Universität Bielefeld

Development of refinement procedures in gas electron diffraction

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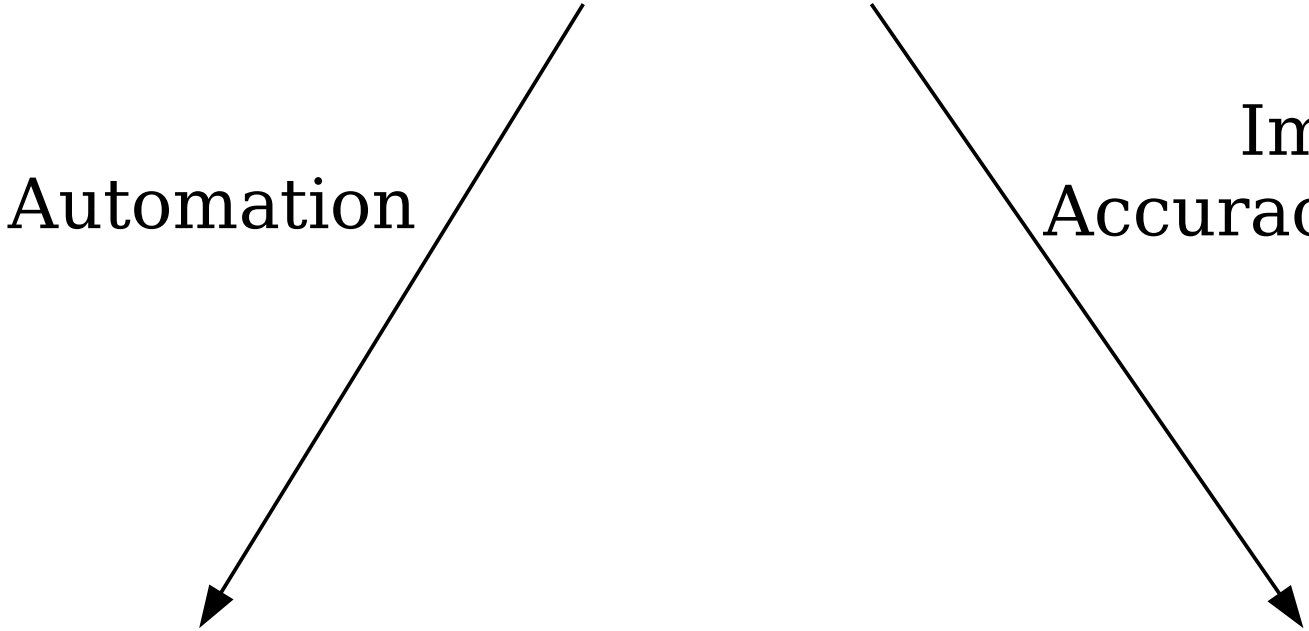
Ways of Development

Current GED method



routine investigations

(like routine XRD) Refine everything, what can be evaporated.

fine investigations

Utilization of additional experimental data.
Limited to small and symmetric molecules.

Monte Carlo in UNEX 1.6

Subject to randomize:

- Scattering intensities
- Geometrical constraints/restraints
- Vibrational amplitudes and corrections
- Wavelengths
- Regularization constants

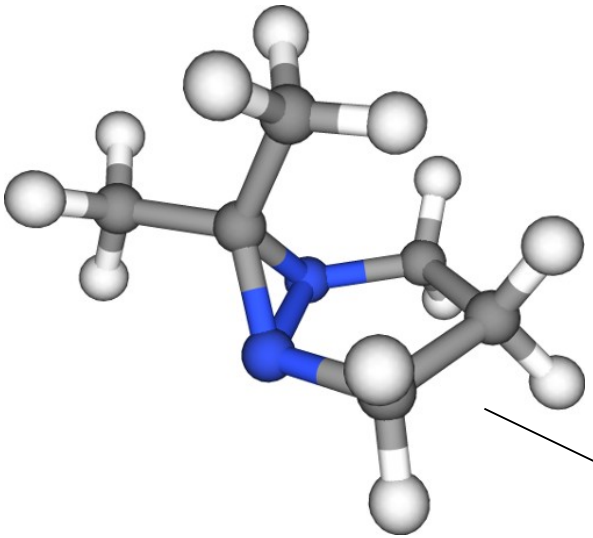
Experimental data set, D_0 → Refined parameters, p_0

Refined parameters, p_0 → Randomized data set/model D_1 → Refined parameters, p_1

Refined parameters, p_0 → Randomized data set/model D_2 → Refined parameters, p_2

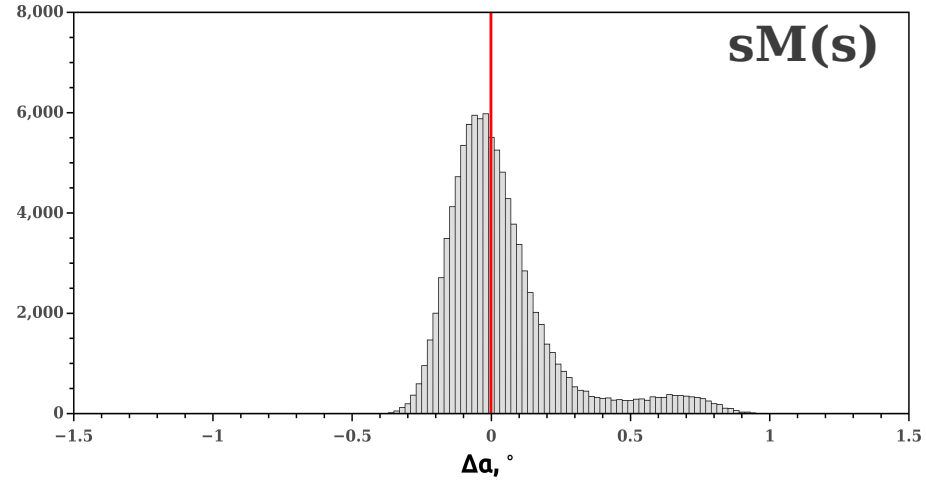
Refined parameters, p_0 → Randomized data set/model D_3 → Refined parameters, p_3

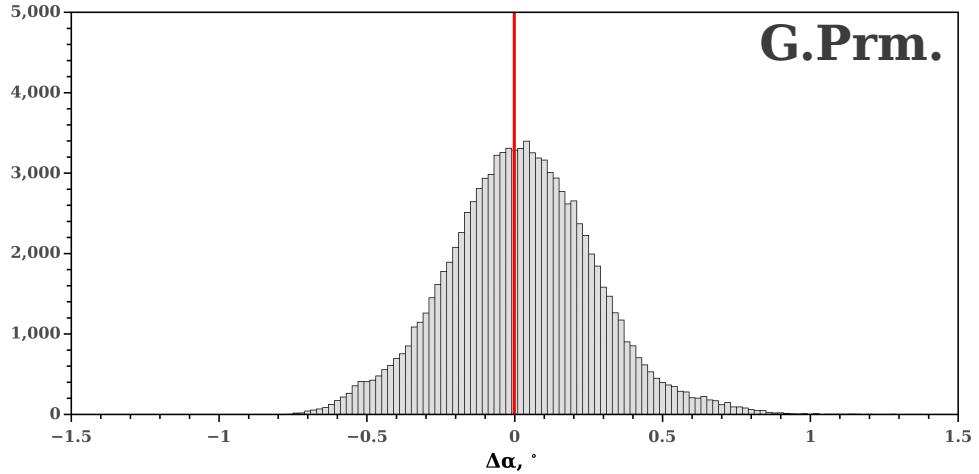
Refined parameters, p_0 → Randomized data set/model D_4 → Refined parameters, p_4

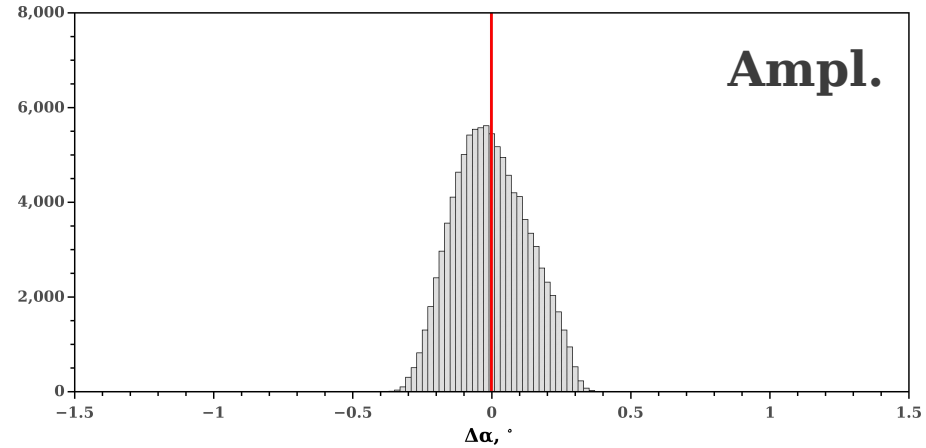


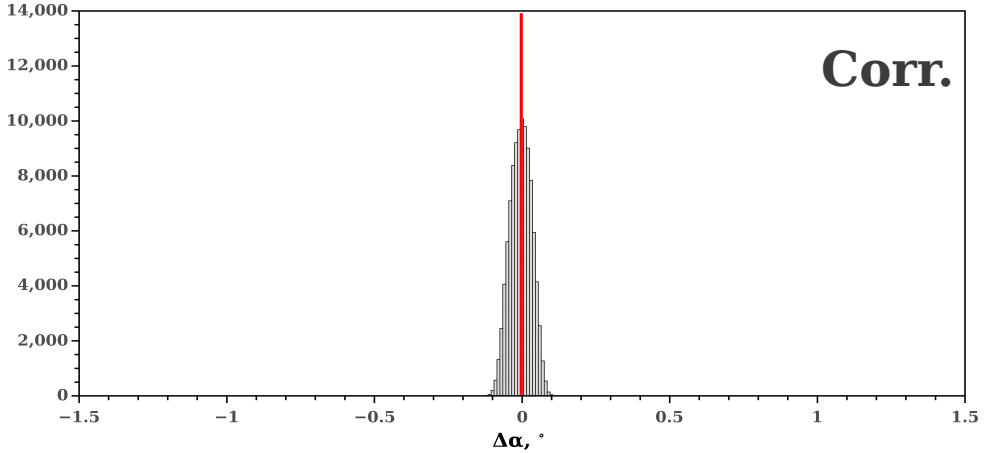
Example (N-N-C angle)

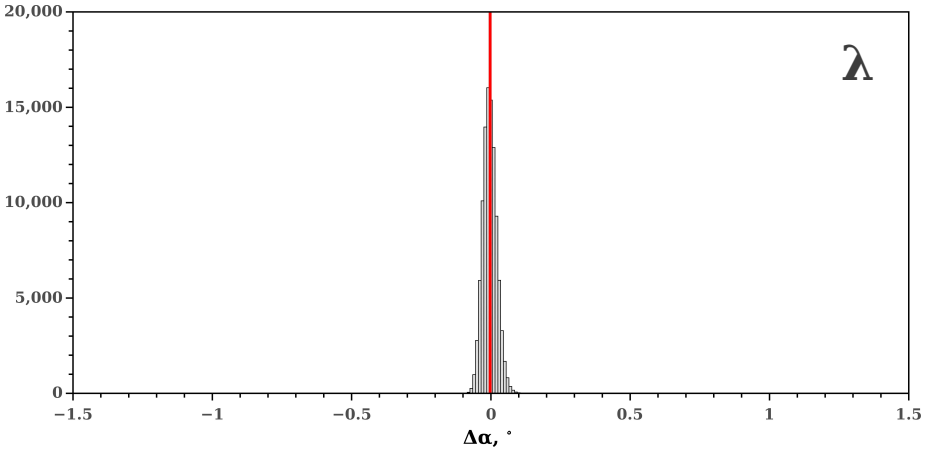
Monte Carlo: Histograms

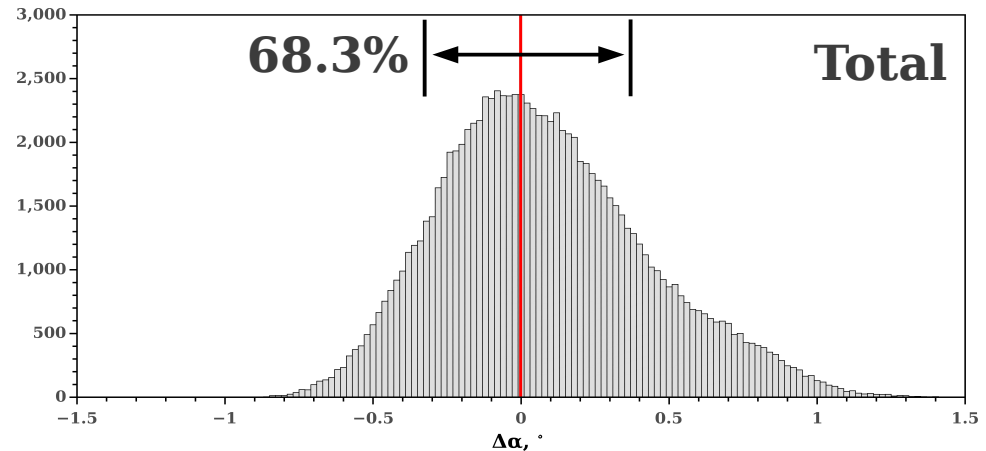




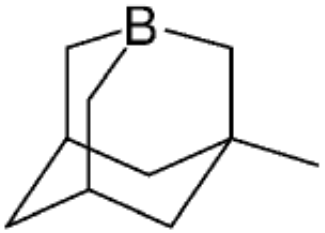








Recent work



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Structure and Bonding Nature of the Strained Lewis Acid 3-Methyl-1-boraadamantane: A Case Study Employing a New Data-Analysis Procedure in Gas Electron Diffraction

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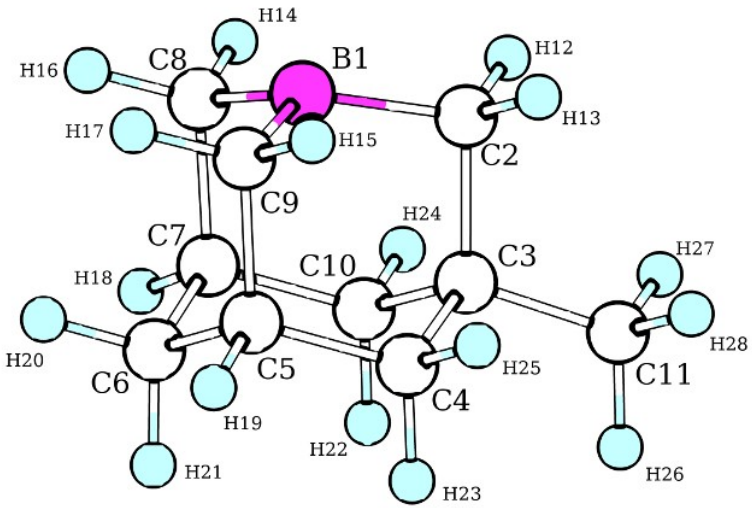
Bartel's “predicate observations”:

$$Q = \sum \left[sM(s)^{e} - sM(s)^{mod} \right]^2 + \alpha \sum_i w_i \left(p_i^0 - p_i^{mod} \right)^2 \rightarrow min$$

	This work	SARACEN
Refined parameters	Cartesian coordinates	Internal parameters and their combinations
Restraints	Internal parameters	Same as refined parameters
Weights	All w_i are equal	Adjusted to formal precision

L. S. Bartell, D. J. Romenesko, T. C. Wong, in *Molecular Structure by Diffraction Methods,* The Chemical Society, London, 1975, Vol. 3, pp 72 – 79.
A. J. Blake, P. T. Brain, H. McNab, J. Miller, C. A. Morrison, S. Parsons, D. W. H. Rankin, H. E. Robertson, B. A. Smart, *J. Phys. Chem.*, 1996, 100, 12280.
A. N. Tychonoff, *Dokl. Akad. Nauk SSSR*, 1943, 39, 195.

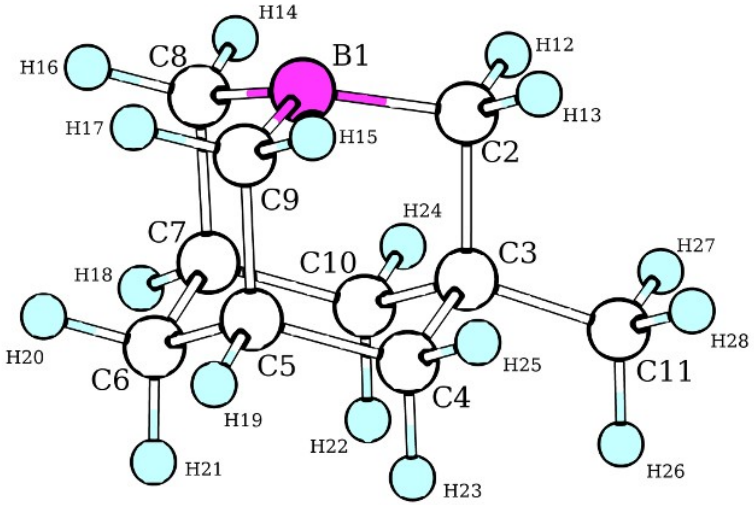
Conventional vs. Regularization

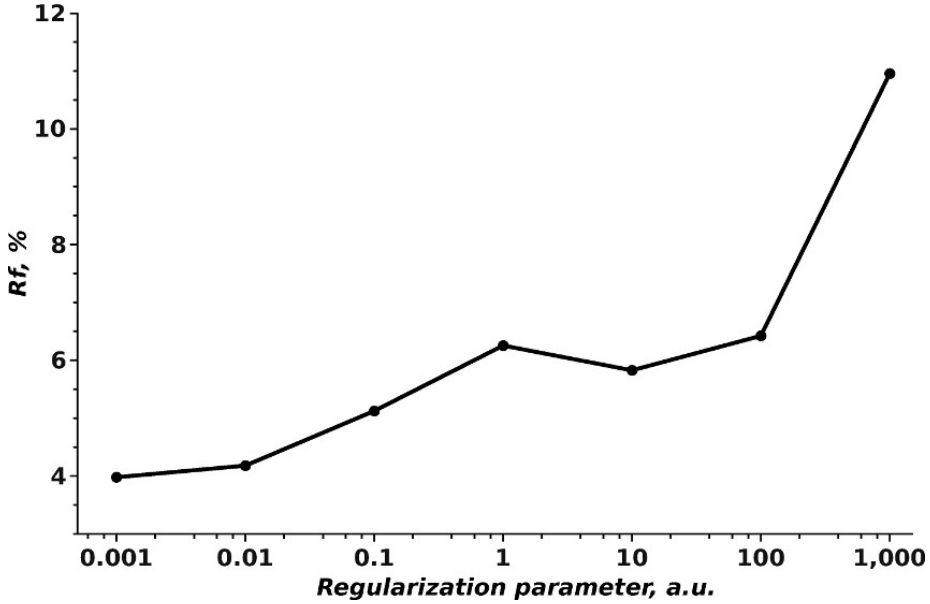


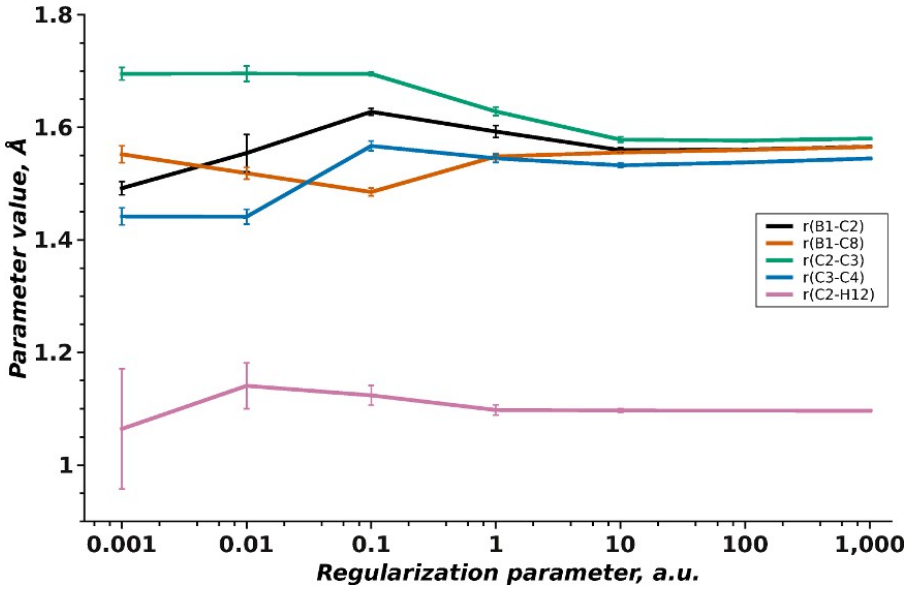
Estimated total errors include:
1. LSQ std. deviations.
2. Scale errors.
3. Effects of geom. model.
4. Ambiguity in α.
5. Inaccuracy in constraints and restraints.

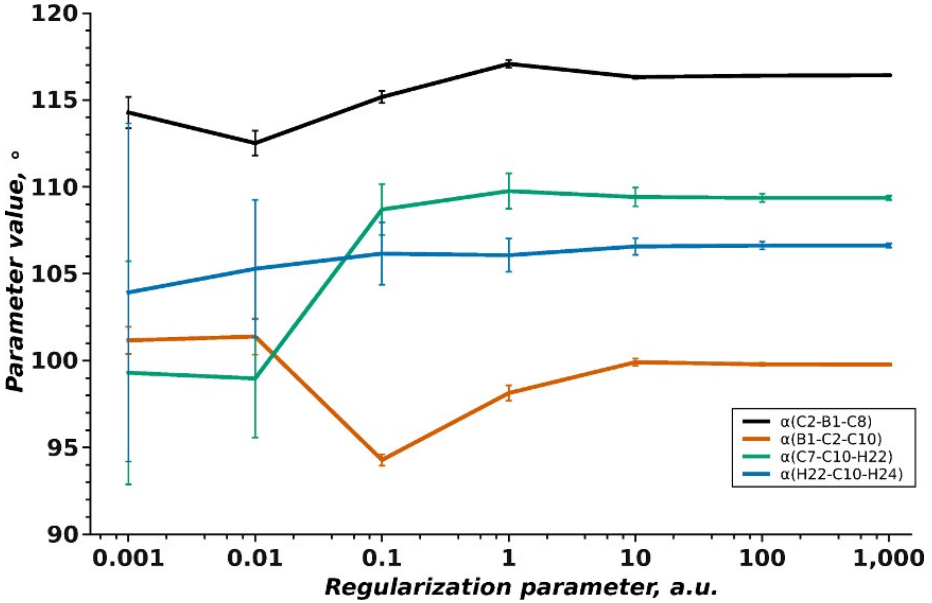
Parameter	GED Conventional	GED with Regularization
r_e(B1-C2)	1.561(10)	1.562(7)
r_e(B1-C8)	1.561(10)	1.553(4)
r_e(C2-C3)	1.575(10)	1.580(8)
r_e(C4-C5)	1.531(6)	1.538(10)
r_e(C3-C11)	1.521(6)	1.524(13)
r_e(C-H)$_{av}$	1.099(8)	1.097(11)
α(C2-B1-C8)	116.4(50)	116.3(2)
α(C8-B1-C9)	116.6(115)	116.8(3)
α(B1-C2-C3)	101.2(21)	100.0(8)
α(C2-C3-C11)	106.2(81)	110.2(8)
φ(B1-C2-C3-C10)	-58.7(21)	-59.1(6)
φ(B1-C8-C7-C10)	59.0(79)	60.4(2)
l_1	0.052(2)	0.051(1)
l_6	0.087(19)	0.093(6)

Degree of Regularization









Cartesian Coordinates

Regularization of internal coordinates:

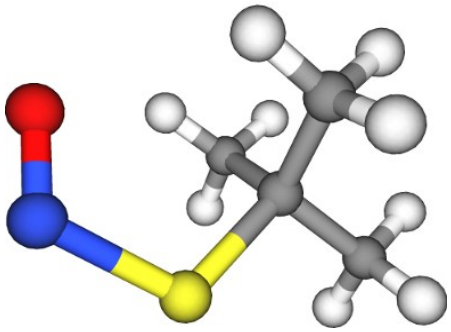
$$Q = \sum \left[sM\left(s\right)^{e} - sM\left(s\right)^{mod} \right]^2 + \alpha \sum_i w_i \left(p_i^0 - p_i^{mod} \right)^2 \rightarrow min$$

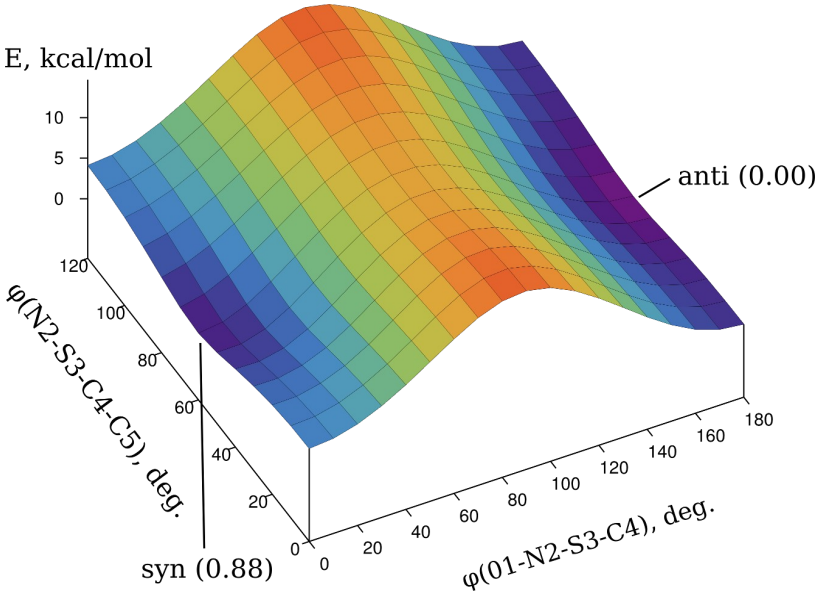
Regularization of Cartesian coordinates:

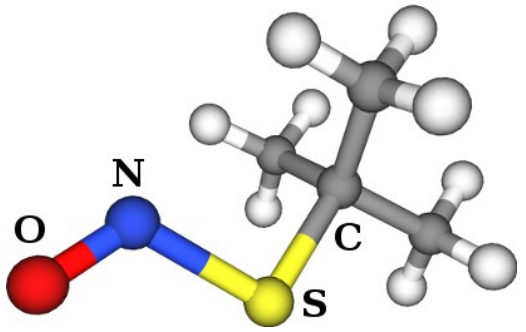
$$Q = \sum \left[sM\left(s\right)^{e} - sM\left(s\right)^{mod} \right]^2 + \alpha \sum_i^{3N} w_i \left(x_i^0 - x_i^{mod} \right)^2 \rightarrow min$$

Parameter	**GED Conventional**	**GED with Regularization**	**GED with Regularization of Cartesian Coordinates**
r_e(B1-C2)	1.561(10)	1.562(7)	1.565(4)
r_e(B1-C8)	1.561(10)	1.553(4)	1.567(3)
r_e(C2-C3)	1.575(10)	1.580(8)	1.584(4)
r_e(C4-C5)	1.531(6)	1.538(10)	1.517(3)
r_e(C3-C11)	1.521(6)	1.524(13)	1.523(3)
α(C2-B1-C8)	116.4(50)	116.3(2)	115.7(1)
α(C8-B1-C9)	116.6(115)	116.8(3)	116.5(2)

Mixtures of Conformers: tBu-SNO





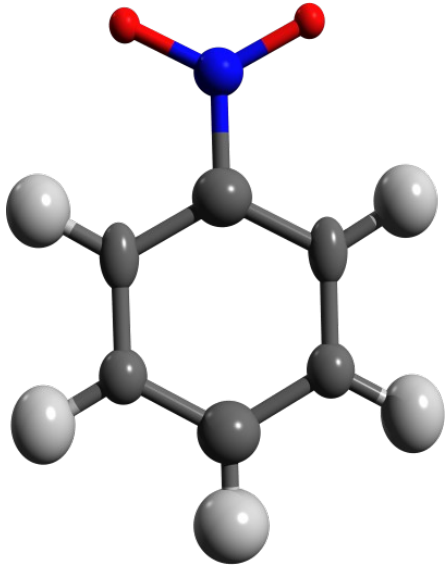


Parameters	*anti*		*syn*	
	Conventional	**Regularization**	**Conventional**	**Regularization**
r_e(O-N), Å	1.198(2)	1.199(2)	1.206(2)	1.207(4)
r_e(N-S), Å	1.770(4)	1.790(6)	1.743(4)	1.744(5)
r_e(S-C), Å	1.826(4)	1.807(5)	1.826(4)	1.820(3)
r_e(C-C), Å	1.520(3)	1.517(3)	1.522(3)	1.519(2)
α_e(O-N-S), °	113.7(4)	114.0(4)	117.0(4)	118.1(3)
α_e(N-S-C), °	97.2(7)	96.1(3)	109.2(7)	108.8(3)
x, %	83(3)	87(3)	17(3)	13(3)

Adding Rotational Constants: $C_6H_5NO_2$

$$Q = \sum [sM(s)^{e} - sM(s)^{mod}]^2 + \alpha \sum_{i}^{3N} w_i (x_i^0 - x_i^{mod})^2 + \beta \sum_{i} w_i (B_i^e - B_i^{mod})^2 \rightarrow min$$

	Exp.	Delta	
A_e	3968.078	-0.003	MHz
B_e	1286.920	-0.002	MHz
C_e	972.661	0.070	MHz



Parameter	Conventional	Cartesian coord. + Regularization	Cartesian coord. + Regularization + Rot. constants
r_e(N-O), Å	1.2227(4)	1.2224(7)	1.2226(6)
r_e(C-N), Å	1.4640(16)	1.4639(24)	1.4619(21)
r_e(C-C(N)), Å	1.3839(7)	1.3836(18)	1.3840(17)
α_e(O-N-O), °	124.10(13)	123.87(17)	123.90(19)
α_e(C-C(N)-C), °	123.08(17)	122.32(21)	122.98(21)

O. V. Dorofeeva, Yu. Vishnevskiy, N. Vogt, J. Vogt, L. Khristenko, S. Krasnoshchekov, I. Shishkov, I. Hargittai, L. Vilkov, *Struct. Chem.*, 2007, 18, 739.

Conclusions

I. It is possible …

… to refine structures in Cartesian coordinates!
… to regularize Cartesian coordinates.
… to refine models with mixtures.
… to use additional rotational constants.

II. Typical **precision** of refined parameters is comparable to that from XRD (50% of XRD structures in 2012 have σ(C-C) > 0.005 Å).

III. We are ready to **refine automatically** large molecules.

IV. Accuracy of restraints plays minor role.

V. Dynamic models with large-amplitude motions are hardly possible.

IV. ToDo:

1). Project out rotations&translations.
2). Find appropriate scale to express “amount of experiment” in refined parameters.
3). Implement automatic calculation of vibrational parameters.

Thank you for attention!