



A new method for the molecular geometry optimization during the quantum-chemical modeling of chemical and biochemical reactions

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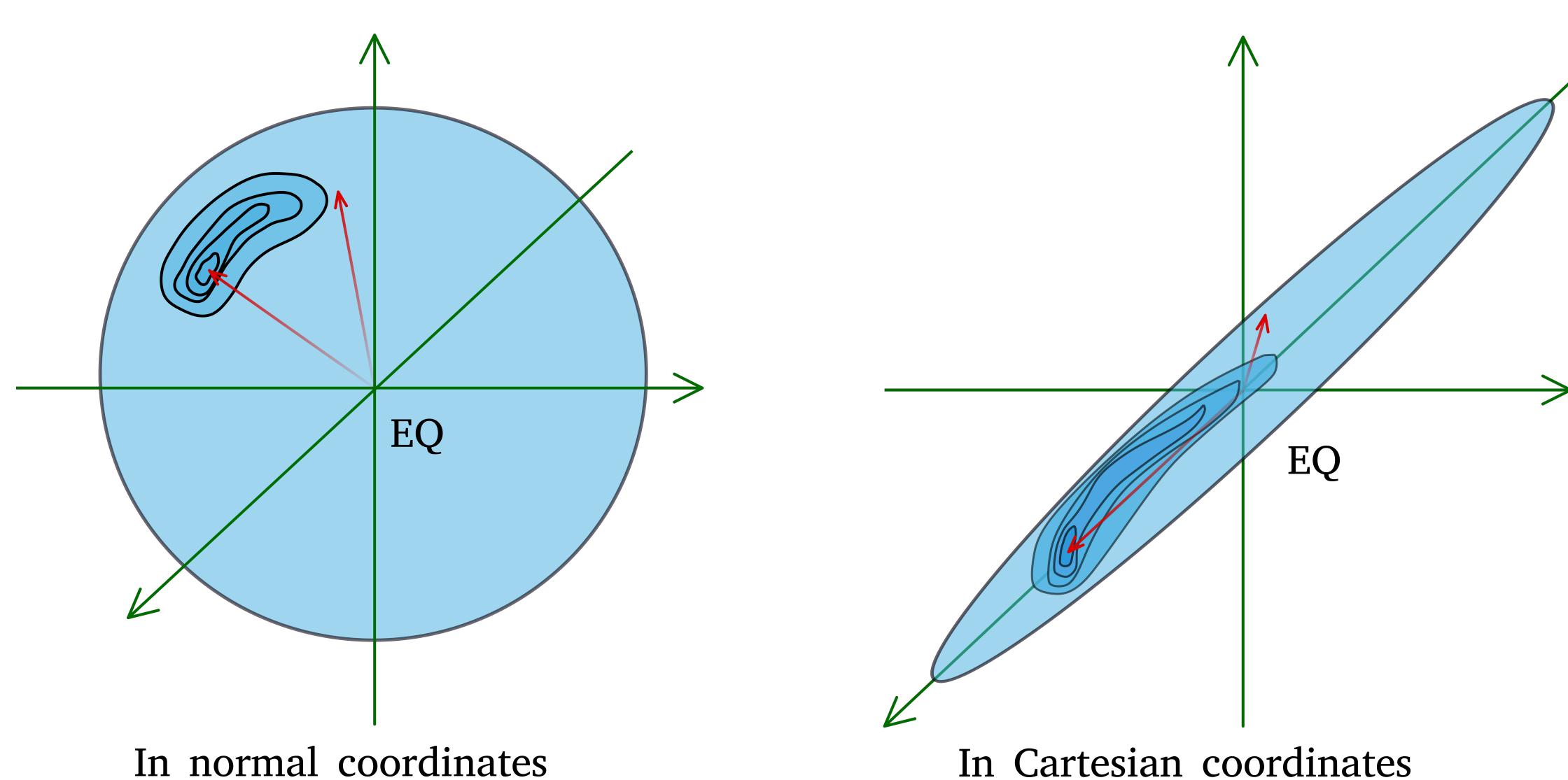
Abstract

Optimization of molecular geometry is a crucial step for all methods that simulate chemical and biochemical reactions. However, the available methods are not very stable and in certain cases can lead to divergences. To overcome this problem we modified a well known RFO method by introducing more sophisticated approaches for deriving the numerical parameters that define the optimization process. We showed that the proposed modifications eliminate the possibility of divergences, and for this reason the modified optimization algorithm can be safely included as a part of automatic algorithms for studying chemical reactions.

Introduction

The key role in the ADDF[1, 2] is played by the optimization of the molecule energy in normal coordinates with a spherical constraint. The classical methods for optimizing the geometry of the RFO/TRM [1] molecule do not take into account many of the features of such an energy parametrization. We propose a modification for RFO/TRM, which consists of re-weighting the coordinates and selecting a scaling factor based on a binary search.

Theory



Standart RFO:

$$E_{RFO}(\Delta x) = \frac{g^T \Delta x + \frac{1}{2} \Delta x^T H \Delta x}{1 + \Delta x^T S \Delta x}, \quad \Delta x^* = \underset{\Delta x \in \mathbb{R}^{3N}}{\operatorname{arg\min}} E_{RFO}(\Delta x)$$

$$S = \alpha I : \alpha = 1 \text{ or } \alpha = \frac{1}{3N}$$

Modification of S-matrix:

$$\Delta x \approx J_{q \rightarrow x} \Delta q \Rightarrow \Delta x^T \Delta x \approx \Delta \theta^T J_{\theta \rightarrow q}^T J_{q \rightarrow x} J_{q \rightarrow x} J_{\theta \rightarrow q} \Delta \theta$$

$$\Delta q \approx J_{\theta \rightarrow q} \Delta \theta$$

$$S = \alpha J_{\theta \rightarrow q}^T J_{q \rightarrow x}^T J_{q \rightarrow x} J_{\theta \rightarrow q}$$

Since the step norm monotonously depends on α , we will search for α with binary search:

$$\Delta \theta^T \Delta \theta = \sum_{i=1}^{3N-7} \left(\frac{g_i}{\lambda \alpha - h_i} \right)^2$$

References

[1] H Bernhard Schlegel.

Optimization of equilibrium geometries and transition structures.
Journal of Computational Chemistry, 3(2):214–218, 1982.

[2] Satoshi Maeda, Koichi Ohno, and Keiji Morokuma.

Systematic exploration of the mechanism of chemical reactions: the global reaction route mapping (grmm) strategy using the addf and afir methods.

Physical Chemistry Chemical Physics, 15(11):3683–3701, 2013.

Results

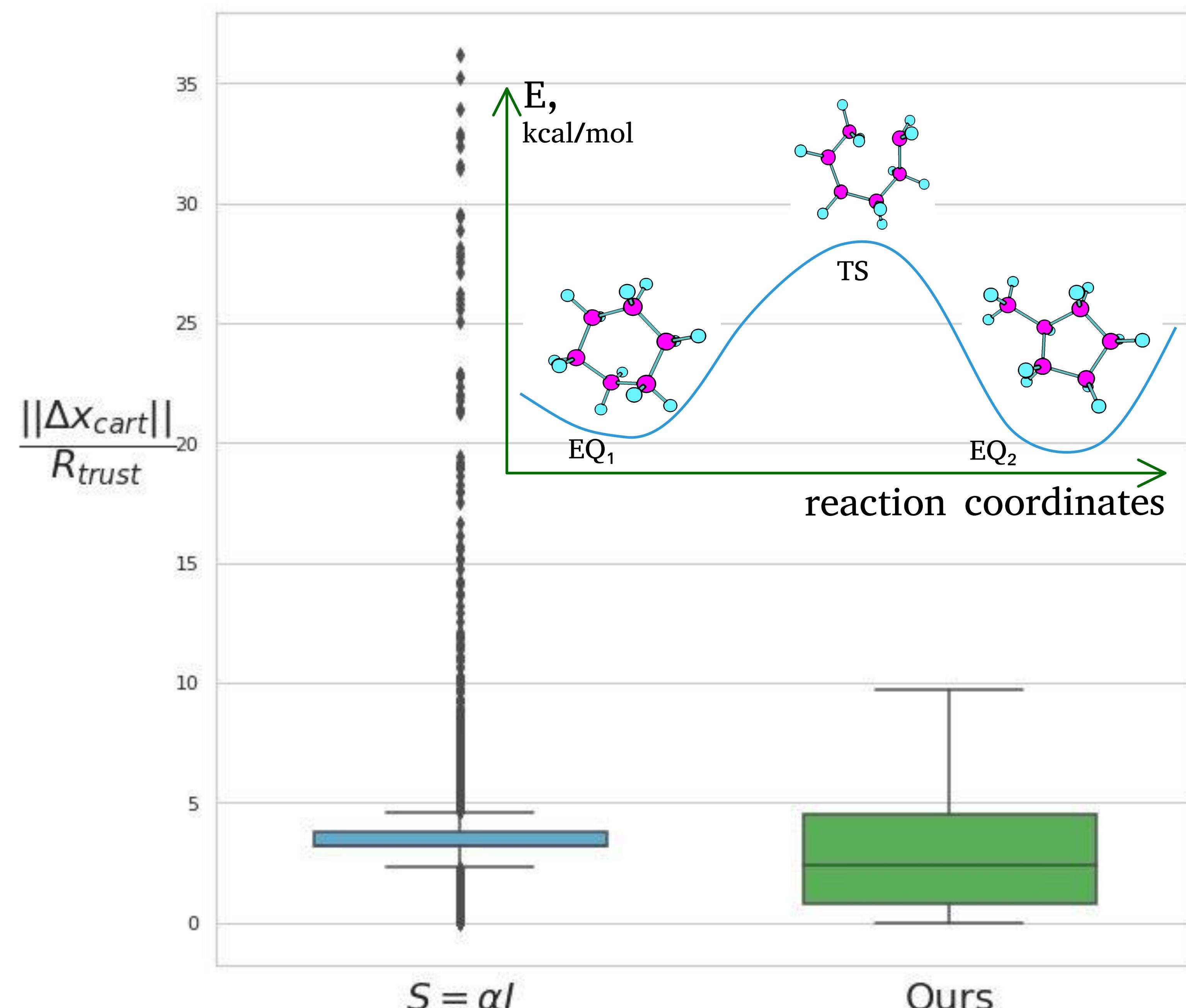


Figure 1: Correlation of the step norm and the trust radius for the standard RFO and modified RFO for optimization on the spheres in the d-ADDF algorithm for cyclohexane.

Molecule	$S = \alpha I$		Transformed S	
	grads	time, s	grads	time, s
HCN (migration H)	234	833	229	815
CH_3O (migration H)	242	1110	203	937
Ethylidenenyl-2-formiate (1-2 migration)	644	15341	506	12053
Vinylalcohol-Acetaldehyde	420	2764	264	1737
Claisen rearrangement	737	15027	676	13783
$HNCH_2$ (migration H)	154	671	116	505
C_6H_8 (migration H)	1502	6031	1364	5810
cis/trans-hexadienamineyl	—	1218	1259	
S-ylid	—	1078	4133	
Rotational acrolein	—	319	2667	

Table 1: Comparison of the convergence of d-ADDF using RFO without transformation of S-matrix and with transformation of S-matrix.

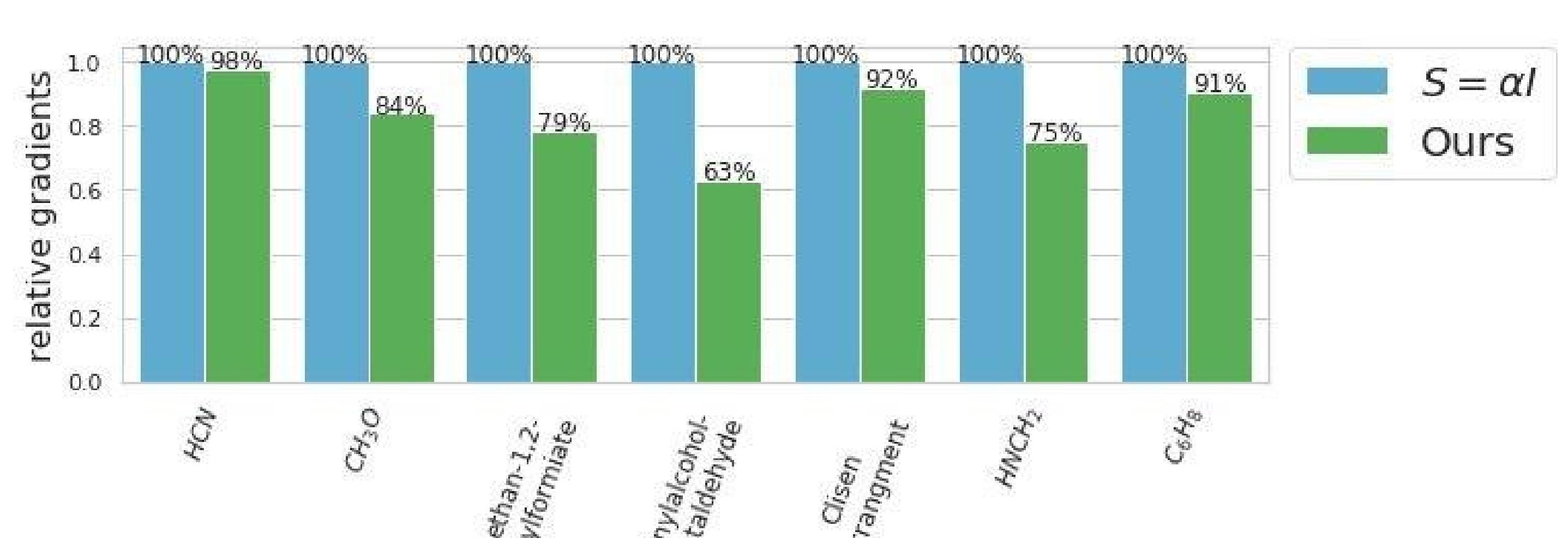


Figure 2: Comparison of the relative amounts of gradient calculations for a number of compounds in the case of using classical RFO and our method.