# Constrained Optimisation in internal coordinates

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## Abstract

We have developed an automated procedure for optimising the relative orientation of several molecular fragments for the use together with highly accurate quantum chemical models that is lacking an implementation of analytical gradients. The optimisation is done in internal coordinates so that all internal movement of the fragments can be constrained. Test calculations shows that we can reproduce the result of unconstrained optimisations down to about 0.1 Å using approximately the same number of geometry iterations. A larger test on a Heme Oxygen complex on the CASPT2-level, something that would not be possible with a full optimisation, is in progress.

## Introduction

For high accuracy quantum mechanical methods that lack implementations of analytical gradients, such as CASPT2 and Coupled Cluster, unconstrained optimisation of the geometric structure in Cartesian coordinates quickly grows impossible as the number of atoms is increased, due to the large number of displacements needed. If internal coordinates (bonds, angles and dihedrals) are used, one can choose them so just a few coordinates link each complex and utilize the fact that many molecules retain its geometry during interaction with others.

In our procedure, outlined in Figure 2, the complex of interest is split into two or more fragments and only relative coordinates are optimised, further constraints are also easily imposed upon the structure. The energy can be calculated with any quantum mechanical method and the geometry optimised with any numerical procedure. As we can see in Table 1 the approximation is mostly useful for a small number of larger fragments, because the number of displacements does not depend on the number of atoms with our approach.

The procedure has been implemented into the computational software MOLCAS [1], findings from the initial testing are reported in the results section.

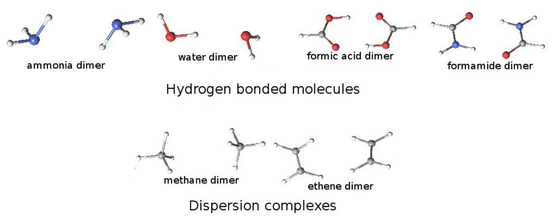


Figure 1: The set of small dimers used for testing.

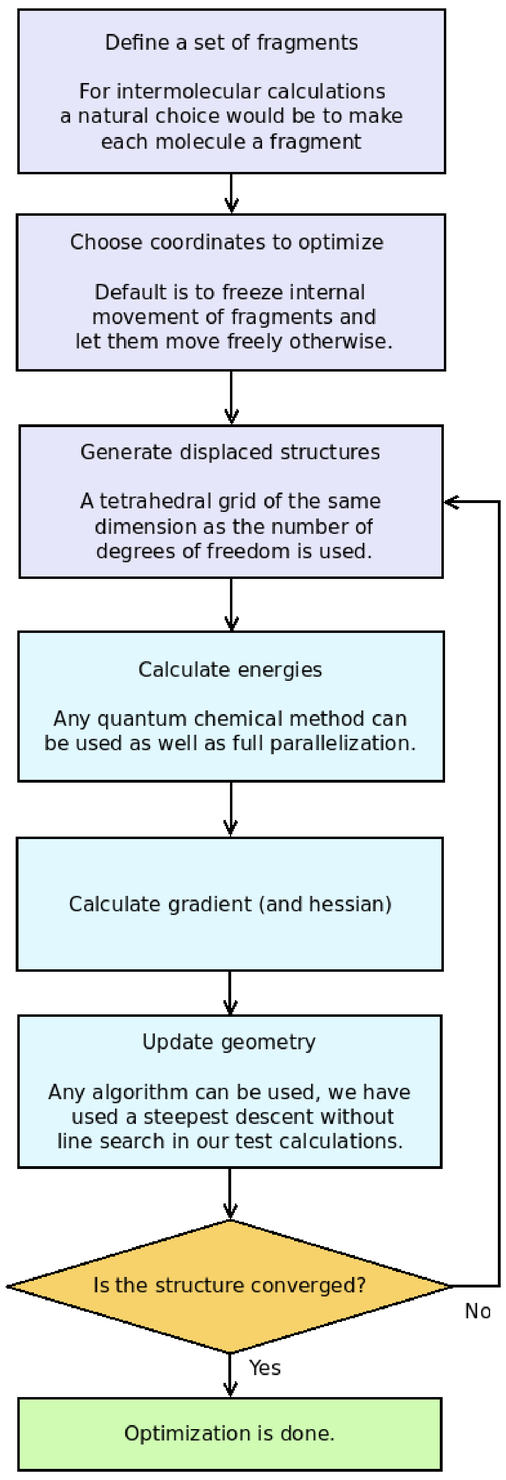


Figure 2: A flowchart of the method

| Complex | Nr of Displacements | |
|---|---|---|
| | Free | Constr. |
| Water Dimer | 36 | 29 |
| 10 Water molecules | 180 | 496 |
| Porphyrine and $O_2$ | 234 | 22 |
| Fullerene ($C_{60}$) dimer | 720 | 29 |
| 10 Fullerenes ($C_{60}$) | 7200 | 496 |
| Metal cluster(200 atoms) and H2O | 1218 | 29 |

Table 1: Number of displacements for an unconstrained calculation vs our constrained procedure

| Dimer | Nr of geometry iterations, MP2 | |
|---|---|---|
| | Free | Constr. |
| Water | 5 | 3 |
| Ammonia | 5 | 5 |
| Formic Acid | 12 | 4 |
| Formamide | 20 | 5 |
| Methane | 6 | 16 |
| Ethene | 9 | 23 |

Table 2: Comparison of the number of geometry iterations used in the unconstrained vs our constrained optimisation procedure.

## Results

The total time consumed depends both on the number of displacements in each geometry step but also on the total number of steps, as can be seen in Table 2 the number of geometry iterations are about the same in our approach as in an unconstrained.

Table 3 shows a comparison between our method and a full optimisation. We get rather small differences of up to 0.1 Å in the distance between most monomers, the exception is for a methane dimer using HF and B3LYP, this may be because these methods are bad at describing dispersion interaction, something also reflected in Table 4.

Comparing Table 3 and 4 we see that the differences between methods are still larger, indicating that there should be possible to find cases were our procedure combined with a high level computational method outperform a fully constrained optimisation on a lower level of theory.

| Dimer | Distance (Å) | | |
|---|---|---|---|
| | HF | B3LYP | MP2 |
| Water | 0.015 | 0.009 | 0.010 |
| Ammonia | 0.012 | 0.005 | 0.0261 |
| Formic Acid | 0.021 | 0.019 | 0.040 |
| Formamide | 0.042 | 0.108 | 0.094 |
| Methane | 0.268 | 0.195 | 0.073 |
| Ethene | 0.091 | 0.064 | 0.028 |

Table 3: Differences in hydrogen bond distance (or center to center distance for the pure hydrocarbons) between our method and unconstrained optimisation, both optimisations are started from a semiempirical reference.

| Dimer | Distance (Å) | | |
|---|---|---|---|
| | HF vs B3LYP | B3LYP vs MP2 | HF vs MP2 |
| Water | 0.145 | 0.009 | 0.154 |
| Ammonia | 0.223 | 0.070 | 0.293 |
| Formic Acid | 0.201 | 0.025 | 0.175 |
| Formamide | 0.189 | 0.013 | 0.202 |
| Methane | 0.329 | 0.629 | 0.958 |
| Ethene | 0.443 | 0.313 | 0.756 |

Table 4: Differences in hydrogen bond distance (or center to center distance for the pure hydrocarbons) between HF, DFT and MP2.

## Work in progress

Besides the small test molecules we have started a sample calculation on a larger molecule, a Heme interacting with an oxygen molecule. We are performing a geometry optimisation on the RASPT2 level, something which would not be possible without constraints. We have started doing calculations but has not gathered many results as of yet.

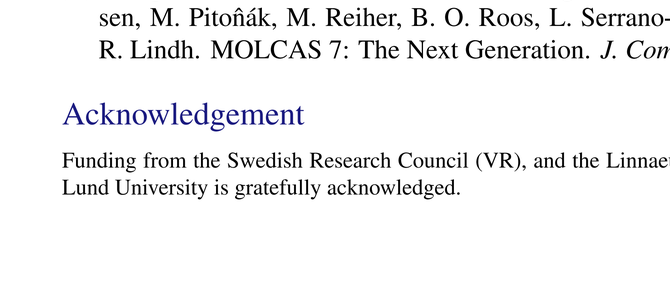

Figure 3: The heme and oxygen complex

- Basis Functions: 292
- Active electrons: 20
- Active space 1 (Ras1/2/3): 9/2/9
  - Time in Rasscf: $\sim$ 30min
  - Time in Raspt2: $\sim$ 2h
- Active space 2 (Ras1/2/3): 8/4/8
  - Time in Rasscf: $\sim$ 3h

## Conclusions

- The procedure can be applied to geometry optimisation of large fragments within CASPT2 level of theory
- The number of displacements do not scale with fragment size
- It does not require more geometry iterations, compared to an unconstrained optimisation

## References

[1] F. Aquilante, L. De Vico, N. Ferré, G. Ghigo, P.-Å. Malmqvist, P. Neogrády, T. B. Pedersen, M. Pitoňák, M. Reiher, B. O. Roos, L. Serrano-Andrés, M. Urban, V. Veryazov, and R. Lindh. MOLCAS 7: The Next Generation. *J. Comput. Chem.*, 31:224–247, 2010.

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