

## Transition-State Searching with NWChem

One of the most exciting uses of ab initio methods is to use them to map out chemical reaction pathways. Mapping chemical reaction pathways involves characterizing the reactants, products, intermediates, and transition states. This is followed by the calculation of a minimum energy path from the transition states to the reactants and products. At first glance this seems like a relatively simple process, however, locating transition states can be an arduous task.

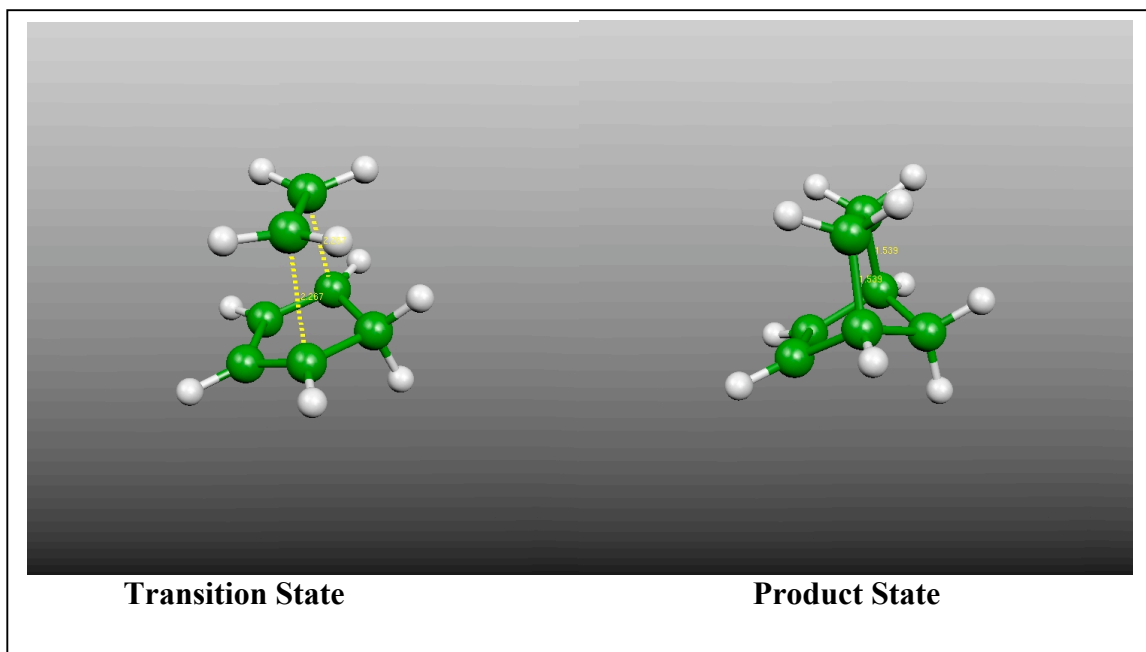
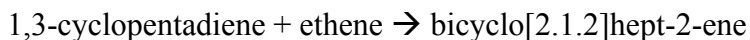
There are three stages involved in locating transition states:

1. Construct a geometry that is near the transition state
2. Refine the transition state by using saddle point optimizer
3. Characterize the transition state (i.e. following the reaction path from the transition state to the reactant and product)

Stage 1 is crucial because saddle point optimizers will not work well unless the gradient points roughly in the direction of the saddle point. The following examples show how to use constrained optimization and constrained the ab initio molecular dynamics methods in NWChem to determine geometries that are close to transition states.

## Example: dielsalder.nw

This example finds the transition state for the following dielsalder reaction:



The initial constrained geometry optimization is used to construct a geometry that is near the transition state. After which the constraints are released and a saddle point optimization is run. In general, a series of constrained geometry optimization will need to be run, because the transition state distance is not known a priori (see Example: session6/disilane.constrained-opt.nw for an example of how to do this).

## From the NWChem Users Manual

### 6.5 `ZCOORD` -- Forcing internal coordinates

By default redundant internal coordinates are generated for use in geometry optimizations. Connectivity is inferred by comparing inter-atomic distances with the sum of the van der Waals radii of the two atoms involved in a possible bond, times a scaling factor. The scaling factor is an input parameter of `ZCOORD` which maybe changed from its default value of 1.3. Under some circumstances (unusual bonding, bond dissociation, ...) it will be necessary to augment the automatically generated list of internal coordinates to force some specific internal coordinates to be included in among the internal coordinates. This is accomplished by including the optional directive `ZCOORD` within the geometry directive. The general form of the `ZCOORD` directive is as follows:

```
ZCOORD
```

```

CVR_SCALING <real value>
BOND      <integer i> <integer j> \
          [<real value>] [<string name>] [constant]
ANGLE     <integer i> <integer j> <integer k> \
          [<real value>] [<string name>] [constant]
TORSION   <integer i> <integer j> <integer k> <integer l> \
          [<real value>] [<string name>] [constant]
END

```

The centers *i*, *j*, *k* and *l* *must* be specified using the numbers of the centers, as supplied in the input for the Cartesian coordinates. The ZCOORD input parameters are defined as follows:

- `cvr_scaling` -- scaling factor applied to van der Waals radii.
- `bond` -- a bond between the two centers.
- `angle` -- a bond angle  $\widehat{ijk}$ .
- `torsion` -- a torsion (or dihedral) angle. The angle between the planes *i-j-k* and *j-k-l*.

A value may be specified for a user-defined internal coordinate, in which case it is forced upon the input Cartesian coordinates while attempting to make only small changes in the other internal coordinates. If no value is provided the value implicit in the input coordinates is kept. If the keyword `constant` is specified, then that internal variable is not modified during a geometry optimization with DRIVER (Section [21](#)). Each internal coordinate may also be named either for easy identification in the output, or for the application of constraints (Section [6.6](#)).

If the keyword `adjust` is specified on the main GEOMETRY directive, only ZCOORD data may be specified and it can be used to change the user-defined internal coordinates, including adding/removing constraints and changing their values.

The following input example use the DFT module, for finding the transition state for the dielsalder reaction:



This example is simple enough so that other ab initio theories can also be used, such as the HF, PSPW, and MP2 modules.

## NWChem Input Deck

```
title "parent diels-alder - constrained geometry optimization + saddle search"  
#dielsalder.nw input deck
```

```
permanent_dir ./perm  
scratch_dir ./perm
```

```
echo  
start
```

```
# tests constrained optimization, saddle search,  
# use of constraints with symmetry
```

```
# norbornene = -45.69811295 au r = 1.539 Angstroms
```

```
geometry autosym # Equil nonbornene geometry
```

```
C 0.48438728 -1.26420666 0.66379632  
C 0.48438728 -1.26420666 -0.66379632  
C -0.32763055 -0.09123377 1.11105174  
C -0.32763055 -0.09123377 -1.11105174  
C -1.36089042 -0.02893165 0.00000000  
C 0.50866739 1.15402721 0.76530727  
C 0.50866739 1.15402721 -0.76530727  
H -0.69016477 -0.11291256 -2.13538649  
H -0.69016477 -0.11291256 2.13538649  
H -1.93888714 0.89733827 0.00000000  
H 1.50914212 1.10998500 -1.19387233  
H 1.50914212 1.10998500 1.19387233  
H 1.09450829 -1.87707752 -1.31279758  
H 1.09450829 -1.87707752 1.31279758  
H -2.02362675 -0.89310262 0.00000000  
H 0.02217904 2.04804733 1.15788544  
H 0.02217904 2.04804733 -1.15788544
```

```
end
```

```
driver
```

```
maxiter 101  
end
```

```
basis
```

```
* library 6-31G*  
end
```

```
dft
```

```
xc b3lyp  
end
```

```
geometry adjust # move to guess geometry & apply constraints
```

```
zcoord  
bond 6 3 2.267 r constant  
bond 7 4 2.267 r constant  
end
```

```
end
```

```
task dft optimize # relax with constraints
```

```
geometry adjust # release constraints
```

```
zcoord  
bond 6 3 2.267 r  
bond 7 4 2.267 r  
end
```

```
end
```

```
task dft saddle # go for the transition state
```

The following input is used to apply constraints to the input geometry. In this example the bond distances between carbon atoms in 1,3-cyclopentadiene and ethane are constrained to be 2.267 Å.

The following input releases the constraints and then runs a saddle point search