Universität Bielefeld

Some Aspects of Accuracy and Precision in GED Method

UNEX Project

Yury V. Vishnevskiy

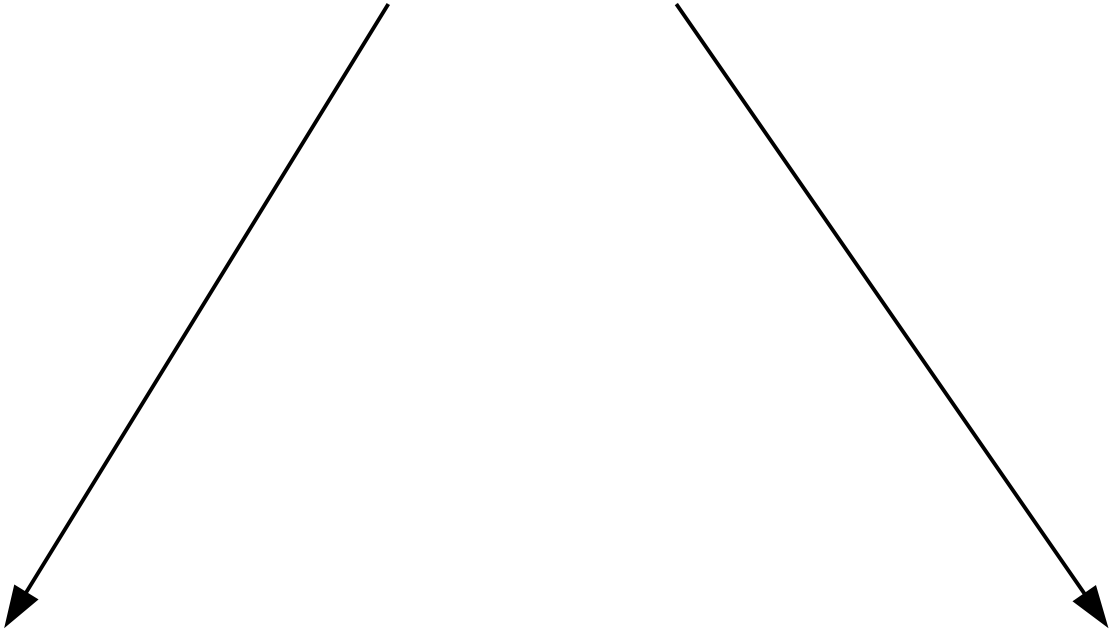
Moscow, June 24th 2011

I. Introduction

Main problems

Ways of GED development

Current GED method



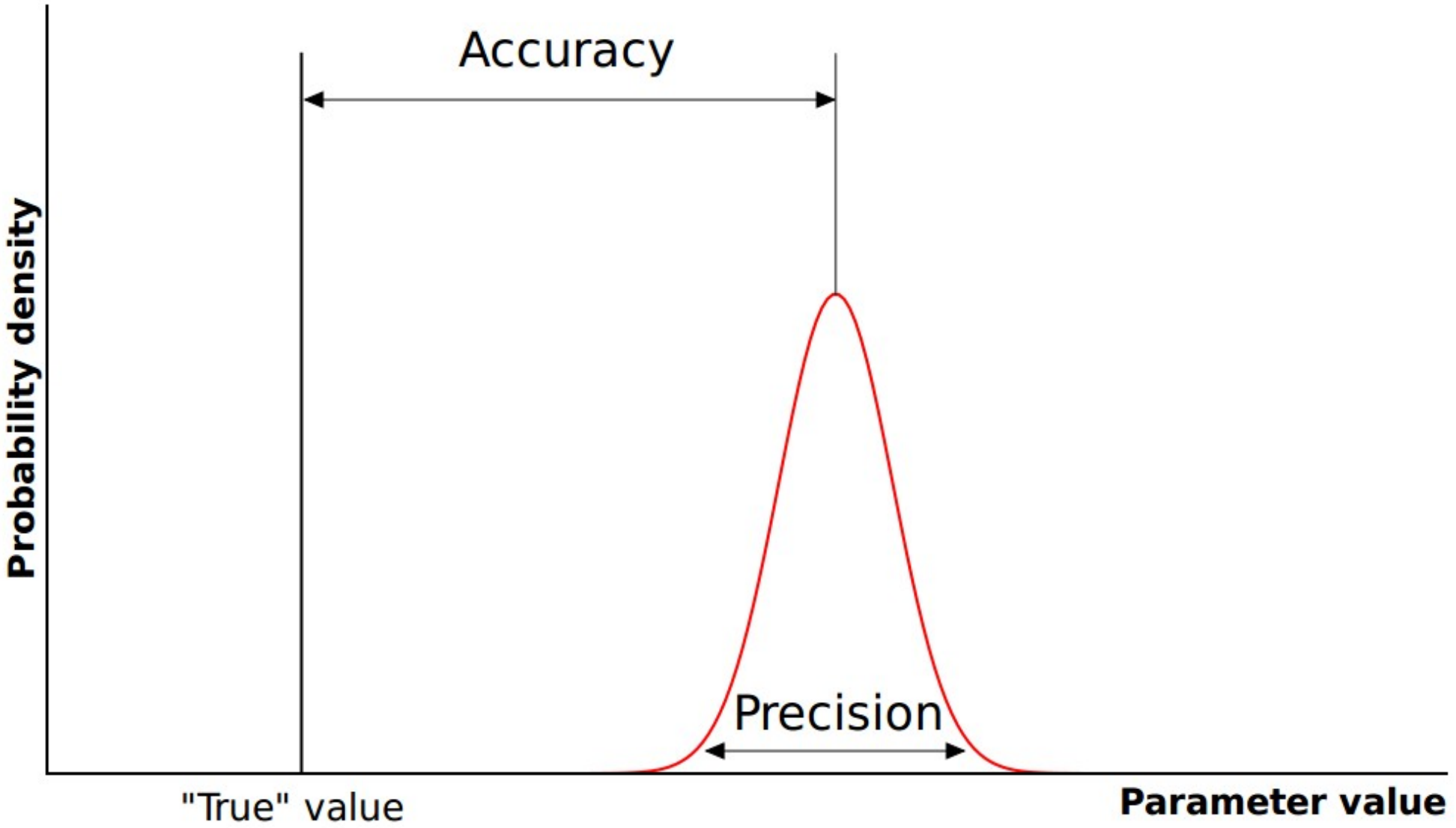
Automation for routine investigations

XRD

Improving reliability for accurate investigations

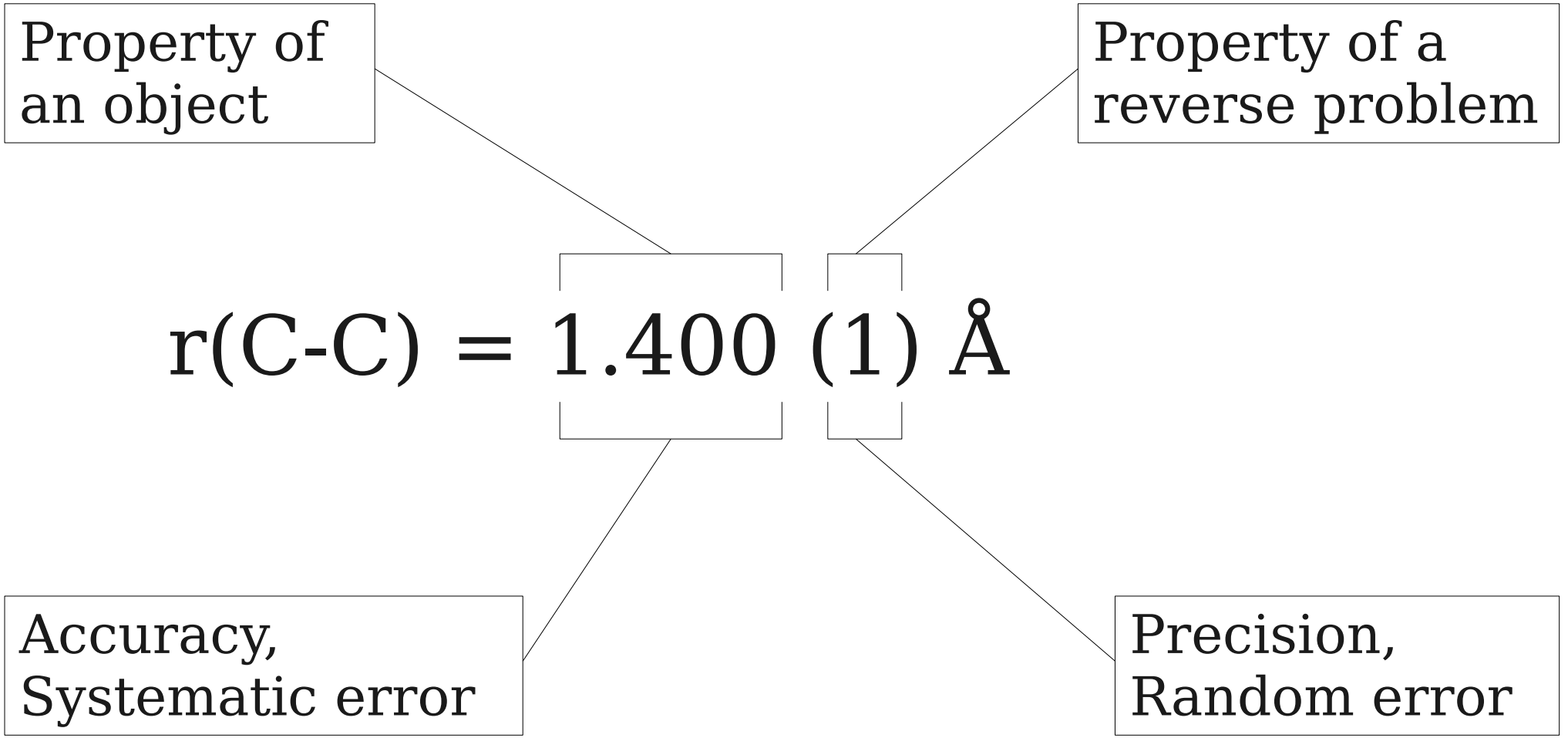
MW

Accuracy & Precision



“Guide to the Expression of Uncertainty in Measurement” (GUM)
“International Vocabulary of Metrology – Basic and General Concepts and Associated Terms” (VIM)

Accuracy vs. Precision



Confusion with precision

JCTC Journal of Chemical Theory and Computation

Geometries of Third-Row Transition-Metal Complexes from Density-Functional Theory

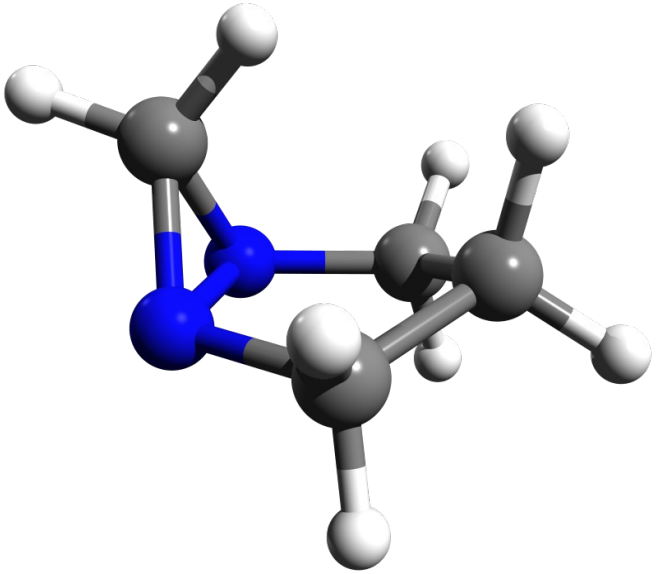
Michael Bühl,*,† Christoph Reimann,‡ Dimitrios A. Pantazis,‡ Thomas Bredow,‡ and Frank Neese*,‡

Drawing from a large compilation of gas-phase structures,[23] we chose complexes for which at least one metal−ligand bond length was determined with a precision better than 1 pm, affording a final set of 25 molecules with 41 individual bond distances with that precision, which should be sufficient for reasonable statistics. We also report computed zero-point corrections to the bond distances[24,25] for this data set in order to furnish increments to estimate r_g^0 from r_e values,[26] thus facilitating the comparison between theory and experiment.

II. Main part

Investigation of Accuracy and Precision

Systematic errors: a simple approach



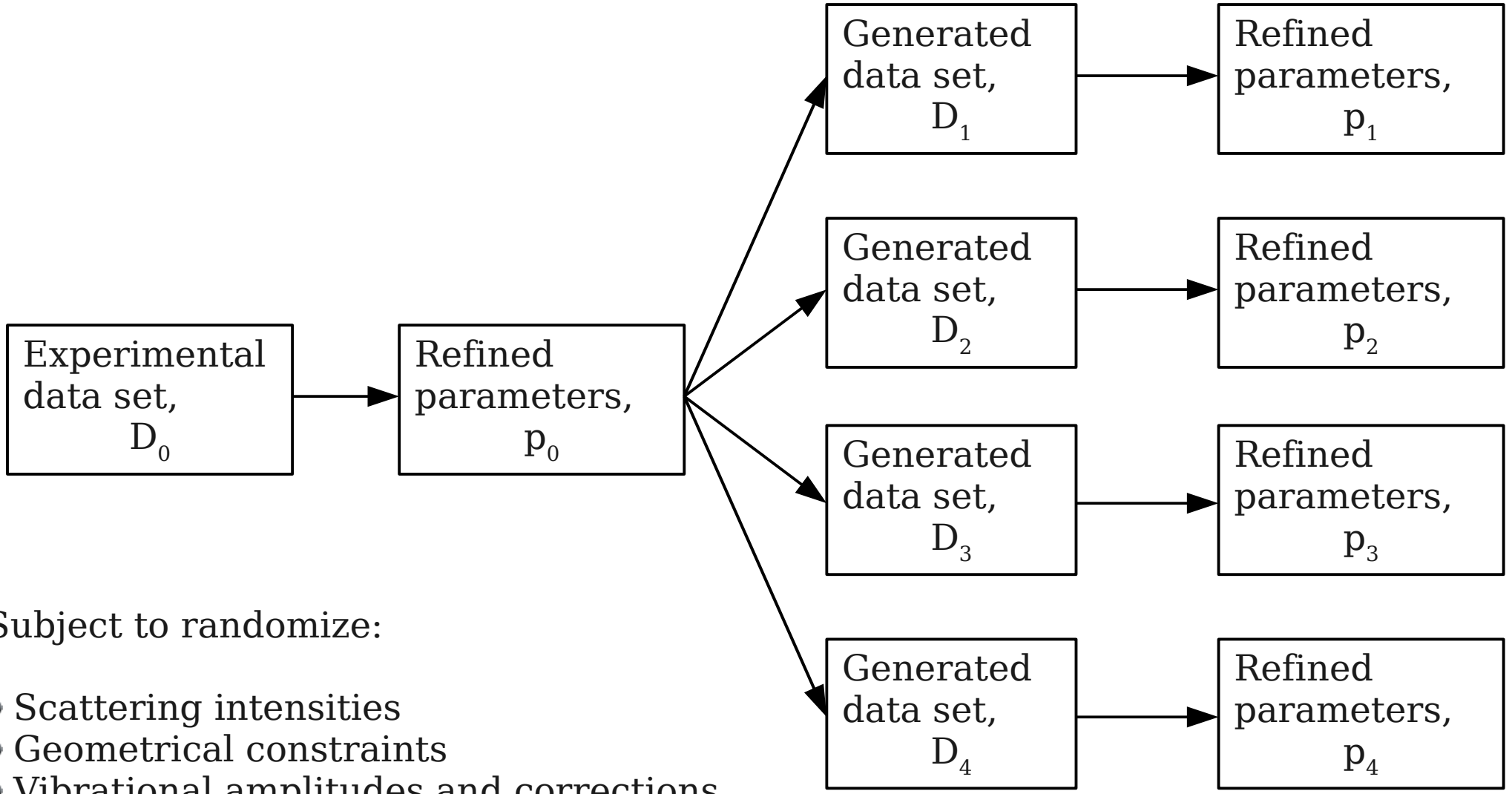
MP2/cc-pVTZ
MP2/aug-cc-pVTZ
MP4(SDQ)/cc-pVTZ
CCSD/cc-pVTZ

B3LYP/6-31G(df,p)
MP2/6-31G(d,p)

Parameter	3σ	S_{err}	Δ_{const}	Δ_{vib}	Δ_{bgl}	Δ_{tot}
r(N-N)	0.001	0.002	0.013	0.001	0.000	0.013
r(C-H)	0.004	0.001	0.004	0.000	0.000	0.005
$\angle$(N-N-C)	0.47	0.00	0.23	0.06	0.17	0.40
l(C-C/C-N)	0.001	0.001	0.001	0.000	0.000	0.001
ΔRf, %			0.08	0.03	1.6	

Yu.V. Vishnevskiy, N. Vogt, J. Vogt, A.N. Rykov, V.V. Kuznetsov, N.N. Makhova, L.V. Vilkov, *J. Phys. Chem. A*, 2008, **112**, 5243-5250.
G. Portalone, A. Domenicano, G. Schultz, I. Hargittai, *J. Mol. Struct.*, 1987, **160**, 97-107

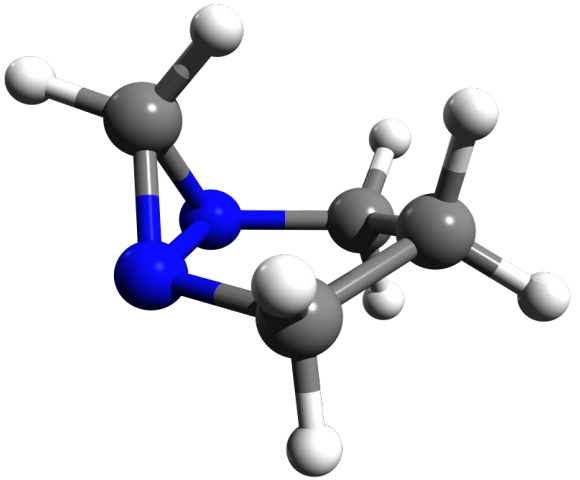
Monte Carlo simulation



Subject to randomize:

- Scattering intensities
- Geometrical constraints
- Vibrational amplitudes and corrections
- Other types of constraints

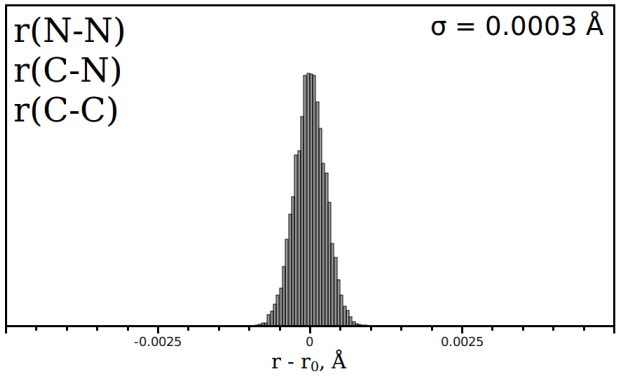
Monte Carlo for DABH

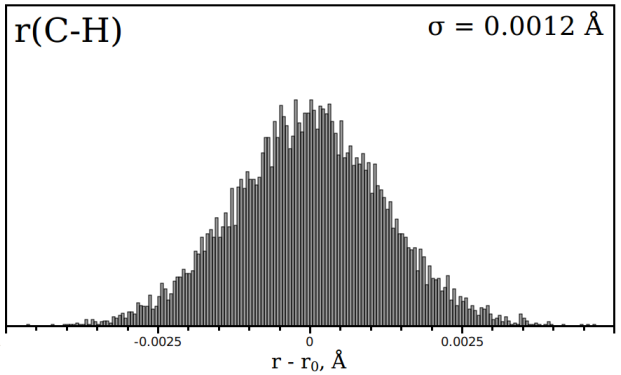


Subject to randomize:

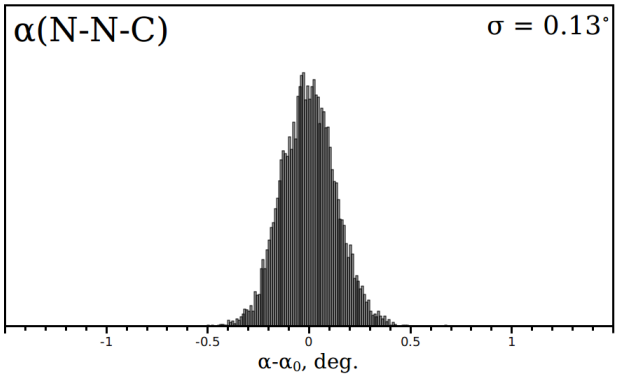
Scattering intensities only

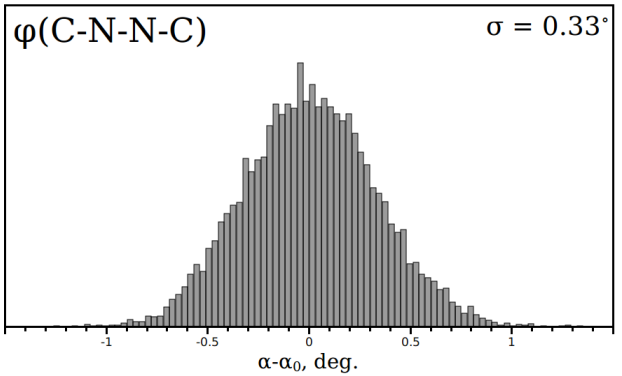
Bond lengths



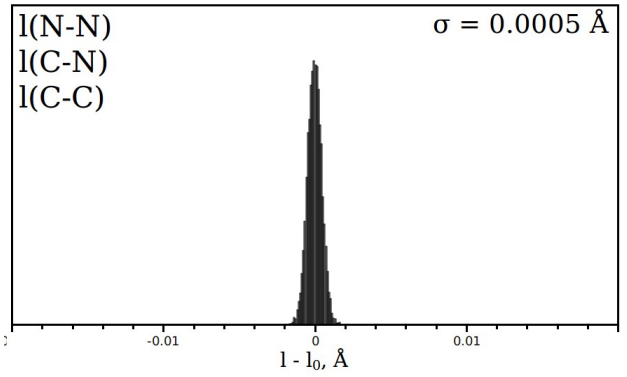


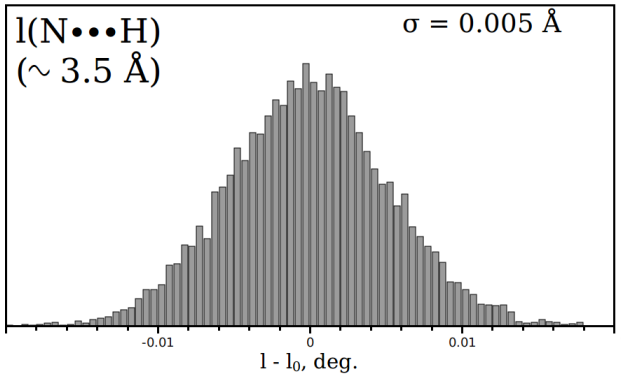
Angles



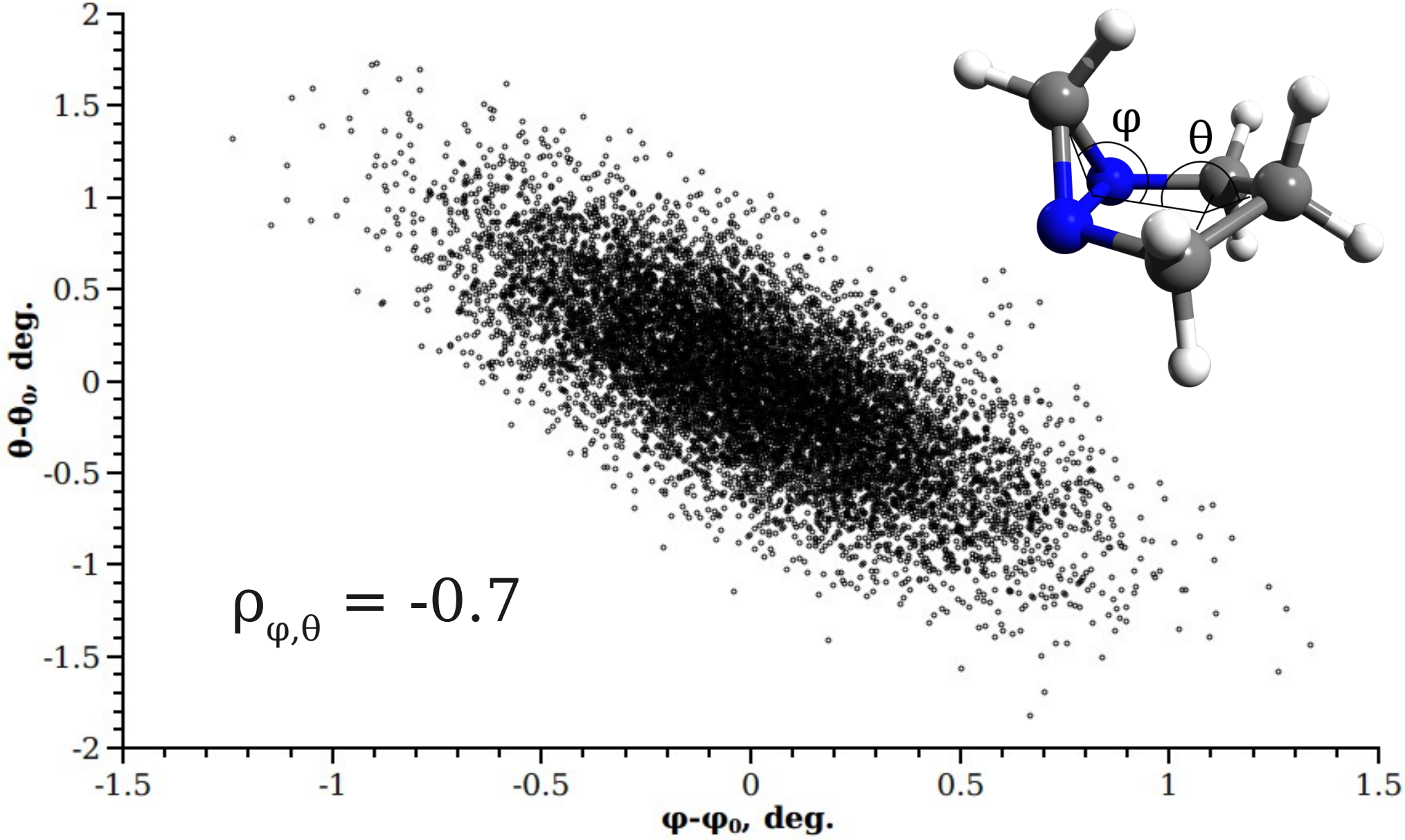


Amplitudes



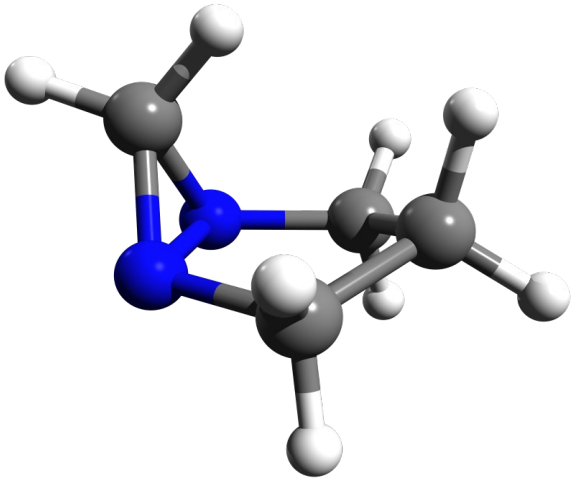


Correlation between φ and θ



In UNEX: “X^2 hyperellipsoid (axes vectors) for P=99.0%”.

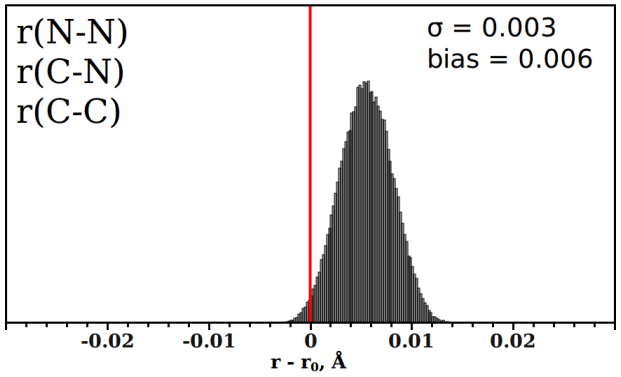
Monte Carlo for DABH

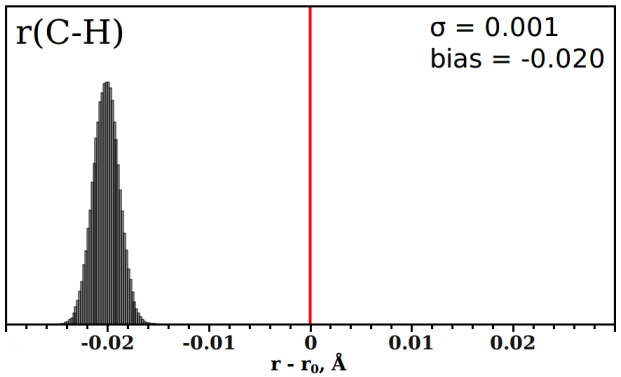


Subject to randomize:

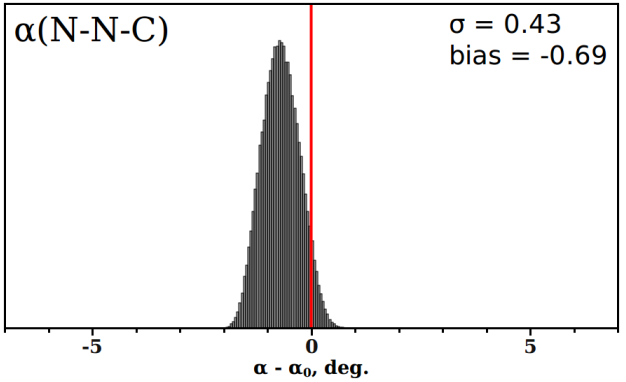
Scattering intensities
+Geometrical constraints

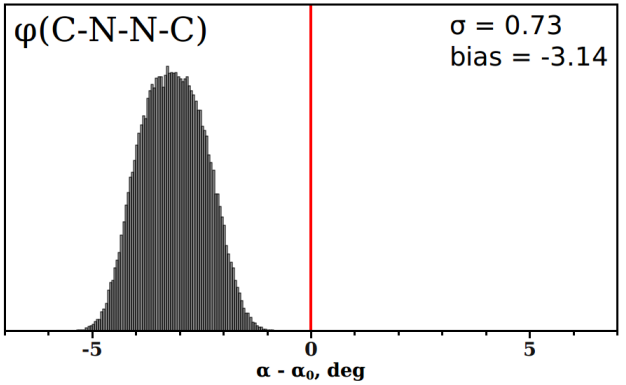
Bond lengths



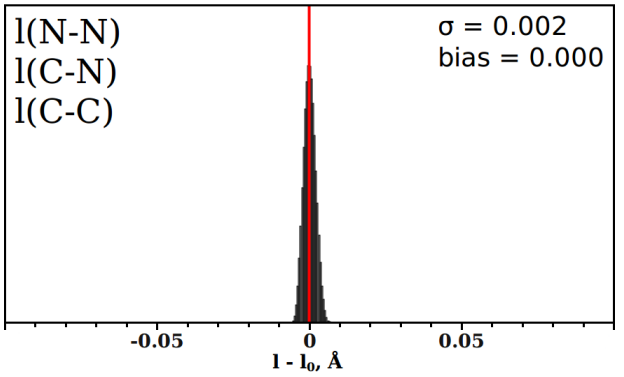


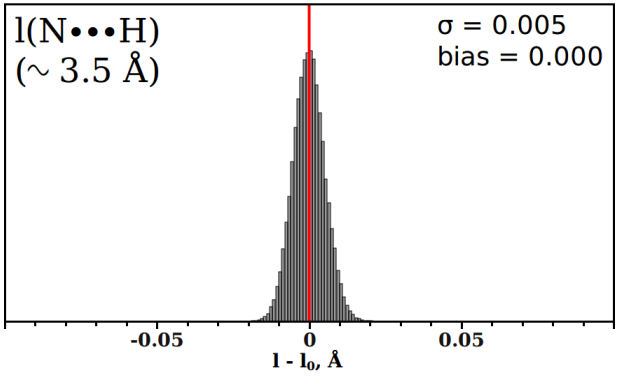
Angles



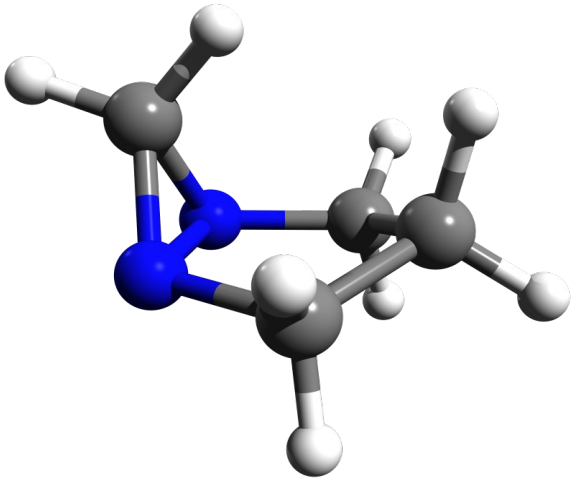


Amplitudes





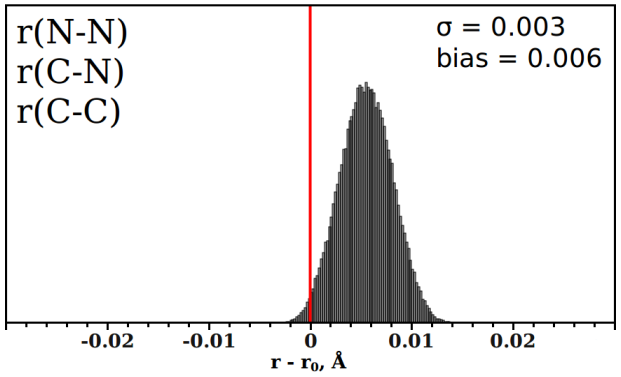
Monte Carlo for DABH

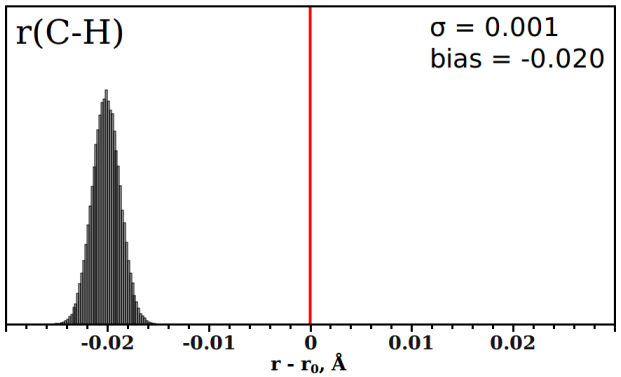


Subject to randomize:

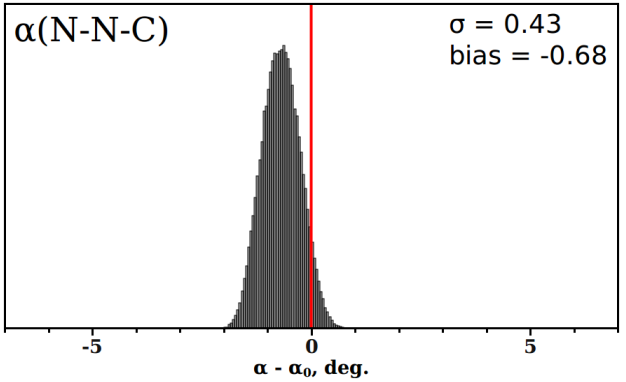
Scattering intensities
+Geometrical constraints
+Vib. amplitudes
+Vib. corrections

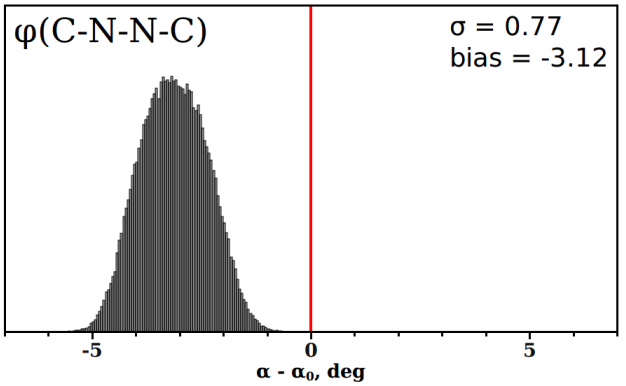
Bond lengths



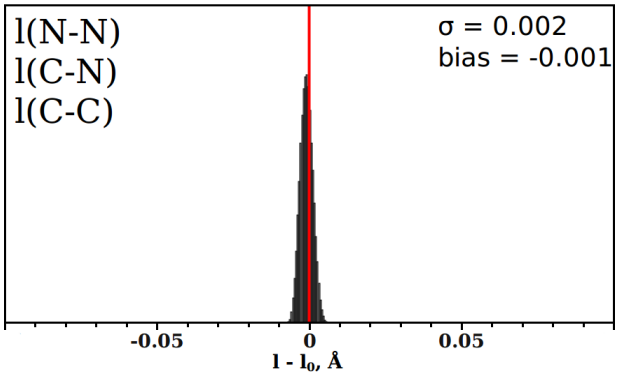


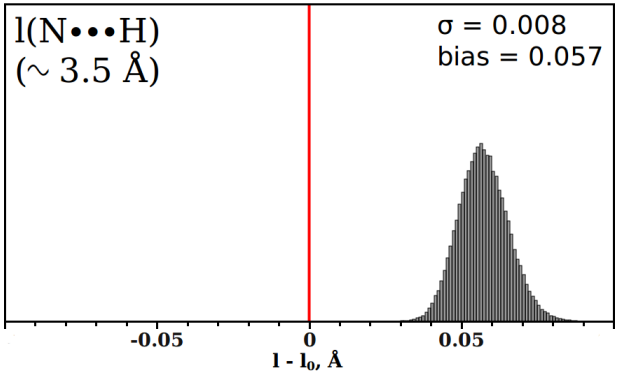
Angles



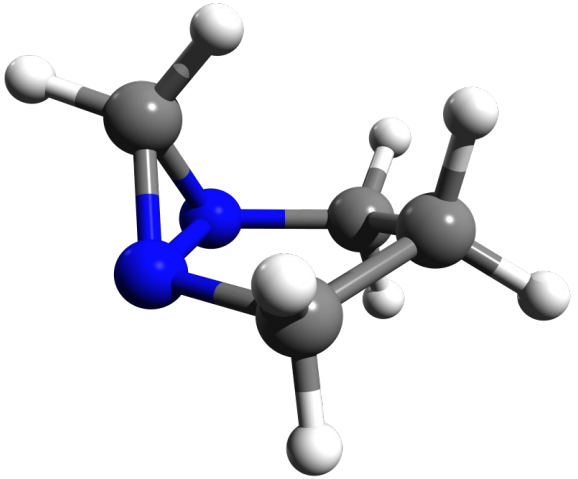


Amplitudes





DABH: Comparison of results



Parameter	GED, Conventional	GED with Bootstrapping	Theory*
r(N-N), Å	1.506(13)	1.513(3)	1.515
$r(C\text{-}H)_{av}$, Å	1.100(5)	1.087(1)	1.088
∠(N-N-C), deg	107.7(4)	107.0(4)	106.9
φ(C-N-N-C),deg	108.7(9)	105.1(8)	105.1
l(N-N), Å	0.057(1)	0.056(2)	0.055
l(N...H), Å	0.076(99)	0.134(8)	0.106

* MP2/aug-cc-pVTZ for the geometry, B3LYP/6-31G(df,p) for the amplitudes.

III. Development of the method

The regularization approach

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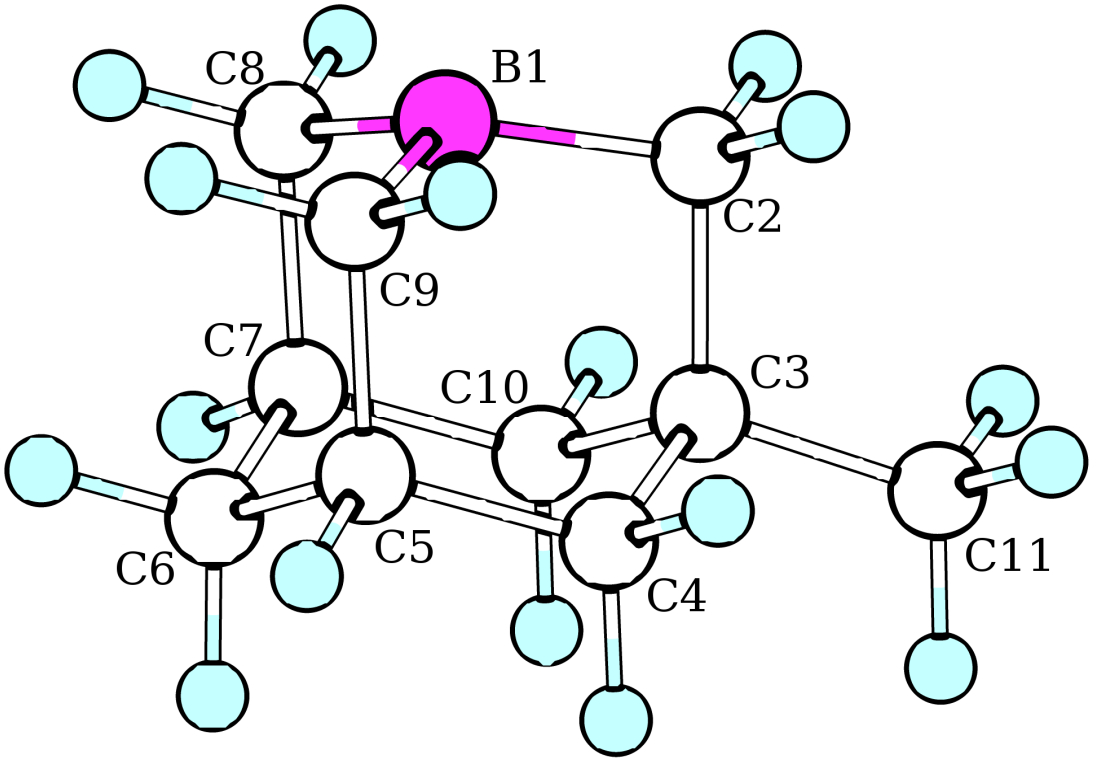
3-Methyl-1-boraadamantane



… see our poster.

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Acknowledgments

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DFG

14 European
Symposium
Gas Electron Diffraction