Structure and Dynamics of Molecules in Gas Electron Diffraction

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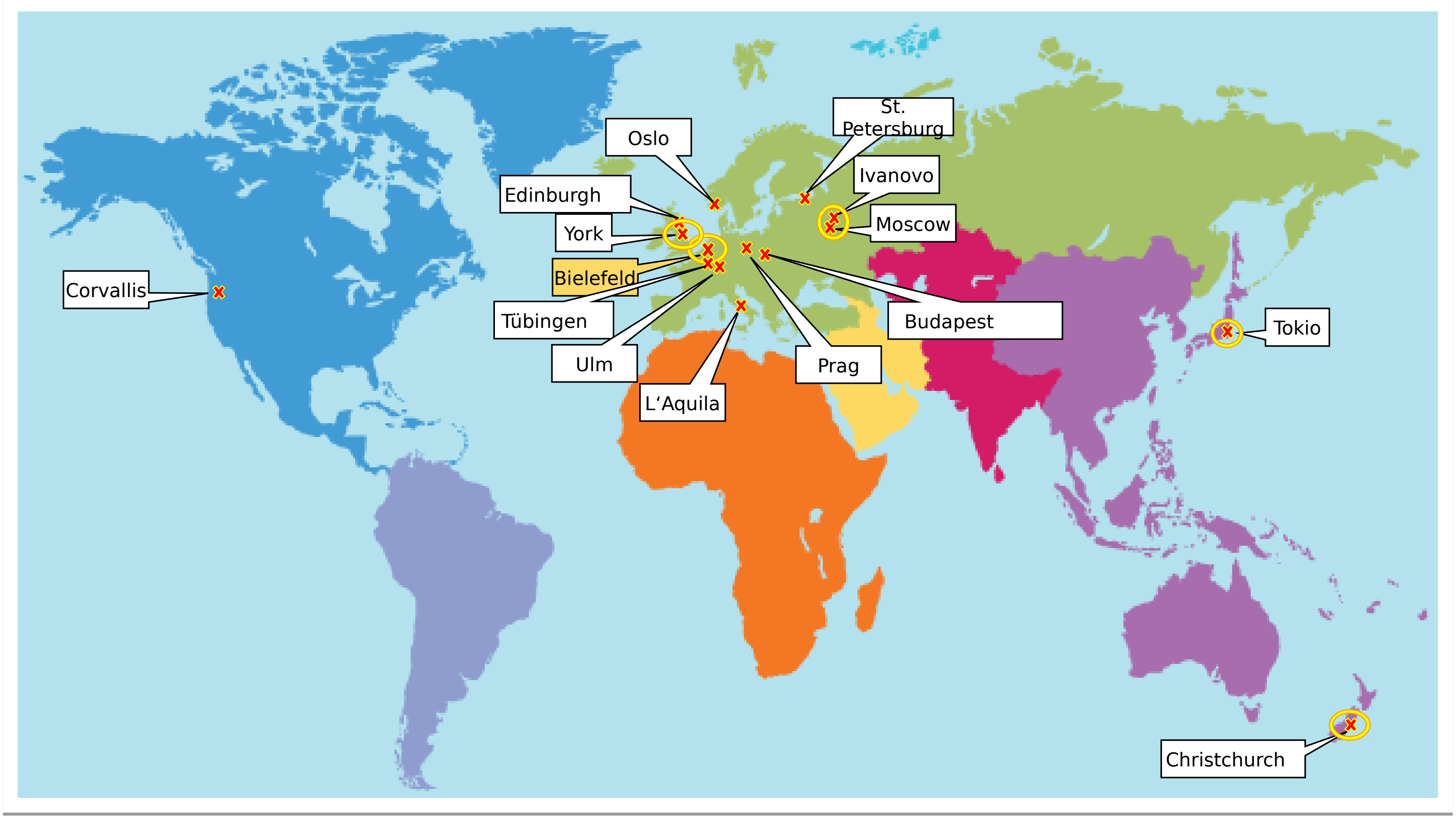
4th IC-MSQUARE, Mykonos, June 6, 2015

GED Worldmap 2015



What is GED?

Diffraction of electrons on gaseous targets.

GED patterns contain information about:

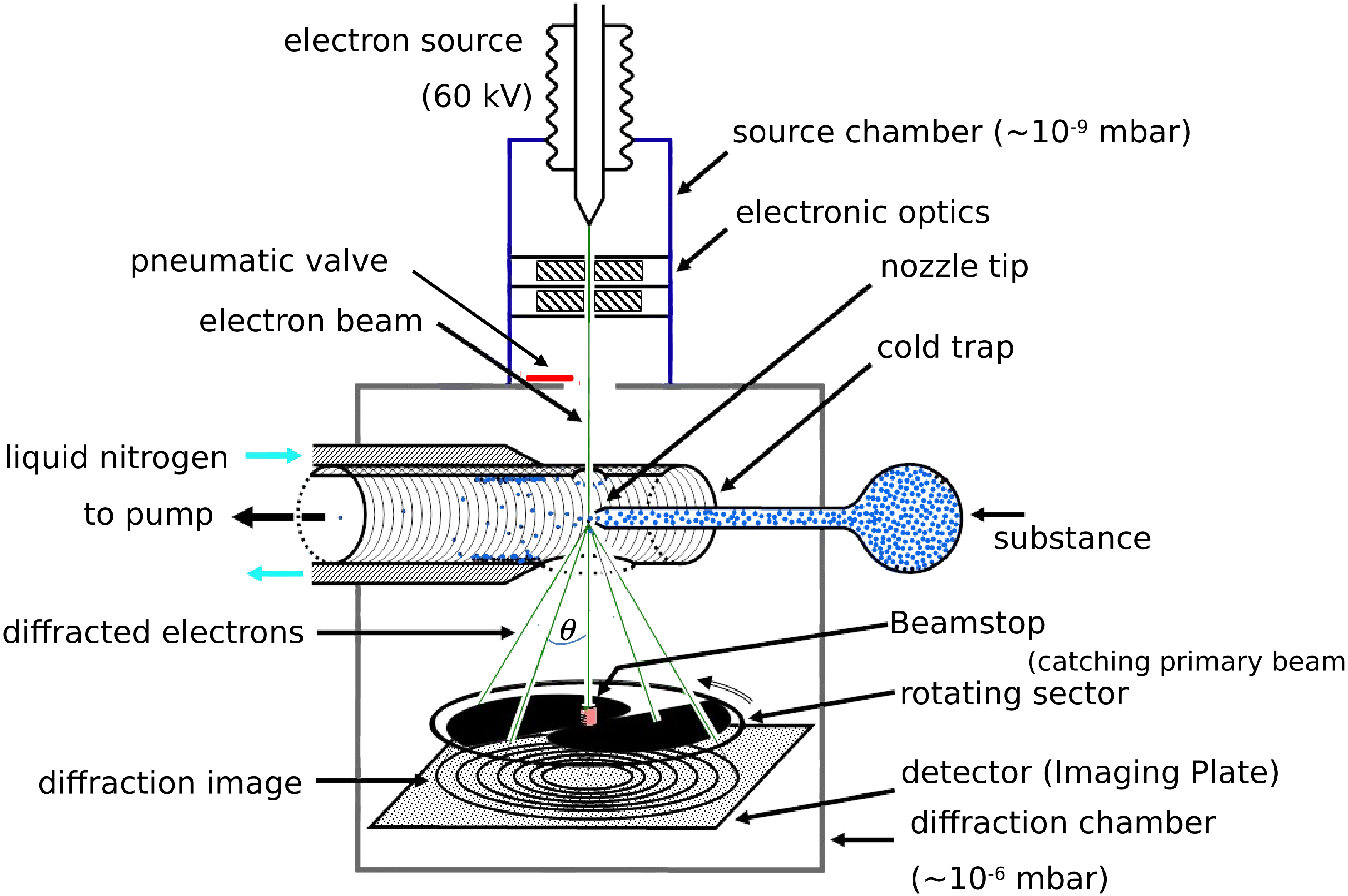
- Molecular structure, conformations.
- Dynamics of molecules (rms interatomic amplitudes, potential functions).
- Composition of different species in mixtures.
- Electron density distribution (in small-angle ED).
- Molecular processes in time (with UED).

- Some compounds exist only in the gas phase.
- Some compounds do not form single crystals.
- No intermolecular interactions and packing effects.
- Conformational studies are possible.
- Results can be used for calibration of QC methods.

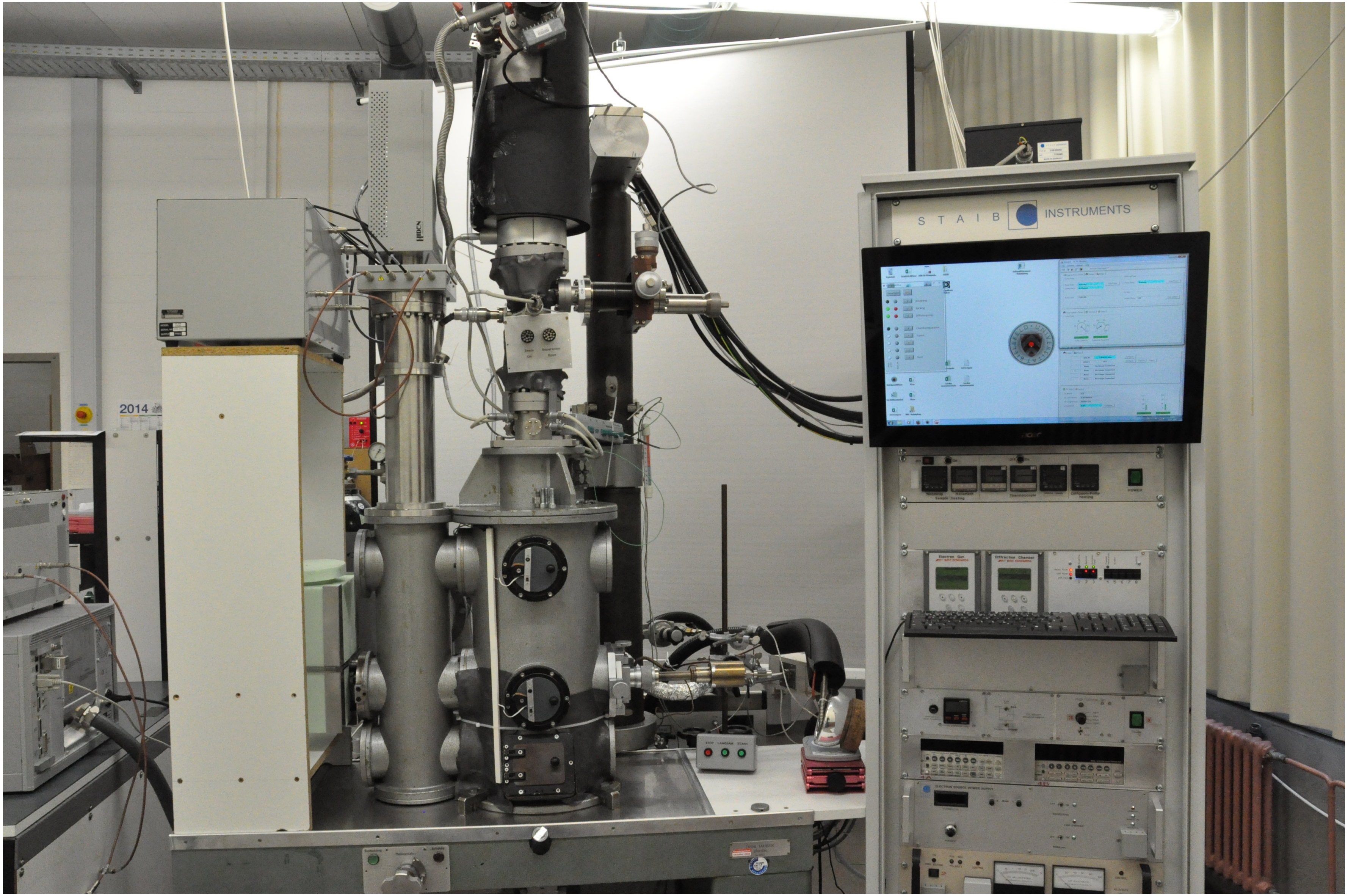
The key values of quantum mechanics are eigenvalues and eigenvectors. Eigenvalues, through energy differences, give spectroscopic methods whereas gas electron diffraction gives information about eigenvectors...

(ascribed to O. Bastiansen)

GED Experiment



Real Setup in Bielefeld



http://molwiki.org/wiki/BielefeldGED:Equipment

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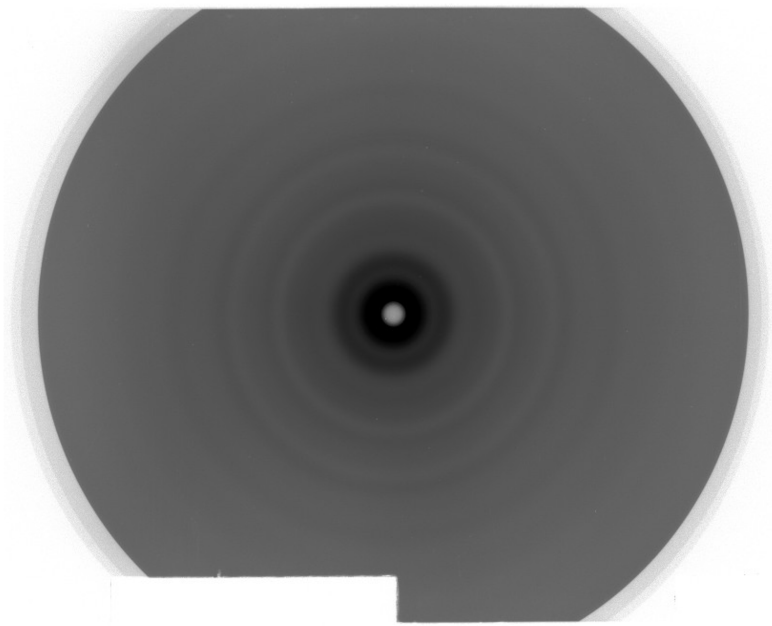
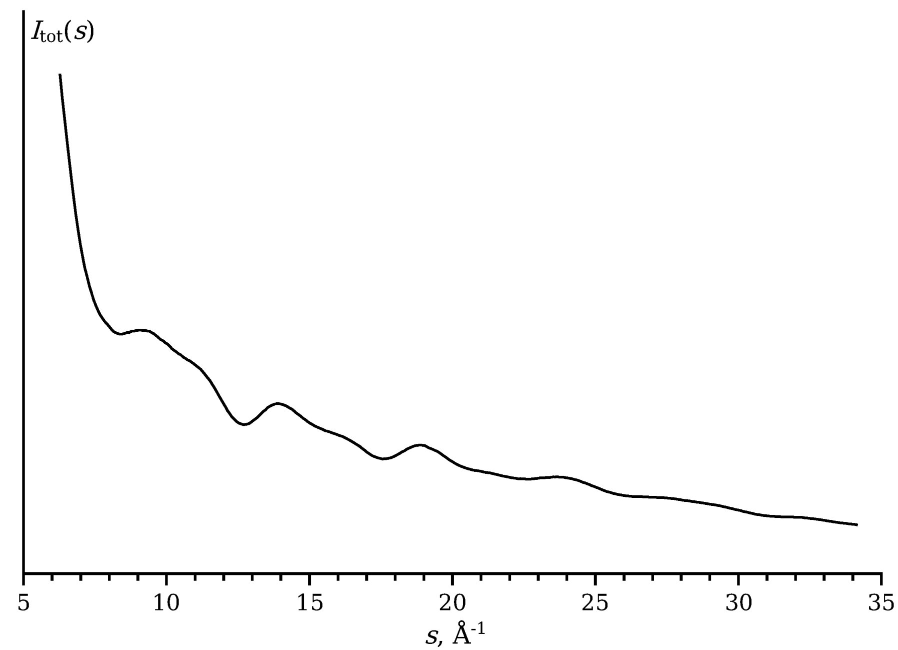
Diffraction pattern

Benzene (L = 250 mm)





GED Theory

$$I_{tot}=I_{mol}+I_{at}+I_{bgl}$$

$$s=\frac{4\pi}{\lambda}\sin\left(\frac{\theta}{2}\right)$$

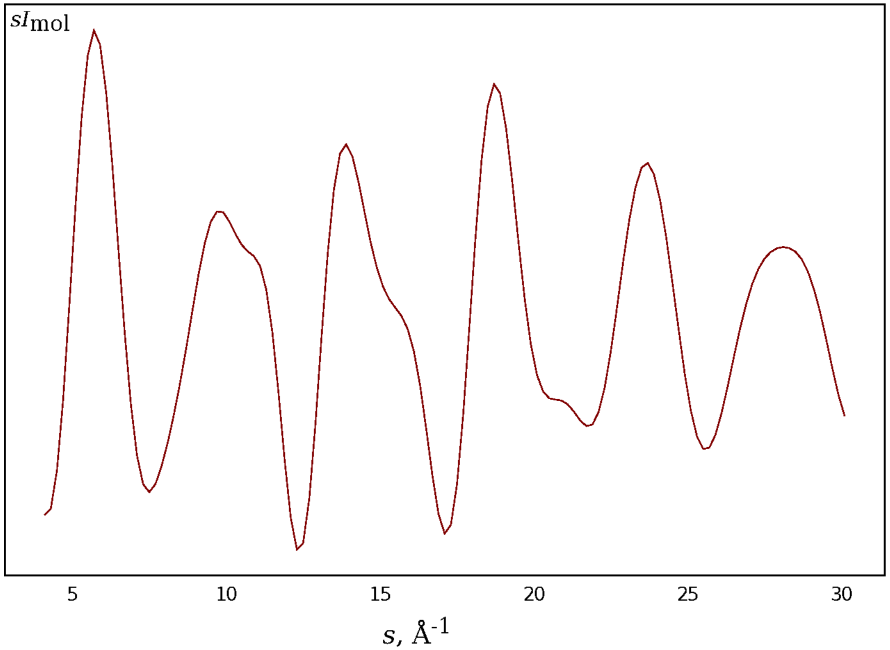
$$sM(s)=\frac{sI_{mol}}{I_{at}}=\sum_{i>j}^{N} g_{i,j}e^{-\frac{(sl_{i,j})^2}{2}}\frac{\sin(sr_{i,j}-a_{i,j}s^3)}{sr_{i,j}}$$

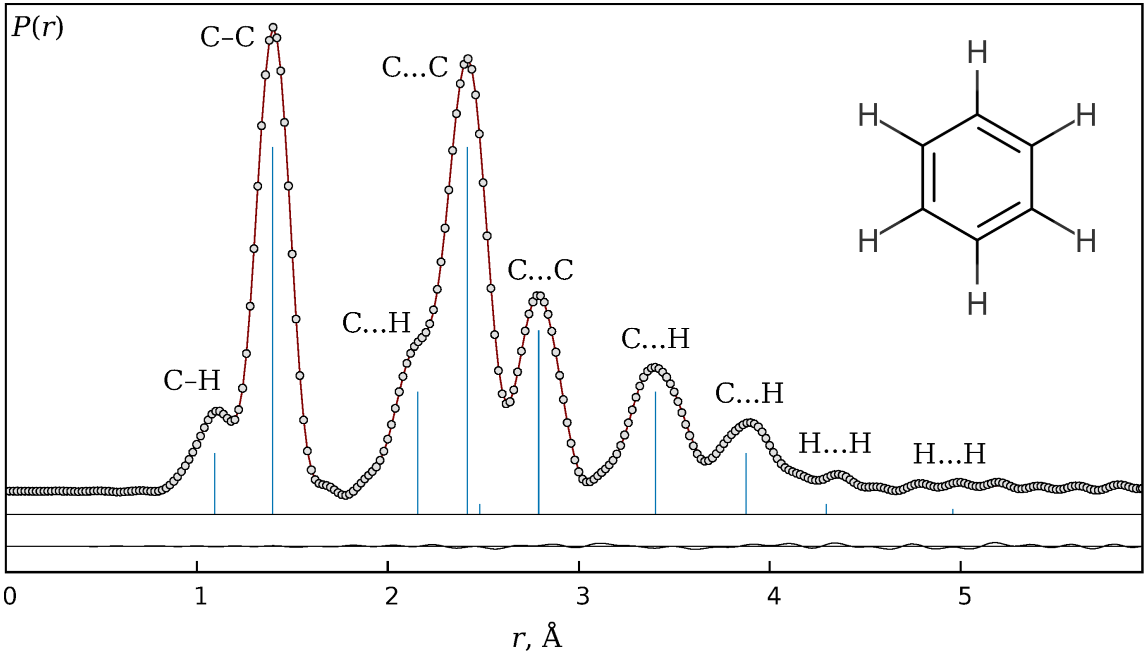
θ – scattering angle,
λ – electron wavelength,
g – scattering factors,
r – interatomic distances,
l – amplitudes,
a – anharmonic constants.

Inverse problem:

$$Q=\sum_{i}^{N}\left(sM(s|r,l,a)_{model}-sM(s)_{exp}\right)^2\rightarrow min$$

RDF





GED Theory, LAM

In case of large amplitude motions:

$$sM(s)_{tot} = \int P(\varphi)\, sM(\varphi, r, l)\, d\varphi$$

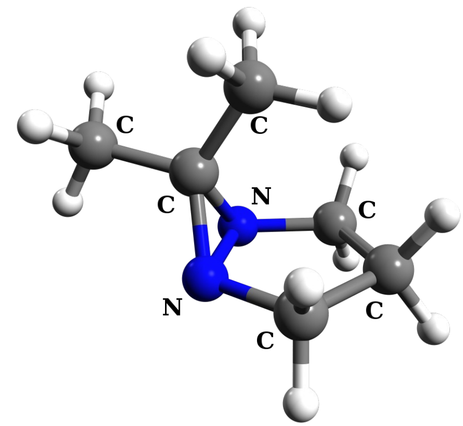
Pseudoconformers:

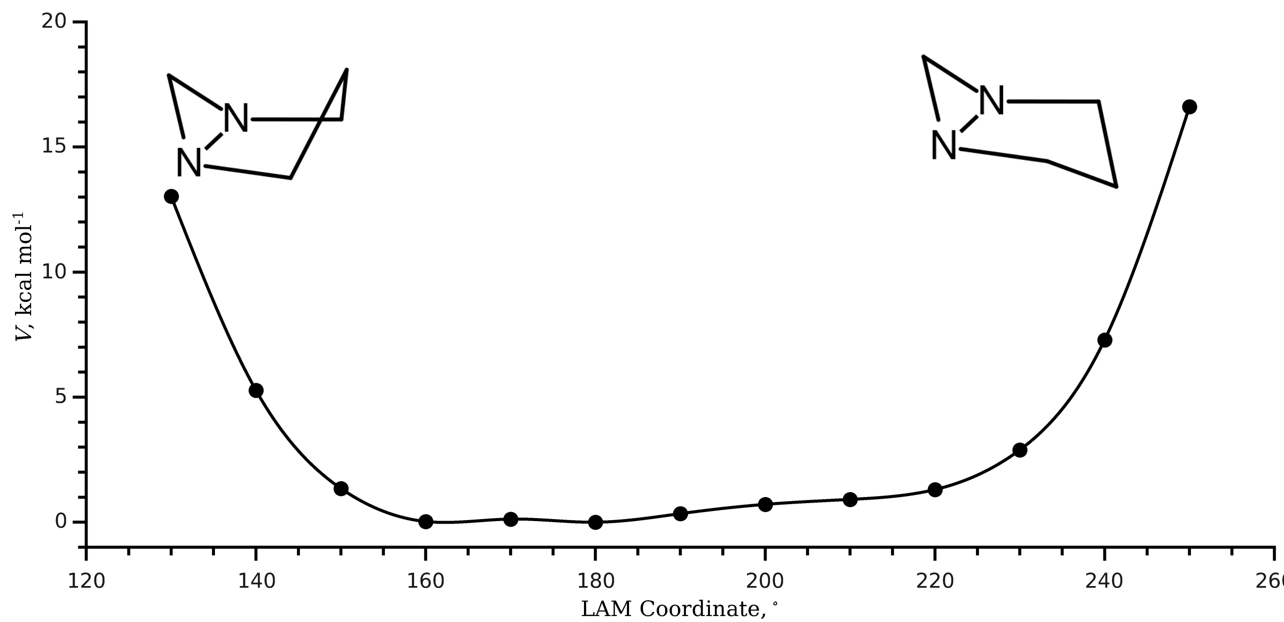
$$sM(s)_{tot} \approx \sum P(\varphi_i)\, sM(s)_i$$

Boltzmann distribution:

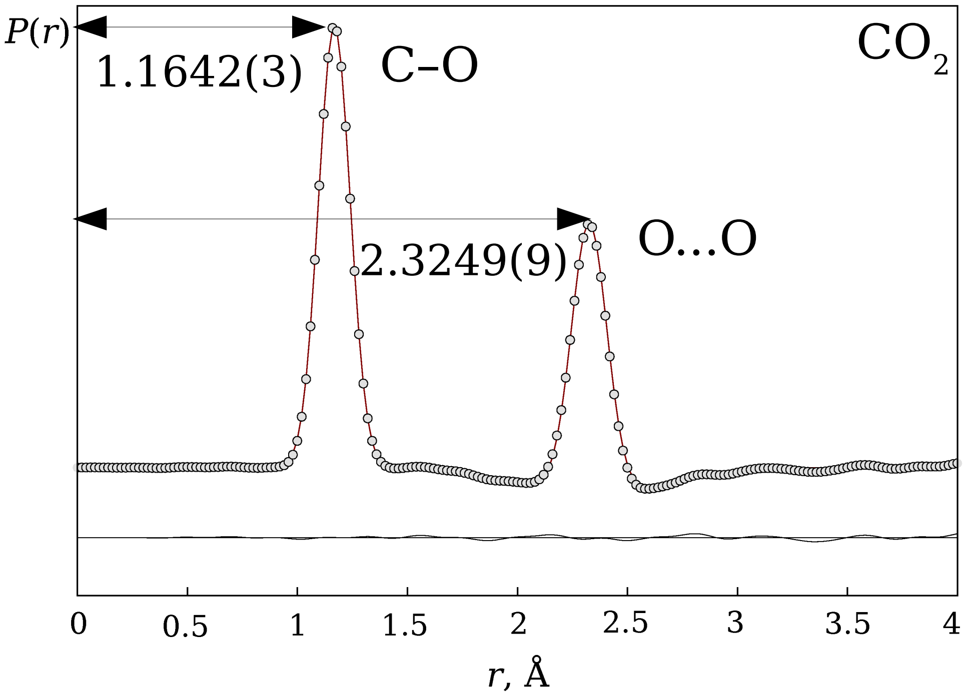
$$P(\varphi) \sim e^{\frac{-V(\varphi)}{kT}}$$

Example:
6,6-dimethyl-1,5-diazabicyclo[3.1.0]hexane





Average Structure



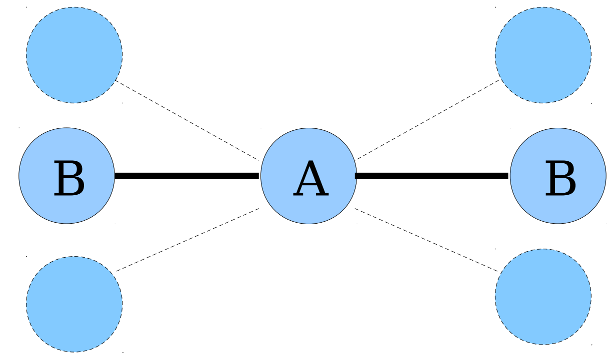
$\delta = 2r_a(\text{C–O}) - r_a(\text{O...O})$

0.0036(5) @ 298 K
0.0059(11) @ 463 K
0.0071(8) @ 627 K
0.0078(10) @ 731 K
0.0093(7) @ 937 K

$r_g = \langle r \rangle$
$r_a = \langle 1/r \rangle^{-1}$

Shrinkage effect:

$r_a(\text{B...B}) < 2r_a(\text{A–B})$



Example:
$\angle_a$(Br–Hg–Br) ~ 170°

Solution: use corrections to geometrically consistent structure (r_{h0}, r_{h1}, r_e).

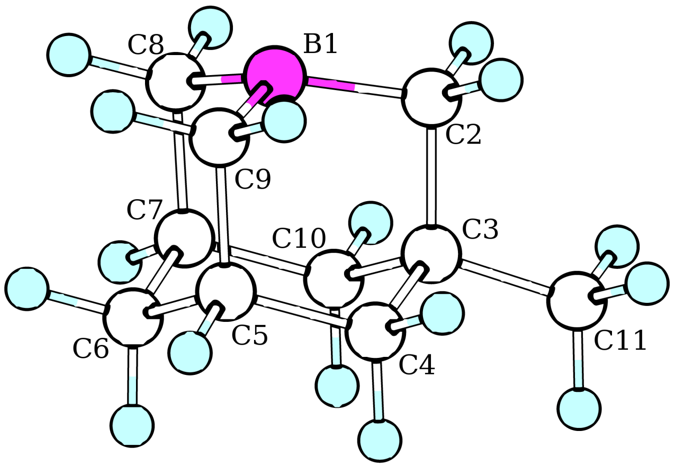
- Perturbation theory
- Molecular dynamics

R. J. Mawhorter, M. Fink, B. T. Archer, *J. Chem Phys.* 79, 1983, 170
R. Z. Deyanov, K. P. Petrov, V. V. Ugarov, B. M. Shchedrin, N. G. Rambidi, *J. Struct. Chem.* 26, 1985, 698.

Real Examples

1. Rigid molecules.
2. Objects with large amplitude motions.
3. Highly flexible molecules.

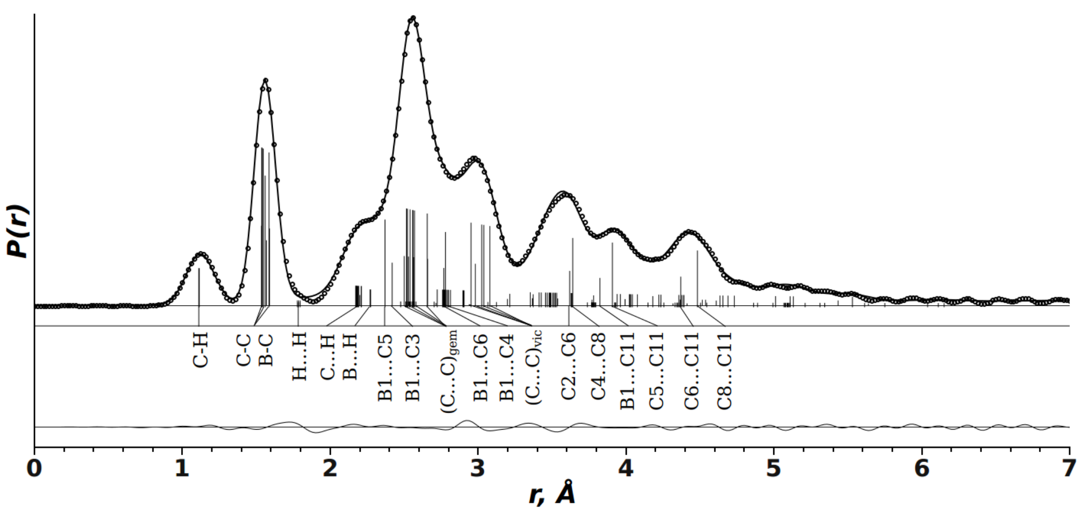
3-Methyl-1-boraadamantane



A typical GED study of an object:
0. Prediction of interesting features.
1. Their experimental detection.
2. Computational explanation.

Step 0:
Cage strain vs. electronic configuration of boron.
Pyramidal boron configuration?

Step 1:



No large amplitude motions.

∠(C-B-C) = 116.5(2)°
∠(C-C-C) = 109.8(5)° in adamantane

r_g(B-C) = 1.565(5) Å
1.578(3) Å in BMe_3
1.560(3) Å in $B(CH{=}CH_2)_3$

r_g(C-C(B)) = 1.589(7) Å
r_g(C-C) = 1.542(2) Å in adamantane

Yu. V. Vishnevskiy, M. A. Abaev, A. N. Rykov, M. E. Gurskii, P. A. Belyakov, S. Yu. Erdyakov, Yu. N. Bubnov, N. W. Mitzel, *Chem. Eur. J.* 18, 2012, 10585.
I. Hargittai, K. Hedberg, *J. Chem. Soc., Chem. Comm.* 1971 1499.
L. S. Bartell and B. L. Carroll, *J. Chem. Phys.* 42, 1965, 3076.
A. Foord, B. Beagley, W. Reade and I. A. Steer, *J. Mol. Struct.* 24, 1975, 131.

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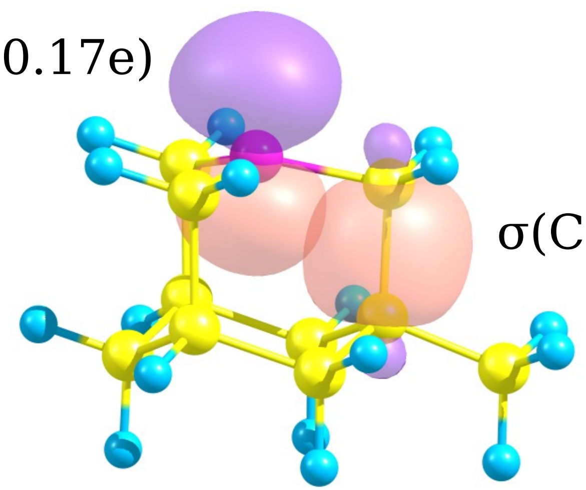
3-Methyl-1-boraadamantane

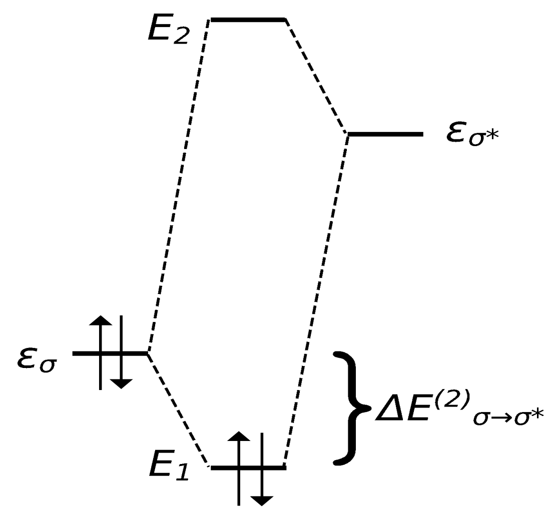
Step 2: explanation.
Natural Bond Orbitals (NBO), Quantum Theory of Atoms in Molecules (QTAIM).

σ(C-C) → p_z(B) hyperconjugation:

Lp*(B), (0.17e)



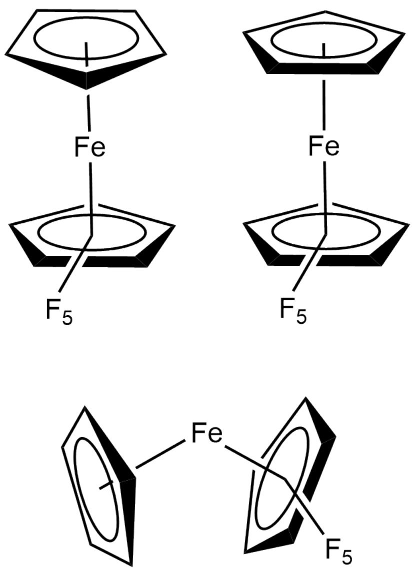
σ(C-C)



$\Delta E^{(2)}$ = 15.4 kcal mol^{-1}

QTAIM: B-C bond ellipticity 0.26 (C-C in benzene 0.21; in ethylene 0.38)

Ferrocenes

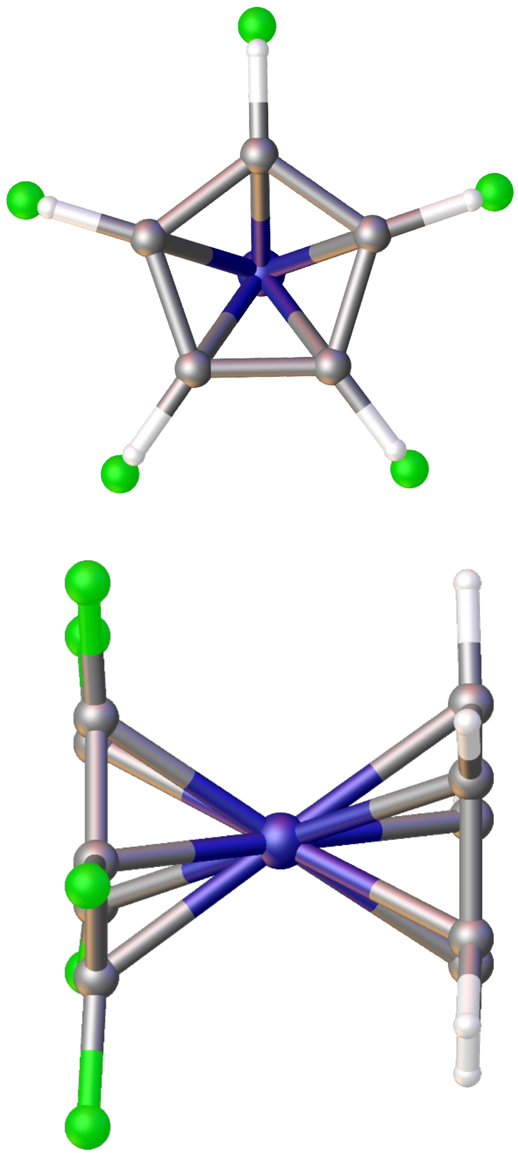


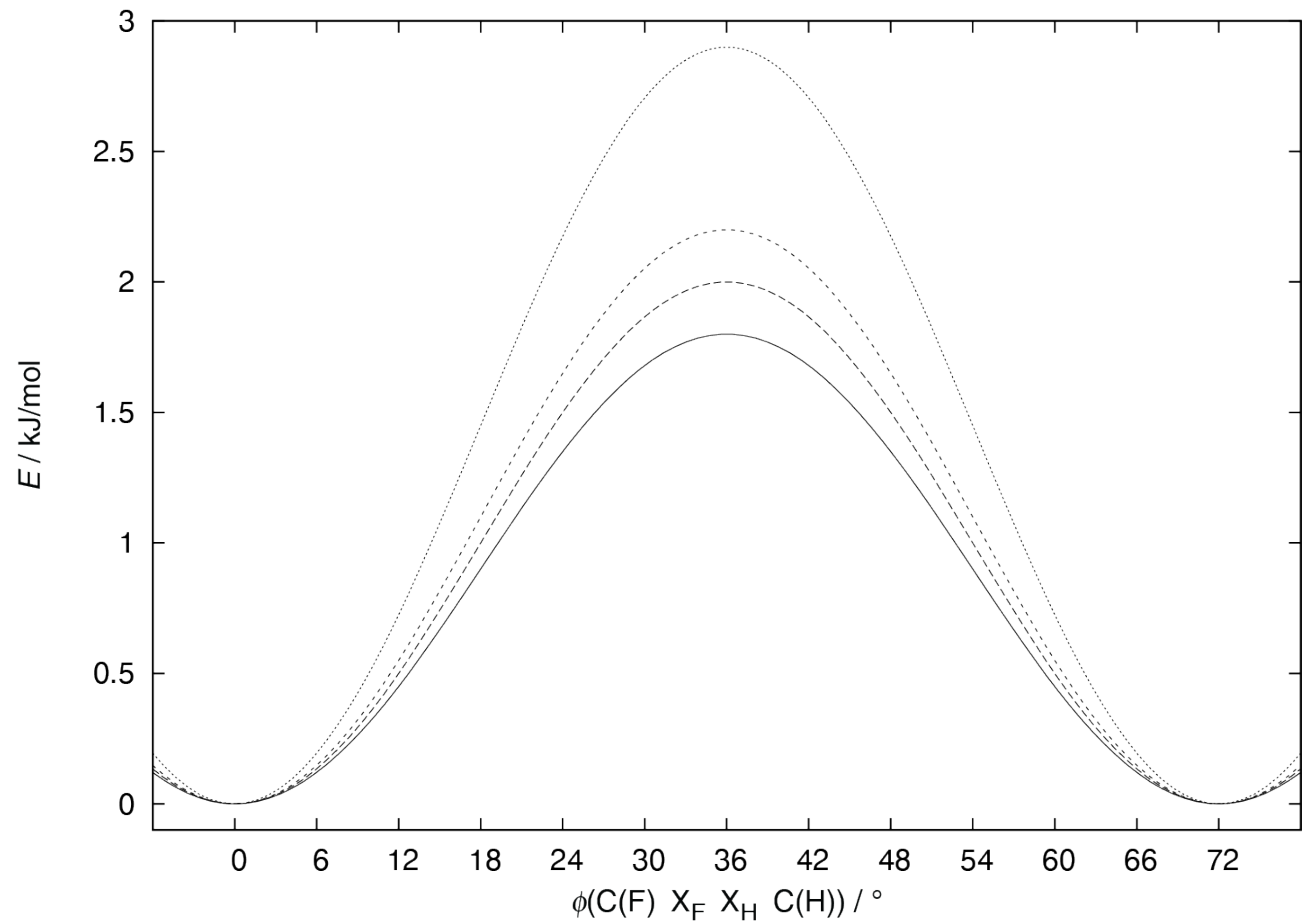
Compound	QC	GED	XRD
$Fe(C_5H_5)_2$	eclipsed[1]	eclipsed[2]	eclipsed[3]
$Fe(C_5Me_5)_2$	staggered[4]	staggered[4]	staggered[5]
$Fe(C_5Cl_5)_2$	staggered[6]	staggered[6]	–
$Fe(C_5F_5)(C_5H_5)$	???	???	eclipsed[7]

[1] S. Coriani, A. Haaland, T. Helgaker, P. Jørgensen, *ChemPhysChem. 7,* 2006, 245.
[2] R. K. Bohn, A. Haaland, *J. Organomet. Chem. 5,* 1966 470.
[3] P. Seiler, J. D. Dunitz, *Acta Crystallogr.* 38, 1982, 1741.
[4] A. Almenningen, A. Haaland, S. Samdal, J. Brunvoll, J. L. Robbins, J. C. Smart, *J. Organomet. Chem.* 173, 1979, 293.
[5] D. P. Freyberg, J. L. Robbins, K. N. Raymond, J. C. Smart, *Acta Chem. Scand.* 23, 1969, 3224.
[6] L. Phillips, M. K. Cooper, A. Haaland, S. Samdal, N. I. Giricheva, G. V. Girichev, *Dalton Trans.* 39, 2010, 4631.
[7] K. Sünkel, S. Weigand, S. Blomeyer, C. G. Reuter, Yu. Vishnevskiy, N. W. Mitzel, *JACS* 137, 2015, 126.

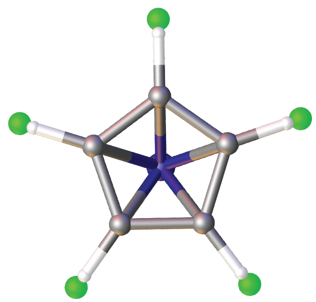
$Fe(C_5H_5)(C_5F_5)$, QC

DFT: PBE0, PBE0+D3, B3LYP, TPSSh, B3P86, B3PW91, B2PLYP
cc-pVTZ, TZVPP+f

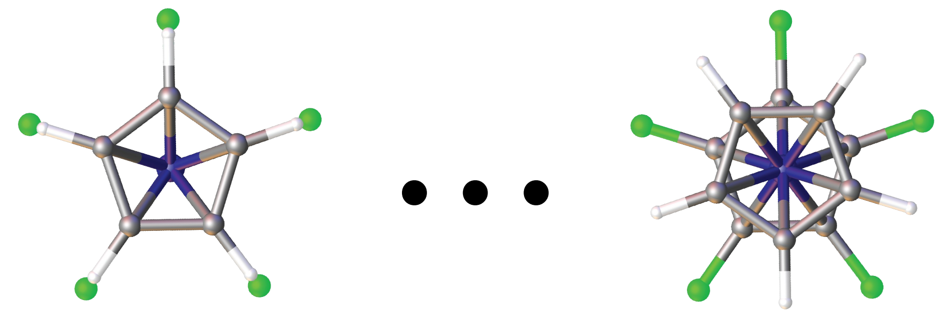




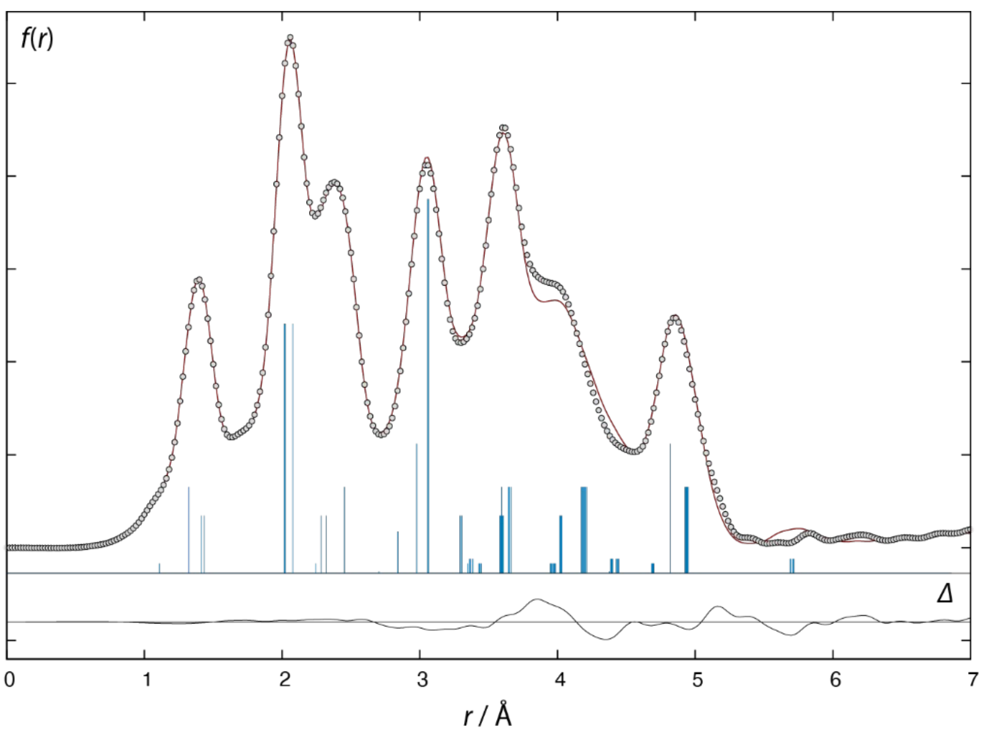
$Fe(C_5H_5)(C_5F_5)$, Static vs. Dynamic



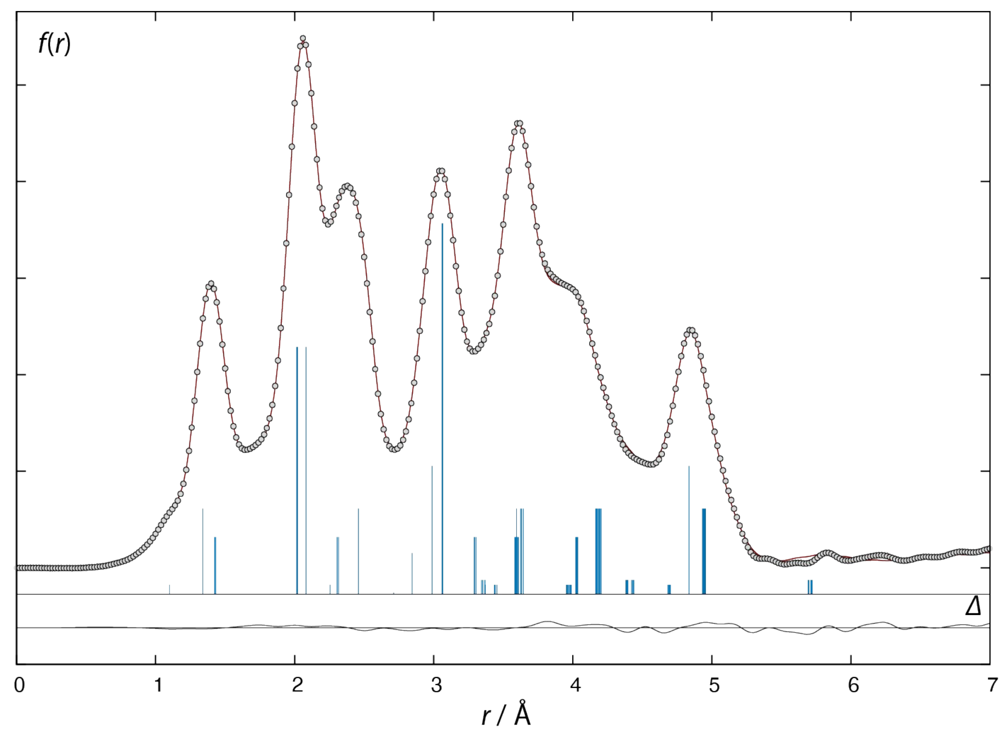
Static



Dynamic
(Pseudoconformers)

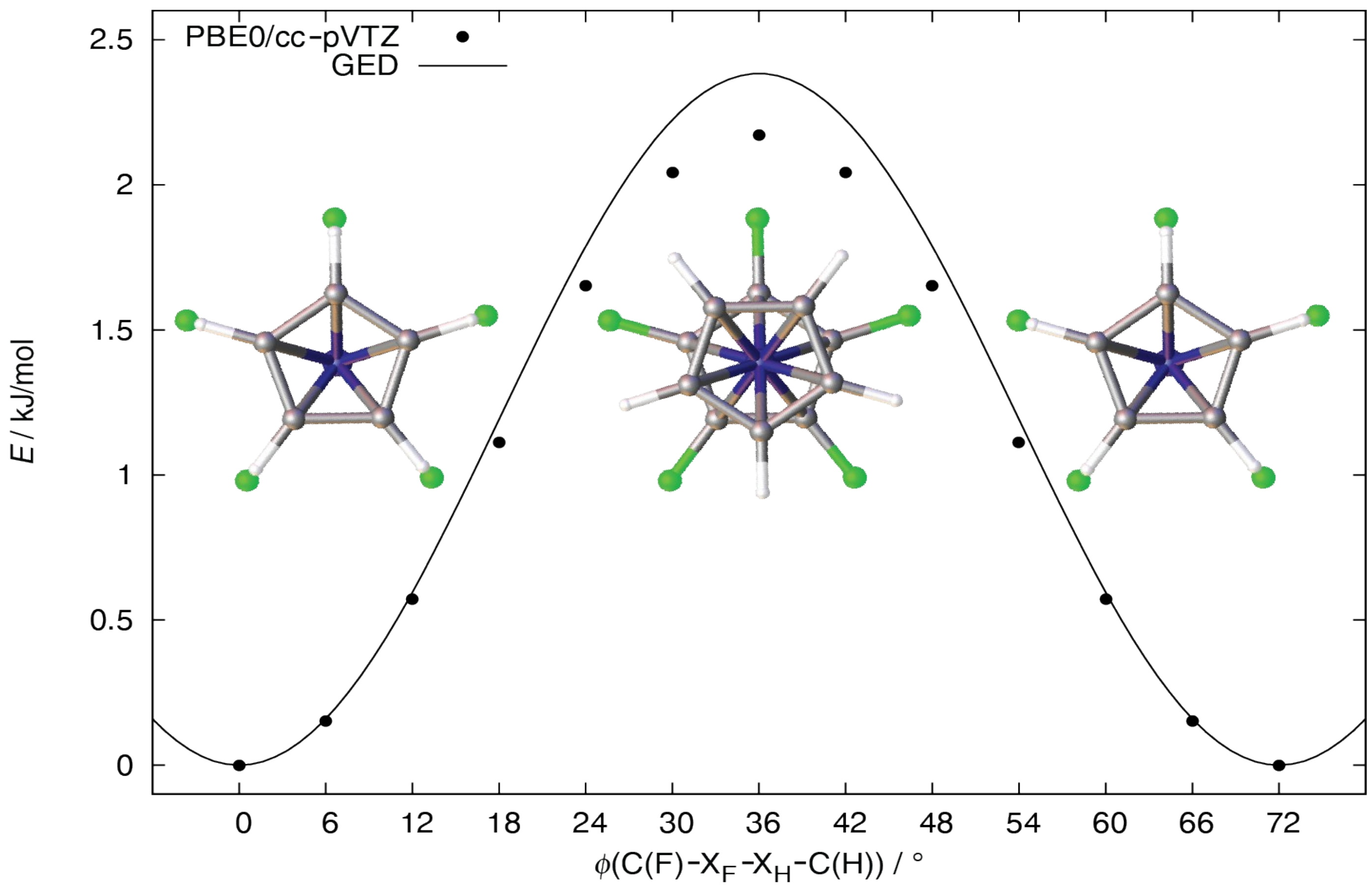


R_f = 5.8 %



R_f = 4.4 %

$Fe(C_5H_5)(C_5F_5)$, Potential



Compound	$V_0 = E_{stag} - E_{ecl}$ / kJ mol^{-1}
$Fe(C_5H_5)_2$	3.8(3)
$Fe(C_5Me_5)_2$	−4.0(3)
$Fe(C_5Cl_5)_2$	−0.8(2)

$$V(\varphi) = V_0(1-\cos(5\varphi))/2$$

$$V_0 = 2.4(3)\ \text{kJ mol}^{-1}$$

$Fe(C_5H_5)(C_5F_5)$, Geometry

Parameter [Å/°]	GED	PBE0	MP2	XRD
r(Fe–CH)	2.071(1)	2.054	1.904	2.048(3) – 2.054(3)
r(Fe–CF)	2.009(1)	2.013	1.856	1.997(3) – 2.005(3)
r(C–H)	1.085(7)	1.079	1.074	0.96(3) – 1.13(2)
r(C–F)	1.333(1)	1.323	1.330	1.331(4) – 1.341(4)
r(HC–CH)	1.425(1)	1.420	1.435	1.417(3) – 1.427(3)
r(FC–CF)	1.419(1)	1.420	1.434	1.410(3) – 1.416(3)
φ(C5-F)	−3.7(1)	−3.0	−1.6	−3.5(3)
φ(C5-H)	+1.6(2)	+1.6	+2.2	+2.1(4)

- PBE0/cc-pVTZ performs well
- MP2/cc-pVTZ fails

1σ Errors

K. Sünkel, S. Weigand, S. Blomeyer, C. G. Reuter, Yu. Vishnevskiy, N. W. Mitzel, *JACS* 137, 2015, 126.

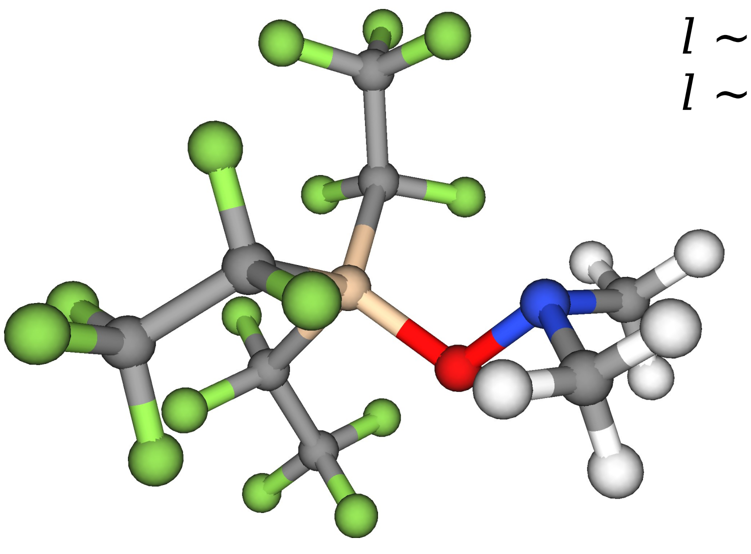
$(C_2F_5)_3Si–O–NMe_2$

Main chemical problem: Si...N interaction

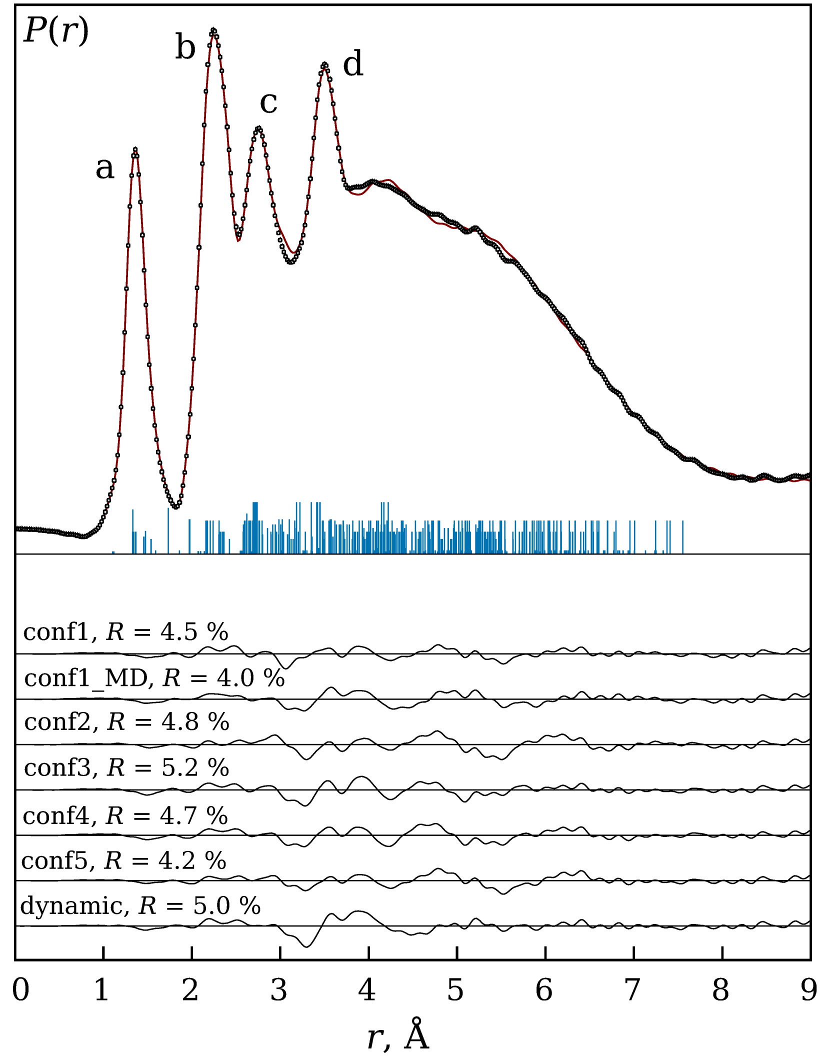
<(Si–O–N), °

82.0(1)	XRD
83.6	MP2/cc-pVTZ
105.0	B3LYP/6-31G(d,p)
105.9(12)	GED

F...H
$r \sim 6.5$ Å
$l \sim 4.5$ Å (refined)
$l \sim 1.5$ Å (MD)
$l \sim 0.2$ Å (PT)



(Unsolved 4D) Dynamic Problem



B. Waerder, S. Steinhauer, J. Bader, B. Neumann, H.-G. Stammler, Yu. V. Vishnevskiy, B. Hoge, N. W. Mitzel, *Dalton Trans*, *submitted*.

Nobody believes theoretical calculations,
except the one who did them.

Everybody believes experimental results,
except the one who obtained them.

Thank you for your attention!