The proper description of chemical processes usually requires high levels ab initio methods such as CASPT2/RASPT2, and CCSD(T). The recent algorithmics developments of the CASPT2 and the CCSD(T) methods together with code improvements in MOLCAS has not been followed by development of the standard MOLCAS geometry optimization module, SLAPAF. For instance, within the Cholesky Decomposition and/or Frozen Natural Orbital approaches a CASPT2/RASPT2, or CCSD(T) energy of medium-sized and large systems can now be calculated pretty fast [1-5]. However, the total number of $3N_{\text{sys}} - 6$ displacements needed to evaluate numerical gradients (with and without constraints) underlines and significantly limits the MOLCAS applicability only to small molecular systems. We have adressed this problem by developing a new module for constrained multi-fragment geometry optimization in internal coordinates [6].

The new geometry optimization algorithm relies on the idea of supramolecular approach when a studied system can be naturally decomposed into smaller rigid groups (or fragments) and their optimal relative positions within the entire structure is a subject of interest. One area is the calculation of photoactive molecules and metal-organic complexes. Another area is non-covalent intermolecular interactions, like, e.g., the chemical or physical absorption on a crystalline surface.

- The system of interest is manually/heuristically divided into $N_{\text{frag}}$ fragments;
- The xyz files for each fragment are used as input data; the order of xyz files determines the connectivity of fragments;
- The global multi-fragment Z-matrix consists of two sets of internal coordinates:
  - active (being optimized) inter-fragment coordinates - one small sub-matrix of 6 variables per each pair of connected fragments;
  - inactive (frozen by default) intra-fragment coordinates - regular Z-matrix for each fragment
- By default, only the relative position and orientation between fragments will be optimized;
- User can provide an own built Z-matrix file with explicitly specified set of active (i.e., optimized) and frozen coordinates; user-friendly editing/altering of any frozen/optimized bonds or angles;
- The step is computed in automatically generated internal "Z-matrix" coordinates using numerical 1st and 2nd order energy derivatives, i.e. analytical gradients are not required;
- The total number of required single points energy evaluations scales with the number of fragments ($\sim N_{\text{frag}}$) rather than with the total number of atoms in the system;
- The single point energy calculations can be proceed in parallel on an arbitrary (f!) number of processors.
- Reliable and easy-to-use restart mechanism

The benzene lithium cation complex - $C_6H_6^+\cdot Li^+$
CCSD(T)

The goal: the optimization of the interaction of (frozen) surface with molecules (catalytic reactions, surface growth, chemical adorption)

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