## More transition state tips & tricks





Transition states 2, TU Delft, 22 January 2021 SCM support: <u>support@scm.com</u>

# Pointers & ideas for TS search

### Good starting point (**geometry** close to TS) 1.

- First explore reactant and product
- (Initially) use low convergence criteria
- Scan the PES with MOPAC or GFNx-TB
  - Sometimes scanning from product side is easier  $\triangleright$
  - Can use complex composite scan coordinates
- Use CI-NEB (See TS 1 by Thomas)
  - > Always a good idea to explore Reactants
- Pass on coordinates (+Hessian) to ADF
- Previous TS 'similar' system
- Consider first doing constrained/partial optimization

### Good description of the **curvature**: lowest Hessian eigenmode(s) 2.

- **Partial Hessian**
- Low-level Hessian from previous, of for ADF choose 'Calculate With Fast Engine'
- TSRC: define (complex) reaction coordinate
- Consider 'TS point characterization' to check only 1 negative eigenmode

### Accuracy? 3.

- Solvent effects: COSMO and/or SM12 (single point only)
- metaGGA? TZP/DZP? Good numerical quality?
- Double hybrids (single point)
- Low-eigenmode corrections to frequencies
- Sometime spurious 2<sup>nd</sup> imaginary modes are hard to get rid of -> ScanFreq





**Reaction Coordinate** 



# Transition State through PES scan

## Exercise (Ziegler-Natta tutorial):

- New DFTB input
- Build Cp<sub>2</sub>ZrMe<sup>+</sup> 0
  - structure tool () => ferrocene
  - Right-click Fe -> Element -> Zr
  - Add C and replace by methyl
  - (Use dummies to change CpMCp angle)
  - Model -> Solvent -> Toluene
  - Add charge and optimize

 $\circ$  Add ethene (use the Q )

- Manipulate it in position
- Right-click + drag = translate
- Left-click + drag = rotate
- Ctrl+M = select molecule
- **Remove dummies**
- Optimize

Alkyl Chains Amino Acids Aromatic		XC functional:	LDA	•
Cyclic Hydrocarbons DNA Ligands	* * *	Relativity.	None	•
Metal Complexes		Porphyrins	D7	
Polyhedra Solvents	*	Sandwiches  M2L10 cluster	Ferrocene Sandwich Nb(C5H5)(C7H7) Sandwich	
Cp-Zr Cp2Zr_m DETDA EPON862 NIPAM bpy bpy2 Manage Structures Save As Structure		M2L8 cluster ML2 Linear ML3 Trigonal Planar ML4 Square Planar ML4 Tetrahedral ML5 Square Pyramidal ML5 Trigonal Bipyramidal ML6 Octahedral	Triple Porphyrin Sandwich	
		ML6 Trigonal Prismatic ML7 Pentagonal Bipyramidal ML8 Cubic ML8 Square Antiprismatic		





AMS hands-on workshop: TS 2, 22 January 2021 © SCM

	DFTB	Main	Model	Pro	operties Details		Q
6					Solvation		⊜ 0
	Solver	nt:		[	Toluene	•	
	Surfac	e grid:			230	•	
	Solvat	ion Free E	inergy:		Yes		
x, o * * ¢							

# Transition State through PES scan

- Set up a PES scan, using **1 combined scan coordinate** 0
  - Zr-C to 2.4 & C-C to 1.55
- Details -> Geometry Optimization:
  - Loosen the Convergence criteria by a factor of 5
- Run, and when finished, open AMSMovie



- Copy the highest energy structure (e.g. Ctrl+U), or save as structure
- Set up a TS run (ideally make a new input)
  - make sure there are no constraints, and regular convergence
  - use a calculate Hessian as initial guess and calculate frequencies



DFTB	Main	Model	Properties	Details			Q
		Geor	netry Const	raints and F	PES Scar	n	• •
Conve	ergence de	etails					Ð
Restra	aints						Ð
Numbe Result	er of scan s for all PE	points fo S points	r coordinate : 🗆 Save			SC-1	: 10
- c	(29) Zr(1)			3.188	2.4	Å	SC- 1 🚖
- c	(28) C(24)			3.290	1.55	Å	SC- 1 🚖

Gradient convergence:	0.005	Hartree/Å •
Energy convergence:	5e-05	Hartree •
Step convergence:	0.05	Å٠

## Transition State, start with NEB - Ziegler-Natta

### Exercise: •

SCM

- Optimize reactant & product from the last PES scan points
- Rotate the Zr-C-C-H dihedral to ~0 (metallacycle Zr-C-C-H) & optimize => alpha-agostic
- Set up a climbing nudged elastic band calculation Task: NEB
- Choose this structure as final, the other product as intermediate, and R as initial (import structures from results/ams.rkf) and choose 14 points
- Don't optimize R&P, relax convergence by factor 5
- Open AMSMovie when finished

## Which is the rate-determining step?





Tip: use CI-NEB to get close enough to TS, use Hessianbased optimization to find it

0-2021> <13:58:17>	Numerical nuclear derivatives calculation	n complete.
0-2021> <13:58:17>	Scanning mode: 7	
0-2021> <13:58:18>	PES point character: Geometry correspond	is to a transition state.
0-2021> <13:58:18>	TS barrier height from the left	0.02270445 Hartree
0-2021> <13:58:18>		14.247 kcal/mol
0-2021> <13:58:18>		59.611 kJ/mol
0-2021> <13:58:18>	TS barrier height from the right	0.06580135 Hartree
0-2021> <13:58:18>		41.291 kcal/mol
0-2021> <13:58:18>		172.761 kJ/mol
0-2021> <13:58:18>	NORMAL TERMINATION	
N-NEB has finished		

## **Transition States: Further considerations**

### Reaction rates: ullet

Calculate  $\Delta G^{\#}$ : include H<sub>vib</sub>, S (AMSoutput -> Other Properties -> Statistical Thermal Analysis)

1	Temp		Transl	Rotat	Vibrat	Total
:	298.15 Entropy (cal/mol-K):		42.601	31.288	52.371	126.261
	Nuclear Internal Energ	y (kcal/mol):	0.889	0.889	160.907	162.684
	Constant Volume Heat C	apacity (cal/mol-K):	2.981	2.981	56.260	62.222
	(c) Constant Volume Heat C	apacity (cal/mol-K):	2.981	2.981	52.800	58.761
	Summary of energy terms					
		hartree	eV	k	cal/mol	kJ/mol
	Energy from Engine:	-37.585024915182686	-1022.7406	-2	3584.96	-98679.47
	Nuclear Internal Energy:	0.259253970109237	7.0547		162.68	680.67
(c)	Nuclear Internal Energy:	0.257445594179003	7.0055	161.55		675.92
	Internal Energy U:	-37.325770945073451	-1015.6859	-2	3422.28	-97998.80
	pV/n = RT:	0.000944186013486	0.0257		0.59	2.48
	Enthalpy H:	-37.324826759059967	-1015.6602	-2	3421.68	-97996.32
	-T*S:	-0.059990510871653	-1.6324		-37.64	-157.51
(c)	-T*S:	-0.058176671371776	-1.5831		-36.51	-152.74
	Gibbs free energy:	-37.384817269931617	-1017.2926	-2	3459.33	-98153.82

(c) The properties marked with this symbol have been corrected using 'low vibrational frequency free rotor interpolation corrections'. For those terms all positive frequencies are used (also ones below 20 1/cm), but the contribution to the partition function of small vibrational frequencies is modified as described in the following paper: S. Grimme, 'Supramolecular Binding Thermodynamics by Dispersion-Corrected Density Functional Theory' (Chem. Eur. J. 2012, 18, 9955-9964) Configuration: Dampener Frequency : 100.000 1/cm . 4 000 Dampener Alpha

Dampener 1	arbua			•	4.000		
Averaging	Moment	of	Inertia	:	1.000E-44	kg	m2

- <u>hTST as first approximation</u>:  $k \sim exp$  (-G<sup>#</sup>/RT), Low-level frequencies: Grimme corrections
- Could also try <u>mircokinetics</u>. More underway (<u>ReaxPro</u>)
- Suggestions & troubleshooting •
  - <u>get close to TS</u>: NEB, PES Scan, constrained opt, previous TS + change ligands (PLAMS script!), ....
  - <u>get a good curvature (Hessian): pre-calc with GFN-xTB, MOPAC; partial Hessian</u>
  - 3. check final curvature / path: Frequency calculation, PES point characterization, IRC
  - 4. Spurious imag. Freq.: displace along that mode (AMSSpectra, Ctrl+8 \*5) & retry



# Periodic systems: surfaces & bulk

- How to get good TS geometry guess?
  - Literature or previous results: 0
    - similar TS + constrained optimization
  - Quick (?) NEB (you want to find R & P anyway)
  - PES scan (can you use ReaxFF, MOPAC, GFN-xTB? Otherwise: cheaper DFT?) (video)
  - Maybe you can get away with periodic DFT/DFTB (video) or DFT/MM ?

## How to get good guess for lowest few Hessian eigenmodes?

- Could try MOPAC or DFTB Hessian
  - Inspect modes first?
- Define reaction coordinate (TSRC)
- Use a partial Hessian ('active' region)



AMSinput 2020.102



Bonds View Help						_		×
	BAND	Main	Model	Properties	Details	MultiLevel		Q
				IR (Frequ	iencies),	VCD	6	?
	Charac	cterize PE	S point:	Yes				
	Freque	ncies:		Yes				
	VCD:			Yes		_		
	Hessiar	n only for	r:	active		•		
	Hessia	n:		Auto		•		
	Re-sca	n modes	:	Yes				
	+ R	le-scan r	ange: -	1000000.0	10	.0 cm-1 •		
	Displac	cements:		Cartesi	an	•		Ø
	Symm	Frequent	cies:	All		v		
	+ 8	Block regi	on:		*			
нх,0⊛□ ★ 🗉 🕄								