# Chapter #3

## Potential Energy Surface Exploration

## Coordinates, File Formats, Scans, and IRC

# Observables

[1] Structure.

[2] Energy.

[3] Properties.

Spectroscopy: MW, IR, UV/Vis, NMR, ESR,…

Thermochemistry and Kinetics.

# Potential Energy Surface, PES

$$\text{Energy} = E(x_1, y_1, z_1, x_2, y_2, z_2, \ldots x_M, y_M, z_M)$$

Nonlinear: M = 3N - 6

Linear: M = 3N - 5

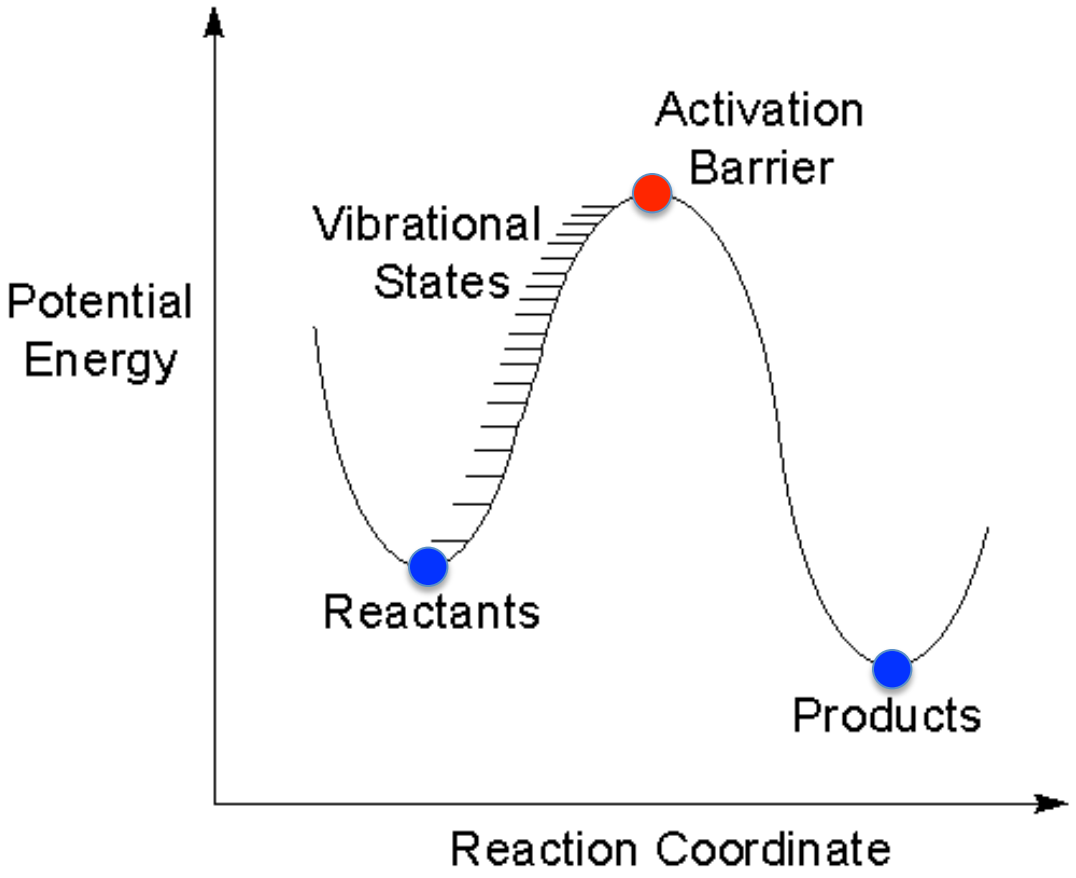
N is the number of atoms.

3N is the total number of degrees of freedom.

M is the number of internal degrees of freedom which describe the structure.

3N – M degrees of freedom describe the motion of the molecule as a whole.

# PES and Stationary Structures



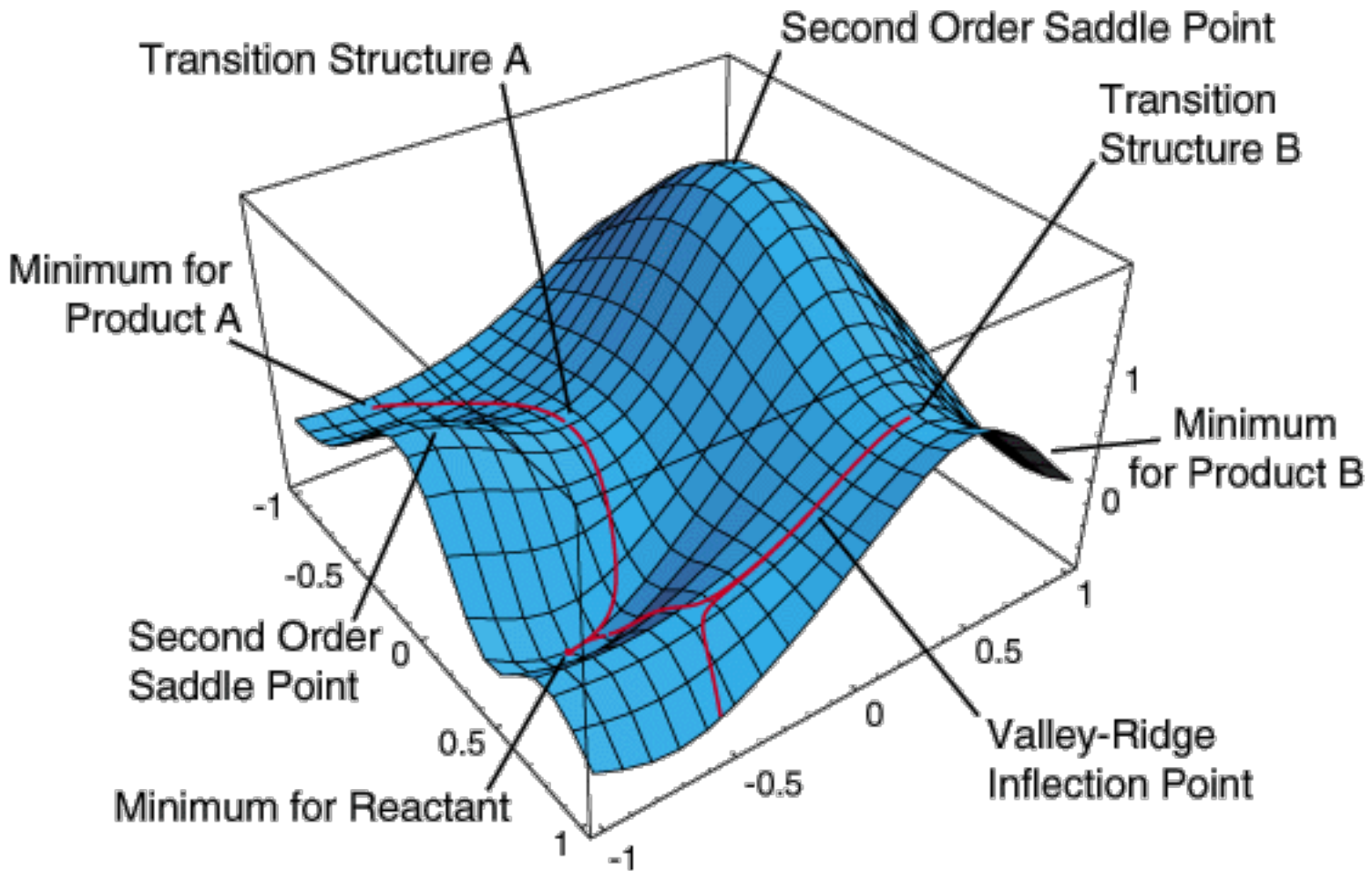

Stationary Structure
Gradient = 0

Minimum (pl.: Minima)
All curvatures are positive

Transition State Structure
ONE curvature is negative

Higher-Order Saddle Point
More than one curvature are negative

# Potential Energy Surface, PES




www.chem.wayne.edu/ ~hbs/chm6440/PES.html

# Chapter #3

## 3.1. Stationary Structures, Symmetry, Step-by-Step Scans – Preparation for Assignment #1

# $NH_3$ Str. Opt.: Internal Coordinates

**Draw $NH_3$ in Active Window without using Point Group**

**Save as internal coordinates from "File" menu**

```
%chk=C:\Users\glaserr\Desktop\ammonia.chk
# hf/6-31G* geom=connectivity

Title Card Required

0 1
 N
 H                  1           B1
 H                  1           B2     2            A1
 H                  1           B3     3            A2     2            D1     0

   B1             1.00000000
   B2             1.00000000
   B3             1.00000000
   A1           109.47120255
   A2           109.47125080
   D1          -119.99998525

 1 2 1.0 3 1.0 4 1.0
 2
 3
 4
```

# $NH_3$ Str. Opt.: Cartesian Coordinates

**Draw $NH_3$ in Active Window without using Point Group**

**Save as Cartesian coordinates from "File" menu (mark "Write Cartesians")**

```
%chk=C:\Users\glaserr\Desktop\ammonia_coord.chk
# hf/6-31G* geom=connectivity

Title Card Required

0 1
 N                  0.00000000    0.00000000    0.00000000
 H                  0.00000000    0.00000000    1.00000000
 H                  0.94280915    0.00000000   -0.33333304
 H                 -0.47140478   -0.81649655   -0.33333304

 1 2 1.0 3 1.0 4 1.0
 2
 3
 4
```

Optimization will still be performed in internal coordinates.

# $NH_3$ Opt.: $C_{3v}$, Internal Coords.

```
%nprocshared=1
%mem=128MW
%chk=C:\Users\glaserr\Desktop\ammonia_C3v.chk
# opt=z-matrix hf/6-31G*

Ammonia in C3v

0 1
 N
 X    1         1.0
 H    1          b1     2          a1
 H    1          b1     2          a1     3   120.0     0
 H    1          b1     2          a1     3  -120.0     0

b1=1.
a1=110.
```

Opt=z-matrix: Optimization will be performed in the internal coordinates specified in the z-matrix.

# $NH_3$ Opt.: $D_{3h}$, Internal Coords. I

```
%nprocshared=1
%mem=128MW
%chk=C:\Users\glaserr\Desktop\ammonia_D3h.chk
# opt=z-matrix hf/6-31G*

Ammonia in D3h

0 1
 N
 X    1         1.0
 H    1          b1    2         90.
 H    1          b1    2         90.    3  120.0    0
 H    1          b1    2         90.    3 -120.0    0

b1=1.
```

# $NH_3$ Opt.: $D_{3h}$, Internal Coords. II

```
%nprocshared=1
%mem=128MW
%chk=C:\Users\glaserr\Desktop\ammonia_D3h_V2.chk
# opt=z-matrix hf/6-31G*

Ammonia in D3h

0 1
 N
 H    1         b1
 H    1         b1    2         120.
 H    1         b1    2         120.   3 -180.0    0

b1=1.
```

# Characterize Your PES Position

Gradient Vector:
Change of energy $E(r_i)$ as a function of coordinate $r_i$

Curvature Matrix: (Hessian)
Change of the change of energy $E$
-- as a function of coordinate $q_i$
-- as a function of coordinates $q_i$ and $q_j$

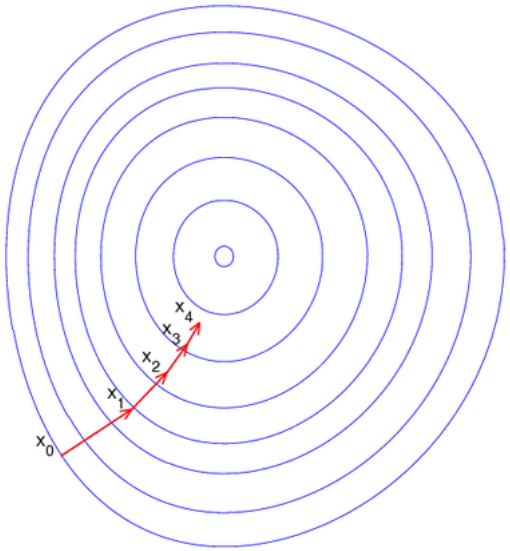
*Estimate and update, opt*
*Compute once, opt=calcfc*
*Compute everytime, opt=calcall*

*Analytically*
*or*
*Numerically*

# Steepest Descent

Steepest Descent: Take steps proportional to the negative of the gradient of the energy of the present structure: Walk to MINIMUM.

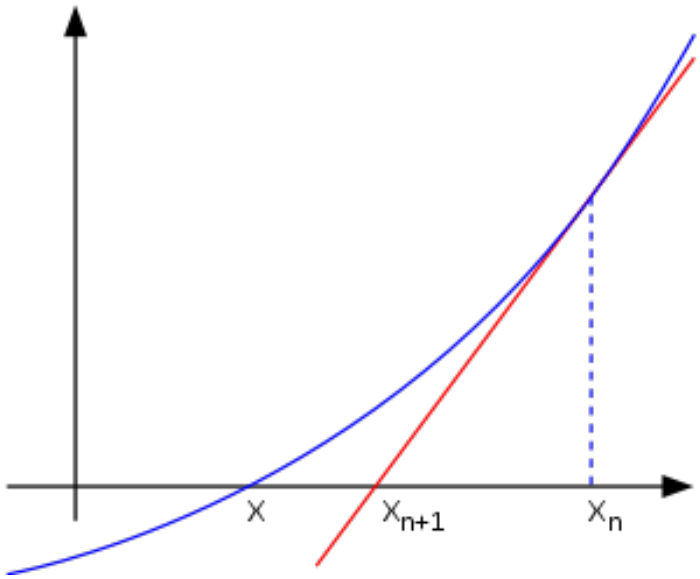
Steepest Ascent: Take steps proportional to the negative of the gradient of the energy of the present structure: Walk to TRANSITION STATE.



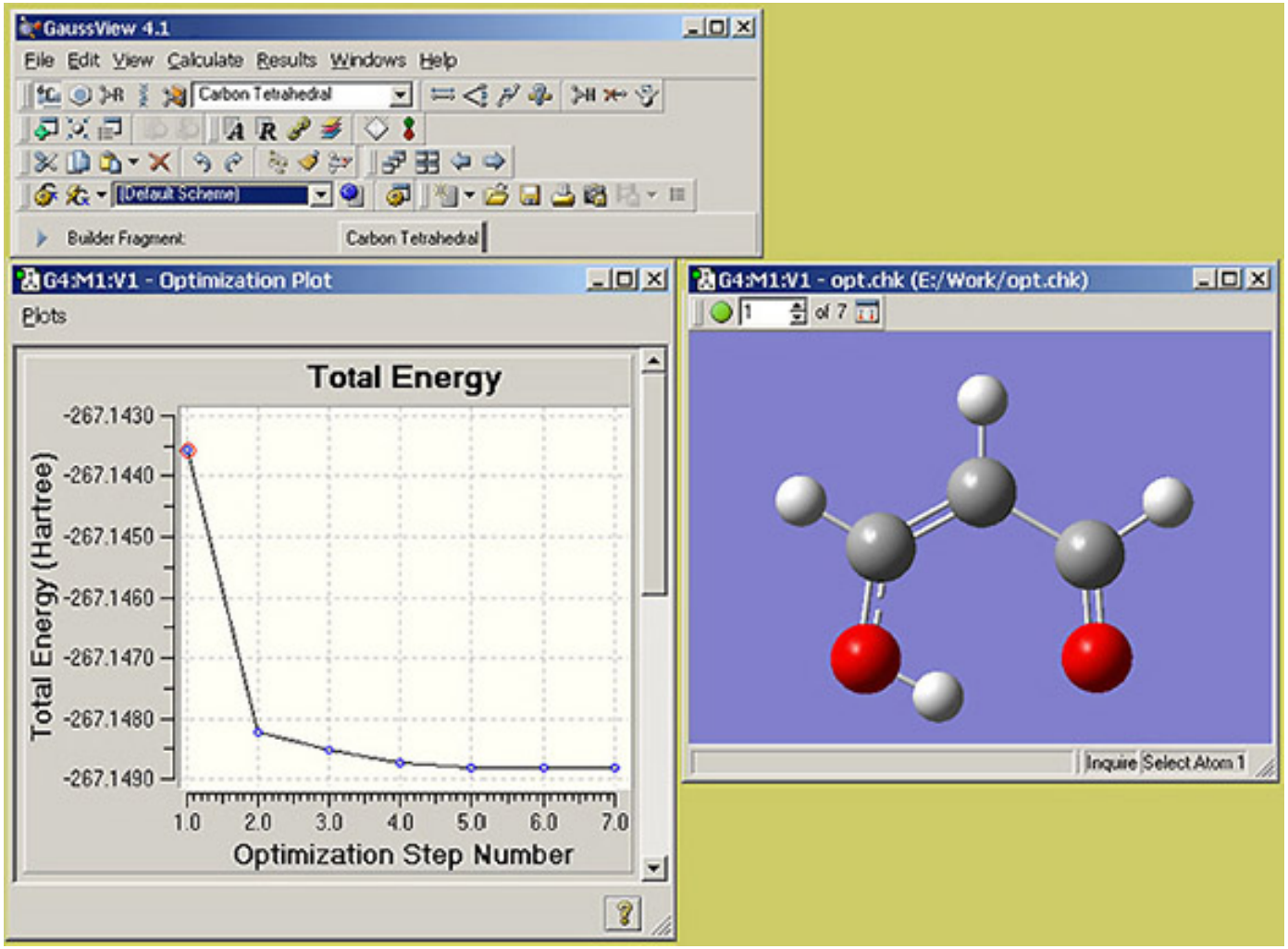
# Newton-Raphson Method

Gradient: Where to go.

Curvature: How far to step.
High curvature, small step.



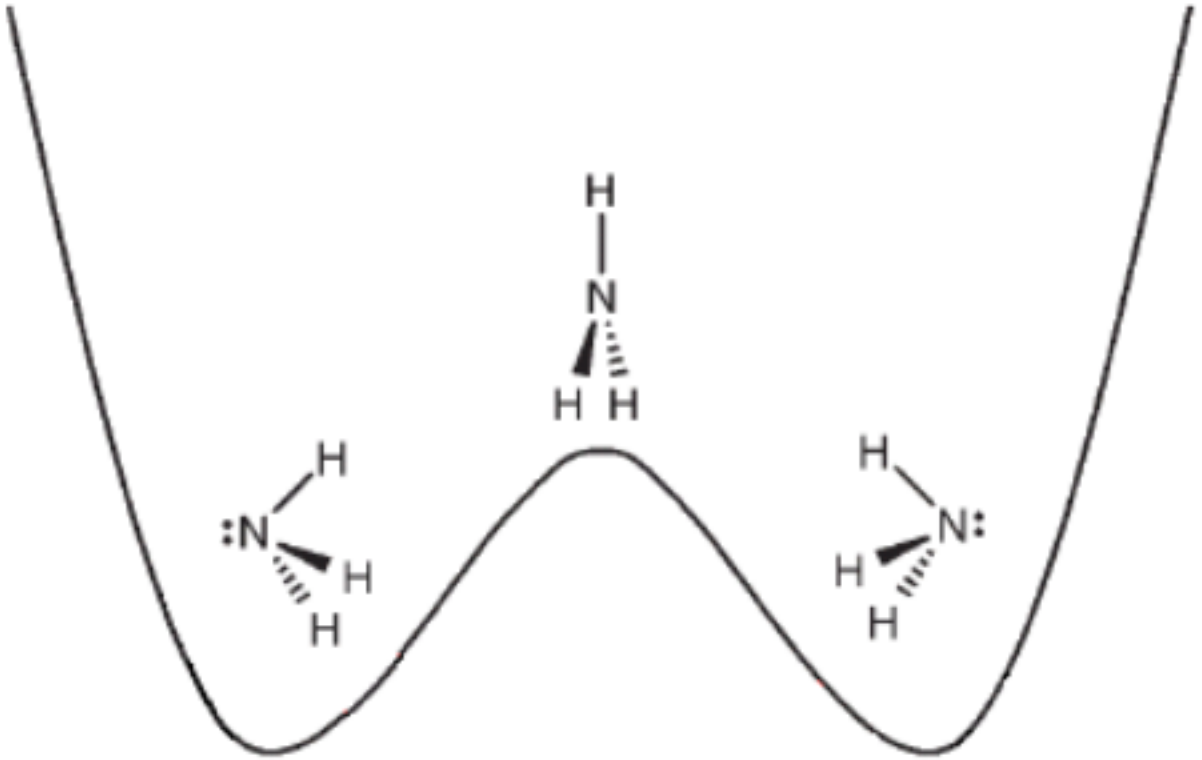
# Optimization Steps



# $NH_3$ Opt.: Locate TS

```
%chk=C:\Users\glaserr\Desktop\ammonia_TS.chk
# hf/6-31G* opt=(TS,calcfc) geom=connectivity

Title Card Required

0 1
 N
 H          1       B1
 H          1       B2     2      A1
 H          1       B3     3      A2     2    D1     0

   B1              1.00000000
   B2              1.00000000
   B3              1.00000000
   A1            118.23587891
   A2            121.47125080
   D1           -115.99998525

 1 2 1.0 3 1.0 4 1.0
 2
 3
 4
```

# PES and Scan of Inversion Path

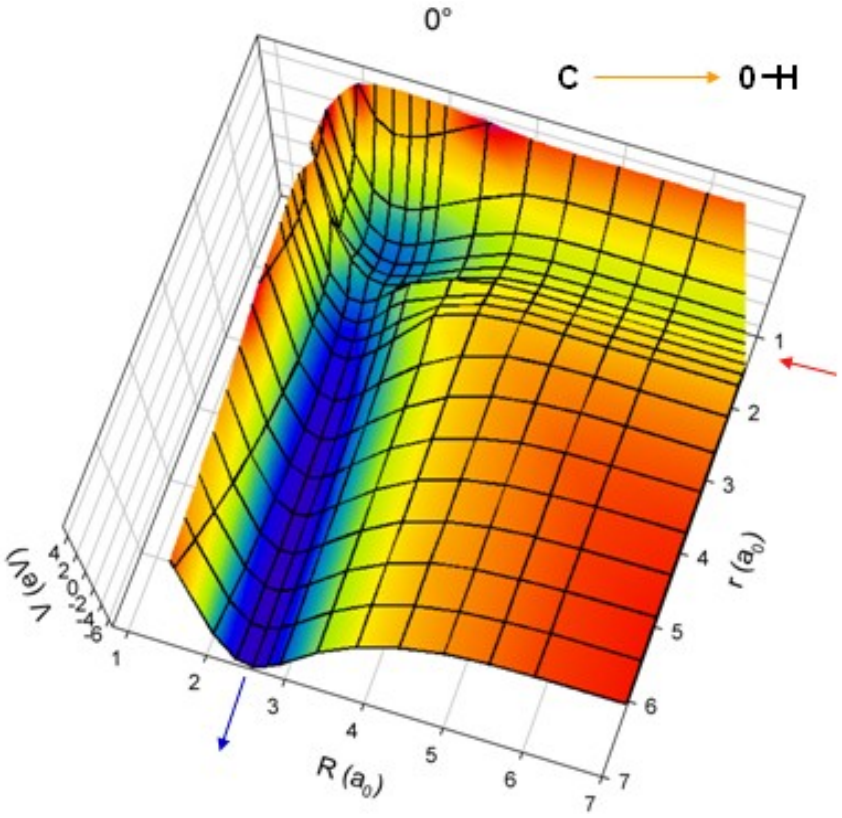



One internal coordinate suffices to define a “good path”

# $NH_3$ Str. Opt.: Constrained

```
%nprocshared=1
%mem=128MW
%chk=C:\Users\glaserr\Desktop\partd_80.chk
# opt=z-matrix hf/6-31G*

Ammonia with a1 angle 80 degrees

0 1
 N
 X    1        1.0
 H    1         b1    2        a1
 H    1         b1    2        a1    3  120.0    0
 H    1         b1    2        a1    3 -120.0    0

b1=1.          Variable will be optimized

a1=80.         Variable after the extra line with NOT be optimized
```

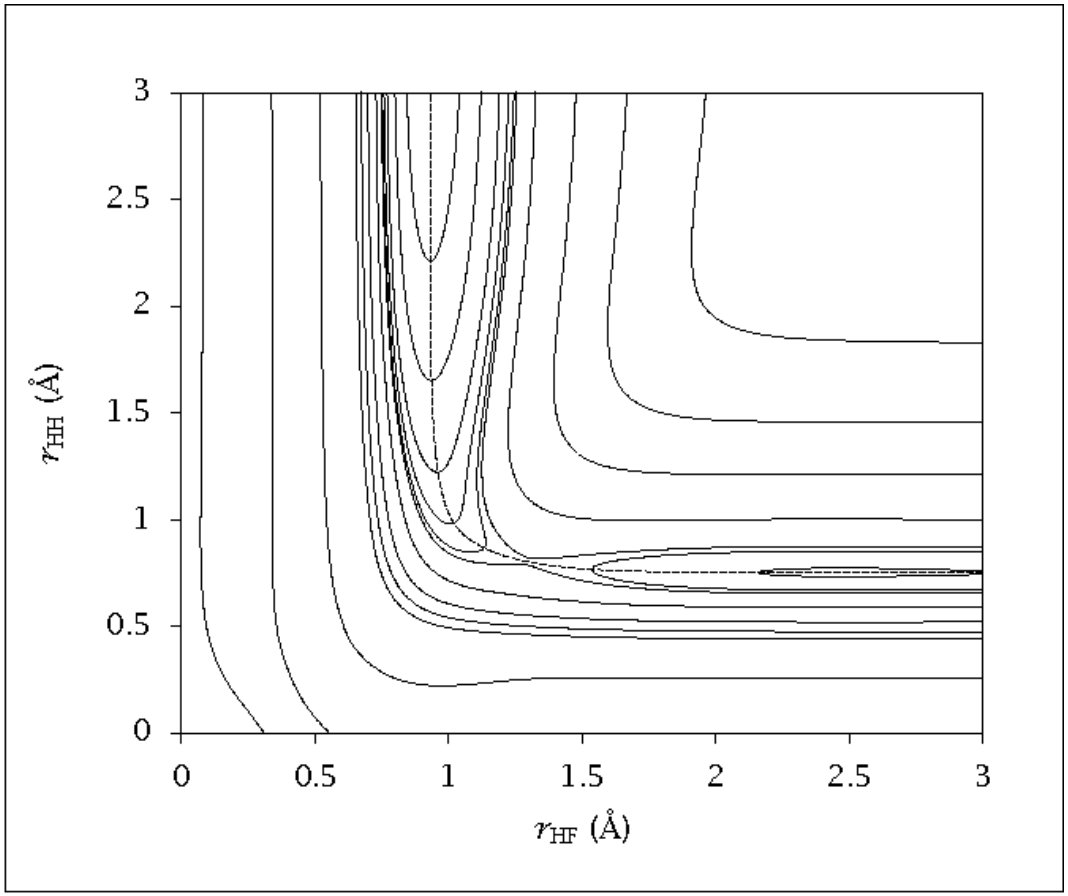
# PES Scan: 2 of 3 Coordinates




C + OH ➔ CO + H

http://www.utinam.cnrs.fr/utinam/IMG/jpg/COHcol.jpg

# PES: PES Scan *versus* IRC




http://jbrwww.che.wisc.edu/home/jbraw/chemreacfun/ch5/figures/hfc.png

# Chapter #3

## 3.2.1 CIF and PDB File Formats – Preparation for Assignment #2

# CIF File @ Acta Cryst.

MU - Chemistry 8330 - FS16 | (IUCr) Acta Crystallographi...

journals.iucr.org/b/issues/2016/04/00/

Search

Acta Cryst B

**Acta Crystallographica Section B**

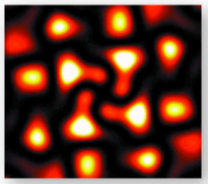
STRUCTURAL SCIENCE, CRYSTAL ENGINEERING AND MATERIALS

search IUC

home | archive | editors | for authors | for readers | submit | subscribe | open access

## research papers

*Acta Cryst.* (2016). B**72**, 571-583
doi: 10.1107/S2052520616005552



### An insight into real and average structure from diffuse X-ray scattering – a case study

**M. L. Chodkiewicz, A. Makal, R. Gajda, D. Vidovic and K. Woźniak**

Diffuse X-ray scattering from an organic salt has been analysed including modeling of the local structure, explaining relationships between symmetry and extinction patterns, and assessing the sensitivity of the calculated diffuse scattering to the model of the average structure.

**CCDC references:** 1472062; 1472063; 1472064; 1472065

**Read article**

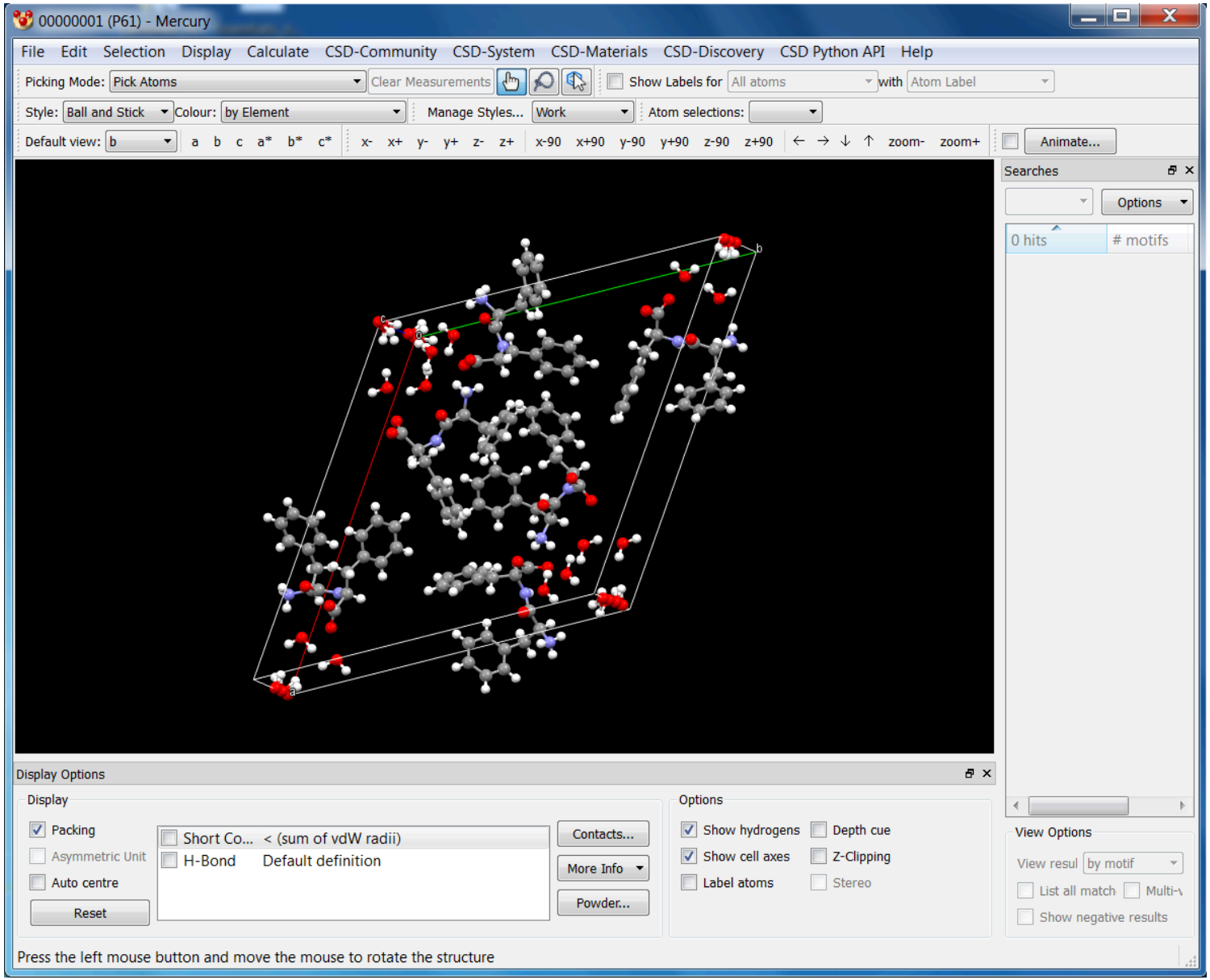
*Acta Cryst.* (2016). B**72**, 584-592
doi: 10.1107/S2052520616008180

### Self-assembly modes of glycyrrhetinic acid esters in view of the crystal packing of related triterpene molecules

# Content of a "Small Molecule" CIF File

```
##############################################################################
#
#                 Cambridge Crystallographic Data Centre
#                                 CCDC
#
##############################################################################
#
# If this CIF has been generated from an entry in the Cambridge
# Structural Database, then it will include bibliographic, chemical,
# crystal, experimental, refinement or atomic coordinate data resulting
# from the CCDC's data processing and validation procedures.
#
##############################################################################

data_00000001
_symmetry_cell_setting            hexagonal
_symmetry_space_group_name_H-M    'P 61'
_symmetry_Int_Tables_number       169
_space_group_name_Hall            'P 61'
loop_
_symmetry_equiv_pos_site_id
_symmetry_equiv_pos_as_xyz
1 x,y,z
2 -x+y,-x,2/3+z
3 -y,x-y,1/3+z
4 y,-x+y,5/6+z
5 x-y,x,1/6+z
6 -x,-y,1/2+z
_cell_length_a                    24.1048(18)
_cell_length_b                    24.1048(18)
_cell_length_c                    5.4459(5)
_cell_angle_alpha                 90
_cell_angle_beta                  90
_cell_angle_gamma                 120
_cell_volume                      2740.36
loop_
_atom_site_label
_atom_site_type_symbol
_atom_site_fract_x
_atom_site_fract_y
_atom_site_fract_z
O23 O 0.30333 0.25106 0.6074
O11 O 0.28335 0.10734 0.5575
…
H3wa H 0.18 0.08 0.2723
H3wb H 0.132 0.112 0.2697

#END
```

# Diphenylalanine in *Mercury*

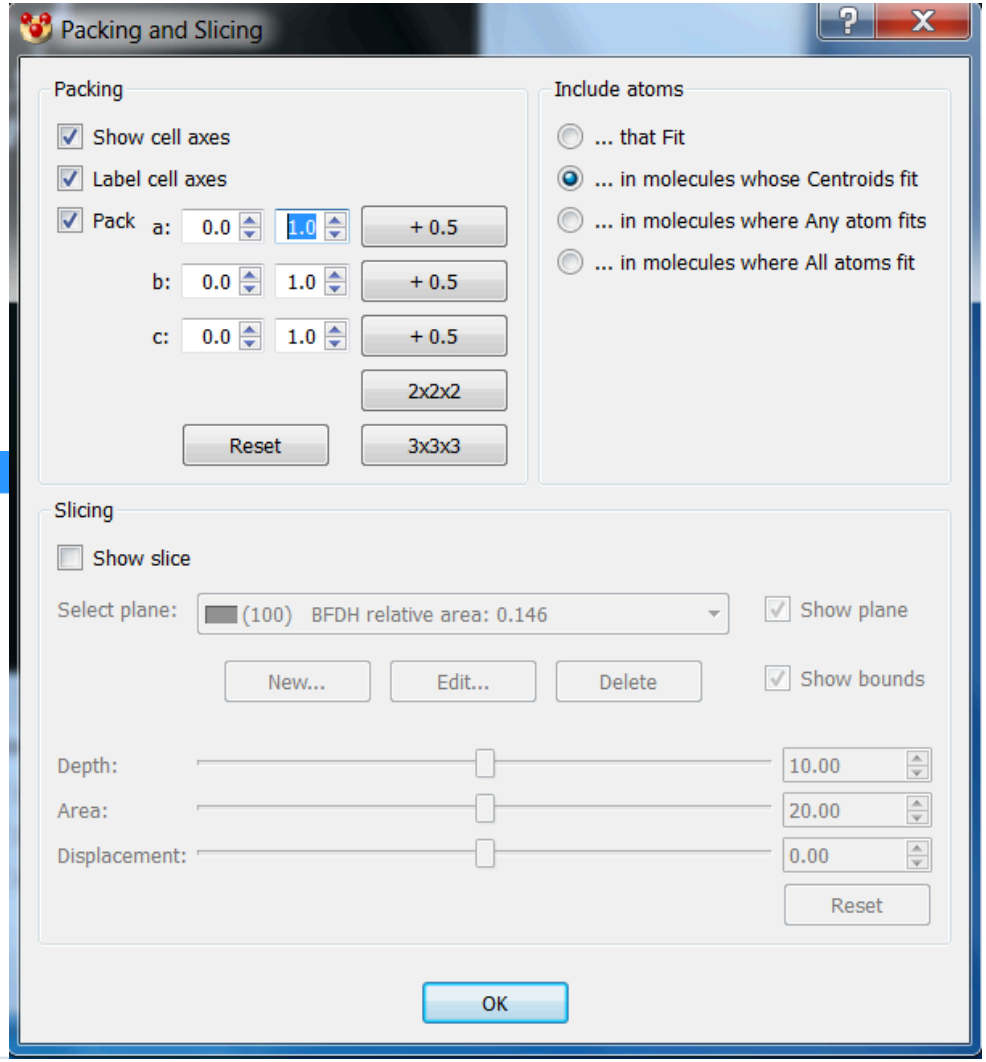


# “Calculate” Menu in *Mercury*

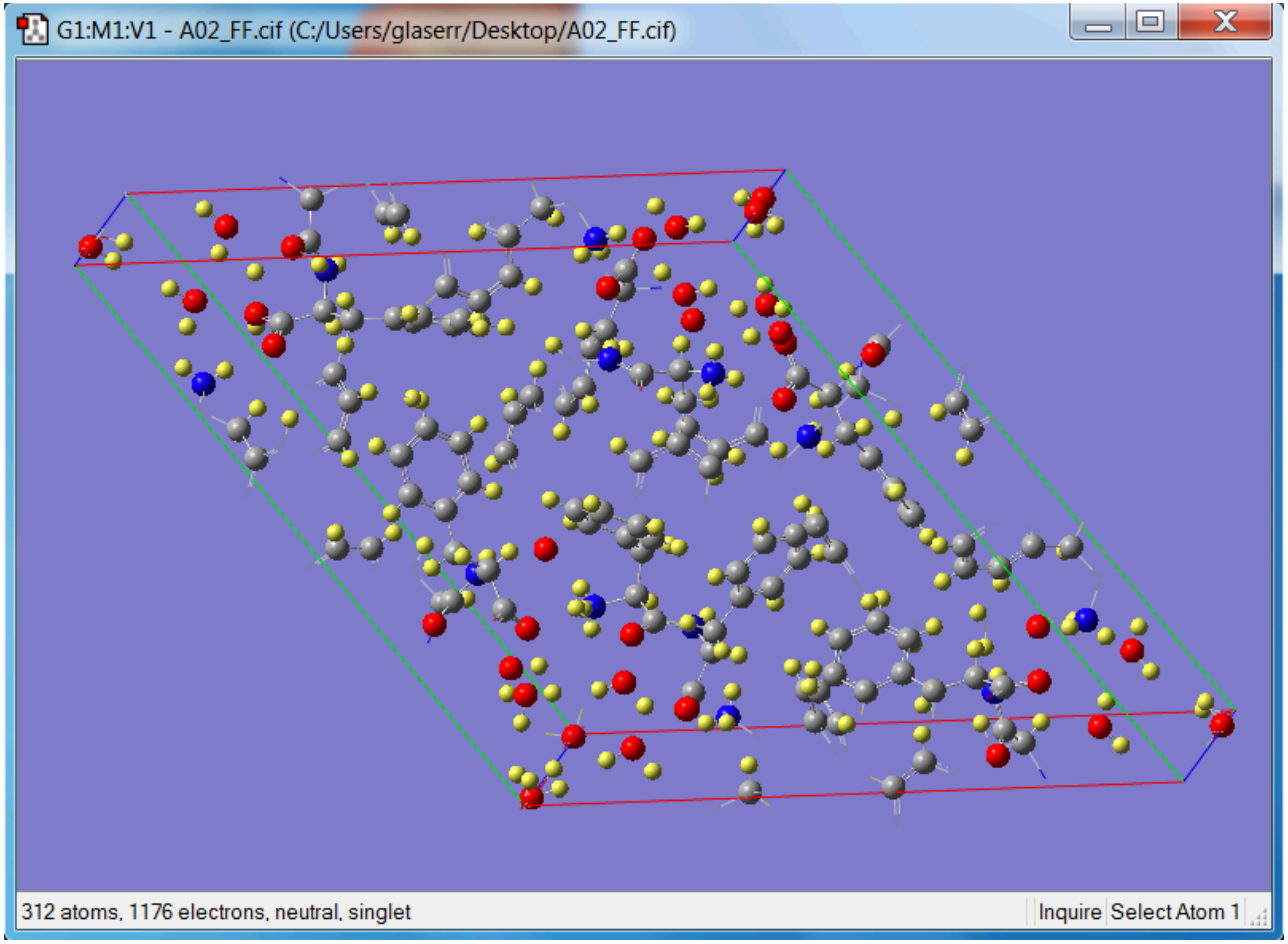
Vary the ranges along the crystal axes until the display matches your target moiety.

Save the atom coordinates of the edited structure in a file format which can be read by *GaussView*.

- Cif files (*.cif *.cmf)
- Debug output file (*.txt)
- MOL files (*.mol *.sdf *.sd *.mdl)
- Mercury compressed XML crystal files (*.mryx)
- Mol2 files (*.mol2 *.mol)
- PDB files (*.pdb *.ent)
- SHELX files (*.res *.ins)
- XMol files (*.xyz)
- BMP (*.bmp)
- JPEG (*.jpg *.jpeg *.jpe *.jfif)
- PDF (*.pdf)
- PNG (*.png)
- POV-Ray (*.pov)
- TIFF (*.tif *.tiff)

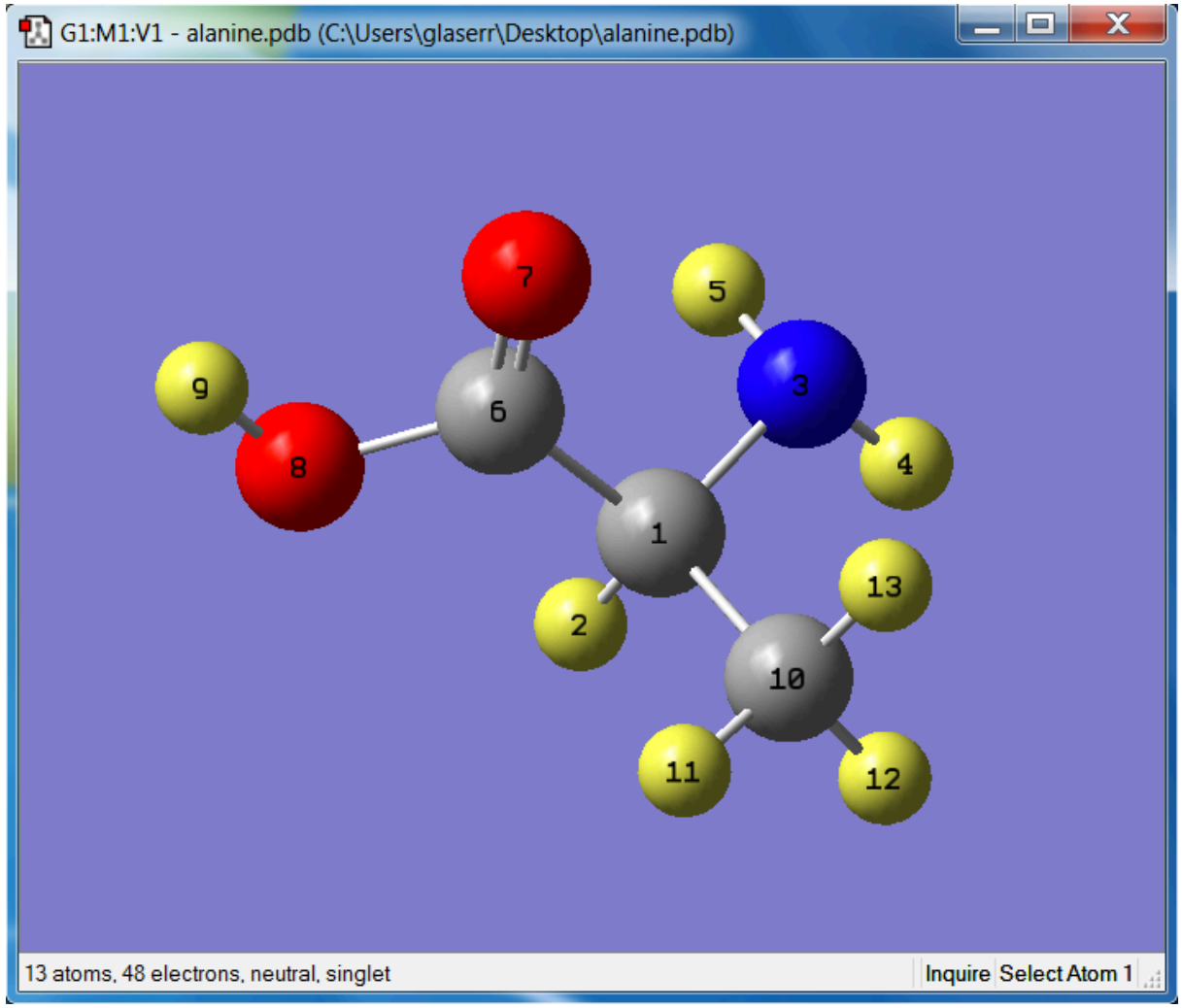


# Diphenylalanine in *GaussView*




Use “Select Atoms by Rubberband” and “Delete” until only the desired moieties of the peptide are left. Save as GJF File.

# Alanine in *GaussView*



```
TITLE       alanine
REMARK   1 File created by GaussView 5.0.9
HETATM    1  C           0        0.000    0.000    0.000                      C
HETATM    2  H           0        0.000    0.000    1.070                      H
HETATM    3  N           0        1.386    0.000   -0.490                      N
HETATM    4  H           0        1.857    0.816   -0.157                      H
HETATM    5  H           0        1.857   -0.816   -0.158                      H
HETATM    6  C           0       -0.726   -1.257   -0.514                      C
HETATM    7  O           0       -0.845   -1.691   -1.659                      O
HETATM    8  O           0       -1.310   -1.961    0.489                      O
HETATM    9  H           0       -1.760   -2.746    0.139                      H
HETATM   10  C           0       -0.726    1.258   -0.512                      C
HETATM   11  H           0       -1.767    1.190   -0.276                      H
HETATM   12  H           0       -0.309    2.125   -0.044                      H
HETATM   13  H           0       -0.604    1.333   -1.573                      H
END
CONECT    1    2    3    6   10
CONECT    2    1
CONECT    3    4    5    1
CONECT    4    3
CONECT    5    3
CONECT    6    7    8    1
CONECT    7    6
CONECT    8    6    9
CONECT    9    8
CONECT   10   11   12   13    1
CONECT   11   10
CONECT   12   10
CONECT   13   10
```

# Alanine Saved by *GaussView* as PDB File

MU - Chemistry 833 | RCSB PDB - 5CJH: Cr

www.rcsb.org/pdb/explore/explore.do?structureId=5CJH

RCSB PDB | Deposit | Search | Visualize | Analyze | Download | Learn | More | MyPDB Login

RCSB PDB PROTEIN DATA BANK — An Information Portal to 122121 Biological Macromolecular Structures

Search by PDB ID, author, macromolecule, sequence, or ligands | Go

Advanced Search | Browse by Annotations

PDB-101 | PDB | EMDataBank | Nucleic Acid Database | StructuralBiology Knowledgebase | Worldwide Protein Data Bank Foundation

Structure Summary | 3D View | Annotations | Sequence | Sequence Similarity | Structure Similarity | Experiment

Biological Assembly 1

View in 3D: NGL or JSmol or PV (in Browser)

Standalone Viewers

Simple Viewer | Protein Workshop | Ligand Explorer | Kiosk Viewer

Biological assembly 1 generated by PISA (software)

Macromolecule Content

- Unique protein chains: 1

# 5CJH

## Crystal Structure of Eukaryotic Oxoiron MagKatG2 at pH 8.5

**DOI**: 10.2210/pdb5cjh/pdb

**Classification**: OXIDOREDUCTASE
**Deposited**: 2015-07-14 **Released**: 2015-09-02
**Deposition author(s)**: Gasselhuber, B., Obinger, C., Fita, I., Carpena, X.
**Organism**: Magnaporthe oryzae
**Expression System**: Escherichia coli

**Structural Biology Knowledgebase**: 5CJH (1 model >18 annotations) SBKB.org

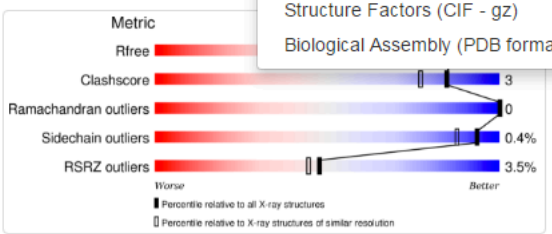
Display Files | Download Files

- FASTA Sequence
- PDB Format
- PDB Format (gz)
- PDBx/mmCIF Format
- PDBx/mmCIF Format (gz)
- PDBML/XML Format (gz)
- Structure Factors (CIF)
- Structure Factors (CIF - gz)
- Biological Assembly (PDB format - gz) (S)

**Experimental Data Snapshot**

**Method**: X-RAY DIFFRACTION
**Resolution**: 1.6 Å
**R-Value Free**: 0.190
**R-Value Work**: 0.165

**wwPDB Validation**




## Literature

Download Primary Citation

Eukaryotic Catalase-Peroxidase: The Role of the Trp-Tyr-Met Adduct in Protein Stability, Substrate Accessibility, and Catalysis of Hydrogen Peroxide Dismutation.

Gasselhuber, B., Carpena, X., Graf, M.M., Pirker, K.F., Nicolussi, A., Sundermann, A., Hofbauer, S., Zamocky, M., Furtmuller, P.G., Jakopitsch, C., Oostenbrink, C., Fita, I., Obinger, C.

(2015) Biochemistry **54**: 5425-5438

Contact Us

5cjh @ PDB

# Beginning of 5cjh.pdb File

## More Section Types

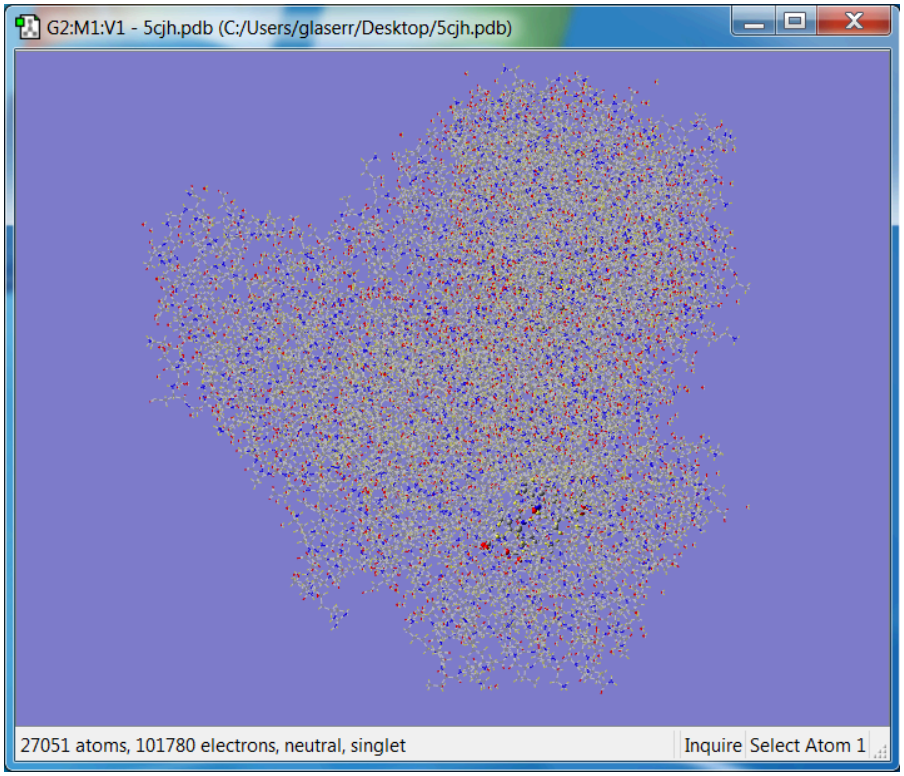
```
HEADER    OXIDOREDUCTASE                          14-JUL-15   5CJH
TITLE     CRYSTAL STRUCTURE OF EUKARYOTIC OXOIRON MAGKATG2 AT PH 8.5
COMPND    MOL_ID: 1;
COMPND   2 MOLECULE: CATALASE-PEROXIDASE 2;
COMPND   3 CHAIN: A, B;
COMPND   4 FRAGMENT: RESIDUES 24-786;
COMPND   5 SYNONYM: CP 2,PEROXIDASE/CATALASE 2;
COMPND   6 EC: 1.11.1.21;
COMPND   7 ENGINEERED: YES
SOURCE    MOL_ID: 1;
SOURCE   2 ORGANISM_SCIENTIFIC: MAGNAPORTHE ORYZAE (STRAIN 70-15 / ATCC MYA-
SOURCE   3 4617 / FGSC 8958);
SOURCE   4 ORGANISM_COMMON: RICE BLAST FUNGUS;
SOURCE   5 ORGANISM_TAXID: 242507;
SOURCE   6 GENE: KATG2, CPXB, MAGKATG2, MGG_09834;
SOURCE   7 EXPRESSION_SYSTEM: ESCHERICHIA COLI;
SOURCE   8 EXPRESSION_SYSTEM_TAXID: 562
KEYWDS    OXIDOREDUCTASE, COMPOUND I, OXOIRON CATALASE-PEROXIDASE
EXPDTA    X-RAY DIFFRACTION
AUTHOR    B.GASSELHUBER,C.OBINGER,I.FITA,X.CARPENA
REVDAT   3   28-OCT-15 5CJH    1
REVDAT   2   16-SEP-15 5CJH    1       JRNL
REVDAT   1   02-SEP-15 5CJH    0
JRNL        AUTH   B.GASSELHUBER,X.CARPENA,M.M.GRAF,K.F.PIRKER,A.NICOLUSSI,
JRNL        AUTH 2 A.SUNDERMANN,S.HOFBAUER,M.ZAMOCKY,P.G.FURTMULLER,
JRNL        AUTH 3 C.JAKOPITSCH,C.OOSTENBRINK,I.FITA,C.OBINGER
JRNL        TITL   EUKARYOTIC CATALASE-PEROXIDASE: THE ROLE OF THE TRP-TYR-MET
JRNL        TITL 2 ADDUCT IN PROTEIN STABILITY, SUBSTRATE ACCESSIBILITY, AND
```

# Extract from 5cjh.pdb File

## More Columns in “Atom” Section

```
ATOM     18  CZ  PHE A  52      44.314  -0.531 -23.438  1.00 22.62           C
ATOM     19  N   GLY A  53      46.658  -4.243 -22.274  1.00 24.05           N
ATOM     20  CA  GLY A  53      45.657  -4.819 -21.373  1.00 23.46           C
ATOM     21  C   GLY A  53      46.059  -6.134 -20.735  1.00 23.57           C
ATOM     22  O   GLY A  53      45.222  -6.816 -20.121  1.00 22.59           O
ATOM     23  N   ARG A  54      47.338  -6.476 -20.855  1.00 24.28           N
ATOM     24  CA  ARG A  54      47.888  -7.712 -20.302  1.00 25.30           C
ATOM     25  C   ARG A  54      49.058  -7.380 -19.396  1.00 24.08           C
ATOM     26  O   ARG A  54      49.948  -6.622 -19.784  1.00 24.13           O
ATOM     27  CB  ARG A  54      48.390  -8.607 -21.436  1.00 27.72           C
ATOM     28  CG  ARG A  54      47.374  -8.849 -22.541  1.00 30.24           C
ATOM     29  CD  ARG A  54      46.314  -9.854 -22.128  1.00 33.50           C
ATOM     30  NE  ARG A  54      46.892 -11.185 -21.925  1.00 38.38           N
ATOM     31  CZ  ARG A  54      46.192 -12.282 -21.638  1.00 41.31           C
ATOM     32  NH1 ARG A  54      44.864 -12.234 -21.525  1.00 44.28           N
ATOM     33  NH2 ARG A  54      46.825 -13.436 -21.459  1.00 41.30           N
ATOM     34  N   CYS A  55      49.060  -7.956 -18.195  1.00 22.69           N
ATOM     35  CA  CYS A  55      50.155  -7.782 -17.252  1.00 22.68           C
ATOM     36  C   CYS A  55      51.288  -8.726 -17.655  1.00 23.63           C
```

# 5cjh.pdb File Read by *GaussView*




27051 atoms!!

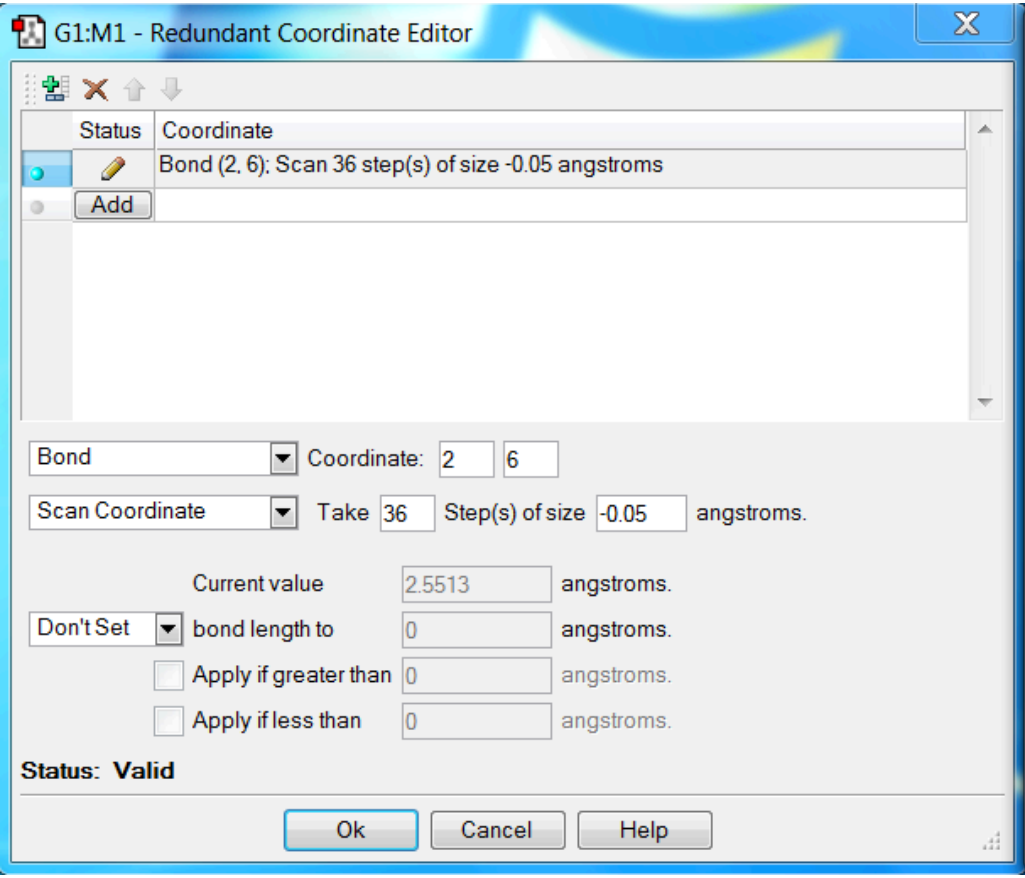
Use “Select Atoms by Rubberband” and “Delete” until only the desired moieties of the protein are left.

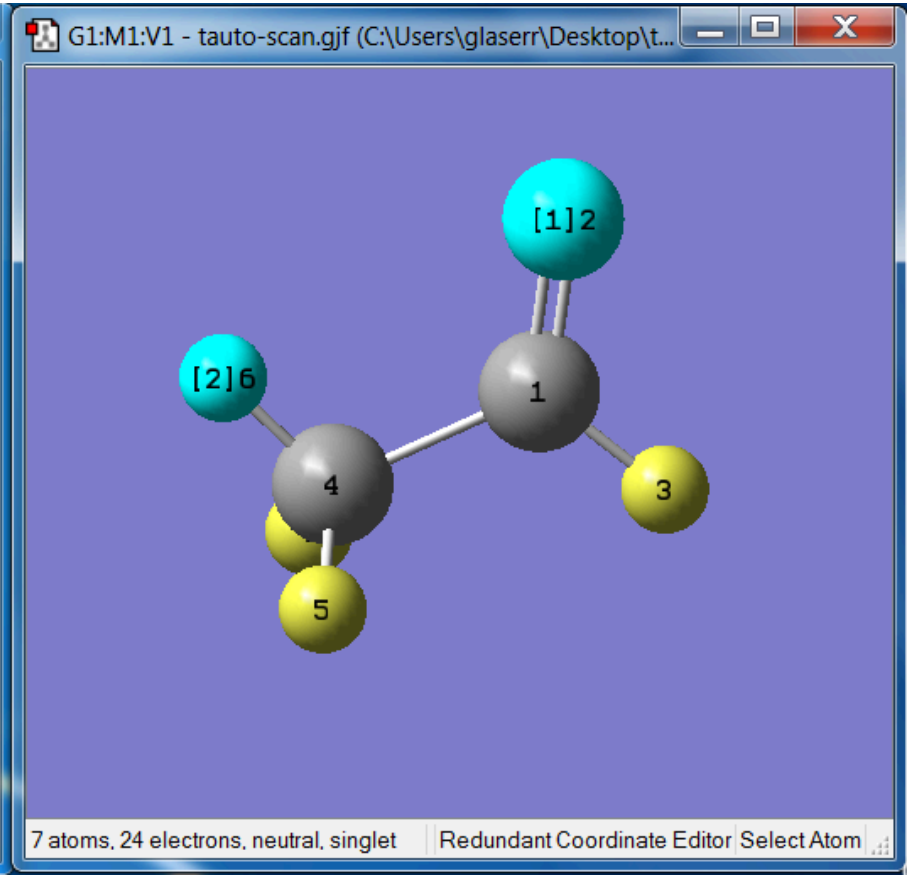
# Chapter #3

## 3.2.2. PES-Scans – Preparation for Assignments #2

# PES-Scan Request in *GaussView*

Tautomerization of acetaldehyde to its enol:  Drive OH distance



# PES-Scan Request in *GaussView*


Define scan coordinate in the “Edit” menu under “Redundant Coordinates”.
Best to define scan coordinate before you request “Scan” type.

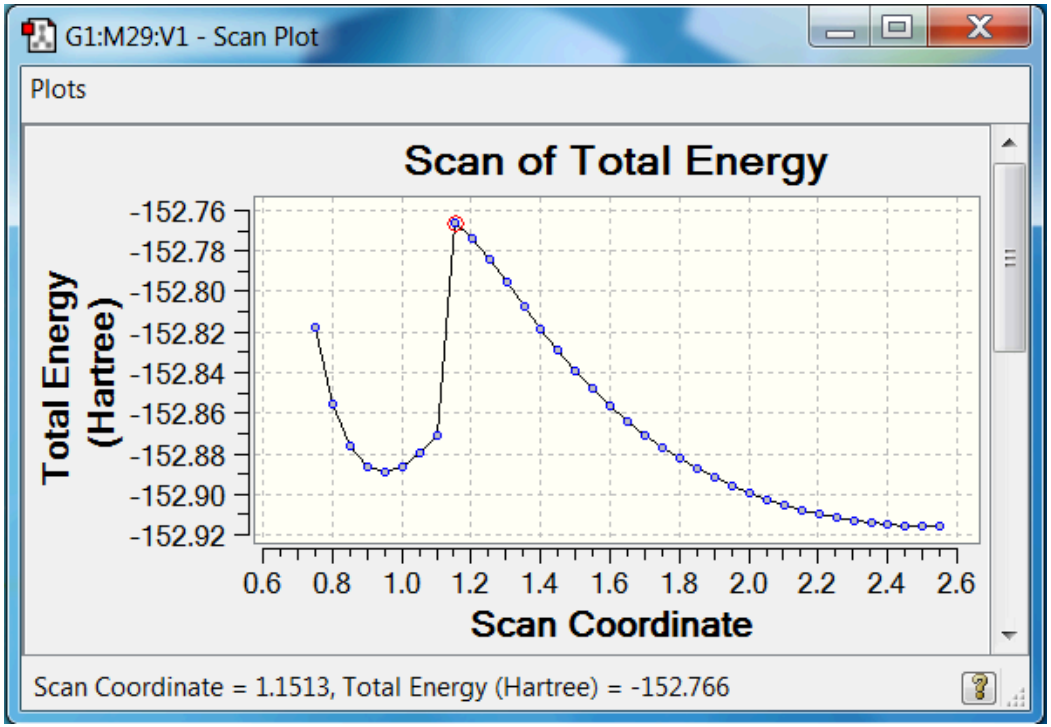
If you request “Scan” type before you define the scan coordinate, GV will remind you to define the scan coordinate in the “Edit” menu under “Redundant Coordinates”.

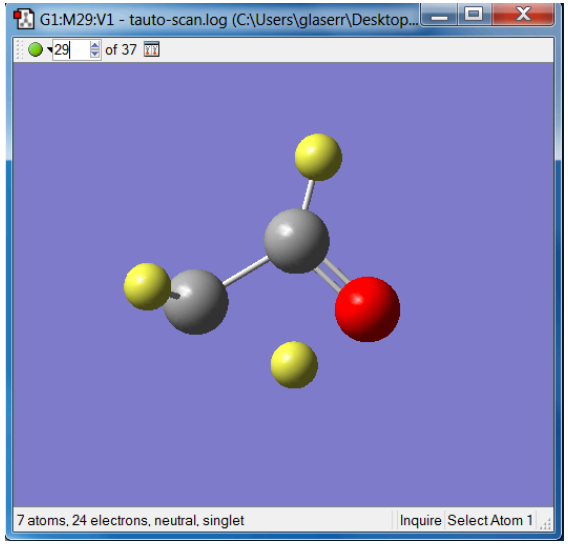
```
# opt=modredundant hf/6-31g(d) geom=connectivity

Tautomerization of acetaldehyde

0 1
 C
 O                    1            B1
 H                    1            B2     2            A1
 C                    1            B3     2            A2     3            D1     0
 H                    4            B4     1            A3     2            D2     0
 H                    4            B5     1            A4     2            D3     0
 H                    4            B6     1            A5     2            D4     0

   B1             1.22731700
   B2             1.11045737
   B3             1.54000000
   B4             1.07000000
   B5             1.07000000
   B6             1.07000000
   A1           122.22491839
   A2           122.22491841
   A3           109.47120255
   A4           109.47120255
   A5           109.47123134
   D1           179.99762133
   D2          -120.11110740
   D3            -0.00000000
   D4           119.88890000

 1 2 2.0 3 1.0 4 1.0
 2
 3
 4 5 1.0 6 1.0 7 1.0
 5
 6
 7

B 2 6 S 36 -0.050000       Bond between atoms 1 and 6 scan 36 steps with stepsize -0.05
```

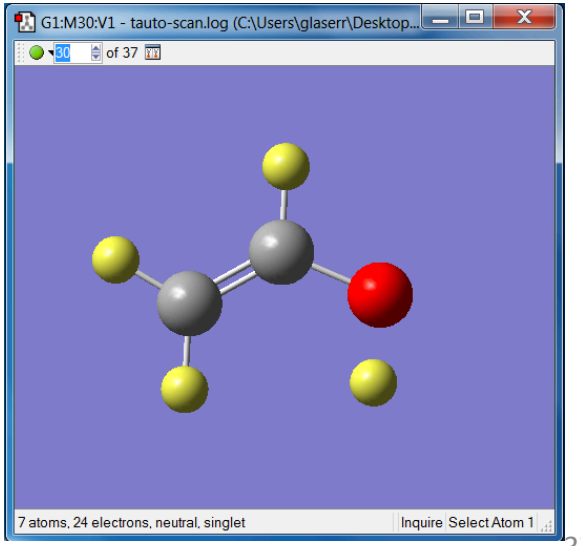
# PES-Scan Request in GJF File

# PES-Scan Output in *GaussView*

Tautomerization of acetaldehyde to its enol:
1. Drive OH distance from the aldehyde.



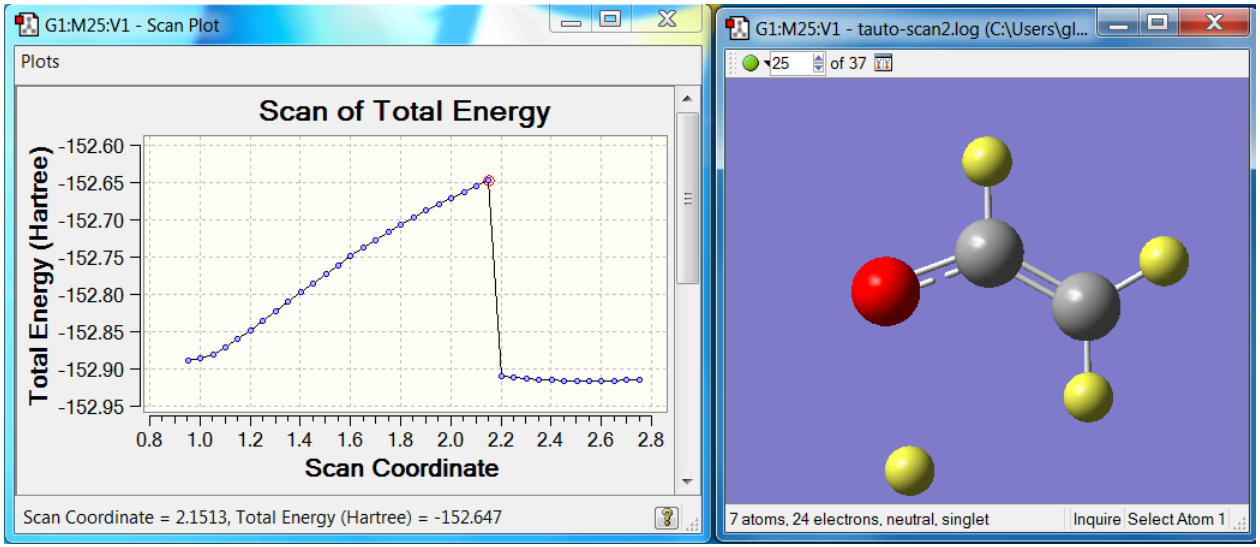




Works well at first, then sudden collapse as CH2 group rotates.

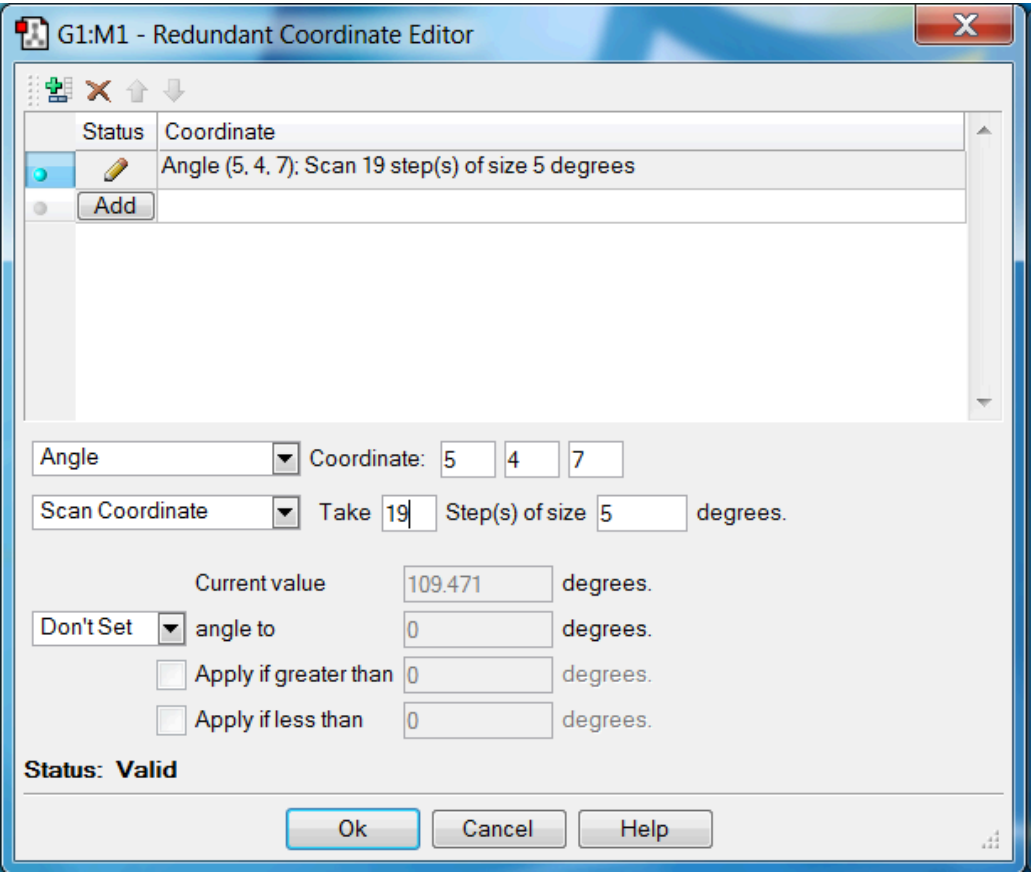
# PES-Scan Output in *GaussView*

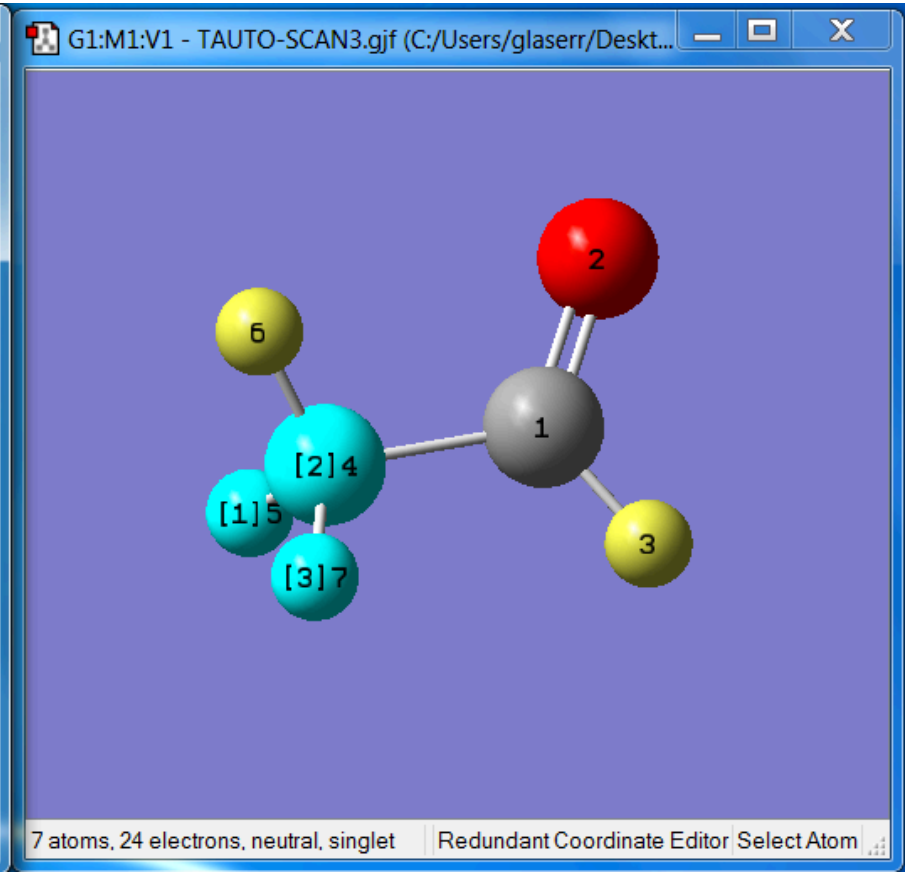
Tautomerization of acetaldehyde to its enol: 2. Drive OH distance from the enol.



# PES-Scan Request in *GaussView*

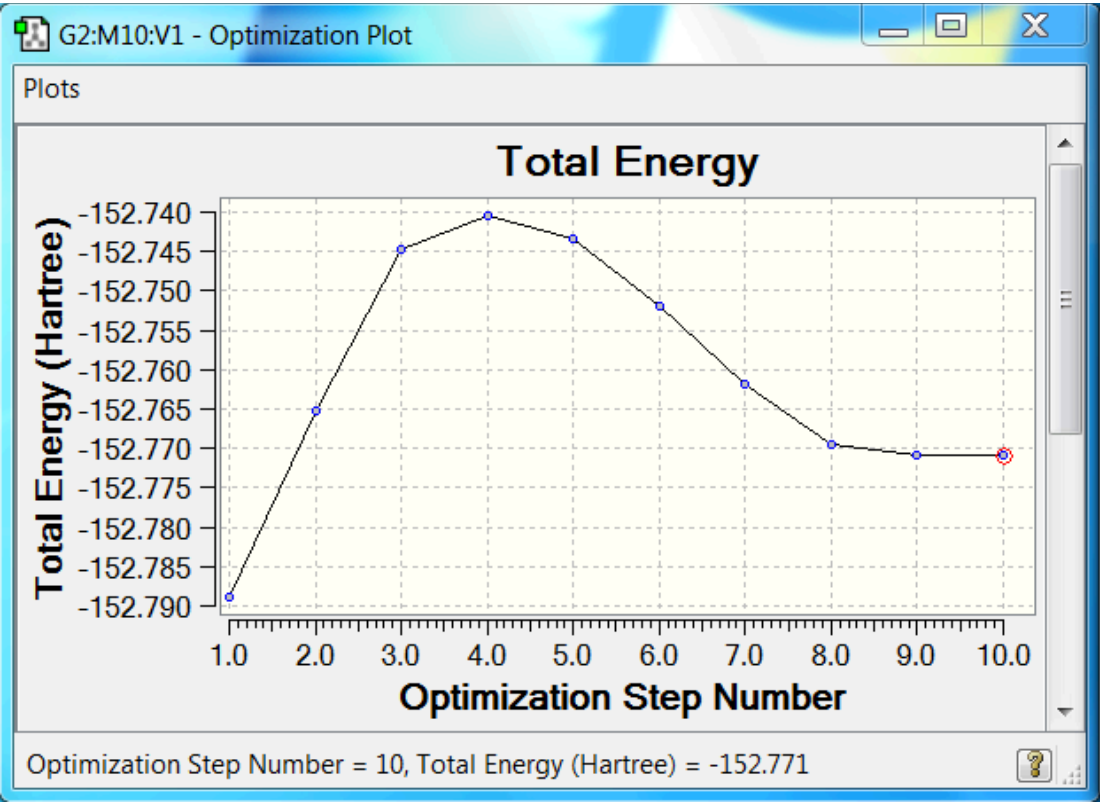
Tautomerization of acetaldehyde to its enol: 3. Drive HCH angle

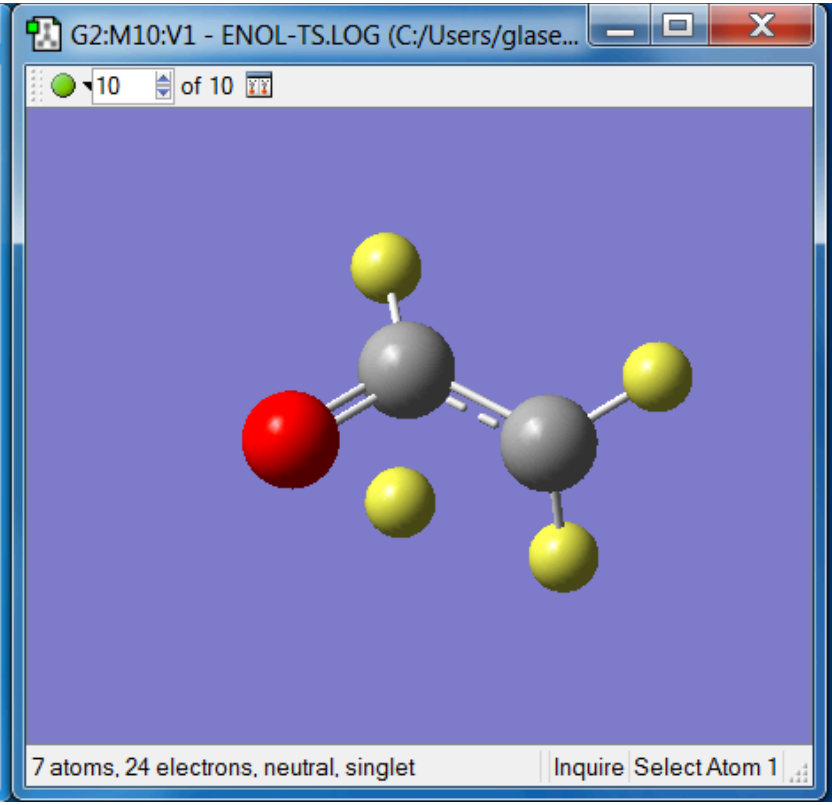


# TS Search with Reasonable Guess

By now we have a pretty good idea of the tautomerization TS:
H close to O; migrating H out of OCC plane; CH2 group rotated



# Chapter #3

## 3.3. Intrinsic Reaction Path – Preparation for Assignments #3

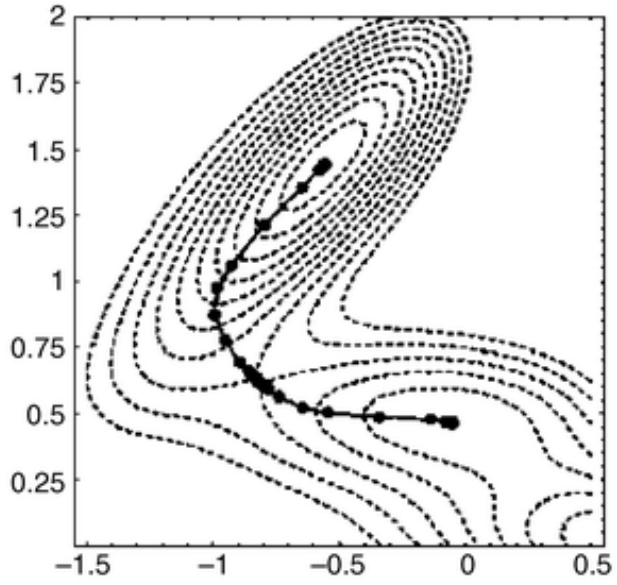
# IRC: Intrinsic Reaction Path

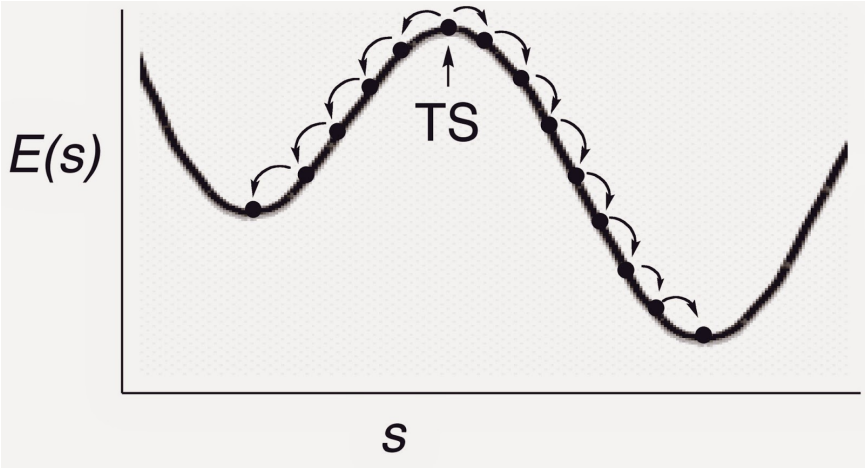
## Introduction

Intrinsic reaction coordinate (IRC), which was proposed by Fukui in 1970 as a path of chemical reactions,[1,2] is the mass-weighted steepest descent path on the potential energy surface (PES), starting from the transition structure (TS), that is, first-order saddle point. The mass-weighted steepest descent path starting from nonstationary structures is called meta-IRC.[3] The IRC is the solution of the following differential equation,

$$\frac{d\mathbf{q}(s)}{ds} = \mathbf{v}(s) \qquad (1)$$

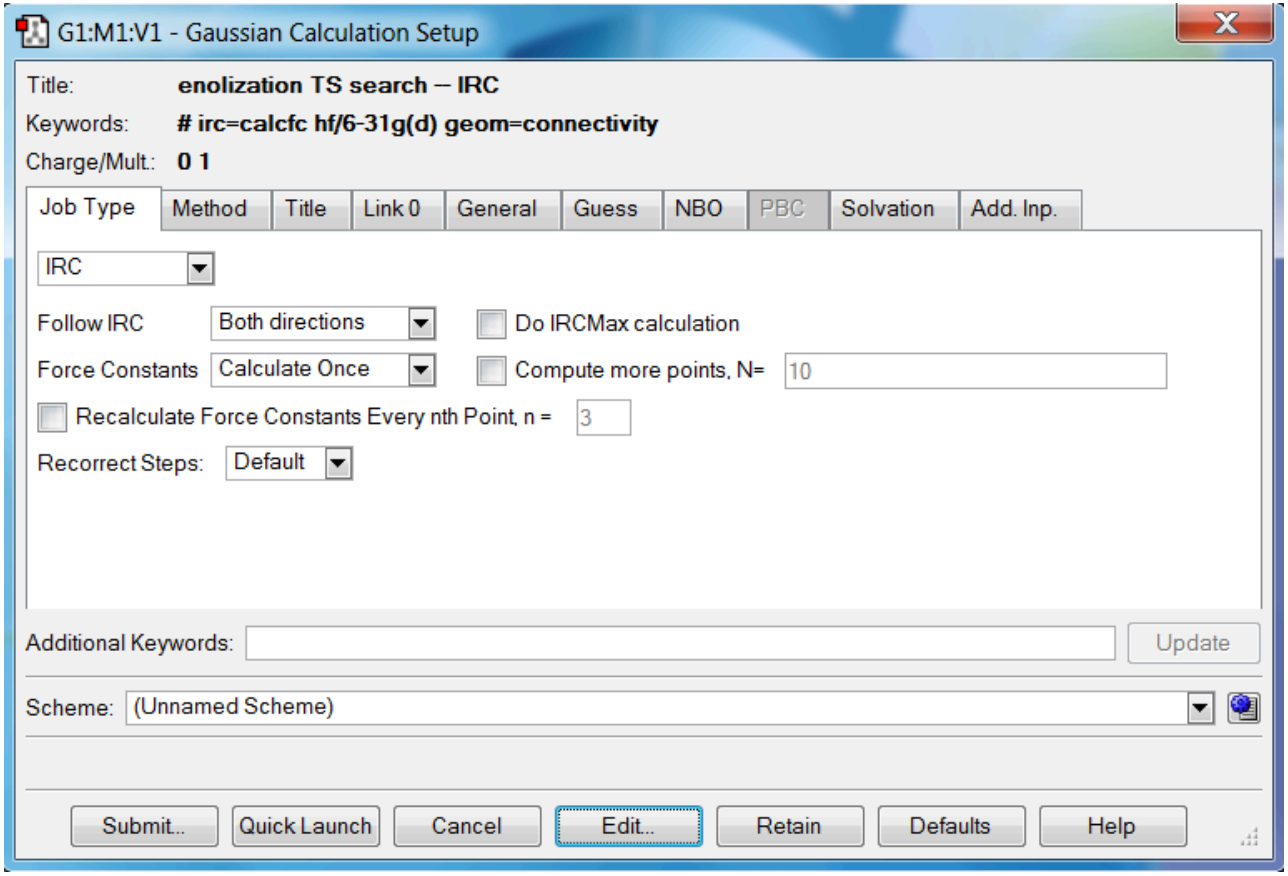
where $\mathbf{q}$ is the mass-weighted Cartesian coordinates and $s$ the coordinate along the IRC. The normalized tangent vector $\mathbf{v}$ of the IRC corresponds to the normal coordinate eigenvector with a negative eigenvalue at the TS with $s = 0$, and, at the other points, the unit vector parallel to the mass-weighted gradient vector $\mathbf{g}$, that is, $\mathbf{v} = -\mathbf{g}/|\mathbf{g}|$ for $s > 0$ and $\mathbf{v} = \mathbf{g}/|\mathbf{g}|$ for $s < 0$. In numerical integration of Eq. (1), $\mathbf{g}$ has to be computed repeatedly. Hence, various IRC-following algorithms have been proposed to reduce the number of gradient calculations.[4–10] With help of these algorithms, the IRC approach has been used extensively in analysis and prediction of mechanisms of a variety of chemical reactions.[11–15]



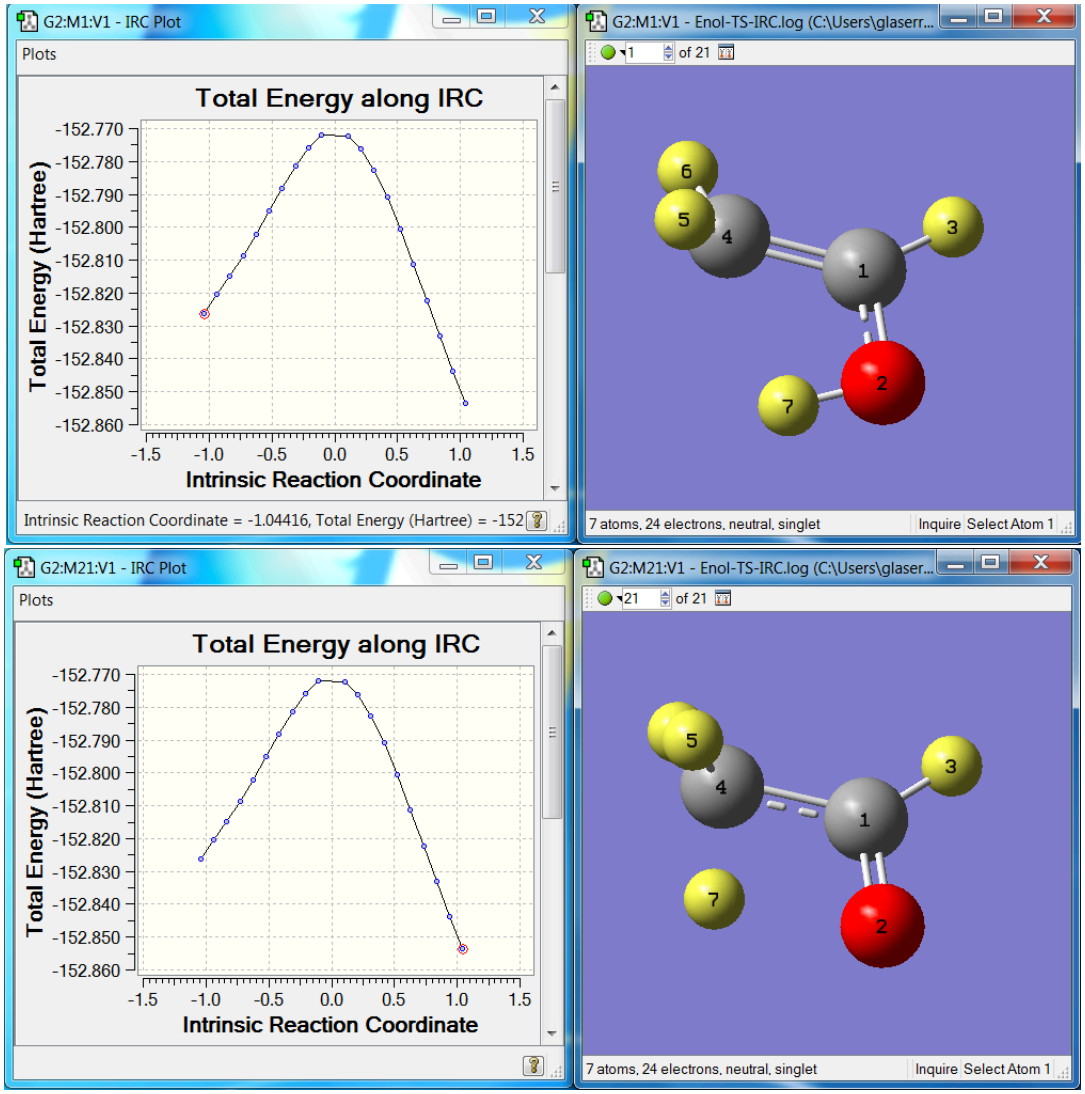



# IRC Request in *GaussView* and in GJF File

```
%nprocshared=2
%mem=128MW
%chk=C:\Users\glaserr\Desktop\Enol-TS-IRC.chk
# irc=rcfc hf/6-31g(d) geom=connectivity

enolization TS search – IRC

0 1
Geometry of TS follows here.
Reads forces from CHK, but not geometry.
```



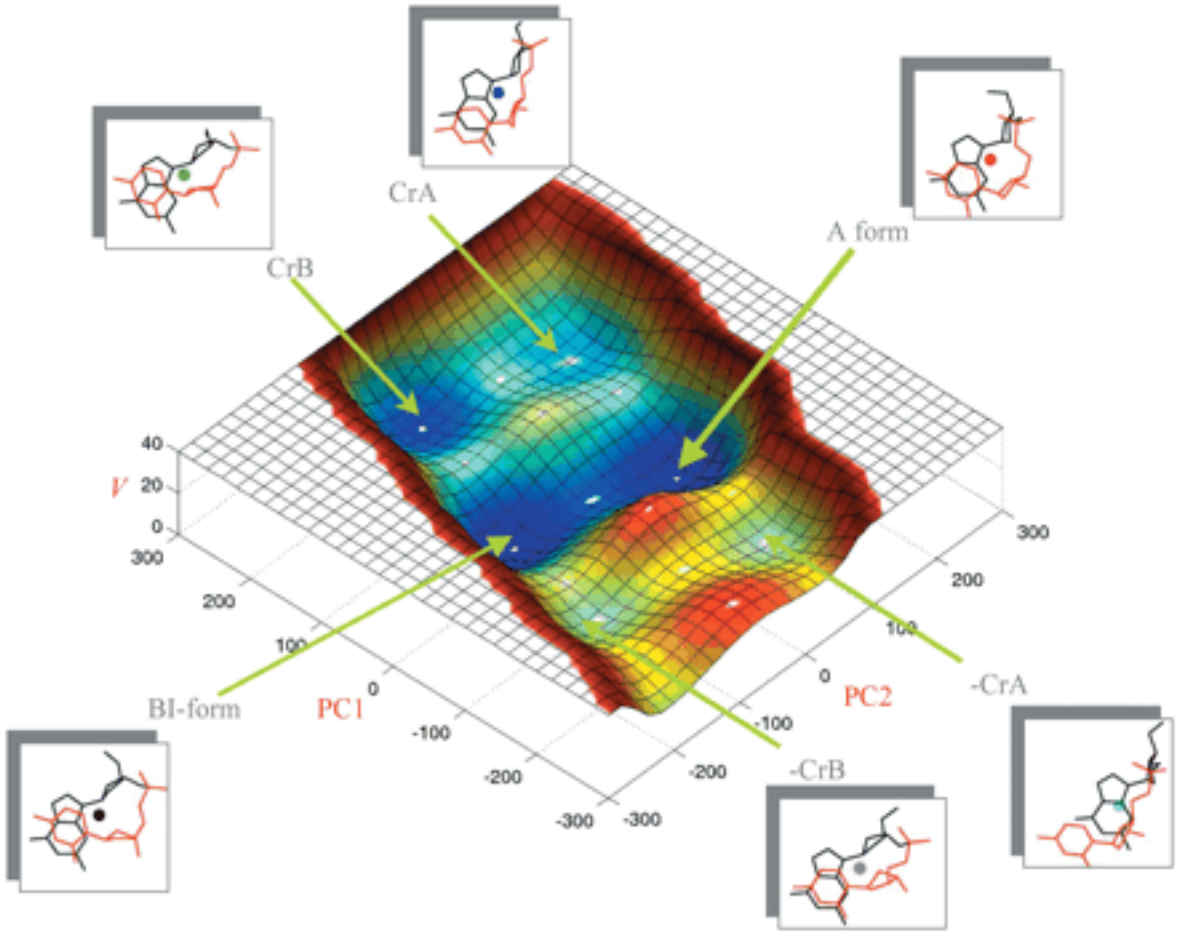
# IRC Output in *GaussView*



# Chapter #3

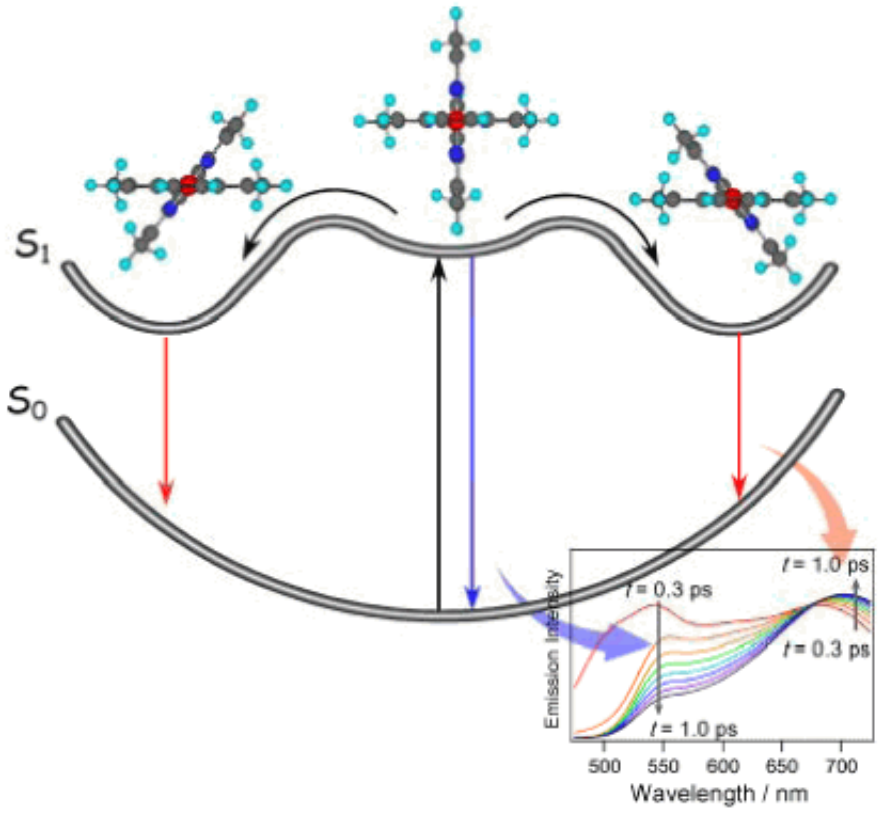
## 3.4. Complicated Systems, Excited States

# Potential Energy Surface, PES



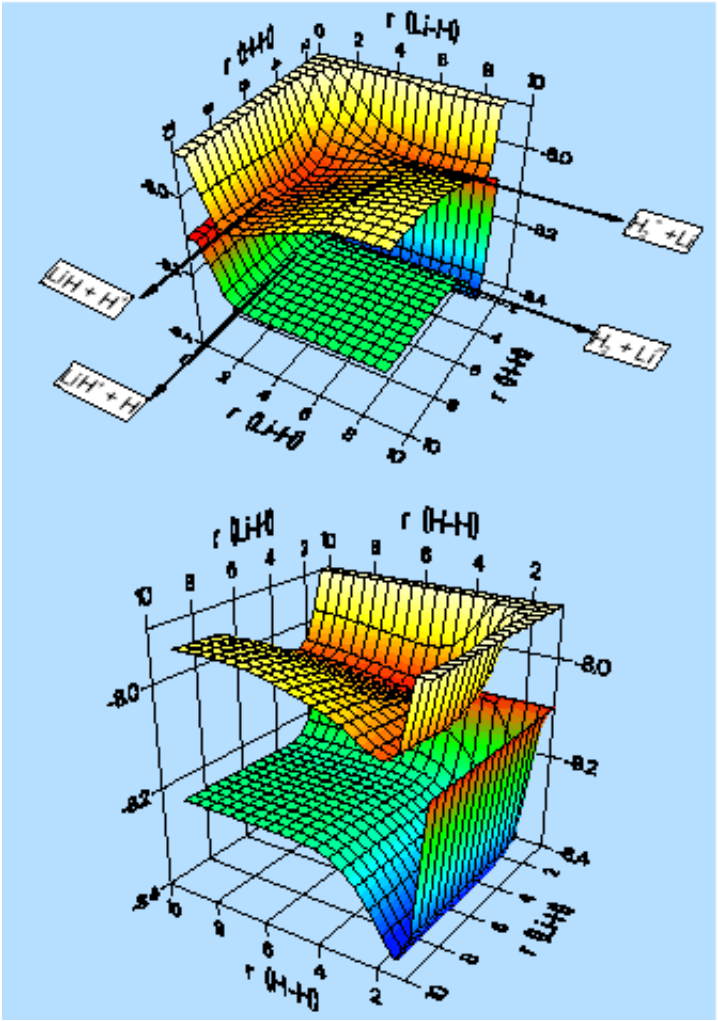

nar.oxfordjournals.org/.../ issue18/cover.dtl

# PES, Excited States




http://www.riken.jp/lab-www/spectroscopy/img/metal_complex_fig3.gif

# PES, Excited States




http://www.dcfe.unimi.it/sezion4.gif