



Optimizations and Frequencies

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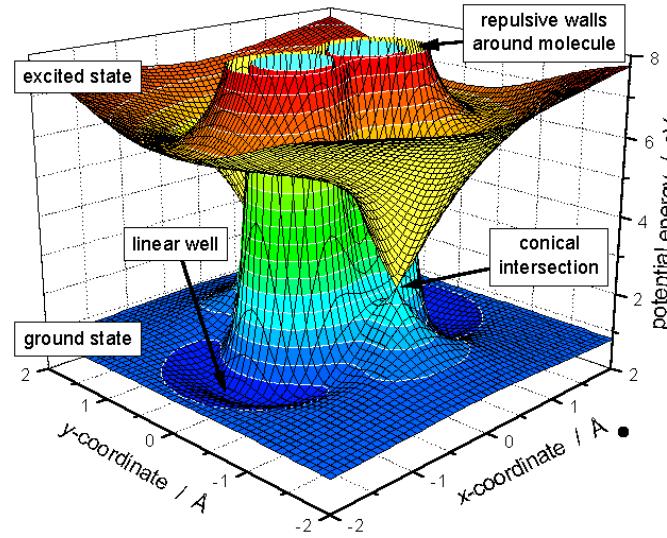
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Items

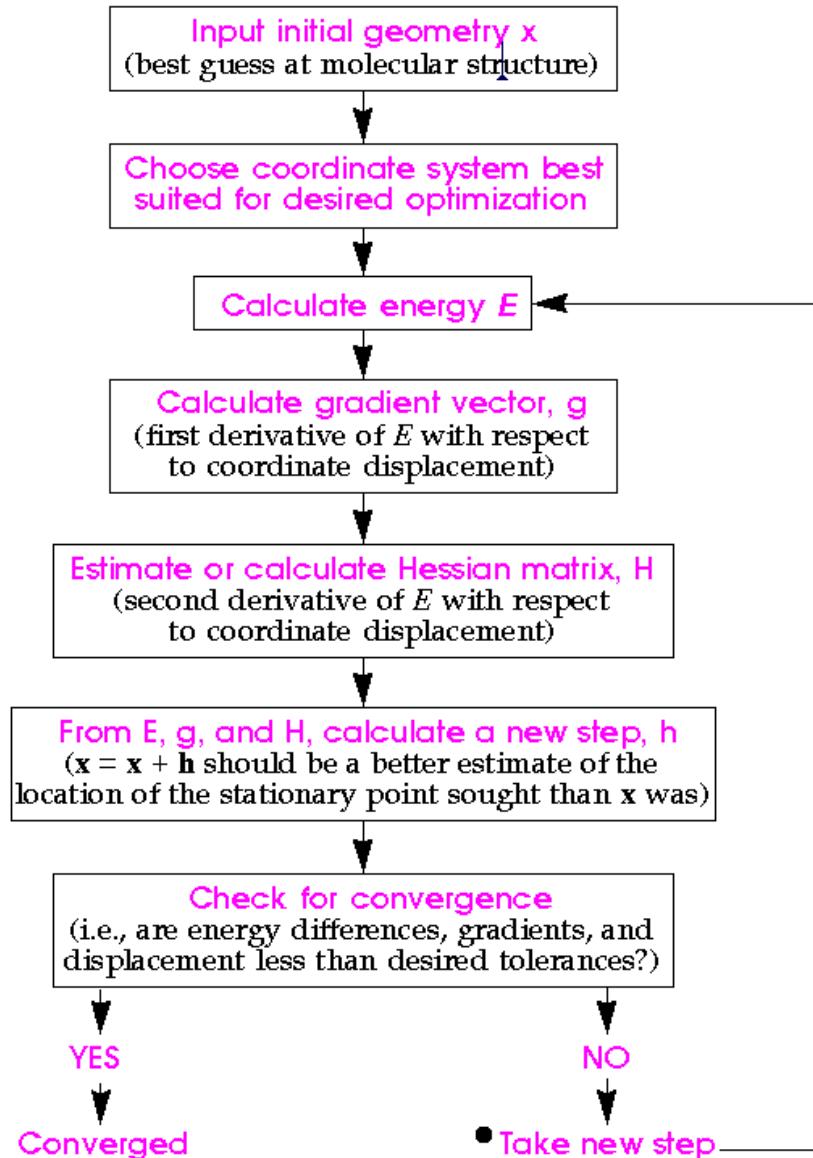
- optimizations
- frequency calculations
- finding transition states (TS)
- exploring the energy as a function of specific internal coordinates
- computing reactions paths, minimum energy paths (MEP)
- finding minimum energy cross point (MECP)
- mapping out the (conical) intersection subspace

Optimizations for minima



- We want to find stationary points and other structures close to a starting structure.
- We want to have procedures in which can walk the "surface in a controlled way.

The SlapAf module controls geometry manipulations.



Optimizations for minima

SlapAf is using a quasi 2nd order method for geometry optimizations

- Restricted Step Rational Function optimization (default)
- quasi-Newton update (BFGS, MSP)
- internal coordinates (default) or cartesian coordinates
- a trust radius

Consult notes by Trygve Helgaker "Optimization of Minima and Saddle points", and the paper by Anglada on RS-RF optimization.

Slapaf Keywords

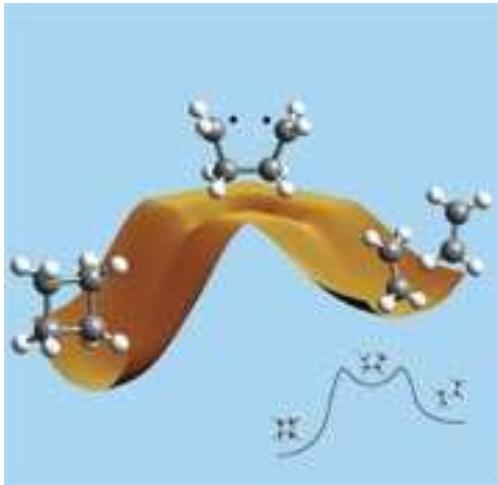
In the lab we will explore

- **Iterations** : max number of iterations
- **MaxStep** : initial trust radius
- **Cartesian** : selection of internal coordinates
- **NoLineSearch** : skip line search

Frequency calculations

- McKinely and MCLR are used for analytic frequencies
- Slapaf enables numerical frequency calculations
- MCLR module envoked automatically
- Analytic: SCF and CASSCF.

TS Optimization



Transition state optimization is like a normal optimization, however, in one dimension we will do a maximization!

Near convergence method.

- Partition technique, RS-P-RF
- Image technique, RS-I-RF

See notes by T. Helgaker!

TS Optimization

The trick is to get to the TS region!

Slapaf commands to controll this process.

- TS
- Mode
- FindTS

Constraint Optimizations

The approach presented here is a

- a 1st order method to separate the minimization and constraints
- a restricted-step procedure with a back-feed mechanism
- use of general constraints which not necessarily are internal coordinates.

Theory

Standard approach is to use so-called Lagrangian multipliers.

$$L(\mathbf{q}, \lambda) = E(\mathbf{q}) - \lambda^T \mathbf{r}(\mathbf{q}) \quad (1)$$

Draw backs

- number of parameters to optimize increase
- mixed minimization and maximization optimization
- implicit separation of subspaces due to Hessian eigen values
- BFGS update method can't be used, H has negative eigen values

The Projected constrained optimization (PCO), by Anglada and Bofill

A Taylor expansion to 2nd order of $L(\mathbf{q}, \lambda)$ around \mathbf{q}_0 and λ_0 gives

$$L(\mathbf{q}_0 + \Delta\mathbf{q}, \lambda_0 + \Delta\lambda) = E(\mathbf{q}_0) + \Delta\mathbf{q}^T \frac{\partial E(\mathbf{q}_0)}{\partial \mathbf{q}} + \frac{1}{2} \Delta\mathbf{q}^T \mathbf{W} \Delta\mathbf{q} - \lambda^T \left(\mathbf{r}(\mathbf{q}_0) + \frac{\partial \mathbf{r}(\mathbf{q}_0)}{\partial \mathbf{q}} \Delta\mathbf{q} \right) \quad (2)$$

where \mathbf{W} is defined as

$$\mathbf{W}(\mathbf{q}, \lambda_0) = \frac{\partial^2 E(\mathbf{q}_0)}{\partial \mathbf{q}^2} - \sum_{i=1,m} (\lambda_0)_i \frac{\partial^2 (\mathbf{r}(\mathbf{q}_0))_i}{\partial \mathbf{q}^2} \quad (3)$$

This sets up the equation for the generalized elimination method. We note that the last term of the RHS in Eq. ?? controls to first order the constraint.

In the subspace which fulfill the constraint any displacement Δq must be such that

$$\frac{\partial \mathbf{r}(\mathbf{q}_0)}{\partial \mathbf{q}} \Delta \mathbf{q} = \mathbf{0} \quad (4)$$

This defines a linear transformation which will to first order subdived the original $3n-6(5)$ space into a m -dimensional space in which the constraints are fulfilled and a $3n-6(5)-m$ subspace in which a normal optimization is made. The unitary transformation matrix \mathbf{T} contains two part and transform as

$$\Delta \mathbf{q} = [\mathbf{T}_c \mathbf{T}_m] \begin{pmatrix} \Delta \mathbf{y} \\ \Delta \mathbf{x} \end{pmatrix} = \mathbf{T}_c \Delta \mathbf{y} + \mathbf{T}_m \Delta \mathbf{x} \quad (5)$$

where, \mathbf{y} and \mathbf{x} are the new parameters. \mathbf{y} is of m dimensions and \mathbf{x} of $3n-6(5)-m$ dimension.

In particular we note that at λ_0

$$\frac{\partial \mathbf{r}(\mathbf{q}_0)}{\partial \mathbf{q}} \mathbf{T}_c \neq \mathbf{0} \quad (6)$$

and

$$\frac{\partial \mathbf{r}(\mathbf{q}_0)}{\partial \mathbf{q}} \mathbf{T}_m = \mathbf{0} \quad (7)$$

These two equations are sufficient for the definition of \mathbf{T} via a Gram-Schmidt procedure.

We now proceed by introducing our transformation matrix into our Lagrangian expression (Eq. ??). The equation now falls into two parts (one of m and a second of $3n-6(5)m$ dimensions), one which depends only on \mathbf{y} ,

$$\Delta\mathbf{y} = -\left(\frac{\partial\mathbf{r}(\mathbf{q}_0)}{\partial\mathbf{q}}\mathbf{T}_c\right)^{-1}\mathbf{r}(\mathbf{q}_0) \quad (8)$$

and a second part which depends on both \mathbf{x} and \mathbf{y} ,

$$\begin{aligned} Q(\mathbf{q}_0 + \Delta\mathbf{q}, \lambda) &= E(\mathbf{q}_0) + \Delta\mathbf{y}^T \mathbf{T}_c^T \frac{\partial E(\mathbf{q}_0)}{\partial \mathbf{q}} + \frac{1}{2} \Delta\mathbf{y}^T \mathbf{T}_c^T \mathbf{W} \mathbf{T}_c \Delta\mathbf{y} \\ &+ \Delta\mathbf{x}^T \mathbf{T}_m^T \left(\frac{\partial E(\mathbf{q}_0)}{\partial \mathbf{q}} + \mathbf{W} \mathbf{T}_c \Delta\mathbf{y} \right) \\ &+ \frac{1}{2} \Delta\mathbf{x}^T \mathbf{T}_m^T \mathbf{W} \mathbf{T}_m \Delta\mathbf{x}. \end{aligned} \quad (9)$$

This equation is the projected energy expression with $\mathbf{T}_m^T \mathbf{W} \mathbf{T}_m$ being the reduced Hessian and $\mathbf{T}_m^T \left(\frac{\partial E(\mathbf{q}_0)}{\partial \mathbf{q}} + \mathbf{W} \mathbf{T}_c \Delta\mathbf{y} \right)$ is the reduced gradient.

Using the quasi-Newton condition applied to Eq.?? we find that the effective gradient to be used in an Hessian update procedure applied only to the molecular part of the Lagrangian Hessian is

$$h(\mathbf{q}, \lambda) = \frac{\partial E(\mathbf{q})}{\partial \mathbf{q}} - \frac{\partial \mathbf{r}(\mathbf{q})}{\partial \mathbf{q}} \lambda. \quad (10)$$

The update procedure is commenced by evaluating a series of $h(\mathbf{q}, \lambda)$ for different values of \mathbf{q} and a fixed value of λ . A suitable value of λ is the first order estimate of λ at convergence as given by

$$h(\mathbf{q}_0, \lambda_0) = 0 \quad (11)$$

To conclude the presentation of the PCO approach of Anglada and Bofill let us here summarize the major advantages the presented method has as compared to a optimization/maximization procedure applied to Eq. ??,

- the PCO approach have an explicit separation of the two subspaces where as a optimization/maximization indirectly separates the two subspaces by identifying the positive and negative eigen vectors of the Hessian of the Lagrangian,
- the presence of negative eigen values in the Hessian of the Lagrangian restricts the selection of Hessian update (variable metric) methods while the PCO approach allows the use of the BFGS update method to be applied to the reduced Hessian, and
- the the PCO technique by Bofill and Anglada does not explicitly

require λ to be determined.

Restricted-step mechanism

- Restricted-Step Rational Function Optimization is used where the max step length is dynamically changed to reflect the agreement between the analytic gradients and the model function used in the optimization.
- Similar arrangement is done for the constrained subspace.
- The max step length in both subspaces are are coupled.

Constrained geometry optimization require 1st and 2nd order derivatives of the constraints with respect to the internal coordinates.

This is trivial for Cartesian coordinates. For curvilinear coordinates Baker et al suggested to include the constraints in the definition of the redundant internal coordinate space followed by a linear transformation after the generation of the non-redundant coordinates such that the constraint equals on of the non-redundant coordinates. In this paper we will present the required derivatives for the case when the constraints not necessarily are explicitly expressed in the redundant space of internal coordinates.

Given

$$\frac{\partial}{\partial \mathbf{x}} = \frac{\partial}{\partial \mathbf{q}} \frac{\partial \mathbf{q}}{\partial \mathbf{x}} \quad (12)$$

the 1st order derivative is trivially expressed as

$$\frac{\partial \mathbf{r}}{\partial \mathbf{q}} = \left(\frac{\partial \mathbf{q}}{\partial \mathbf{x}} \right)^{-1} \frac{\partial \mathbf{r}}{\partial \mathbf{x}} \quad (13)$$

and the 2nd derivative is expressed as

$$\frac{\partial^2 \mathbf{r}}{\partial \mathbf{q}^2} = \left(\frac{\partial \mathbf{q}}{\partial \mathbf{x}} \right)^{-1} \left[\frac{\partial^2 \mathbf{r}}{\partial \mathbf{x}^2} - \frac{\partial \mathbf{r}}{\partial \mathbf{q}} \frac{\partial^2 \mathbf{q}}{\partial \mathbf{x}^2} \right] \left(\frac{\partial \mathbf{q}}{\partial \mathbf{x}} \right)^{-1} \quad (14)$$

Applications

- Single geometrical constraint constraint
- Multiple geometrical constraint constraints
- Minimum Energy Path
- Minimum Energy Cross Point
- Spacial extension of a intersection subspace

Single geometrical constraint

As an example of a geometry optimization with a simple geometrical constraint we study energy profile of the hindered rotation of ethane. In this series of optimizations we fix the HCCH dihedral angle, i.e. the constraint is

$$r_1 = \phi_{\text{HCCH}} - \phi_{\text{HCCH}}^0. \quad (15)$$

The geometry optimizations converged on average after 6 iterations for each selected angle.

C₂H₄ Hindered internal rotation

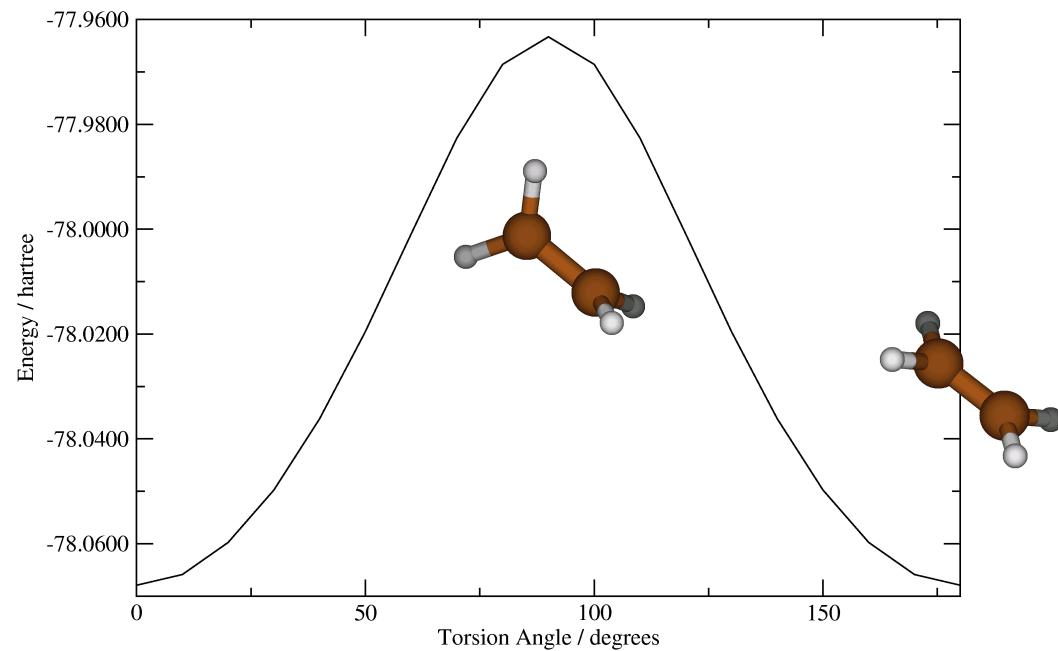


Figure 1: C₂H₄ Hindered rotation.

Multiple geometrical constraints

As an example of a geometry optimization with multiple geometry constraints we study the energy surface of the triplet 1,2-dioxoethane around the biradical minimum as a function of the OO bond distance and the OCCO dihedral angle, i.e. the constraints are

$$r_2 = r_{\text{OO}} - r_{\text{OO}}^0, \quad (16)$$

and

$$r_2 = \phi_{\text{OC CO}} - \phi_{\text{OC CO}}^0. \quad (17)$$

The geometry optimization typically converge after 5 iterations for each selected pair of constraints.

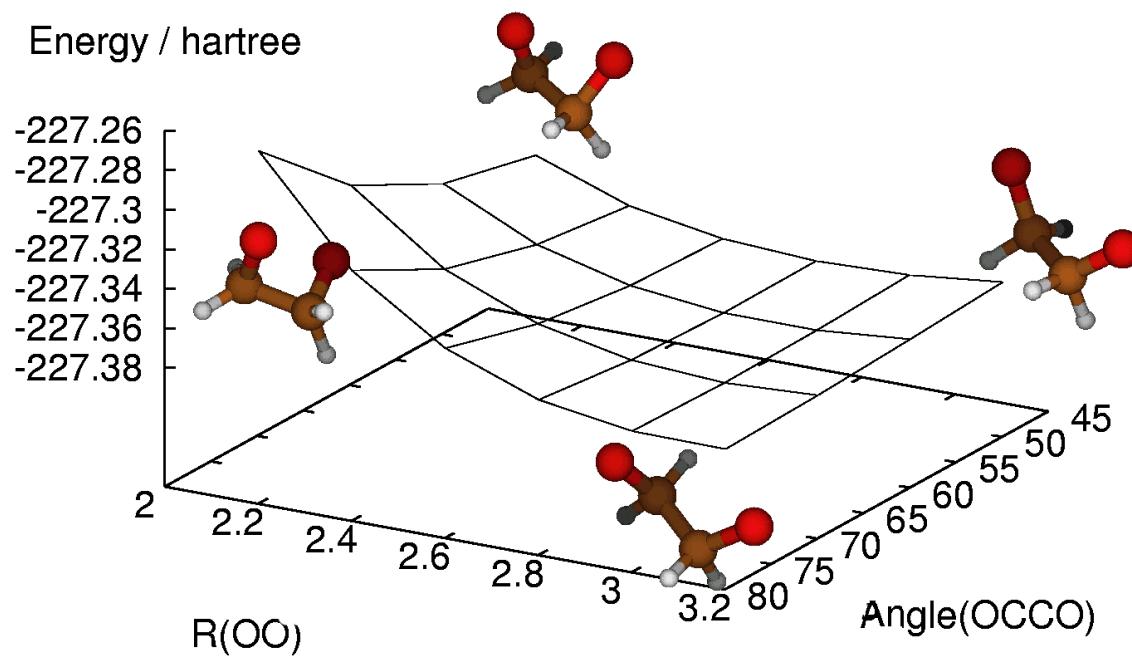


Figure 2: The potential energy surface of triplet 1,2-dioxetane as a function of the OO bond distance (Angstrom) and the OCCO dihedral angle (degrees).

Minimum Energy Path

A minimum energy path (MEP) can be found by minimizing the energy of the hypersphere with a fixed radius, where the origin of the sphere is the geometry of some reference structure. For a MEP the reference structure is selected to be the resulting structure of the previous step. If one starts from the TS one get the reaction path of the Intrinsic Reaction Coordinates (IRC). The hypersphere optimization is performed in mass weighted Cartesian coordinates,

$$\mathbf{R}(\mathbf{q}) = (\sqrt{m_1}\mathbf{r}_1(\mathbf{q}), (\sqrt{m_2}\mathbf{r}_2(\mathbf{q}), \dots, (\sqrt{m_n}\mathbf{r}_n(\mathbf{q})). \quad (18)$$

For this purpose the constraint is defined as

$$r_1 = \frac{(\sqrt{(\mathbf{R}(\mathbf{q}) - \mathbf{R}(\mathbf{q}_{ref}))^2} - R)}{\sqrt{M_{tot}}} \quad (19)$$

where R is the radius of the hypersphere and M_{tot} is the total mass of

the system.

As an example we take 1,2-dioxoethane as it is dropped on the triplet state surface at a geometry close to the singlet transition state between the cyclic and biradical structure.

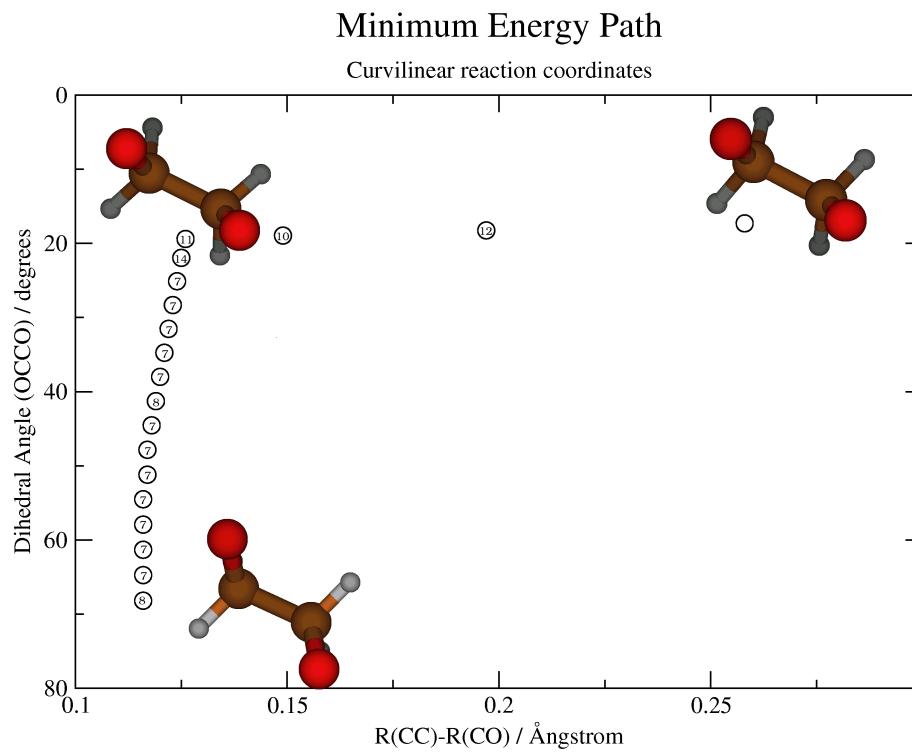


Figure 3: The minimum energy path of 1,2-dioxoethane on the triplet state surface starting at a geometry close to the singlet transition state.

Minimum Energy Cross Point

A minimum energy cross point is found by finding the lowest energy of the excited state at which two states are degenerate. The constraint is the energy difference between the two states,

$$r = E_1 - E_0. \quad (20)$$

Here we will as an example display some statistic in the search for a intersection between the ^3A and ^1A state of N-methyl thioacetamid.

The statistic of the energy of the excited state, and the energy difference, display a robust and conservative convergence.

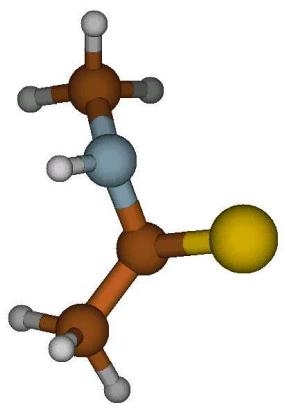


Figure 4: N-methyl thioacetamid.

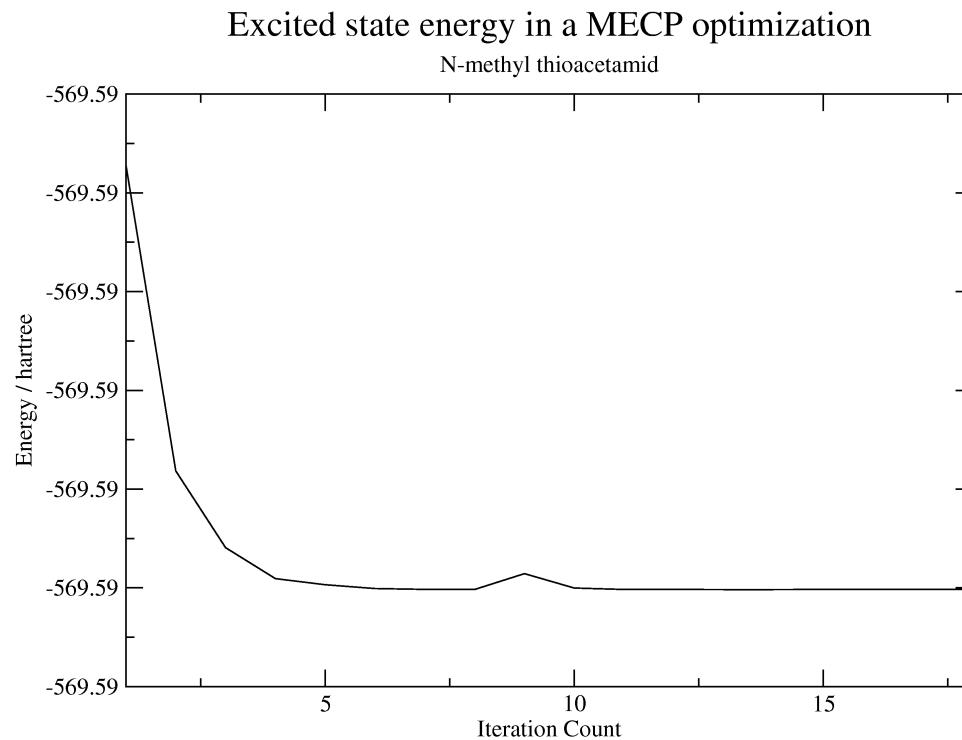


Figure 5: The excited triplet state energy of N-methyl thioacetamid as a function of the iteration count during the MECP optimization.

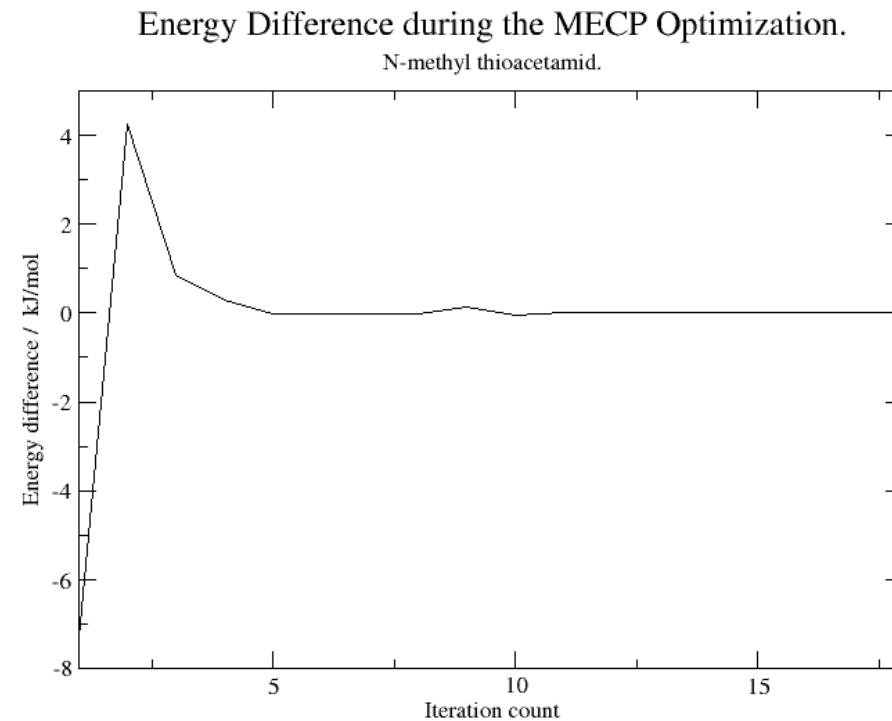


Figure 6: The energy difference as a function of the iteration count during the MECP optimization.

Exploring the conical intersection

To explore the spatial extension of the intersection subspace we will combine the constraints of the intersection

$$r = E_1 - E_0. \quad (21)$$

with those of the MEP search

$$r_1 = \frac{(\sqrt{(\mathbf{R}(\mathbf{q}) - \mathbf{R}(\mathbf{q}_{ref}))^2} - R)}{\sqrt{M_{tot}}} \quad (22)$$

We demonstrate the results of such a search for acrolein.

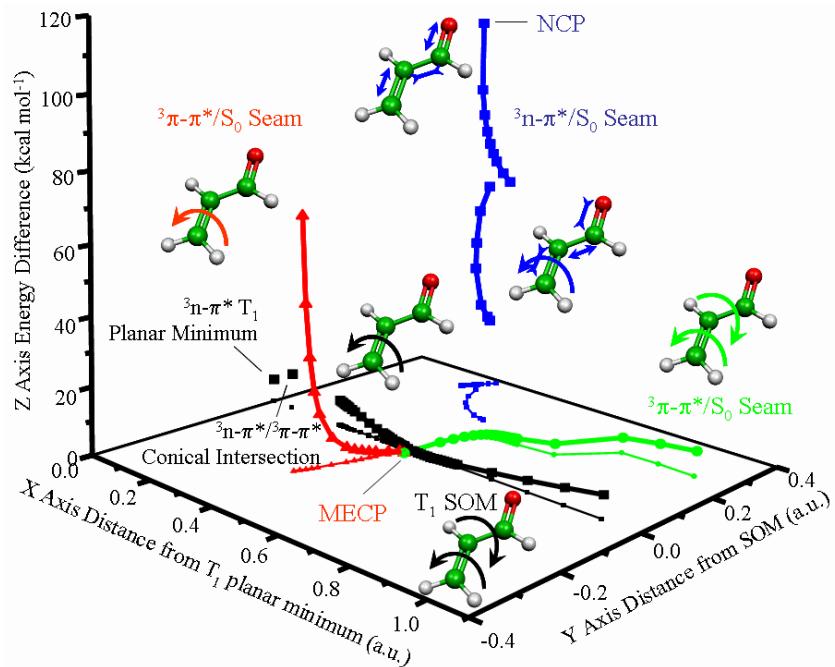


Figure 7: Intersection subspaces

Important MOLCAS Keywords and notes

We will in the lab explore

- Constraints ... End of Constraints
- MaxStep
- definition of a hypersphere
- definition of energy differences
- how to define internal coordinates