Quantum Chemical Calculations of NMR Parameters

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OUTLINE

INTRODUCTION

Relating NMR parameters to geometric and electronic structure
Classical calculations of EFG tensors
Molecular properties from quantum chemical calculations
Quantum chemistry methods

DENSITY FUNCTIONAL THEORY FOR CALCULATIONS OF NMR PARAMETERS

Introduction to DFT
Software
Practical examples
Tutorial

RELATING NMR OBSERVABLES TO MOLECULAR STRUCTURE

NMR Spectrum ←→ NMR Parameters ←→ Local geometry

↕

Chemical structure (reactivity)

I. Calculation of experimental NMR parameters

Find unique solution to C_Q, η_Q, δ_σ, η_σ, α, β, γ

II. Theoretical prediction of fine structure constants from molecular geometry

Classical electrostatic model (EFG)- only in simple ionic compounds
Quantum mechanical calculations (Density Functional Theory) (EFG, CSA)

ELECTRIC FIELD GRADIENT (EFG) TENSOR: POINT CHARGE MODEL

EFG TENSOR IS DETERMINED BY THE COMBINED ELECTRONIC AND NUCLEAR WAVEFUNCTION, NO ANALYTICAL EXPRESSION IN THE GENERAL CASE

THE SIMPLEST APPROXIMATION: CLASSICAL POINT CHARGE MODEL

$$\langle V_{2,k} \rangle = \sum_{i=1}^{n} \frac{Z_i e}{d_i^3} \sqrt{\frac{4\pi}{5}} Y_{2,k}(\theta_i, \phi_i)$$

ATOMS CONTRIBUTING TO THE EFG TENSOR ARE TREATED AS POINT CHARGES, THE RESULTING EFG TENSOR IS THE SUM WITH RESPECT TO ALL ATOMS

VERY CRUDE MODEL, WORKS QUANTITATIVELY ONLY IN SIMPLEST IONIC SYSTEMS, BUT YIELDS QUALITATIVE TRENDS AND GENERAL UNDERSTANDING OF THE SYMMETRY AND MAGNITUDE OF THE EXPECTED TENSOR

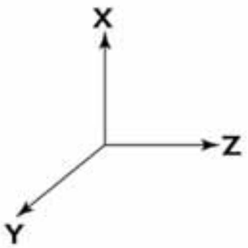
ELECTRIC FIELD GRADIENT (EFG) TENSOR: POINT CHARGE MODEL

$$\langle V_{2,k}\rangle = \sum_{i=1}^{n} \frac{Z_i e}{d_i^3}\sqrt{\frac{4\pi}{5}}Y_{2,k}(\theta_i,\phi_i)$$

Linear, one-coordinate:

$\theta = 0,\ \phi = 0$

$$\langle V_{2,0}\rangle = \frac{Ze}{d^3};\ \langle V_{2,\pm1}\rangle = 0;\ \langle V_{2,\pm2}\rangle = 0$$



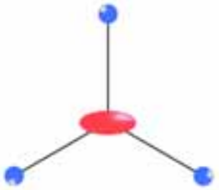
Linear, two-coordinate:

$\theta_1 = 0,\ \phi_1 = 0;\ \theta_2 = \pi,\ \phi_2 = 0$

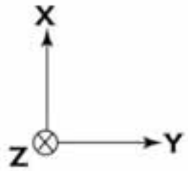
$$\langle V_{2,0}\rangle = \frac{2Ze}{d^3};\ \langle V_{2,\pm1}\rangle = 0;\ \langle V_{2,\pm2}\rangle = 0$$

Trigonal planar:

$\theta_1 = \pi/2,\ \phi_1 = 0;\ \theta_2 = \pi/2,\ \phi_2 = 2\pi/3;\ \theta_3 = \pi/2,\ \phi_3 = -2\pi/3$

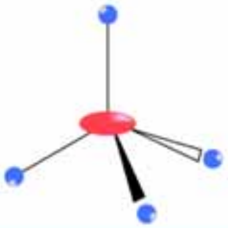


$$\langle V_{2,0}\rangle = -\frac{3}{2}\frac{Ze}{d^3};\ \langle V_{2,\pm1}\rangle = 0;\ \langle V_{2,\pm2}\rangle = 0$$



Tetrahedral:

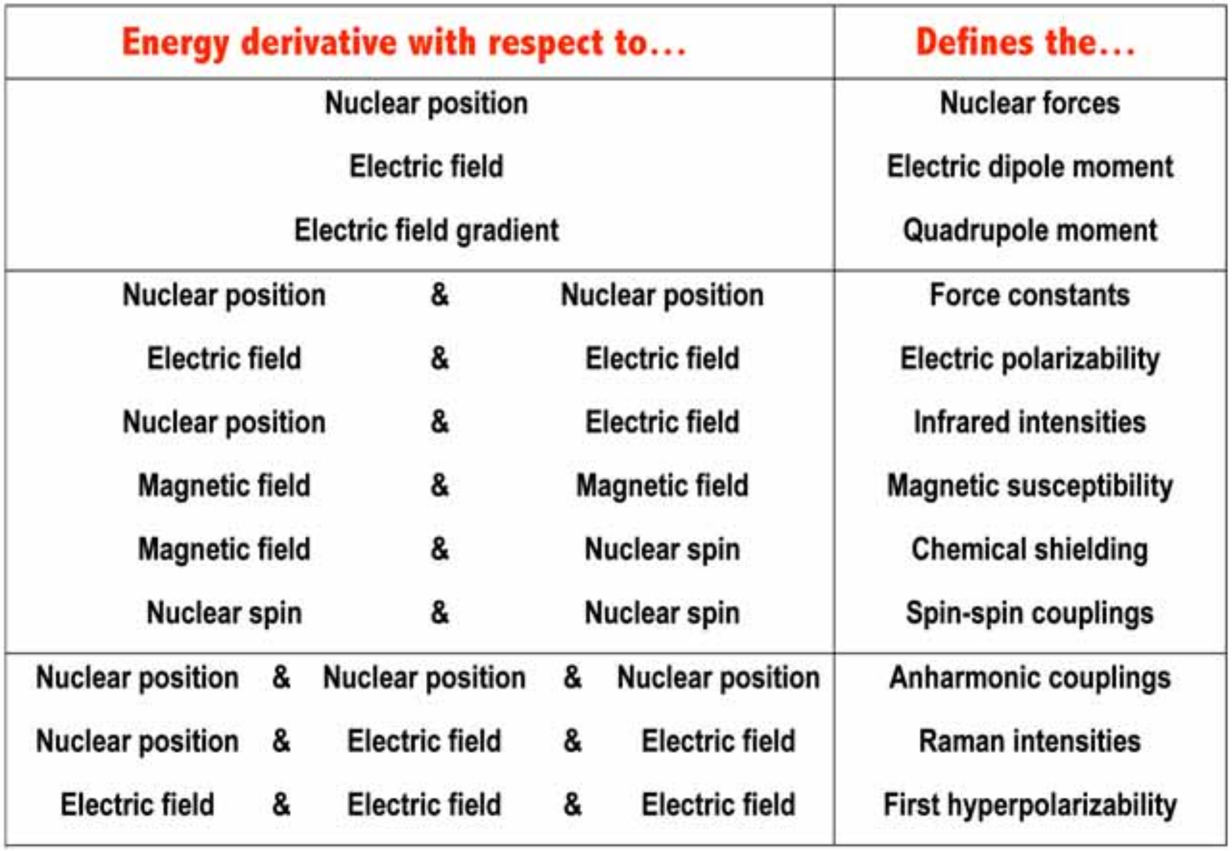
$\theta_1 = 0,\ \phi_1 = 0;\ \theta_2 = 2\pi/3,\ \phi_2 = 0;\ \theta_3 = 2\pi/3,\ \phi_3 = 2\pi/3;\ \theta_4 = 2\pi/3,\ \phi_4 = -2\pi/3$



$$\langle V_{2,0}\rangle = 0;\ \langle V_{2,\pm1}\rangle = 0;\ \langle V_{2,\pm2}\rangle = 0$$

MOLECULAR PROPERTIES FROM QUANTUM CHEMICAL CALCULATIONS

$$H \Psi = E \Psi$$



Energy derivative with respect to…	Defines the…
Nuclear position	Nuclear forces
Electric field	Electric dipole moment
Electric field gradient	Quadrupole moment
Nuclear position & Nuclear position	Force constants
Electric field & Electric field	Electric polarizability
Nuclear position & Electric field	Infrared intensities
Magnetic field & Magnetic field	Magnetic susceptibility
Magnetic field & Nuclear spin	Chemical shielding
Nuclear spin & Nuclear spin	Spin-spin couplings
Nuclear position & Nuclear position & Nuclear position	Anharmonic couplings
Nuclear position & Electric field & Electric field	Raman intensities
Electric field & Electric field & Electric field	First hyperpolarizability

See for example M. Head-Gordon (1996) J. Phys. Chem. 100, 13213-13225

QUANTUM CHEMISTRY METHODS

$$H\,\Psi = E\,\Psi$$

Schrödinger equation- cannot be solved exactly for multi-electron systems, and approximations have to be made

SEMI-EMPIRICAL METHODS

Based on Hartree-Fock approach. A Fock matrix is constructed, and the Hartree-Fock equations are iteratively solved. The approximations are in the construction of the Fock matrix (the energy expressions) and are based upon empirical data.

AB INITIO METHODS

Make no use of empirical information, except for the fundamental constants of nature, such as the mass of the electron, Planck's constant, etc.
Do not confuse "ab initio" with "exact"!

DENSITY FUNCTIONAL THEORY METHODS

Include the electron correlation, which is introduced by adapting the expression for the density of a uniform electron gas to the molecular orbital environment. Replace the many-body electronic wavefunction with the electronic density as the basic quantity.

USEFUL DEFINITIONS

AO (ATOMIC ORBITAL)

An orbital described by a wavefunction for a single electron centered on a single atom.

ORBITAL

The wavefunction describing where an electron is within an atom or a molecule.

BASIS SET

Finite set of functions used to approximately express the molecular orbital (MO) wavefunction(s) of a system, normally atom centered, consisting of AOs differing in local angular momentum for each atom. The basis set can be interpreted as restricting each electron to a particular region of space.

ELECTRON CORRELATION

Explicitly considering the effect of the interactions of specific electron pairs, rather than the effect that each electron feels from the average of all the other electrons.

GAUSSIANS

Functions frequently used as primitive functions to expand the total wavefunction.

USEFUL DEFINITIONS

GIAO (GAUGE INDEPENDENT ATOMIC ORBITALS)

Ditchfield's method for canceling out the arbitrariness of the choice of origin & form (gauge) of the vector potential used to introduce the magnetic field in the Hamiltonian when calculating chemical shielding and chemical shift tensor. An exponential term containing the vector potential is included with each atomic orbital. Originally developed based on Hartree-Fock, improved by Pulay w/ DFT to be faster, also used w/MP2 & CCSD. Pros: less basis set dependence than IGAIM.

FOR MORE DEFINITIONS, SEE

http://www.chamotlabs.com/Freebies/Acronyms.html

SEMI-EMPIRICAL METHODS

LIMITED TO HUNDREDS OF ATOMS

MNDO, AM1, PM3

Were designed to reproduce heats of formation and structures of a large number of organic molecules

INDO/S, CNDO/S

Good at prediction of electronic transitions in the UV/VIS spectral region

AB INITIO METHODS

LIMITED TO TENS OF ATOMS

GIVE THE ABSOLUTE ENERGY OF THE SYSTEM OF FIXED NUCLEI AND MOVING ELECTRONS

One of the most useful features of the ab initio MO theory is that it allows the definition of “model chemistries”. A theoretical model chemistry entails a method (e.g., Hartree-Fock or MP2 etc.) and a basis set. The philosophy of a model chemistry is that it should be uniformly applicable and tested on as many systems as possible to learn about its performance.

DENSITY FUNCTIONAL THEORY (DFT) METHODS

INCLUDE THE ELECTRON CORRELATION

Electron correlation is introduced by adapting the expression for the density of a uniform electron gas to the molecular orbital environment.

Replace the many-body electronic wavefunction with the electronic density as the basic quantity. Many-body wavefunctions- dependent on 3N variables (3 spatial variables for each of the N electrons), the density- dependent on 3 spatial variables.

http://en.wikipedia.org/wiki/Density_functional_theory

DENSITY FUNCTIONAL THEORY (DFT) METHODS

MOST COMMON IMPLEMENTATION- KOHN-SHAM METHOD

The intractable many-body problem of interacting electrons in a static external potential is reduced to a tractable problem of non-interacting electrons moving in an effective potential.

Effective potential- includes the external potential and the effects of the Coulomb interactions between the electrons, e.g. the exchange and correlation interactions.

To model the latter, the local-denisty approximation (LDA) is used, which is based upon exact exchange energy for a uniform electron gas (obtained from the Thomas-Fermi model), and from fits to the correlation energy for a uniform electron gas.

http://en.wikipedia.org/wiki/Density_functional_theory

DENSITY FUNCTIONAL THEORY (DFT) METHODS

MANY-ELECTRON SCHRÖDINGER EQUATION:

$$H\Psi = [T + V + U]\Psi = \left[\sum_{i}^{N} -\frac{\hbar^2}{2m}\nabla_i^2 - \sum_{i}^{N} V(\vec{r}_i) + \sum_{i<j} U(\vec{r}_i, \vec{r}_j)\right]\Psi = E\Psi$$

U- interaction term for many-particle problem

Approaches: expansion of wave function in Slater determinants (HF and post-HF metthods)

Problem: computationally expensive, impractical in large systems

http://en.wikipedia.org/wiki/Density_functional_theory

DENSITY FUNCTIONAL THEORY (DFT) METHODS

DFT ALTERNATIVE:

Introduce a new variable, the particle density

$$n(\vec{r}) = N\int d^3r_2 \int d^3r_2 \ldots \int d^3r_N \Psi^*(\vec{r}_1,\vec{r}_2,\ldots,\vec{r}_N)\Psi(\vec{r}_1,\vec{r}_2,\ldots,\vec{r}_N)$$

Hohenberg and Kohn- proved (1964) that the expression is unique, i.e. to a given ground state density $n_0(r)$ it is possible to calculate the corresponding ground state wavefunction

$$\Psi_0(\vec{r}_1,\vec{r}_2,\ldots,\vec{r}_N)$$

Ψ_0 is a unique functional of n_0, i. e.

$$\Psi_0 = \Psi_0[n_0]$$

Therefore, all other ground state observables (including energy) are also functionals of n_0

$$\langle \boldsymbol{O} \rangle [n_0] = \langle \Psi_0[n_0] | \boldsymbol{O} | \Psi_0[n_0] \rangle$$
$$\boldsymbol{E_0} = \boldsymbol{E}[n_0] = \langle \Psi_0[n_0] | \boldsymbol{T+V+U} | \Psi_0[n_0] \rangle$$

where the contribution of the external potential $\langle \Psi_0[n_0] | \boldsymbol{U} | \Psi_0[n_0] \rangle$ can be written explicitly in terms of the density

$$V[n] = \int V(\vec{r})n(\vec{r})d^3r$$

http://en.wikipedia.org/wiki/Density_functional_theory

DENSITY FUNCTIONAL THEORY (DFT) METHODS

For a particular system with V specified, minimize the functional

$$E[n] = T[n] + U[n] + \int V(\vec{r})\, n(\vec{r})\, d^3 r$$

with respect to n(r), assuming reliable expressions are known for $T[n]$ and $U[n]$. Successful minimization- yields ground state density n_0 and thus all other ground-state observables.

Minimization of energy functional $E[n]$ - by Lagrangian method of undetermined multipliers. Rewrite the functional as a fictitious density functional of a non-interacting system

$$E_s[n] = < \Psi_s [n] | T_s + V_s | \Psi_s [n] >$$

T_s -non-interacting kinetic energy, V_s - external effective potential in which particles are moving

Then solve Kohn-Sham equations of this auxillary non-interacting system

$$\left[-\frac{\hbar^2}{2m} \nabla^2 + V_s(\vec{r}_i) \right] \phi_i(\vec{r}) = \varepsilon_i \phi_i(\vec{r})$$

Which yields the orbitals ϕ_i that reproduce the density n(r) of the original many-body system

$$n(\vec{r}) \overset{def}{=} n_s(\vec{r}) = \sum_{i}^{N} \left| \phi_i(\vec{r}) \right|^2$$

http://en.wikipedia.org/wiki/Density_functional_theory

DENSITY FUNCTIONAL THEORY (DFT) METHODS

EFFECTIVE SINGLE-PARTICLE POTENTIAL CAN BE WRITTEN AS

$$V_s = V + \int \frac{e^2 n_s(\vec{r}\,')}{|\vec{r} - \vec{r}\,'|} d^3 r' + V_{XC}[n(\vec{r})]$$

$\int \frac{e^2 n_s(\vec{r}\,')}{\lvert\vec{r} - \vec{r}\,'\rvert} d^3 r'$	Hartree term (describes the electron-electron Coulomb repulsion)
V_{XC} -	Exchange correlation potential, includes all the many-particle interactions

Since the Hartree term and V_{XC} depend on n(r), which depends on the orbitals ϕ_i, which in turn depend on V_S, the problem of solving the Kohn-Sham equations has to be done in a self-consistent (iterative) way. Start with an initial guess of n(r), then calculate the corresponding V_S and solve the Kohn-Sham equations for ϕ_i. From these calculate a new density and start again, repeat until convergence is reached.

http://en.wikipedia.org/wiki/Density_functional_theory

DENSITY FUNCTIONAL THEORY (DFT) METHODS

APPROXIMATIONS

Problem: exact functionals for exchange and correlation are not known except for the free electron gas. Approximations are needed.

Local-density approximation (LDA)- the functional depends only on the density at the coordinate where the functional is evaluated:

$$E_{XC}[n] = \int \varepsilon_{XC}(n)n(r)d^3r$$

Local spin-density approximation (LSDA)- generalization of LDA to include electron spin:

$$E_{XC}[n_\uparrow, n_\downarrow] = \int \varepsilon_{XC}(n_\uparrow, n_\downarrow)n(r)d^3r$$

Generalized gradient approximations (GGA)- take into account the gradient of the density at the same coordinate:

$$E_{XC}[n_\uparrow, n_\downarrow] = \int \varepsilon_{XC}(n_\uparrow, n_\downarrow, \vec{\nabla} n_\uparrow, \vec{\nabla} n_\downarrow)n(r)d^3r$$

GGA- yields very good results for molecular geometries and ground state energies.

http://en.wikipedia.org/wiki/Density_functional_theory

BASIS SETS

THE SET OF ONE-ELECTRON WAVEFUNCTIONS USED TO BUILD MOLECULAR ORBITAL WAVEFUNCTIONS

Examples of Gaussian basis sets:

- STO-3G, 3-21G (H-Xe), 6-31G (H-Cl), 6-311G (H-Kr);
- 6-31G (d); 6-31G (d,p); 6-31+G (d,p); 6-311+G (3df,2p);
- Aug-cc-pVTZ;
- Effective core potentials: LANL2MB (H-Ba, La-Bi); LANDZ; SDD- entire Periodic Table

And many more basis sets tailored to specific systems...

Useful basis set depository- EMSL basis set exchange:

http://gnode2.pnl.gov/bse/portal

http://www.gaussian.com/00000485.htm

DENSITY FUNCTIONAL THEORY (DFT): SOFTWARE

- Abinit
- ADF
- AIMPRO
- Atomistix Toolkit
- Atompaw/PWPAW
- CADPAC
- CASTEP (NMR CASTEP)
- CPMD
- CRYSTAL06
- DACAPO
- DALTON
- deMon2K
- DFT++
- DMol3
- EXCITING
- Fireball
- FLEUR
- Fsatom
- GAMESS (UK)
- GAMESS (US)
- GAUSSIAN
- GPAW
- JAGUAR (no EFG)
- MOLPRO
- NRMOL
- NWChem
- OCTOPUS
- OpenMX
- ORCA
- ParaGauss
- PARATEC
- PARSEC
- PCGAMESS
- PLATO
- Parallel Quantum Solutions
- Priroda
- Q-Chem
- SIESTA
- Socorro
- S/PHI/nX
- SPR-KKR
- TURBOMOLE
- VASP
- WIEN2k (no CSA)

http://en.wikipedia.org/wiki/Density_functional_theory

DENSITY FUNCTIONAL THEORY: ELECTRIC FIELD GRADIENT TENSOR

RECALL THE BASIC DEFINITIONS FOR EFG TENSOR:

Electric field (vector property):

$$E = -\nabla\phi$$

where ϕ is the electrostatic potential:

$$\phi_1 = \int \frac{\rho_2 dV_2}{4\pi\varepsilon_0 r_{12}}$$

Electric field gradient:

$$V = \nabla E$$ (tensor of rank 2)

Quadrupolar coupling constant:

$$C_Q = \frac{V_{ZZ}(eQ)}{h}, \; Q - electric\ quadrupole\ moment$$

DENSITY FUNCTIONAL THEORY: MAGNETIC SHIELDING TENSOR

RECALL THE DEFINITION OF THE MAGNETIC SHIELDING ANISOTROPY TENSOR:

$$\sigma_{i,j} = \frac{\partial^2 E}{\partial \mu_i \partial B_j}$$

where μ is the nuclear magnetic moment, and B is an external magnetic field.

Early chemical shift calculations: C. Jameson, A. DeDios, E. Oldfield

CALULATING NMR PARAMETERS IN GAUSSIAN03

DEVELOPED BY THE GROUP OF J. A. POPLE

USES GAUSSIAN BASIS SETS

ONE OF THE MOST USER-FRIENDLY PROGRAMS FOR RUNNING ELECTRONIC STRUCTURE CALCULATIONS

CAPABILITIES RELEVANT TO NMR SPECTROSCOPISTS:

- Geometry optimization
- Calculations of EFG tensors
- Calculations of magnetic shielding anisotropy tensors
- Calculations of spin-spin coupling constants

TYPES OF CALCULATIONS:

- Semi-empirical
- Ab initio
- DFT
- Hybrid QM/MM

CALULATING NMR PARAMETERS IN GAUSSIAN03

GAUSSIAN CAN RUN MANY TYPES OF CALCULATIONS, AND THE USER SELECTS WHICH BY GIVING A SERIES OF "KEYWORDS", WHICH REPRESENT THE DESIRED TYPE OF CALCULATION. EACH OF THE KEYWORDS USUALLY HAS A NUMBER OF OPTIONS, SPECIFIED IN THE FORM

```
KEYWORD=(OPTION1,OPTION2,OPTION3)
```

The ordering of keywords and options is not important, and lower and upper case characters are treated equal.

Gaussian reads the keywords and other information (e.g., geometry) from an input file, which must have a name of the type

```
jobname.com
```

To run the program, type

```
g03 jobname.com &
```

which produces an output file called jobname.log

CALULATING NMR PARAMETERS IN GAUSSIAN03

THE BASIC STRUCTURE OF A GAUSSIAN INPUT:		EXAMPLE:	
Link 0 Commands: Locate and name scratch files. 2 processors Memory allocation - 120 MB		--- %chk=formald.chk %nproc=2 %mem=120MB	
Route section (# lines): Specify desired calculation type, (blank line terminated).		# B3LYP/6-31G(d) opt NMR EFG	
Title section (blank line terminated).	Title →	Formaldehyde optimization	
Molecule specification (blank line terminated).	Charge →	0 1 ← multiplicity C 0.0 0. 0 0.0 O 0.0 1.22 0.0 H 0.94 -0.54 0.0 H -0.94 -0.54 0.0	Cartesian Coordinates or Z-matrix
Optional additional sections (usually blank line terminated).			

CALULATING NMR PARAMETERS IN GAUSSIAN03

THE ROUTE SECTION OF A GAUSSIAN03 INPUT FILE SPECIFIES THE TYPE OF CALCULATION TO BE PERFORMED. THERE ARE THREE KEY COMPONENTS TO THIS SPECIFICATION:

The job type

(OPT, FREQ, NMR, PROP=EFG)

http://www.gaussian.com/g_ur/m_jobtypes.htm

The method

(HF, AM1, B3LYP, CASSCF)

The basis set

(3-21G, 6-31G(d),6-311+G(d,p), cc-pVTZ, etc.)

http://www.gaussian.com/g_ur/m_basis_sets.htm

CALULATING NMR PARAMETERS IN GAUSSIAN03

The first line of the molecule specification section specifies the net electric charge (a signed integer) and the spin multiplicity (a positive integer).

Thus, for a neutral molecule in a singlet state, the entry 0 1 is appropriate.

For a radical anion, -1 2 would be used.

This is the only molecule specification input required if Geom=Check is used.

The entire molecule specification (and title section) may be omitted
by including Geom=AllCheck in the route section.

CALULATING NMR PARAMETERS IN GAUSSIAN03

SAMPLE INPUT FILE FOR CALCULATING ^{51}V CSA AND EFG TENSORS FOR VOCl$_3$

```
%nproc=1
%mem=700MB
%Chk=./VOCl3_opt_6311Gdp.chk
# b3lyp/6-311+G(d,p) opt=(maxcycle=100) scf=(vshift=100,maxcycle=256)

VOCl3

 0 1
 V  -0.000056   -0.000022    0.230882
 O -0.000052   -0.000075    1.803662
 Cl 1.215304   -1.787943   -0.387058
 Cl -2.156194   -0.158336   -0.387084
 Cl  0.940990    1.946345   -0.387011
```

CALULATING NMR PARAMETERS IN GAUSSIAN03

SAMPLE OUTPUT FILE FOR CALCULATING ^{51}V CSA AND EFG TENSORS FOR VOCl$_3$ (CSA ENTRIES)

```
Calculating GIAO nuclear magnetic shielding tensors.
 SCF GIAO Magnetic shielding tensor (ppm):
  1  V    Isotropic = -2279.3913   Anisotropy =   369.7210
   XX= -2032.9731   YX=    -0.0448   ZX=    -0.0097
   XY=    -0.0404   YY= -2032.9397   ZY=    -0.0515
   XZ=     0.0107   YZ=    -0.1385   ZZ= -2772.2612
   Eigenvalues: -2772.2612 -2033.0021 -2032.9106
  2  O    Isotropic = -1148.8385   Anisotropy =  1752.5744
   XX= -1732.9364   YX=    -0.0137   ZX=    -0.0339
   XY=    -0.0159   YY= -1733.1237   ZY=     0.0761
   XZ=    -0.0323   YZ=     0.0549   ZZ=    19.5444
   Eigenvalues: -1733.1248 -1732.9352    19.5444
  3  Cl   Isotropic =   -51.5475   Anisotropy =   998.2683
   XX=   376.6950   YX=   -34.6272   ZX=  -476.2807
   XY=   -34.6678   YY=   340.4831   ZY=   286.9402
   XZ=  -494.8562   YZ=   298.1174   ZZ=  -871.8206
   Eigenvalues: -1088.1035   319.4962   613.9647
  4  Cl   Isotropic =   -51.5914   Anisotropy =   998.3747
   XX=   379.3590   YX=    33.0426   ZX=   487.1986
   XY=    33.1260   YY=   337.8399   ZY=   268.1242
   XZ=   506.2733   YZ=   278.5711   ZZ=  -871.9731
   Eigenvalues: -1088.3077   319.5417   613.9917
  5  Cl   Isotropic =   -52.0678   Anisotropy =   998.7335
   XX=   318.8621   YX=     1.5137   ZX=   -11.0368
   XY=     1.4978   YY=   397.5075   ZY=  -556.1673
   XZ=   -11.4555   YZ=  -577.4015   ZZ=  -872.5730
   Eigenvalues: -1088.7912   318.8333   613.7545
```

CALULATING NMR PARAMETERS IN GAUSSIAN03

SAMPLE OUTPUT FILE FOR CALCULATING ^{51}V CSA AND EFG TENSORS FOR VOCl$_3$ (EFG ENTRIES)

```
 -----------------------------------------------------------------
   Center          ---- Electric Field Gradient ----
                  XX              YY              ZZ
 -----------------------------------------------------------------
   1 Atom     -33460.854654   -33460.854707   -33459.870669
   2 Atom      -1241.359443    -1241.359442   -1241.173551
   3 Atom     -13077.544551   -13077.182276   -13076.272504
   4 Atom     -13077.571052   -13077.155932   -13076.272663
   5 Atom     -13076.975620   -13077.751573   -13076.272758
 -----------------------------------------------------------------
 -----------------------------------------------------------------
   Center          ---- Electric Field Gradient ----
                  XY           XZ           YZ
 -----------------------------------------------------------------
   1 Atom        -0.000012       -0.000023        0.000045
   2 Atom         0.000001       -0.000002        0.000087
   3 Atom         0.344135        0.652327       -0.394042
   4 Atom        -0.328898       -0.667307       -0.368130
   5 Atom        -0.015211        0.014992        0.761941
 -----------------------------------------------------------------
 -----------------------------------------------------------------
   Center          ---- Electric Field Gradient ----
                   ----       Eigenvalues       ----
 -----------------------------------------------------------------
   1 Atom     -33460.854709   -33460.854651   -33459.870669
   2 Atom      -1241.359444    -1241.359441   -1241.173551
   3 Atom     -13078.074600   -13076.974518   -13075.950213
   4 Atom     -13078.074716   -13076.974577   -13075.950354
   5 Atom     -13078.074258   -13076.975322   -13075.950371
 -----------------------------------------------------------------
```

CALULATING NMR PARAMETERS IN GAUSSIAN03

SAMPLE OUTPUT FILE FOR CALCULATING ^{51}V CSA AND EFG TENSORS FOR VOCl$_3$ (EFG ENTRIES)

```
 -----------------------------------------------------------------
   Center           ---- Electric Field Gradient ----
                        ( tensor representation )
                   3XX-RR        3YY-RR        3ZZ-RR
 -----------------------------------------------------------------
   1 Atom        -0.327977      -0.328030       0.656008
   2 Atom        -0.061964      -0.061963       0.123928
   3 Atom        -0.544774      -0.182499       0.727273
   4 Atom        -0.571170      -0.156050       0.727220
   5 Atom         0.024364      -0.751590       0.727226
 -----------------------------------------------------------------
 -----------------------------------------------------------------
   Center           ---- Electric Field Gradient ----
                        ( tensor representation )
                     ----       Eigenvalues       ----
 -----------------------------------------------------------------
   1 Atom        -0.328033      -0.327975       0.656008
   2 Atom        -0.061965      -0.061962       0.123928
   3 Atom        -1.074823       0.025259       1.049564
   4 Atom        -1.074834       0.025306       1.049528
   5 Atom        -1.074274       0.024662       1.049612
 -----------------------------------------------------------------
```

VISUALIZING THE RESULTS OF NMR PARAMETER CALCULATIONS IN GAUSSIAN03

GAUSSVIEW CAN GRAPHICALLY DISPLAY A VARIETY OF GAUSSIAN CALCULATION RESULTS, INCLUDING THE FOLLOWING:

- Optimized molecular structures
- Molecular orbitals
- Atomic charges
- Electron density surfaces from any computed density
- Electrostatic potential surfaces
- NMR shielding density
- Animation of the normal modes corresponding to vibrational frequencies

http://www.hoffmann-oberhausen.de/gvbroc.htm

CONVERTING GAUSSIAN03 RESULTS TO STANDARD NMR NOTATION

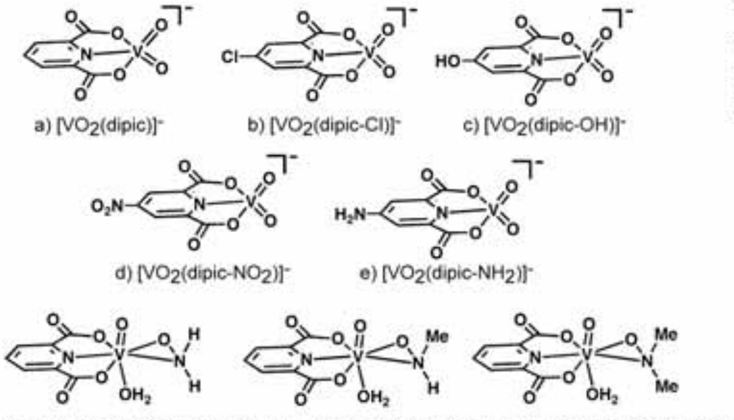
MATHEMATICA ROUTINE GAUSSIAN

- Reads every Gaussian output file in a specified directory
- Searches for CSA and EFG tensor entries for V (can be modified for any nucleus)
- Outputs EFG tensor (C_Q in MHz) and η_Q and CSA tensor (δ_σ in ppm and η_σ)
- Outputs a summary table with the NMR tensors and the Euler angles
- Available from Tatyana Polenova upon request

DFT CALCULATIONS OF NMR PARAMETERS FOR METALS: PRACTICAL CONSIDERATIONS

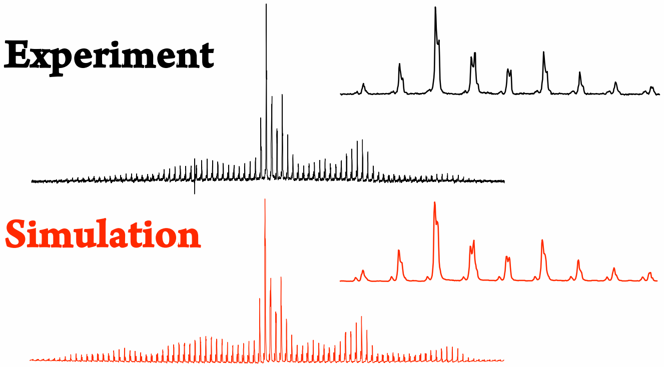
INCLUDING COUNTER IONS AND GENERALLY CHARGES OUTSIDE OF THE IMMEDIATE COORDINATION SPHERE IS NECESSARY

^{51}V SSNMR AND DFT STUDIES OF V(V) DIPICOLINIC ACID DERIVATIVES

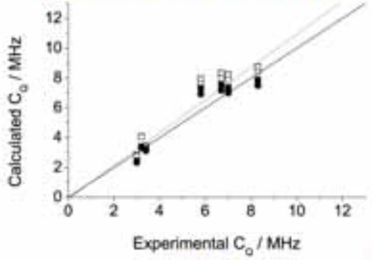

a) [VO$_2$(dipic)]$^-$ b) [VO$_2$(dipic-Cl)]$^-$ c) [VO$_2$(dipic-OH)]$^-$

d) [VO$_2$(dipic-NO$_2$)]$^-$ e) [VO$_2$(dipic-NH$_2$)]$^-$

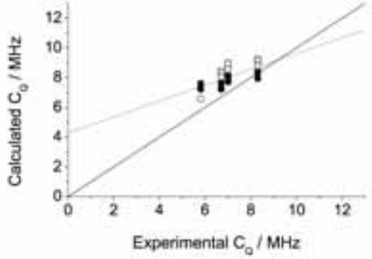
f) [VO(H$_2$O)dipic(ONH$_2$)] g) [VO(H$_2$O)dipic(ONHCH$_3$)] h) [VO(H$_2$O)dipic(ON(CH$_3$)$_2$)]



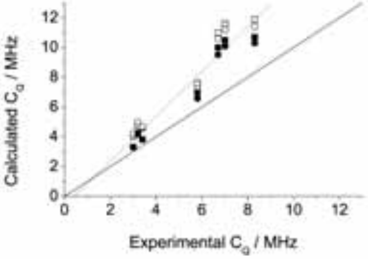
Counter ions, X-ray geometry



No counter ions, X-ray geometry



No counter ions, optimized geometry



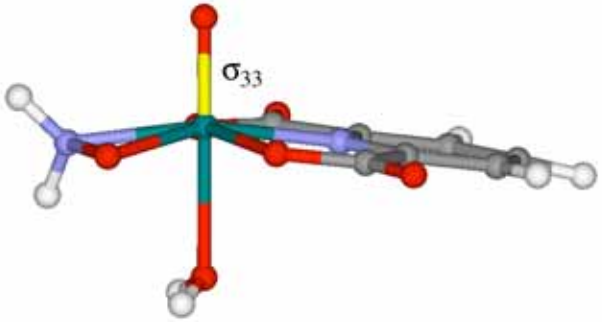
S. Bolte, K. J. Ooms, B. Baruah, J. Smee, D. Crans, T. Polenova (2008) J.Chem. Phys.

DFT CALCULATIONS CAN EXPLAIN THE MAGNITUDE OF C_Q

^{51}V SPECTROSCOPY OF DIPICOLINIC ACID DERIVATIVES

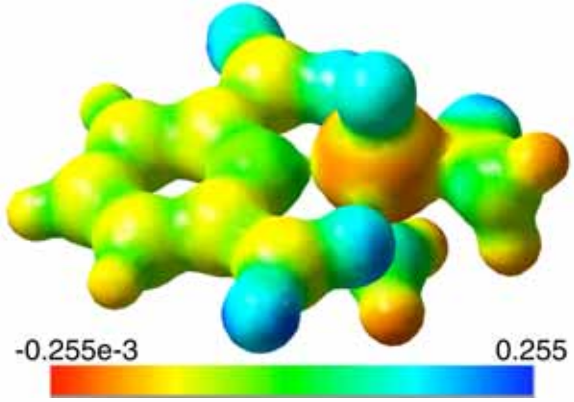
Nominal coordination geometry: heptacoordinate, large C_Q expected

Experimental C_Q: 3.43 MHz (small)



Electrostatic potential surface (ESP):

Reveals capped square planar charge distribution, consistent with small C_Q

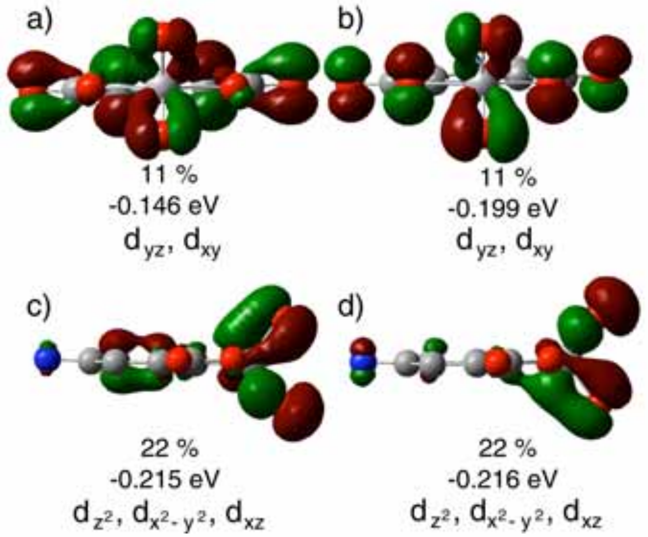


Ooms, Bolte, Baruah, Smee, Crans, Polenova (2007) Inorg. Chem. 46, 9285-9293

DFT ANALYSIS OF MOLECULAR ORBITALS

^{51}V SPECTROSCOPY OF DIPICOLINIC ACID DERIVATIVES

EXAMINE THE SYMMETRY OF MO’S USING THE NCS METHOD TO UNDERSTAND THE CONTRIBUTIONS OF CHEMICAL BONDS AND LONE ELECTRON PAIRS TO THE ^{51}V MAGNETIC SHIELDING TENSOR



Bolte, Ooms, Baruah, Smee, Crans, Polenova (2008) J.Chem. Phys.

DFT CALCULATIONS OF NMR PARAMETERS FOR METALS: PRACTICAL CONSIDERATIONS

ACCURACY OF EXPERIMENTALLY MEASURED EFG TENSORS

5-15% for small molecules
10-30% for proteins

BASIS SET

Compromise between the desired accuracy and the size of the system
For heavier elements- need custom basis sets with additional functions for core electrons (to account for non-spherical charge distribution)
Check for the basis set convergence on small model systems first

METHOD

Choice of functional and basis set-
check on small model systems first

PRACTICAL EXERCISE: CALCULATION OF NMR PARAMETERS AND MOLECULAR ORBITALS FOR VOCl3

1. CREATE A DIRECTORY ON CRUNCH (4-PROCESSOR LINUX AMD OPTERON WORKSTATION IN T. POLENOVA'S LABORATORY) YOU WILL NEED AN X11 APPLICATION (MAC) OR USE PUTTY

The login and password are available from Tatyana Polenova upon request;
Once on crunch,

```
$ mkdir yourlastname                  #  this will make a directory for you
$ cp -r VOCl3/*.com  yourlastname     # copy the Gaussian executable .com files in VOCl3
                                         directory to your directory
$ ls VOCl3                            # list the contents of the VOCl3 directory; you
                                         should see a number of files (.com, .log, .chk, and
                                        .xyz) representing the input, output, checkpoint,
                                         and coordinate files for the Gaussian jobs in this
                                         tutorial


$ cd yourlastname                     # change directory to your directory
$ ls                                  #  list the contents; you should see two entries:
                                       VOCl3_NMR_afteropt_Zampella.com, VOCl3_opt_b3lyp.com
```

PRACTICAL EXERCISE: CALCULATION OF NMR PARAMETERS AND MOLECULAR ORBITALS FOR VOCl3

2. EXAMINE THE CONTENTS OF YOUR GAUSSIAN INPUT FILES

```
$ more VOCl3_opt_6311Gdp.com              # to see the VOCl3_opt_6311Gdp.com file
$ more VOCl3_NMR_afteropt_b3lyp.com       # to see the VOCl3_NMR_afteropt_b3lyp.com file
```

Questions:

1. What type of jobs each of the two input files is written for?
2. What DFT method is used?
3. What basis sets are used?
4. Identify the coordinate entries
5. List the molecular parameters that are calculated in each file
6. In your spare time, identify other keywords that are used in the two files (consult Gaussian03 manual)

PRACTICAL EXERCISE: CALCULATION OF NMR PARAMETERS AND MOLECULAR ORBITALS FOR VOCl3

3. RUN GEOMETRY OPTIMIZATION ON THE VOCl$_3$ MOLECULE

```
$ setGauss                              # set Gaussian03 environment variables
$ nohup g03 VOCl3_opt_Zampella.com &    # executes VOCl3_opt_Zampella.com in Gaussian03
```

Note that the job uses a custom basis set:
On vanadium- a LanL2DZ modified by Couty and Hall (Couty and Hall, J. Comput. Chem. 1996, 17, 1359-1370) and used by Zampella et al. for calculations of QM models of VCPO (Zampella et al., Inorg. Chem. 2004, 43, 4127-4136), and to make the geometry optimization quicker

This job will take approximately 4-15 minutes (depending on how many jobs are running simultaneously on crunch)
After this job is done, examine the corresponding log file. The coordinates for the optimized geometry will be given in the last “Input Orientation” and “Standard Orientation” entries of the file.

To check whether the job is running, type “top” at any stage. Gaussian job names start with “l” followed by 3 or 4 numbers, e.g. “l703.exe”, “l502.exe”, “l1110.exe”, etc. (read Gaussian manual for more information). To exit top, type “q”.

PRACTICAL EXERCISE: CALCULATION OF NMR PARAMETERS AND MOLECULAR ORBITALS FOR VOCl3

5. CALCULATE THE EFG AND CSA TENSORS FOR THE GEOMETRY-OPTIMIZED $VOCl_3$

```
$ g03 VOCl3_NMR_afteropt_b3lyp.com &        # executes VOCl3_NMR_afteropt_b3lyp.com in
                                              Gaussian03
```

This job will take approximately 20-45 minutes depending on the how many jobs are running in parallel

This job will calculate the EFG and CSA tensors on the geometry-optimized $VOCl_3$ molecule, and perform the NCS (Natural Chemical Shielding) analysis to determine the contributions of the individual bonds and lone electron pairs to the shift.

After the job is done, examine the contents of the corresponding log file. The CSA tensors will be printed for each atom; the EFG tensors will be given as well (in atomic units).

Note that the 6-311+G(d,p) basis set is used, and the starting geometry is that optimized for a $VOCl_3$ job at the same level of theory (which we will not do because it takes 33 min, so I have run the optimization in advance)

PRACTICAL EXERCISE: CALCULATION OF NMR PARAMETERS AND MOLECULAR ORBITALS FOR VOCl3

6. EXAMINE THE RESULTS OF GEOMETRY OPTIMIZATION IN MOLDEN

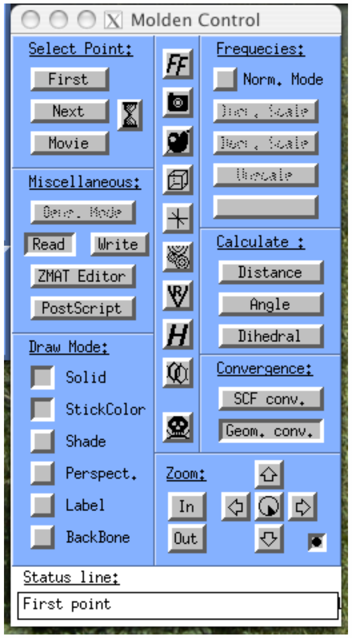
Molden- a free visualization program for displaying molecular structures; reads of Gaussian input and output files, and an easy analysis of geometry and SCF convergence

http://www.cmbi.ru.nl/molden/molden.html;
http://www.cmbi.ru.nl/molden/howtoget.html

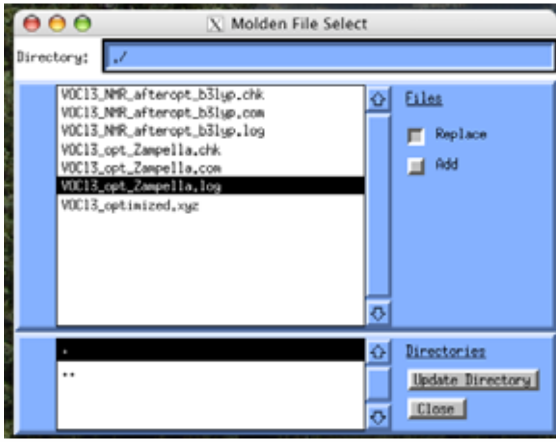
```
$ molden &                    # executes Molden
```

From the Molden Control menu, read VOCl3_opt_Zampella.log;
Select Draw Mode: Solid/Ball-and-Stick

(ignore the error message about being unable to read the basis set- this is irrelevant)



Status line:
First point



Directory: ./

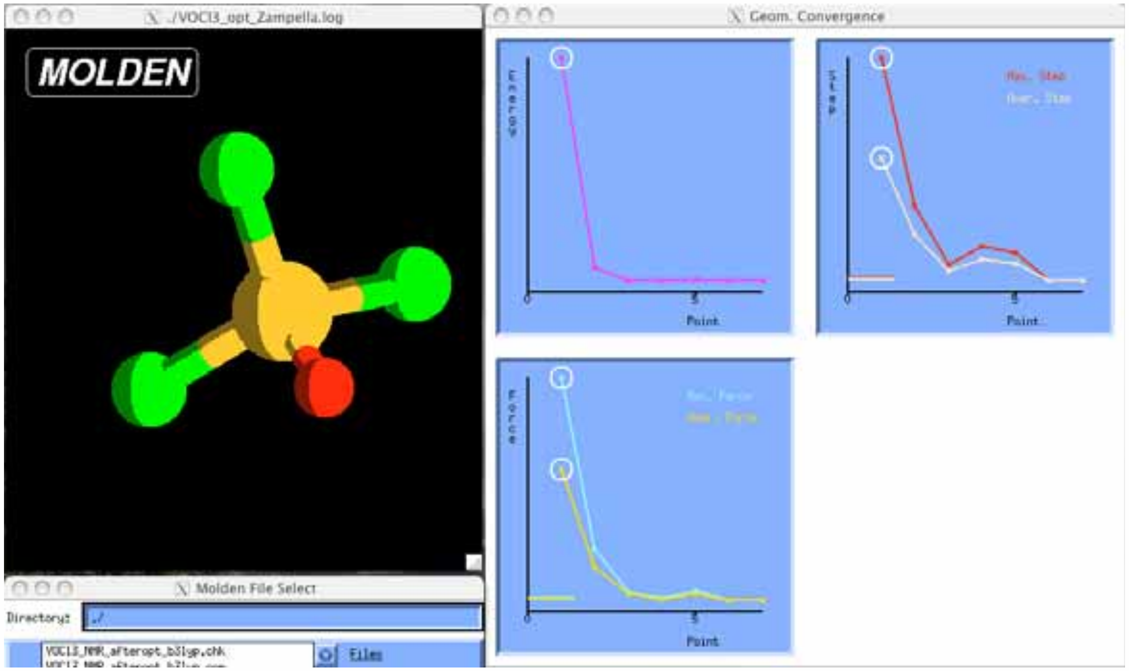
```
VOCl3_NMR_afteropt_b3lyp.chk
VOCl3_NMR_afteropt_b3lyp.com
VOCl3_NMR_afteropt_b3lyp.log
VOCl3_opt_Zampella.chk
VOCl3_opt_Zampella.com
VOCl3_opt_Zampella.log
VOCl3_optimized.xyz
```

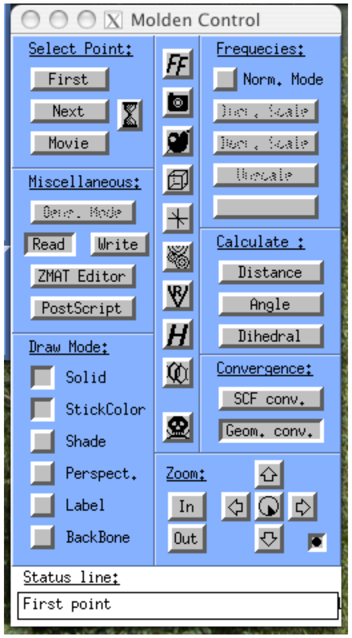
```
.
..
```

PRACTICAL EXERCISE: CALCULATION OF NMR PARAMETERS AND MOLECULAR ORBITALS FOR VOCl3

6. EXAMINE THE RESULTS OF GEOMETRY OPTIMIZATION IN MOLDEN (CON'D)

Examine the geometry convergence by selecting:
Convergence/Geom. Conv.



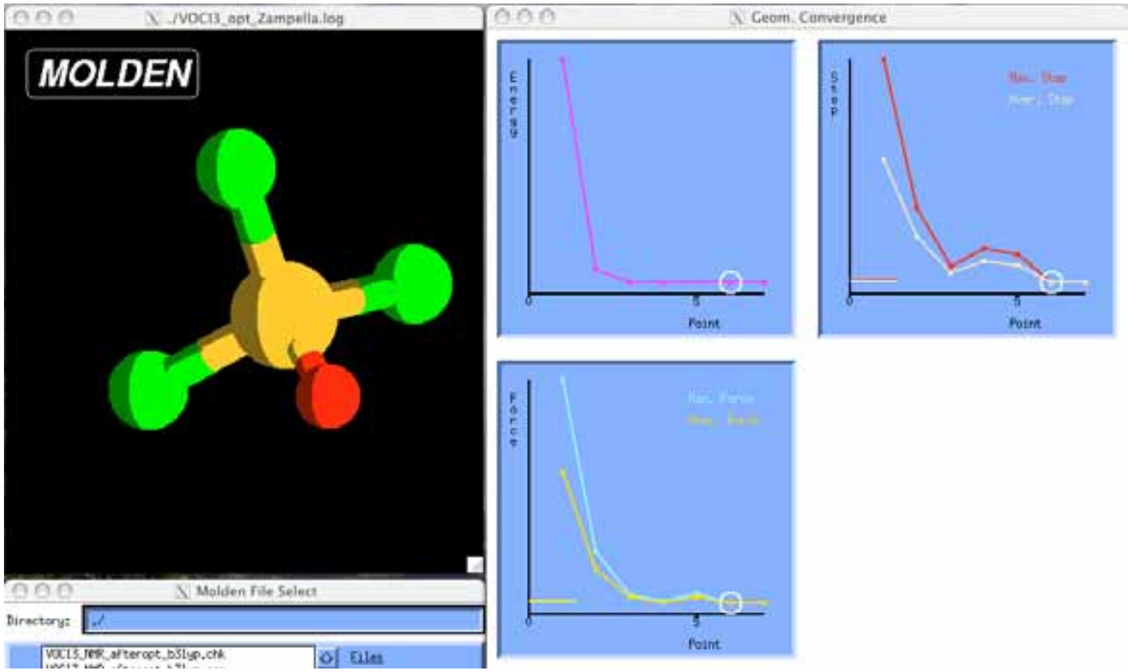


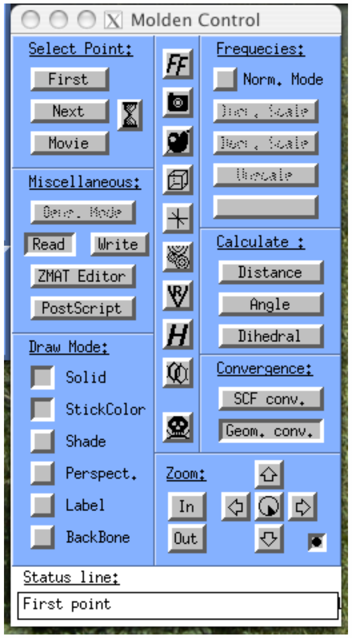
Status line: First point

PRACTICAL EXERCISE: CALCULATION OF NMR PARAMETERS AND MOLECULAR ORBITALS FOR VOCl3

6. EXAMINE THE RESULTS OF GEOMETRY OPTIMIZATION IN MOLDEN (CON'D)

Click on each of the points along the plot; the corresponding geometry will be displayed in the molecule window





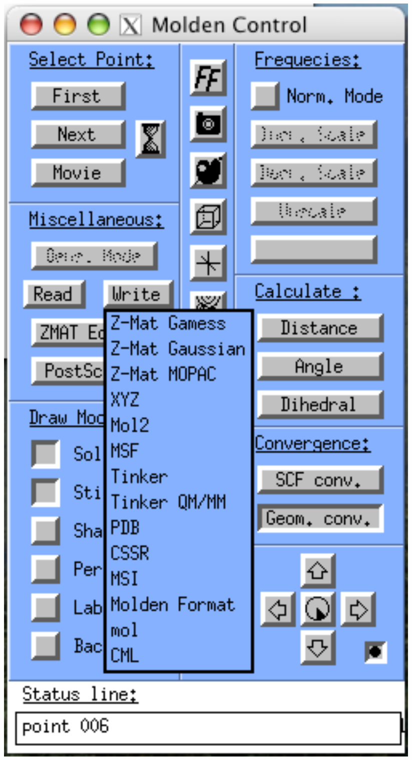
First point

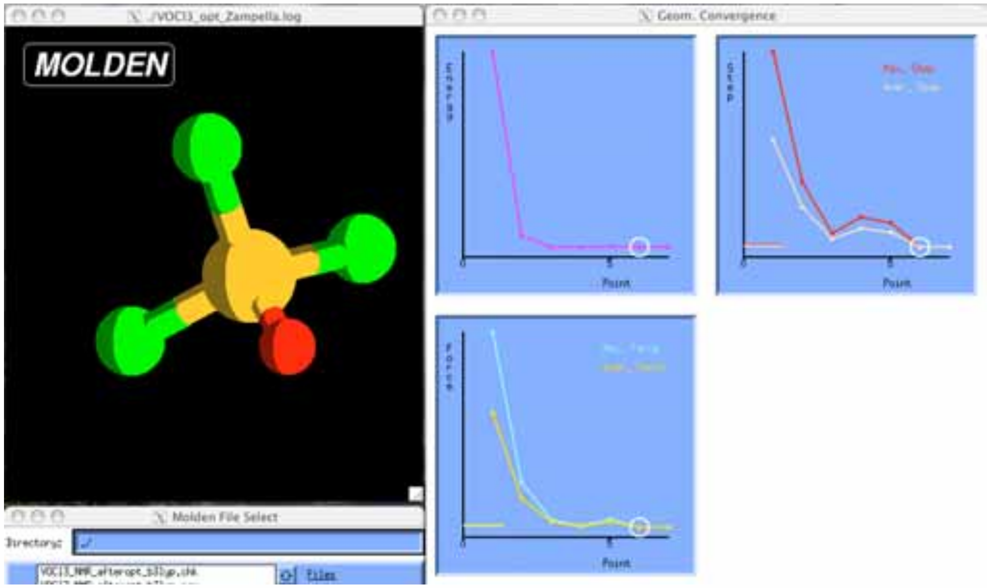
PRACTICAL EXERCISE: CALCULATION OF NMR PARAMETERS AND MOLECULAR ORBITALS FOR VOCl3

6. EXAMINE THE RESULTS OF GEOMETRY OPTIMIZATION IN MOLDEN (CON'D)

You can save the geometry produced at any step of the optimization:
Select Write/XYZ (or any other coordinate file that is supported by the program)

Note that you can then directly paste the coordinates produced by saving the XYZ file into the input file for the single point calculations of the NMR parameters that you will be executing subsequently



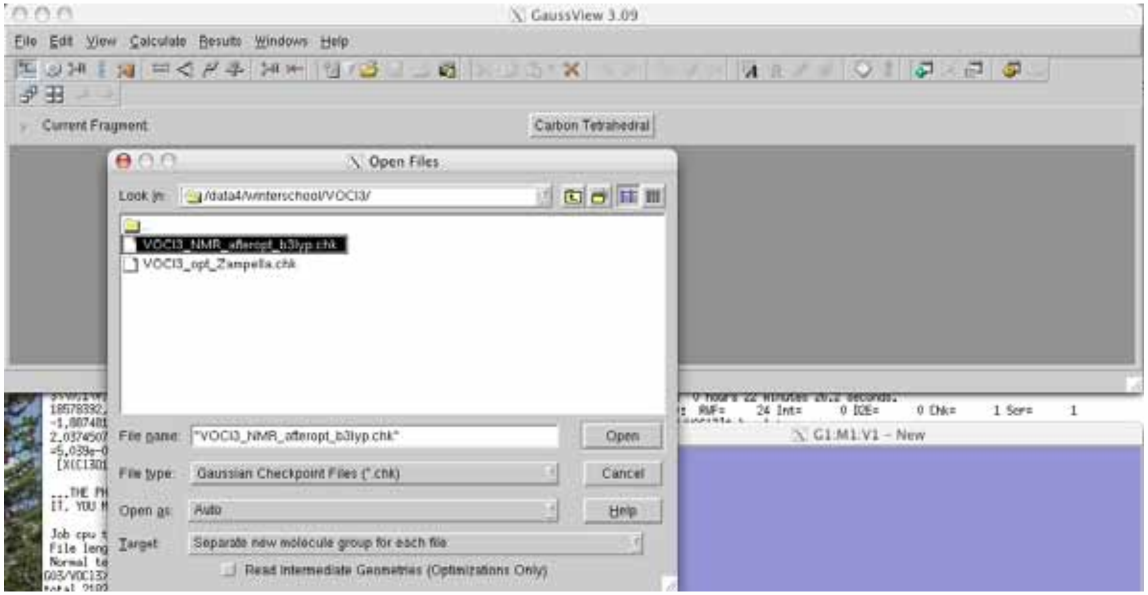


PRACTICAL EXERCISE: CALCULATION OF NMR PARAMETERS AND MOLECULAR ORBITALS FOR VOCl3

7. EXAMINE THE RESULTS OF NMR PARAMETER CALCULATIONS USING GAUSSVIEW

```
$ gview                                    #executes GaussView
```

In GaussView, open the checkpoint file VOCl_NMR_afteropt_b3lyp.chk



Look in: /data4/winterschool/VOCl3/

VOCl3_NMR_afteropt_b3lyp.chk
VOCl3_opt_Zampella.chk

File name: "VOCl3_NMR_afteropt_b3lyp.chk"

File type: Gaussian Checkpoint Files (*.chk)

Open as: Auto

Target: Separate new molecule group for each file

☐ Read Intermediate Geometries (Optimizations Only)

PRACTICAL EXERCISE: CALCULATION OF NMR PARAMETERS AND MOLECULAR ORBITALS FOR VOCl3

7. EXAMINE THE RESULTS OF NMR PARAMETER CALCULATIONS USING GAUSSVIEW: ESP SURFACE

After opening the checkpoint file, go to Results/Surfaces; under cube actions, select New Cube; Kind: Total Density, leave all the settings at default

It will take a minute or so for the program to generate the cube; then a line of data will appear under “Cubes Available”

Under “Cube Actions”, select “New Cube”/Kind: ESP, leave all the settings as defaults

It will take a few minutes to generate the ESP cube; then a line of data will also appear under “Cubes Available”

Next, select an appropriate isosurface value (0.0002 is appropriate for this example); generally adjust the isosurface value until the visualization if the difference densities is ideal

For more details, see: http://educ.gaussian.com/visual/ESP/html/ESPGaussView.htm

PRACTICAL EXERCISE: CALCULATION OF NMR PARAMETERS AND MOLECULAR ORBITALS FOR VOCl3

7. EXAMINE THE RESULTS OF NMR PARAMETER CALCULATIONS USING GAUSSVIEW: ESP SURFACE (CON'D)

Under Cubes Available, select "Electron Density from Total SCF Density"

Select Surface Actions; New Mapped Surface

Under Surface Mapping window, select "Use an Existing Cube"

Under Cubes Available, select "Electrostatic Potential from Total SCF Density"; click OK

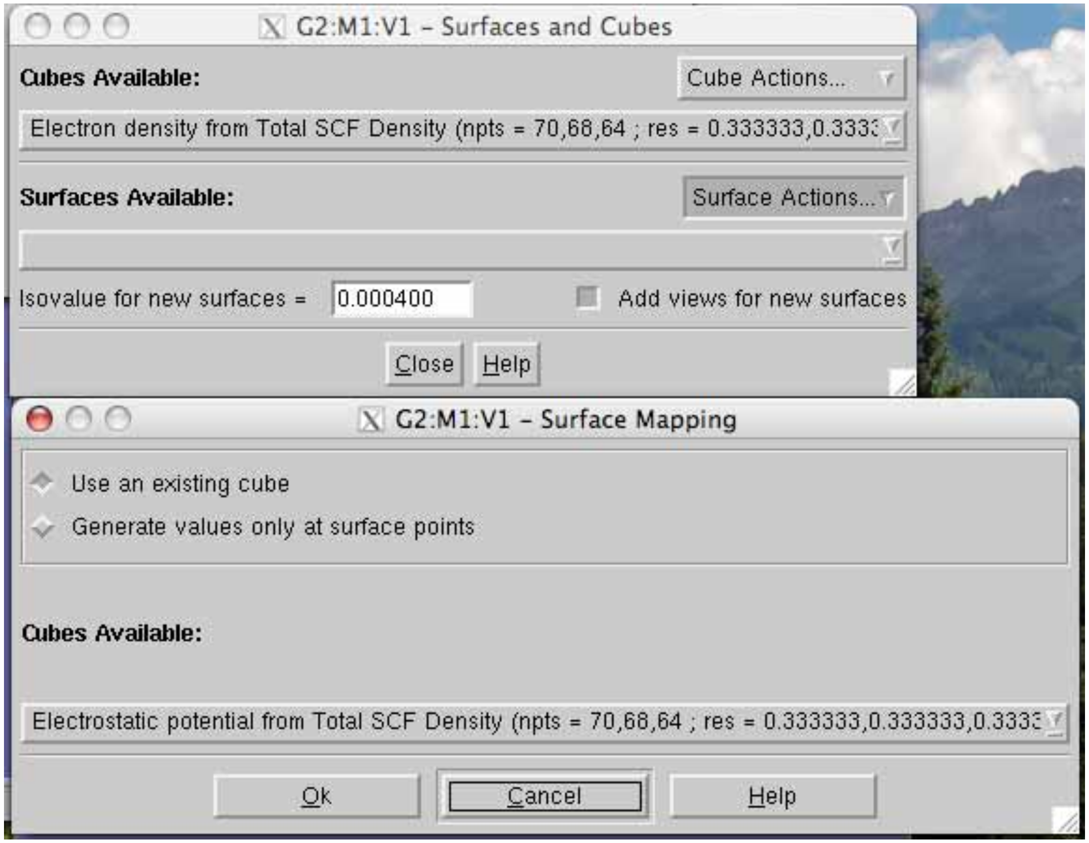
A line of data will appear under Surfaces Available;

The mapped ESP surface will be displayed in the graphical window

For more details, see: http://educ.gaussian.com/visual/ESP/html/ESPGaussView.htm

PRACTICAL EXERCISE: CALCULATION OF NMR PARAMETERS AND MOLECULAR ORBITALS FOR VOCl3

7. EXAMINE THE RESULTS OF NMR PARAMETER CALCULATIONS USING GAUSSVIEW: ESP SURFACE (CON'D)



Cubes Available:

Electron density from Total SCF Density (npts = 70,68,64 ; res = 0.333333,0.3333

Surfaces Available:

Isovalue for new surfaces = 0.000400

☐ Add views for new surfaces

◇ Use an existing cube

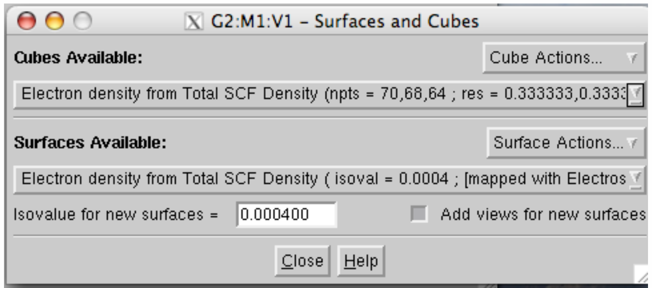
◇ Generate values only at surface points

Cubes Available:

Electrostatic potential from Total SCF Density (npts = 70,68,64 ; res = 0.333333,0.333333,0.3333

PRACTICAL EXERCISE: CALCULATION OF NMR PARAMETERS AND MOLECULAR ORBITALS FOR VOCl3

7. EXAMINE THE RESULTS OF NMR PARAMETER CALCULATIONS USING GAUSSVIEW: ESP SURFACE (CON'D)


G2:M1:V1 – Surfaces and Cubes

Cubes Available:

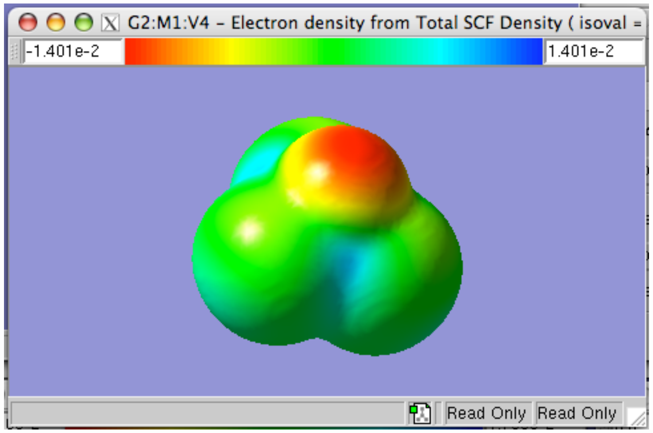
Electron density from Total SCF Density (npts = 70,68,64 ; res = 0.333333,0.3333

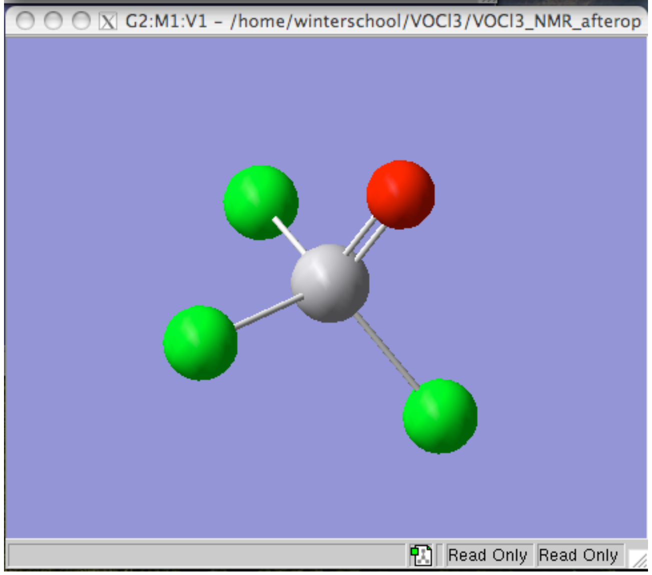
Surfaces Available:

Electron density from Total SCF Density (isoval = 0.0004 ; [mapped with Electros

Isovalue for new surfaces = 0.000400

☐ Add views for new surfaces


G2:M1:V4 – Electron density from Total SCF Density (isoval =


G2:M1:V1 – /home/winterschool/VOCl3/VOCl3_NMR_afterop

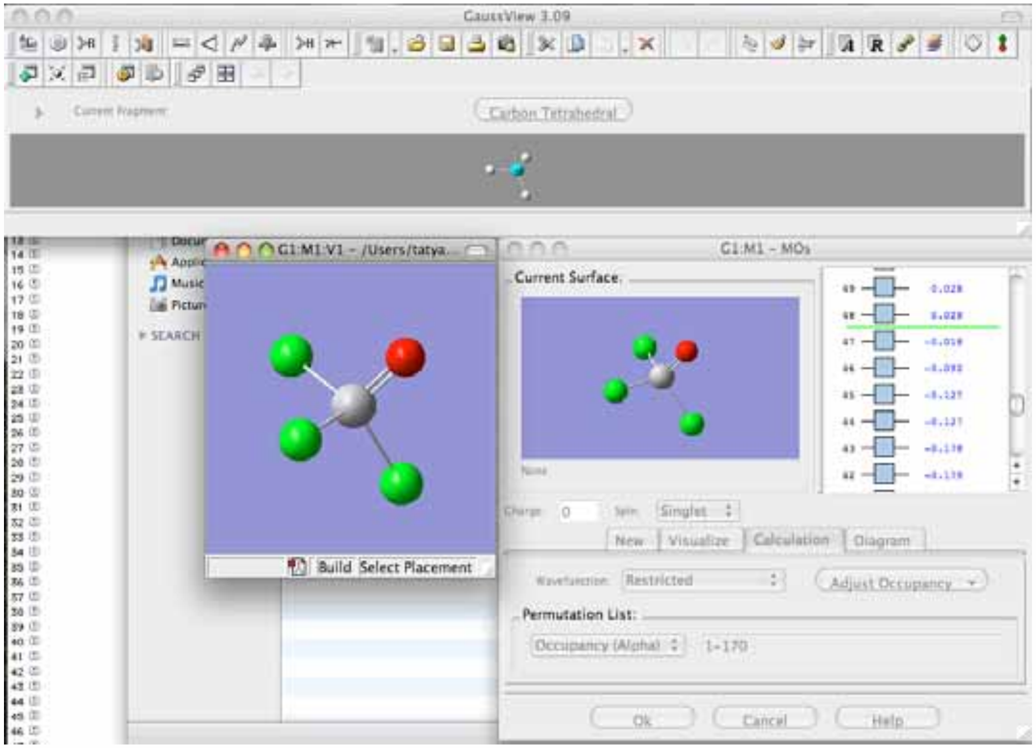
PRACTICAL EXERCISE: CALCULATION OF NMR PARAMETERS AND MOLECULAR ORBITALS FOR VOCl3

7. VISUALIZE MOLECULAR ORBITALS IN GAUSSVIEW

Open the checkpoint file
VOCl3_NMR_afteropt_b3lyp.chk
in GaussView;
Go to the Orbital Editor

On the right side,
orbitals are listed

Under Diagram, you can
arrange those with respect to
Energy or occupancy



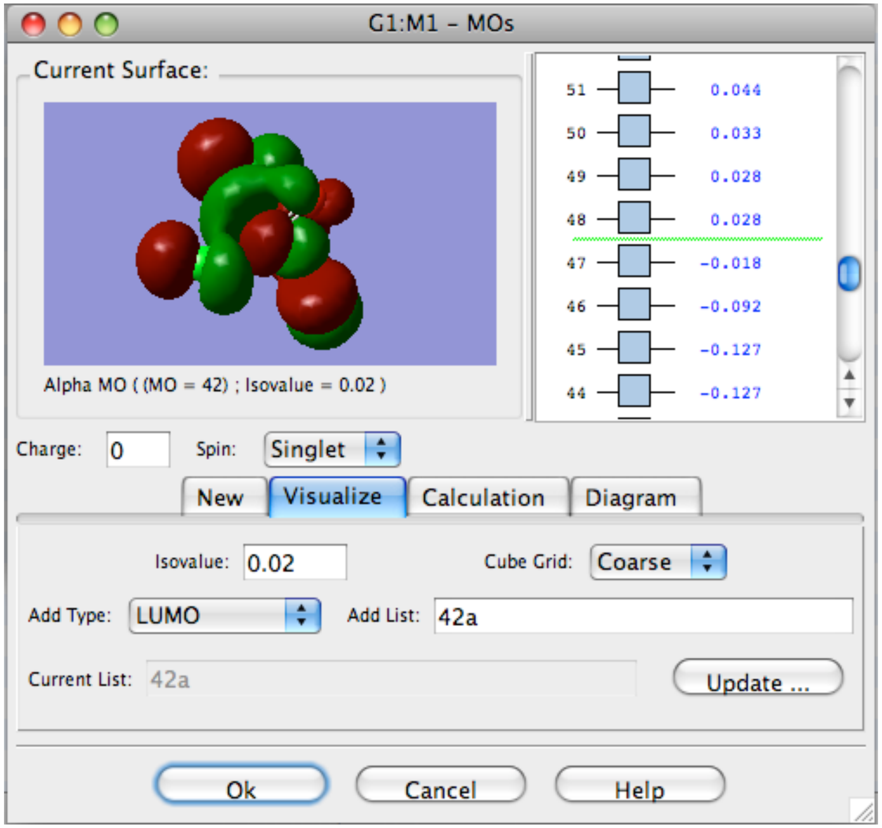
For more details, see: http://educ.gaussian.com/visual/ESP/html/ESPGaussView.htm

PRACTICAL EXERCISE: CALCULATION OF NMR PARAMETERS AND MOLECULAR ORBITALS FOR VOCl3

7. VISUALIZE MOLECULAR ORBITALS IN GAUSSVIEW

Under Visualize, select the set of orbitals you would like to display (e.g., LUMO)

Keep the settings as default



Alpha MO ((MO = 42) ; Isovalue = 0.02)

51	0.044
50	0.033
49	0.028
48	0.028
47	-0.018
46	-0.092
45	-0.127
44	-0.127

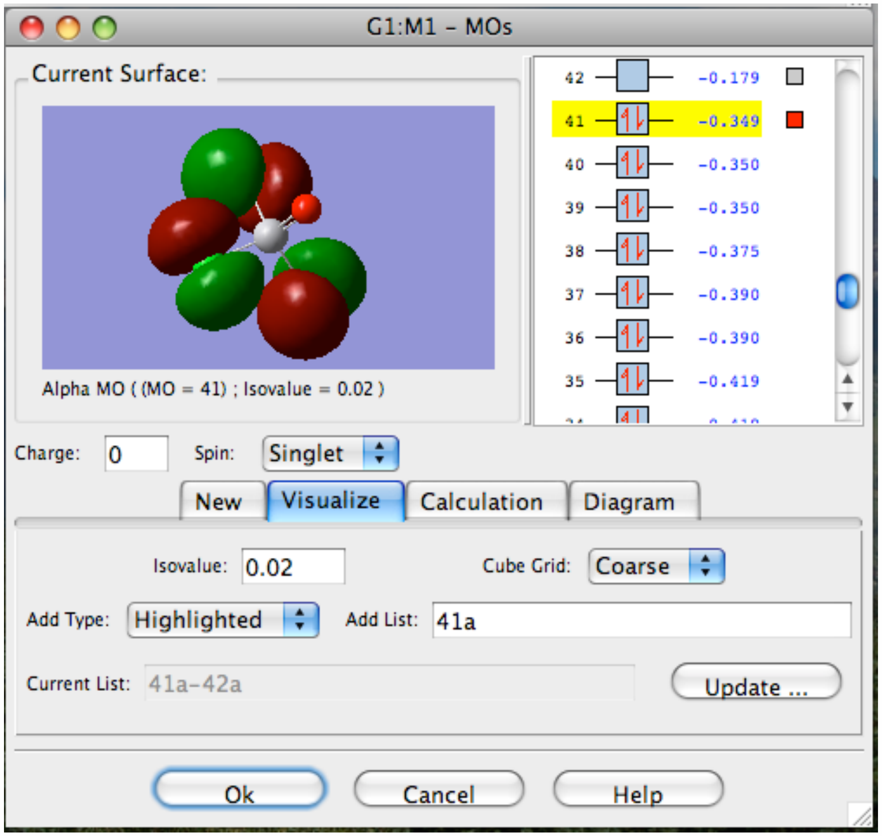
Charge: 0
Spin: Singlet
Isovalue: 0.02
Cube Grid: Coarse
Add Type: LUMO
Add List: 42a
Current List: 42a

For more details, see: http://educ.gaussian.com/visual/ESP/html/ESPGaussView.htm

PRACTICAL EXERCISE: CALCULATION OF NMR PARAMETERS AND MOLECULAR ORBITALS FOR VOCl3

7. VISUALIZE MOLECULAR ORBITALS IN GAUSSVIEW

To display another orbital, select it in the menu on The right side and click "Update"



Alpha MO ((MO = 41) ; Isovalue = 0.02)

42	-0.179
41	-0.349
40	-0.350
39	-0.350
38	-0.375
37	-0.390
36	-0.390
35	-0.419

Charge: 0

Spin: Singlet

Isovalue: 0.02

Cube Grid: Coarse

Add Type: Highlighted

Add List: 41a

Current List: 41a-42a

For more details, see: http://educ.gaussian.com/visual/ESP/html/ESPGaussView.htm

SOME LITERATURE

E. Oldfield “Quantum Chemical Studies of Protein Structure” Phil. Trans. R. Soc. B 360: 1347-1361 (2005)

M. Head-Godron “Quantum Chemistry and Molecular Processes” J. Phys. Chem. 100: 13213-13225 (1996)