



Geometry optimizations with and without constraints

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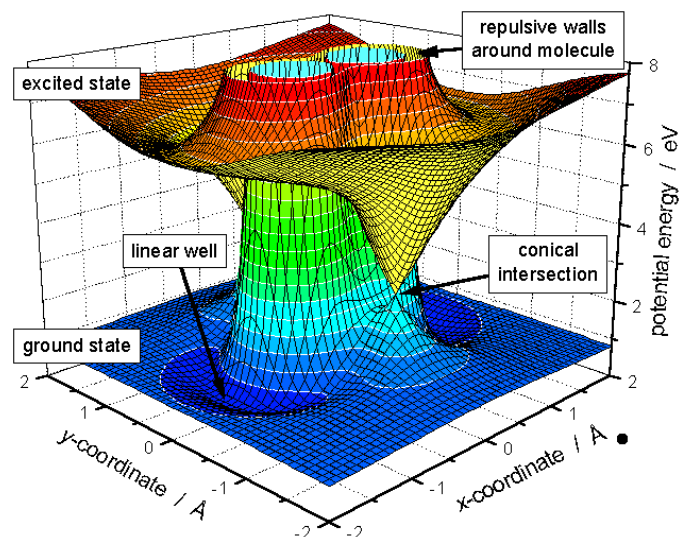
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Sweden

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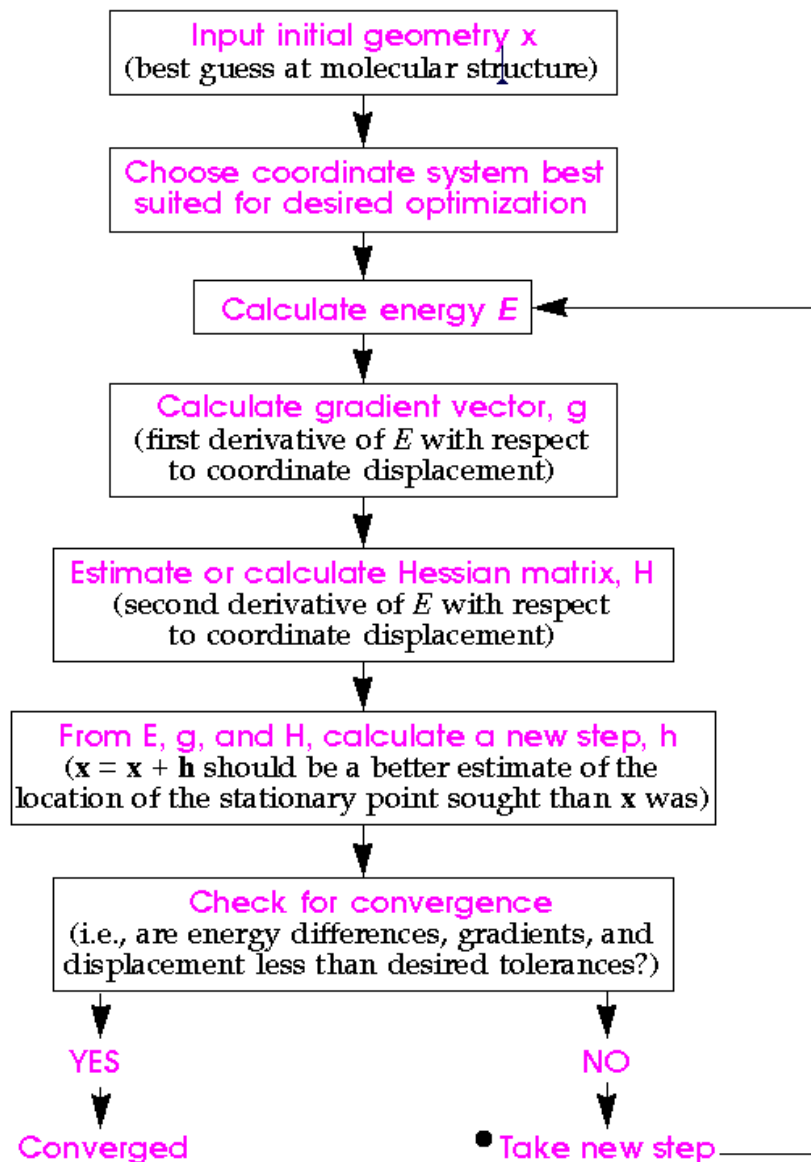
- Equilibrium structure optimizations
- Transition state (TS) optimizations
- Frequency calculations
- Exploring the energy as a function of specific internal coordinates
- Computing reactions paths, minimum energy paths (MEP), IRCs
- Finding minimum energy cross point (MECP)
- Mapping out the Conical Intersection / Interstate Crossing 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 we can "walk the surface" in a controlled way.

The SlapAf module controls geometry manipulations.



Optimizations for minima

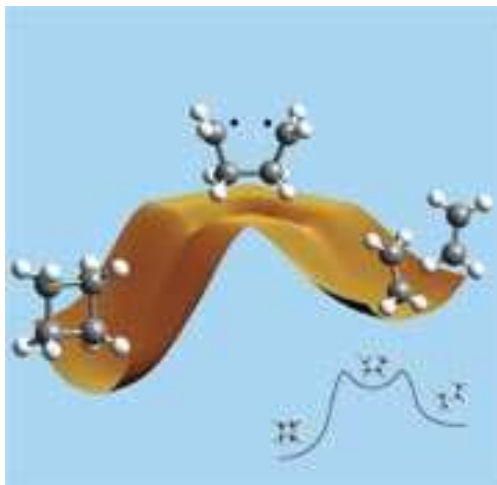
SlapAf is using a quasi 2nd order method for geometry optimizations

- Restricted Step Rational Function optimization (default)
- Approximate Hessian (Hessian Model Function)
- Quasi-Newton update (BFGS, MSP)
- Internal coordinates or Cartesian coordinates
- A dynamic trust radius

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

```
&Gateway  
...  
> Do While  
  &Seward  
  ... wavefunction module(s)  
  &Slapaf  
>End Do
```

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. Mixed optimization.
- Image technique, RS-I-RF. All minimization.

See notes by T. Helgaker (ESQC)!

TS Optimization

The trick is to get to the TS region!

Slapaf commands to control this process.

- TS (brute)
- Mode (better)
- FindTS (smarter)
- RP-Coor: the Saddle method (the best)

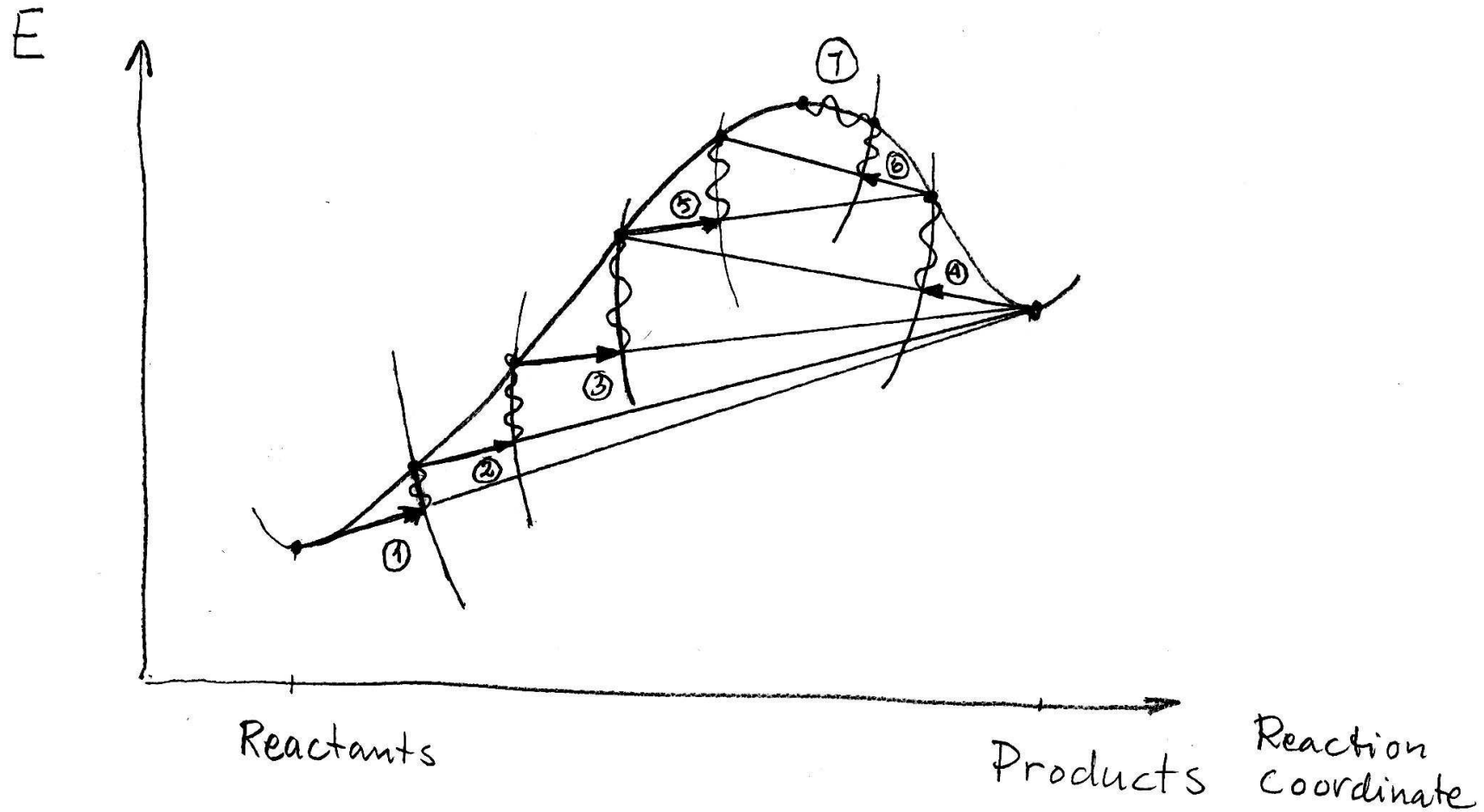
Confirm that it is a TS with a frequency calculation.

Confirm that the TS is the correct TS with an IRC analysis!


```
&Gateway
...
> Do While
  &Seward
... wavefunction module(s)
  &Slapaf; FindTS          <----- note the FindTS option
  Constraints
    a = Bond .....
  Value
    a= 1.8 Angstrom
  End of Constraints
>End Do
```

The Saddle method for TS optimization

The Saddle method



Standard Input: RP-Coor

```
&Gateway
  RP-Coor
    nCoord
    E1          <--- Energy of the reactants
    x y z      <--- nCoord Cartesian coordinates
    . . . .
    E2          <--- Energy of the products
    x y z      <--- nCoord Cartesian coordinates
    . . . .
> Do While
  &Seward
... wavefunction module(s)
  &Slapaf
>End Do
```

Standard Input: RP-Coor and IRC

```
&Gateway
  RP-Coor          <- Saddle TS optimization
  . . . .
> Do While
  &Seward
... wavefunction module(s)
  &Slapaf
>End Do

> Do While
  &Seward
... wavefunction module(s)
  &Slapaf; IRC      <- IRC option
>End Do
```

Frequency calculations

- Module McKinely (and MCLR) for frequencies
- Analytic: SCF and CASSCF
- MCLR module is invoked automatically
- Numerical frequency calculations are automatic

Frequency calculations

A typical input

```
&Gateway  
...  
>Do While  
  &Seward  
  ... wave function module(s)  
  &Slapaf  
>End Do  
&McKinley
```

Constraint Optimizations

The approach presented here is a

- a 1st order method to separate the minimization and constraints
- use of general constraints which not necessarily are internal coordinates.

Theory

The standard approach is to use the so-called Lagrangian multipliers technique.

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

Draw backs

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

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. 2 controls to first-order the constraint.

In the subspace which fulfill the constraint any displacement $\Delta \mathbf{q}$ 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 subdivided 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. 2). 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.1 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 let us summarize the major advantages the presented method has as compared to a optimization/maximization procedure applied to Eq. 1,

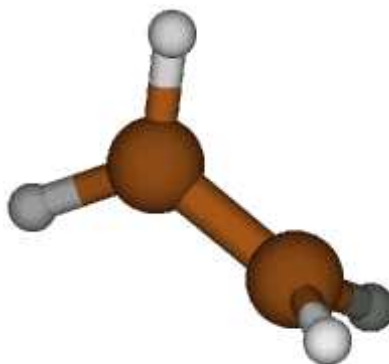
- the PCO approach have an explicit separation of the two subspaces where as a optimization/maximization indirectly separates the two subspaces by identifying the positive and negative eigen vectors of the Hessian of the Lagrangian,
- the presence of negative eigen values in the Hessian of the Lagrangian 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.

- Single geometrical constraint constraint
- Multiple geometrical constraint constraints
- Minimum Energy Path
- Minimum Energy Cross Point
- Two cases of 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

$$r_1 = \phi_{\text{HCCH}} - \phi_{\text{HCCH}}^0. \quad (12)$$



The constraint input to the Gateway (or the Slapaf) module for a dihedral angle of 70 degree would read

...

Constraints

a = Dihedral H1 C1 C2 H3

Value

a = 70 degree

End of Constraints

...

The assembled energy curve for several fixed values of the dihedral angle will look like, The geometry optimizations converged on average

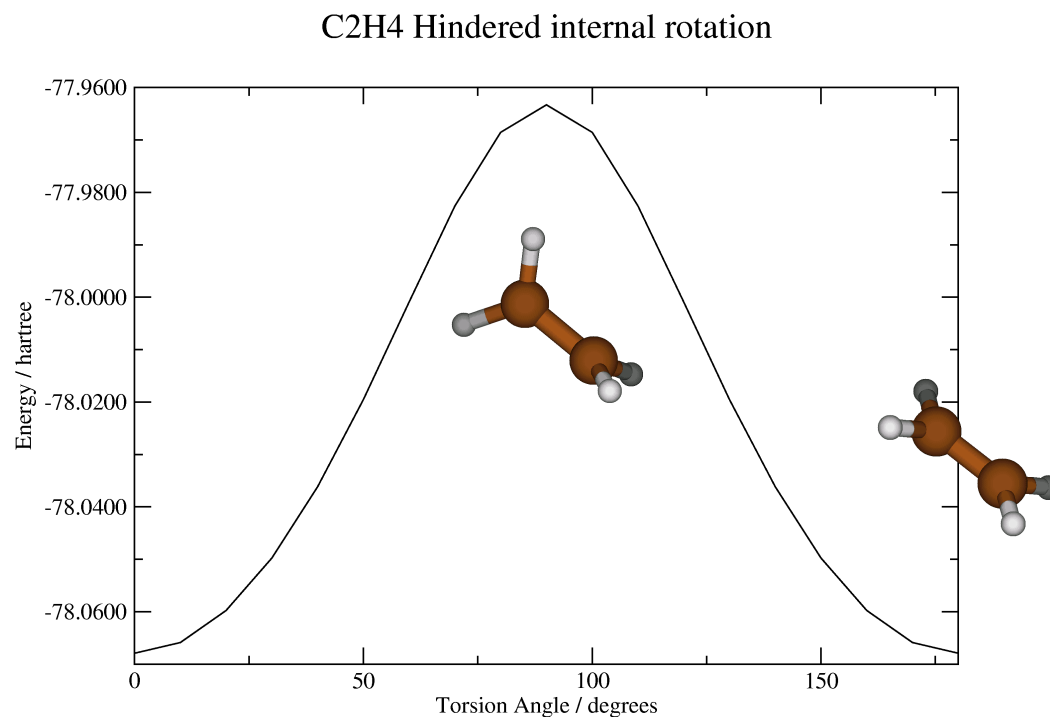


Figure 1: C₂H₄ Hindered rotation.

after 6 iterations for each selected angle.

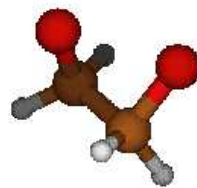
Multiple geometrical constraints

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

$$r_2 = r_{OO} - r_{OO}^0, \quad (13)$$

and

$$r_2 = \phi_{OCCO} - \phi_{OCCO}^0. \quad (14)$$



The constraint input to the Gateway (or the Slapaf) module for a dihedral angle of 30 degree and a OO bond distance of 1.4 Ångström would read

...

Constraints

a = Dihedral 01 C1 C2 02

b = Bond 01 02

Value

a = 30 degree

b = 1.4 Angstrom

End of Constraints

...

The assembled energy surface for several fixed values of the OO bond distance and the OCCO dihedral angle will look like, The geometry

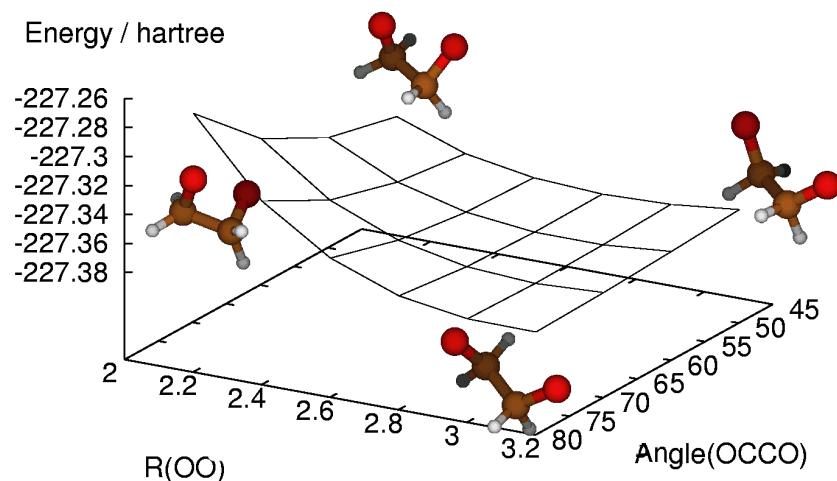
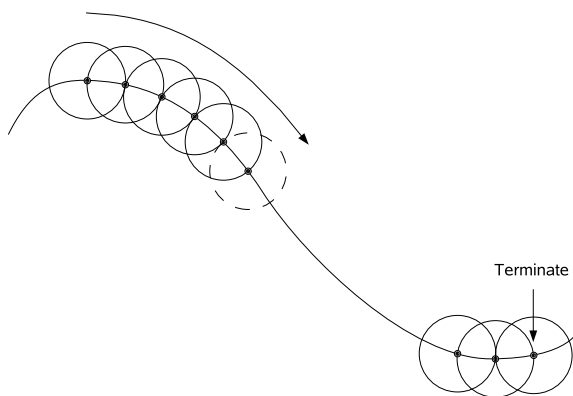


Figure 2: The potential energy surface of triplet 1,2-dioxetane as a function of the OO bond distance (Angstrom) and the OCCO dihedral angle (degrees).

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

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 the selected to be the resulting structure of the previous step. If one starts from a TS one get the reaction path of the Intrinsic Reaction Coordinates (IRC).



The hypersphere optimization is performed in mass weighted Cartesian coordinates,

$$\mathbf{R}(\mathbf{q}) = (\sqrt{m_1}\mathbf{r}_1(\mathbf{q}), (\sqrt{m_2}\mathbf{r}_2(\mathbf{q}), \dots, (\sqrt{m_n}\mathbf{r}_n(\mathbf{q})). \quad (15)$$

For this purpose the constraint is defined as

$$r_1 = \frac{(\sqrt{(\mathbf{R}(\mathbf{q}) - \mathbf{R}(\mathbf{q}_{ref}))^2} - R}{\sqrt{M_{tot}}} \quad (16)$$

where R is the radius of the hypersphere and M_{tot} is the total mass of the system. $\mathbf{R}(\mathbf{q}_{ref})$ is the origin of the hypersphere and $\mathbf{R}(\mathbf{q})$ are the coordinates of the current structure.

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

The constrained input to the Slapaf module will read as

...

Constraint

a = sphere

Value

a = 0.2

End of Constraints

MEP-search

nMEP

20

...

The computed reaction path, projected on to the space spanned of the difference between the CC and CO bond length and the OCCO dihedral angle, will look like,

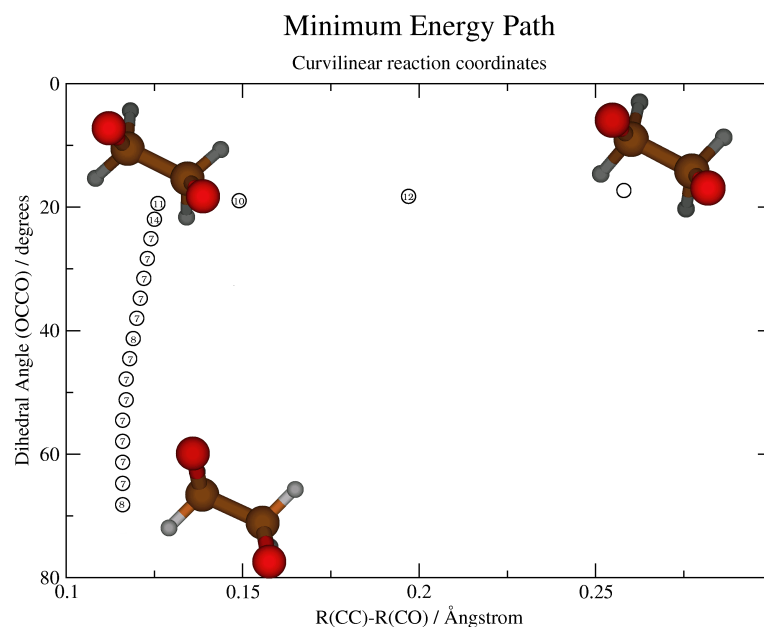


Figure 3: The minimum energy path of 1,2-dioxoethane on the triplet state surface starting at a geometry close to the singlet transition state.

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,

$$r = E_1 - E_0. \quad (17)$$

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.

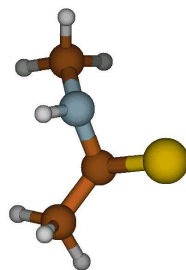


Figure 4: N-methyl thioacetamid.

The Slapaf input would read as follow

...

Constraints

dE = EDiff

Value

dE = 0.0

End of Constraints

...

Note that the MOLCAS setup is a bit complicated since the input will describe the *simultaneous calculation of two different states*. The states will be formally handled as two different MOLCAS projects and the Slapaf module will have access to the runfile of both projects.

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

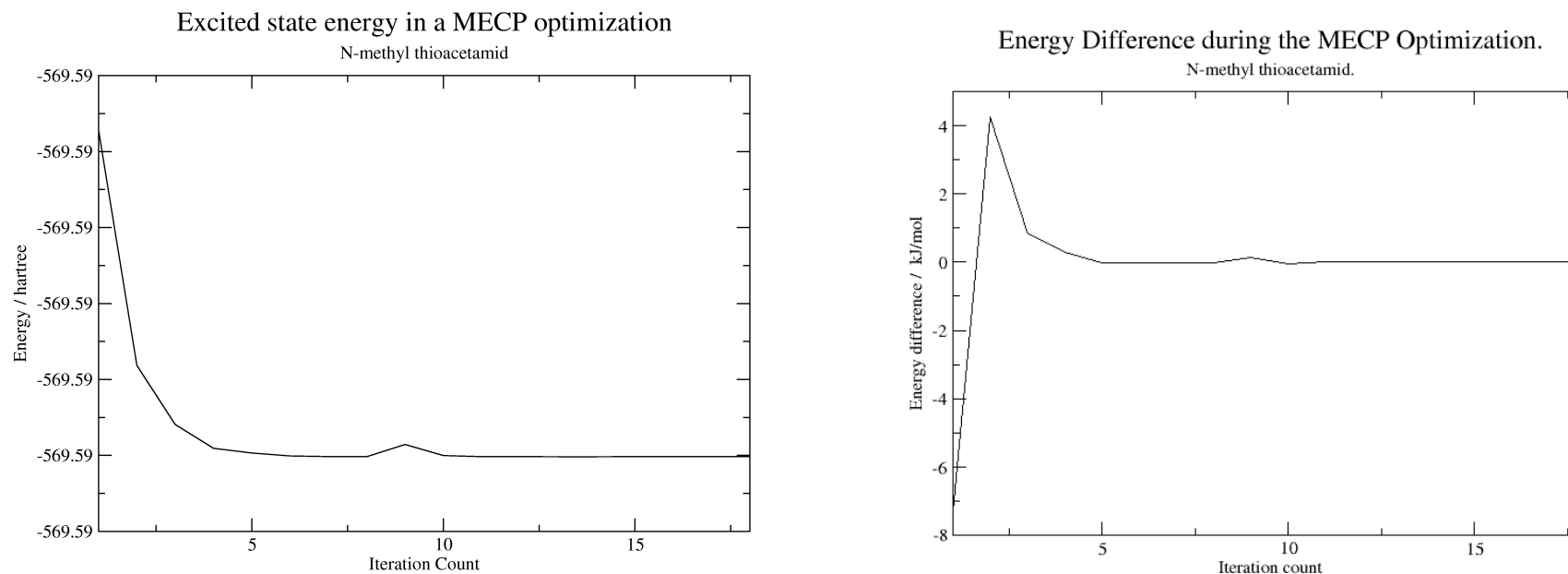


Figure 5: The excited triplet state energy of N-methyl thioacetamid and the energy difference as a function of the iteration count during the MECP optimization.

Exploring the conical intersection: seam of minimum energy points

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

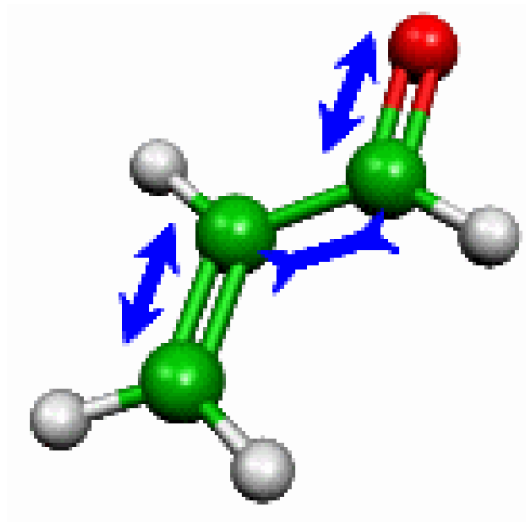
$$r = E_1 - E_0. \quad (18)$$

with those of the MEP search

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

Seam of minimum energy points

We demonstrate the results of such a search for acrolein.





Seam of minimum energy points



The Slapaf input for one point in the conical intersection subspace will read as follow

```
...  
Reference Geometry  
....  
Constraints  
dE = EDiff  
r = Sphere  
value  
dE = 0.0  
r = 0.1  
End of Constraints  
....
```

Here the **Reference** ... keyword is followed by the coordinate list of the structures at the MECP, which defined the center of the hypersphere. After convergence the next point is found by starting from the previous optimized structure with an *increased* value for r .

Seam of minimum energy points

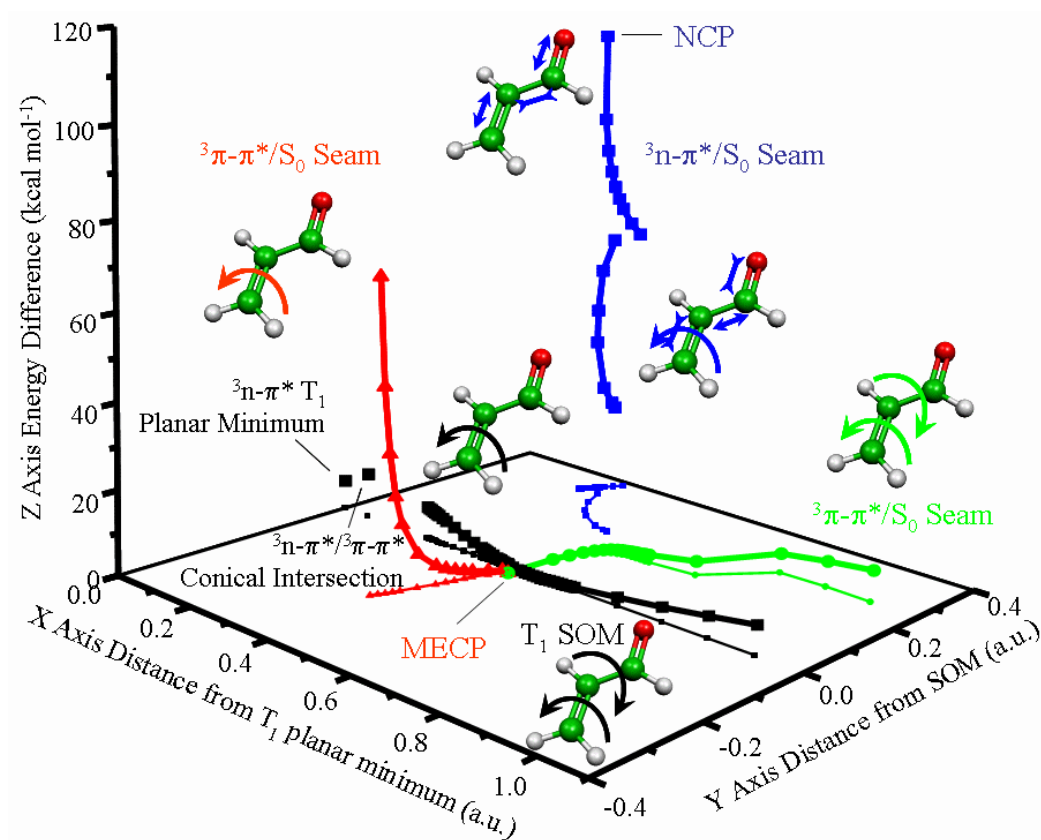


Figure 6: Intersection subspaces

Exploring the conical intersection: one-to-one mapping MEP to CI seam

To explore the CI seams perpendicular to a MEP we use the two constraints of 1) the intersection

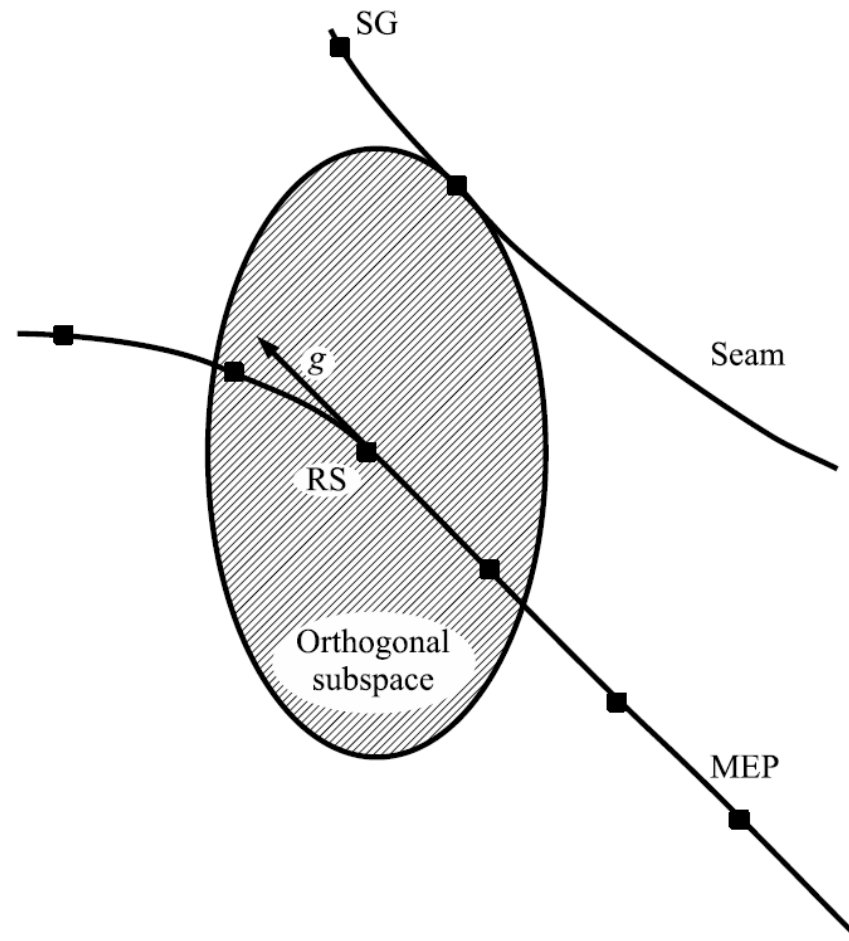
$$r = E_1 - E_0. \quad (20)$$

and 2) that two vectors are perpendicular.

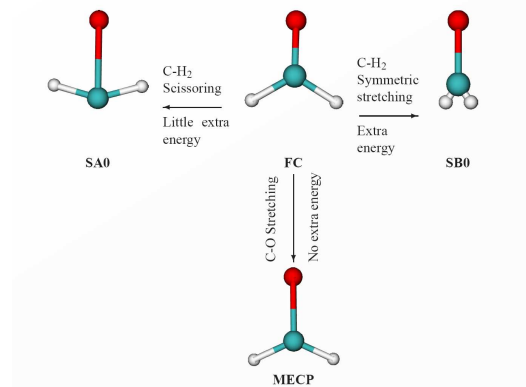
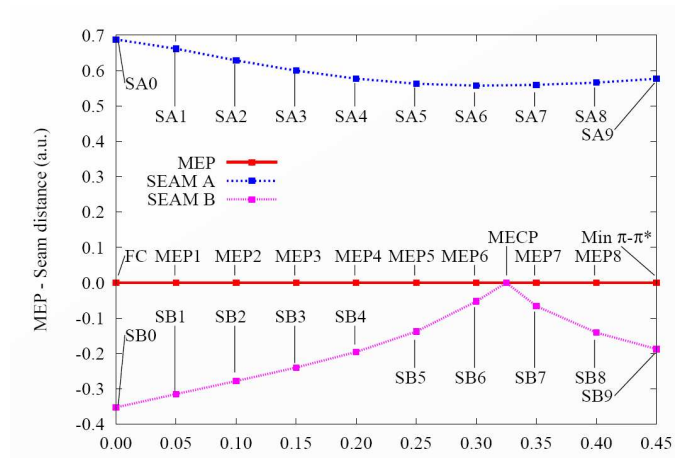
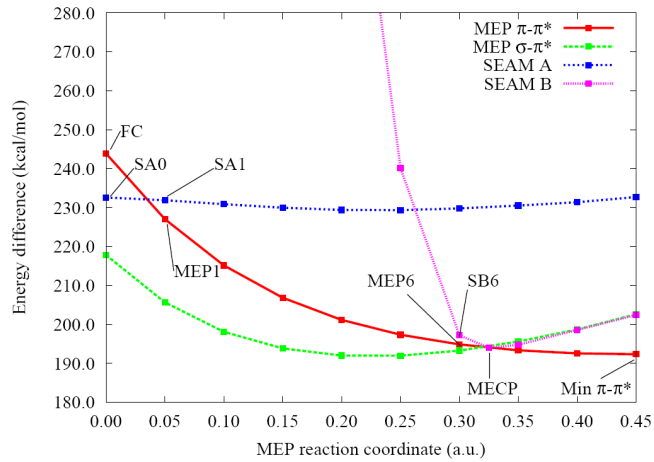
$$0 = (\mathbf{R}(\mathbf{q}) - \mathbf{R}(\mathbf{q}_{ref})) \cdot \mathbf{g}(\mathbf{q}_{ref}) \quad (21)$$

where $\mathbf{g}(\mathbf{q}_{ref})$ is the gradient of the MEP at \mathbf{q}_{ref} . Additional constraints of type 2 can later be added to explore other CI seams.

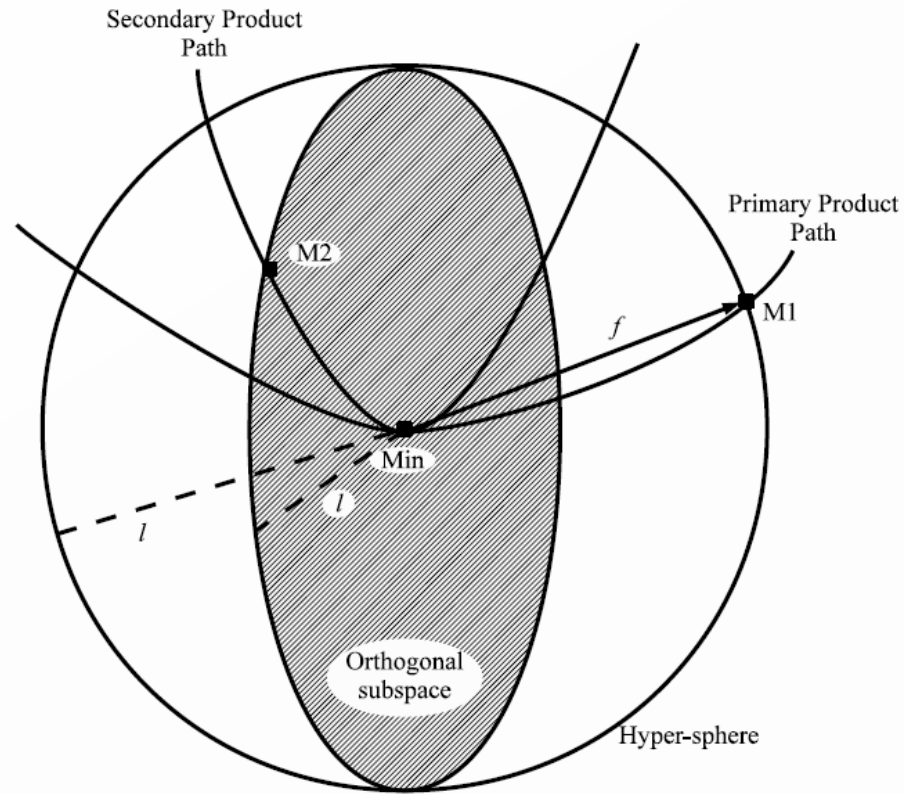
Exploring the conical intersection: one-to-one mapping MEP to CI seam



One-to-one mapping MEP to CI seam: formaldehyde



Novel constrained optimizations



General Slapaf Keywords

In the lab we will explore

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

- **Constraints ... End of Constraints**
- how to define internal coordinates
- definition of a hypersphere
- definition of energy differences
- **RP-Coordinates**
- **IRC**
- **REACTION vector**