoc#0809 (where # is 01-25)
Login:

- You are at CICA (Sevilla) in your account:
eucheme#@pool.cica.es (where # is 01-25)
Policy:

- Each student must work exclusively on the assigned account.

- The system works with queues (it is forbidden to run interactively any program) and it is necessary to create the specific script file \texttt{lanza.sge} (example in your account) to run the Gaussian program.

- For working on the CICA system (pool.cica.es), it is necessary to known a few UNIX commands and also to know the use of vi editor.

Selected UNIX and vi commands are available at:

http://personal.us.es/galindo/Commands.pdf
- Practice for a few minutes with the UNIX commands…

* List files in directory          * ls

   You have the files: NiCO4.com and lanza.sge *

* To know the working directory   * pwd

   This is: /home/eucheme#

* Copy file f1 into f2            * cp f1 f2

* Delete (remove) file f2         * rm f2

* List file contents by screen    * more f1

…

* NiCO4.com is the input file of the Ni(CO)$_4$ molecule.
lanza.sge is the script file for submitting the job.
- Edit the file NiCO4.com and practice a few minutes with vi commands:

  > vi NiCO4.com

  move to the last line in the file                           G
  delete character under cursor                           x
  delete line under cursor                                dd
  replace character under cursor with next character typed r
  finds a word going backwards                           ?word
  finds a word going forwards                             /word
  undoes last command issued                             u

**IMPORTANT:**

Do not use the mouse with the vi mode.

Do not change now the files, exit with :q!

To exit vi and save changes :wq
To exit vi without saving changes :q!
- Edit the file lanza.sge and practice a few minutes with vi commands:
  
  > vi lanza.sge

**Inserting**

*insert before cursor*  
```
i
```

*append after cursor*  
```
a
```

*open line above cursor and enter append mode*  
```
O
```

*To enter vi command mode*  
```
[esc]
```

**IMPORTANT:**

*Do not use the mouse with the vi mode.*

*Do not change now the files, exit with :q!*
- To submit a job and run the Gaussian program it is necessary to prepare the corresponding script file: `lanza.sge` (it exists in your directory)

- When you have edited this file, its structure is:

```bash
#$ -S /bin/bash
#$ -N pruebaGaussian
#$ -cwd
#$ -q acaoc
#$ -o IP.out
#$ -pe make 2

export g03root=/home/deposito/G03Linda/
export G03BASIS=/home/deposito/G03Linda/g03/basis
export GAUSS_ARCHDIR=/home/deposito/G03Linda/g03/arch
export GAUSS_EXEDIR=/home/deposito/G03Linda/g03/bsd:/home/deposito/G03Linda/g03

/home/deposito/G03Linda/g03/g03 /home/eucheme01/NiC04.com
```

Order to execute the program  Input file to be calculated
Gaussian files:

Gaussian program

Read carefully the document GaussFiles.

See it at

http://personal.us.es/galindo/GaussFiles.pdf

More information at

http://www.gaussian.com/
- To run the Gaussian program it is necessary to prepare the corresponding input file: NiCO4.com (it exists in your directory)
- When you have edited this file, its structure is:

```
%mem=1GB
%nproc=2
%CHK=NiCO4.chk
# B3LYP 6-31G* opt

Ni(CO)4 Td

0 1
Ni   0.000000  0.000000  0.000000
C   1.045712  1.045712  1.045712
O   1.707458  1.707458  1.707458
C  -1.045712 -1.045712  1.045712
O  -1.707458 -1.707458  1.707458
C  -1.045712  1.045712 -1.045712
O  -1.707458  1.707458 -1.707458
C   1.045712 -1.045712 -1.045712
O   1.707458 -1.707458 -1.707458
```
Input file structure

Filename.com (or Filename.inp or Filename.gjf)
Free format, case insensitive
Spaces, commas, tabs as delimiters between keywords
! as comment line/section

Divided into sections (in order)

• Link 0 commands (%)
• Route section – what calculation is to do
• Title
• Molecular specification
• Optional additional sections
%mem=1GB
%nproc=2
%CHK=NiCO4.chk
# B3LYP 6-31G* opt

Ni(CO)4 Td

0 1
Ni 0.000000 0.000000 0.000000
C 1.045712 1.045712 1.045712
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O  -1.707458  1.707458 -1.707458
C   1.045712 -1.045712 -1.045712
O   1.707458 -1.707458 -1.707458
Link ‘0’ commands

Locate and name scratch files; System Resources Required
Not blank line terminated

Some “Link 0” options (Examples)
%chk
 %chk=name.chk
 (Location and name of checkpoint file)
%mem
 %mem=1Gb
 (Sets the amount of dynamic memory, default is 32Mb.
 Units allowed: kb, mb, gb, kw, mw, or gw.)
%nproc
 %nproc=2
 (Sets the number of processors to use)
%mem=1GB
%nproc=2
%CHK=NiCO4.chk

# B3LYP 6-31G*  opt

Ni(CO)4 Td

0 1
Ni  0.000000  0.000000  0.000000
C   1.045712  1.045712  1.045712
O   1.707458  1.707458  1.707458
C  -1.045712 -1.045712  1.045712
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O  -1.707458  1.707458 -1.707458
C   1.045712 -1.045712 -1.045712
O   1.707458 -1.707458 -1.707458
Route section

Specify desired calculation type, model chemistry and other options
Start with # , can be multiple lines
Blank line terminated
Keywords can be specified in any order
Options are grouped in parentheses, ()
Keywords should not be repeated
Route section can be up to 5 lines long

3 key components to this specification:
The method
The basis set
The job type

Syntax: Method    Basis Set    Job type
Route section

Selected job types
SP  (Single point energy. Default)
Opt (Geometry optimization.)
Freq (Frequency and thermochemical analysis)

Selected methods
HF  (Hartree-Fock calculation, by default, RHF for singlets and UHF for higher multiplicities)
B3LYP (DFT calculation with B3LYP functional)
MPx (HF calculation and a MPx correction (x=2, 3, 4, 5))
CCD (CCD calculation)
CCSD (CCSD calculation)
CID (CI doubles only calculation)
CISD (CI singles and doubles calculation)
AM1 (semiempirical calculations with AM1)
PM3 (semiempirical calculations with PM3) no basis set spec needed
Route section

Some basis sets:

STO-3G, 3-21G, 6-21G, 4-31G, 6-31G, 6-311G
Polarization: *, **
6-31G*=6-31G(d), 6-31G** = 6-31G(d, p)
Diffuse functions: +, ++

Background Reading for Basis Sets
http://www.shodor.org/chemviz/basis/teachers/background.html
### Selecting a Basis Set: Quick Reference

<table>
<thead>
<tr>
<th>Name of Basis Set</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>STO-3G</td>
<td>Minimal basis set (stripped down in the interest of performance) use for more qualitative results on big systems</td>
</tr>
<tr>
<td>3-21G</td>
<td>Double zeta; 2 sets of functions in the valence region provide a more accurate description of orbitals. Use when 6-31G* is too expensive</td>
</tr>
<tr>
<td>6-31G*</td>
<td>Adds polarization functions to heavy atoms; use for most jobs on up to medium-size systems (these are the 6-component type d functions)</td>
</tr>
<tr>
<td>6-31G** [6-31G(p,d)]</td>
<td>Adds polarization functions to the hydrogens as well; use when the hydrogens are the site of interest (for example, bond energies) and for final, accurate energy calculations</td>
</tr>
<tr>
<td>6-31+G*</td>
<td>Adds diffuse functions; important for systems with lone pairs, anions, excited states</td>
</tr>
<tr>
<td>6-31+G** [6-31+G(p,d)]</td>
<td>Adds p functions to the hydrogens as well; use when you would use 6-31G** and diffuse functions are needed</td>
</tr>
<tr>
<td>6-311+G** [6-311+G(p,d)]</td>
<td>Triple zeta; adds extra valence electrons (3 sizes of s and p functions) to 6-31+G** (five pure component d functions are used)</td>
</tr>
</tbody>
</table>

Note: At least 6-31G needed for research

Standard for our calculations: 6-31G*
Gaussian program

Route section

#N (normal print level (default))
#P (additional output is generated)

TEST (do not save an archive file)

Geom (specify source of molecular specification input)
=connection (specify explicit atom bonding data via additional input section)
=check (take input from checkpoint file)
=allcheck (everything from checkpoint file)

Guess (initial guess of HF wavefunction)
=check (read from checkpoint file)
=only (terminate calc. once guess is done)
%mem=1GB
%nproc=2
%CHK=NiCO4.chk
# B3LYP 6-31G* opt

Ni(CO)₄ Td

<p>| | | | |</p>
<table>
<thead>
<tr>
<th></th>
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<th></th>
</tr>
</thead>
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<tr>
<td>Ni</td>
<td>0.000000</td>
<td>0.000000</td>
<td>0.000000</td>
</tr>
<tr>
<td>C</td>
<td>1.045712</td>
<td>1.045712</td>
<td>1.045712</td>
</tr>
<tr>
<td>O</td>
<td>1.707458</td>
<td>1.707458</td>
<td>1.707458</td>
</tr>
<tr>
<td>C</td>
<td>-1.045712</td>
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O  -1.707458  1.707458 -1.707458
C   1.045712 -1.045712 -1.045712
O   1.707458 -1.707458 -1.707458
Molecular Geometry

1st line: Charge and spin multiplicity (2S+1)

Element label and location
   Cartesian coordinates
       Label  x  y  z
   Z-matrix
       Label atoms bondlength atom2 angle atom3 dihedral

Blank line terminated
%mem=1GB
%nproc=2
%CHK=NiCO4.chk
# B3LYP 6-31G* opt
Ni(CO)4 Td

0 1
Ni 0.000000 0.000000 0.000000
C 1.045712 1.045712 1.045712
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O -1.707458 1.707458 -1.707458
C 1.045712 -1.045712 -1.045712
O 1.707458 -1.707458 -1.707458
EXERCISE 1:  Optimize the following compound:

\[ \text{Ni(CO)}_4 \]

Name of the input file: NiCO4.com

Ni\(_{\text{(CO)}}^4\) contains nickel in the zero oxidation state (\(d^{10}\)). It has 18 valence electron, and is a tetrahedral molecule with four carbonyl ligands attached to nickel. Ni\(_{\text{(CO)}}^4\) was first synthesised, as a pale-yellow liquid, in 1890 by Ludwig Mond by the direct reaction of nickel metal with CO. It is an intermediate in the Mond process for the purification of nickel and a reagent in organometallic chemistry. It is a extremely toxic compound.

See structure at:  
http://www.3dchem.com/3dmolecule.asp?ID=96
Running the calculation

- To submit a job and run the Gaussian program, type:
  
  > qsub <file>

  (an ID number is created for your job)

- To see the jobs in queue or running, type:
  
  > qstat

The system replies, for instance:

```
job-ID   name      user       state  submit/start at    queue
-----------------------------------------------
351443   pruebaGaus  eucheme08   r       07/06/2012 18:05:51  eucheme@nodo14.hpc.cica.es
```

running
- When the program is running there are several files (type Gau-*.*) that disappear when the work is correctly finished. Type:

   > ls

   to see these files.

- You can check the evolution of your calculation by the command qstat and also by editing the file NiCO4.log (with the vi program).

- The presence of a file named core.* indicates an error.
- When the calculation is finished, it is necessary to check the *.log file.

Edit the NiCO4.log file (with the vi program) and:

- go to the end of the output file (press “G”) and see:

  Normal termination of Gaussian 03 at ...

- type ?YES and see four YES and:

  Optimization completed.

    -- Stationary point found.
Information from the output files: NiCO4.log

- Optimized structure and the corresponding structural parameters (bond distances and angles, …).
- Spectroscopic data (IR, Raman, NMR, …).
- Molecular orbitals.

Use of Gaussview program
From the SSH program, open the SSH File Transfer Client
Transfer the NiCO4.log file from CICA to your terminal
From your terminal, open the program
Go to Open file
Select * .log as File type

and open the file: NiCO4 .log
EXERCISE 2:

Run frequency calculations on the optimize Ni(CO)$_4$ compound.

The optimization carried out with Ni(CO)$_4$ molecule afforded the geometry of a stationary point. It is necessary to check if this point is an actual global ground state (NImag = 0) or a transition state (NImag = 1) through the calculation of frequencies. This calculation computes force constants and the resulting vibrational frequencies.
Checkpoint file

For example: NiCO4.chk

When a subsequent calculation is to use results from a previous calculation as its inputs, these results can be kept in a special file to avoid having to type them into the new input file. Many such results are put in a file called a checkpoint file. It is a binary file. The use of a checkpoint file can be specified using the correct options on line ‘0’ commands at the input file.
Use of Checkpoint file. Example: Frequency calculations:

- At CICA: copy the files NiCO4.com and NiCO4.chk to NiCO4f.com and NiCO4f.chk:

> cp NiCO4.com NiCO4f.com
> cp NiCO4.chk NiCO4f.chk

- Edit the NiCO4f.com and change it until:

```
%mem=1GB
%nproc=2
%CHK=NiCO4f.chk

# B3LYP 6-31G* geom=check guess=check freq
Ni(CO)4 Td Frequency calculation

0 1
```

- Run the Gaussian program with the file NiCO4f.com (IMPORTANT: it is necessary to modify the *lanza.sge* file).
- Check the NiCO4f.log file and use the Gaussview program to view the calculated frequencies.
- Check the NiCO4f.log file and use the Gaussview program to view the calculated frequencies.
EXERCISE 3:
Optimize the following compounds and run the corresponding frequency calculation:

http://www.3dchem.com/3dinorgmolecule.asp?ID=948
http://www.3dchem.com/3dinorgmolecule.asp?ID=979
Optimize the molecules: \( \text{Cr(CO)}_6 \) \( \text{Fe(CO)}_5 \)

Name of the files: \( \text{CrCO6} \) \( \text{FeCO5} \) respectively

Suggestion:

- Build up the new molecules with Gaussview.

Open a new window
Select: octahedral Cr atom
IMPORTANT!: Symmetrize the molecule

Oh = octahedral
- Save the Cr(CO)$_6$ molecule in your terminal as CrCO6.gjf file.

**IMPORTANT**

Thick Write Cartesians
- At CICA: Copy the NiCO4.com file into the CrCO6.com file. Edit the CrCO6.com file (with the vi editor) and:
  - change the name of NiCO4.chk file by CrCO6.chk
  - modify the title section
  - remove the old coordinates.
  - edit the file CrCO6.gfj that has just created (with a text editor) and copy the cartesian coordinates.
  - insert the coordinates into the CrCO6.com file.
  - Add the instruction freq to the Route section:

```plaintext
# B3LYP 6-31G* opt freq
```
(in order to do in a single job both the optimization and the frequency calculations).

- Save the CrCO6.com file
%mem=1Gb
%nproc=2
%CHK=CrCO6.chk
# B3LYP 6-31G* opt freq

Cr(CO)6 Oh

0 1

<table>
<thead>
<tr>
<th>Atom</th>
<th>x</th>
<th>y</th>
<th>z</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr</td>
<td>0.00000000</td>
<td>0.00000000</td>
<td>-0.00000000</td>
</tr>
<tr>
<td>C</td>
<td>0.00000000</td>
<td>0.00000000</td>
<td>1.90000000</td>
</tr>
<tr>
<td>C</td>
<td>0.00000000</td>
<td>1.90000000</td>
<td>0.00000000</td>
</tr>
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<tr>
<td>C</td>
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<td>0.00000000</td>
<td>0.00000000</td>
</tr>
<tr>
<td>O</td>
<td>0.00000000</td>
<td>0.00000000</td>
<td>3.01540000</td>
</tr>
<tr>
<td>O</td>
<td>-3.01540000</td>
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<td>0.00000000</td>
<td>-3.01540000</td>
<td>-0.00000000</td>
</tr>
</tbody>
</table>
- For the CrCO6.com file, run the Gaussian program.

**IMPORTANT**: it is necessary to modify the *lanza.sge* file.

- Check the corresponding output CrCO6.log file.

- Repeat the same procedure for the Fe(CO)$_5$ molecule (FeCO5.com file).
%mem=1Gb
%nproc=2
%CHK=FeCO5.chk
# B3LYP 6-31G*  opt freq

Fe(CO)5  D3h

0 1
   Fe   -0.00000000  -0.00000000  0.00000000
   C    -1.67142903   0.96500000  -0.00000000
   C     0.00000000  -1.93000000  -0.00000000
   C     0.00000000   0.00000000   1.93000000
   C     1.67142903   0.96500000  -0.00000000
   C    -0.00000000  -0.00000000  -1.93000000
   O    -0.00000000  -0.00000000   3.04540000
   O     2.63739377   1.52270000   0.00000000
   O     0.00000000  -3.04540000   0.00000000
   O    -0.00000000  -0.00000000  -3.04540000
   O    -2.63739377   1.52270000   0.00000000
EXERCISE 4:

Draw the following molecular orbitals:

HOMO
HOMO-1
HOMO-2

HOMO
HOMO-1

HOMO
HOMO-1
HOMO-2
Generation of additional outputs (CICA):

**FormCheck file**

Transform the checkpoint file in a readable file

```
> /home/deposito/G03Linda/g03/formchk CrCO6.chk
```

This generates a new file CrCO6.fchk

- Transfer the CrCO6.fchk file to your terminal and open it with the Gaussview program.
Open the MO editor
Select the three degenerate HOMO orbitals.
Click: Visualize

Click: Update
Gaussian Calculations of Simple Organometallic Molecules: technical aspects

- Introduction

- Types of complexes to be analyzed
- Metal carbonyls
- Metal olefin complexes

- Practical theoretical chemistry
- Gaussian program
- Input file
- Running the calculation
- Information from output
- Theoretical chemistry “on paper”
Metal carbonyls Coordination complexes of transition metals with carbon monoxide. These complexes may be homoleptic, i.e. contain only CO ligands.

Selected examples:

http://www.3dchem.com/3dinorgmolecule.asp?ID=979
http://www.3dchem.com/3dinorgmolecule.asp?ID=948
http://www.3dchem.com/3dmolecule.asp?ID=96
Simplified MO diagram for CO

Frontier orbitals
**Back donation** (also known as the Chatt-Dewar-Duncanson model):

http://goldbook.iupac.org/

A description of the bonding of π-conjugated *ligands* to a transition metal which involves a synergic process with donation of electrons from the filled π-orbital or lone electron pair orbital of the ligand into an empty orbital of the metal (donor-acceptor bond), together with release (back donation) of electrons from an *nd* orbital of the metal (which is of π-symmetry with respect to the metal-ligand axis) into the empty π*-antibonding orbital of the ligand.
MO diagram of an octahedral compound

Symmetry-adapted $\sigma$ orbitals for an octahedral complex $ML_6$

Orbitals of the same symmetry on the metal centre
MO diagram of an octahedral compound
MO diagram of an octahedral compound

d_π orbitals (t_{2g})
MO diagram of an octahedral compound

\[ \pi \text{-interactions} \]

\[ \pi \text{-donor} \quad \pi \text{-acceptor} \]
MO diagram of an octahedral compound

Perturbation of the d block (in the centre, σ interactions only) of an octahedral complex ML₆ by the π interactions with:
- double-face π-donor ligands (L = Cl, for example) on the left, and
- double-face π-acceptor ligands (L = CO, for example) on the right.
MO diagram of an octahedral compound

\[
\text{Cr(CO)}_6 \quad \text{d}^6
\]
HOMO of Cr(CO)$_6$: $t_{2g}$ orbitals

Outputs from Gaussview
MO diagram of a bpt compound

d-block
MO diagram of a Td compound

d-block

\[ t_2 \]

\[ e \]
EXERCISE 5: Optimize the compounds:

[Fe(CO)$_4$(C$_2$H$_4$)]

[Cr(CO)$_4$(C$_2$H$_4$)$_2$]

Name of the files:

FeC2H4CO4

CrC2H42CO4

- Build up the new molecules with Gaussview and prepare the corresponding input files.
Gaussian Calculations of Simple Organometallic Molecules: technical aspects

- Introduction

- Practical theoretical chemistry
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  - Input file
  - Running the calculation
  - Information from output

- Types of complexes to be analyzed
  - Metal carbonyls
  - Metal olefin complexes

- Theoretical chemistry “on paper”
Ethylene metal complexes

Selected examples:

$[\text{PtCl}_3(\text{C}_2\text{H}_4)]^-$

$[\text{Fe(CO)}_4(\text{C}_2\text{H}_4)]$

$[\text{Cr(CO)}_4(\text{C}_2\text{H}_4)_2]$
Ethylene metal complexes

Frontier orbitals for ethylene ligand

Orbital interactions metal-ethylene
Ethylene metal complexes

Orbital interactions metal-ethylene

Donation

Back-donation
Ethylene metal complexes

Oh, d^{6}
Ethylene metal complexes

Conformational preferences

eclipsed

staggered

SS

SA
Ethylene metal complexes

Interactions between the π and π* orbitals on ethylene (in the centre) and the orbitals of the same symmetry on the \( d^6-ML_5 \) fragment in eclipsed (left) and staggered (right) conformations.
Ethylene metal complexes

Construction of the MO for the eclipsed (left) and staggered (right) conformations of the $d^6$-[ML$_5$(η$^2$-ethylene)] complex, by interaction between the $\pi$ and $\pi^*$ orbitals on ethylene (centre) and the orbitals of the $d^6$-ML$_5$ fragment.
Ethylene metal complexes

Conformational preferences

perpendicular

coplanar
Ethylene metal complexes

Comparison of the back-donation interactions \((d\rightarrow\pi^*)\) in the perpendicular (on the left) and coplanar (on the right) conformations of a \(d^8-[ML_4(\eta^2\text{-ethylene})]\) complex. The energy levels and symmetries of the \(d\) orbitals involved are given in the centre of the diagram.
Ethylene metal complexes

Conformational preferences

coplanar

perpendicular
Ethylene metal complexes

Diagram for the interaction between the nonbonding $d$ orbitals (in the centre) and the $\pi^*$ orbitals on the ethylene ligands in the coplanar ($D2h$, on the left) and perpendicular ($D2d$, on the right) conformations of an octahedral $trans$-$[ML_4(\eta^2-C_2H_4)_2]$ complex with a $d^6$ electronic configuration.