

# From Electrons to Materials Properties

Density Functional Theory for Engineers and Materials Scientists

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# Chapter VI

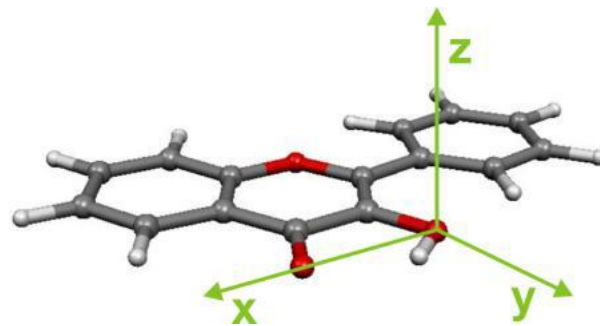
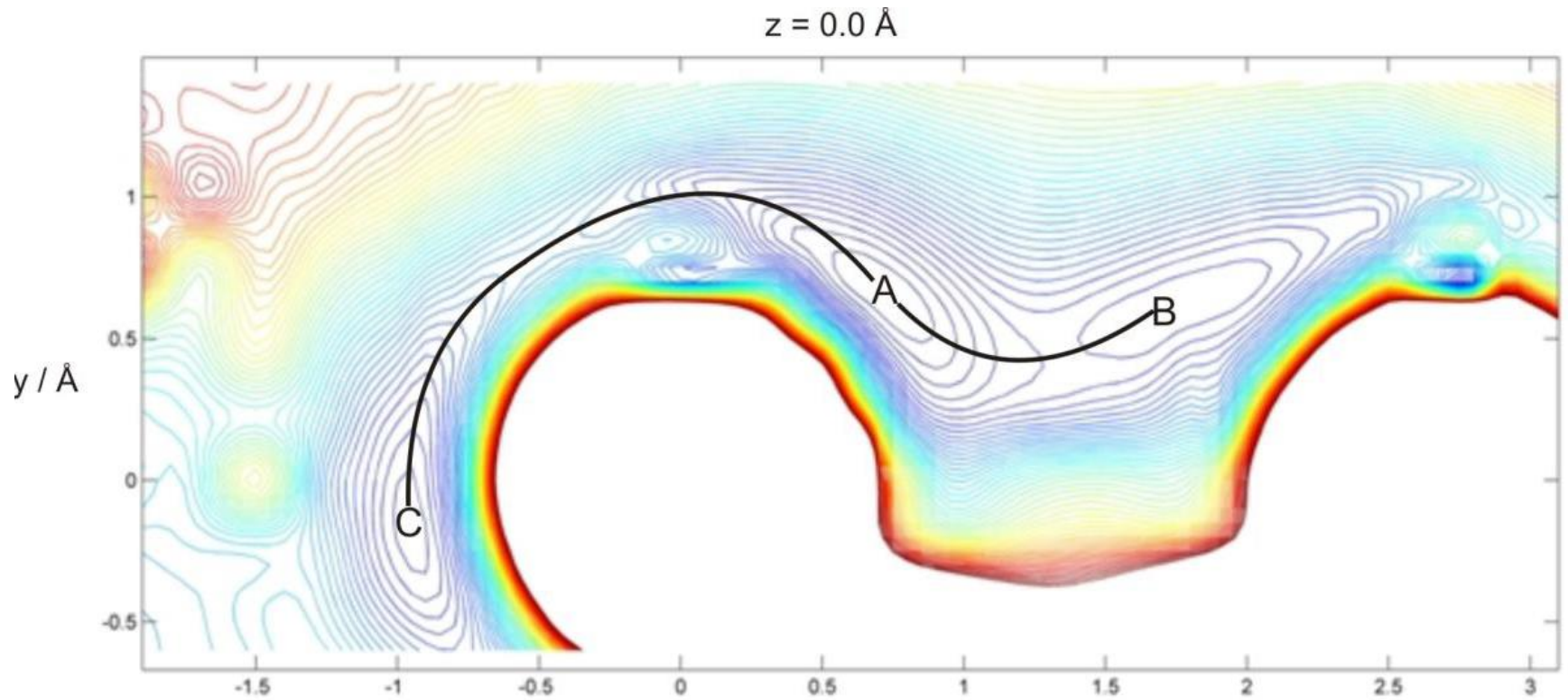
## Potential Energy Surfaces

## Potential energy surfaces (PES's)

Whenever we are dealing with the chemistry of a system we have to understand that any stable conformation of atoms is a minimum on the potential energy surface (PES). A PES is defined as a surface of co-dimension 1 to the atomic degrees of freedom, meaning that it is a scalar function of the atomic coordinates. Physically, it is a field of potential energy.

As stable conformers are minima, reaction paths connect two or more minima in a way that the connecting path (the reaction path) always has the lowest energy possible. The point with highest energy on the reaction path, the transition state, is then a first-order saddle point.

Hence, finding stable conformers is mathematically the task of finding minima, and finding transition states is identical to the task of finding first-order saddle points.



This means that whenever we are going to analyze our PES, we need to know at least the first derivatives of the (potential) energy, hence the gradients of the energy

$$(1) \quad \mathbf{g} = \sum_n \frac{\partial E}{\partial R_n}$$

In principle we can obtain these numerically, yet this is rather costly. Yet, there exists a theorem (the Hellmann-Feynman theorem), which allows us to obtain gradients analytically:

$$(2) \quad \frac{\partial \langle \psi | \hat{H} | \psi \rangle}{\partial R_n} = \frac{E \partial \langle \psi | \psi \rangle}{\partial R_n} = E \left\langle \psi \left| \frac{\partial}{\partial R_n} \right| \psi \right\rangle = \left\langle \psi \left| \hat{H} \frac{\partial}{\partial R_n} \right| \psi \right\rangle = \left\langle \psi \left| \frac{\partial \hat{H}}{\partial R_n} \right| \psi \right\rangle$$

This is quite helpful, as we can now simply obtain the derivatives of our Hamiltonian and apply the new operator to our converged wavefunctions.

In principle, we can try something similar for second derivatives.

Alternatively, we can approximate the Hessian (matrix of second derivatives) from the gradients. We define

$$(3) \quad \boldsymbol{\delta} = \mathbf{R}^{(k+1)} - \mathbf{R}^{(k)}$$

$$(4) \quad \boldsymbol{\gamma} = \mathbf{g}^{(k+1)} - \mathbf{g}^{(k)}$$

We initialize our Hessian as the unit matrix and update its inverse matrix whenever we change the positions of one or all atoms

$$(5) \quad (\mathbf{G}^{(k+1)})^{-1} = (\mathbf{G}^{(k)})^{-1} + \left( \mathbf{1} + \frac{\boldsymbol{\gamma}^T (\mathbf{G}^{(k)})^{-1} \boldsymbol{\gamma}}{\boldsymbol{\delta}^T \boldsymbol{\gamma}} \right) \frac{\boldsymbol{\delta} \boldsymbol{\delta}^T}{\boldsymbol{\delta}^T \boldsymbol{\gamma}} - \frac{\boldsymbol{\delta} \boldsymbol{\gamma}^T (\mathbf{G}^{(k)})^{-1} + (\mathbf{G}^{(k)})^{-1} \boldsymbol{\gamma} \boldsymbol{\delta}^T}{\boldsymbol{\delta}^T \boldsymbol{\gamma}}$$

## Geometry Optimization

Now as we have both, first and second derivatives, we can do some analysis. We have either an extremal point if the necessary condition

$$(6) \quad \mathbf{g} = \mathbf{0}$$

is fulfilled. Furthermore, if the Hessian is positive definite we have a minimum and we have a transition state if one and only one eigenvalue of the Hessian is negative and all others are positive.

We have found a global minimum if our energy value is lower than at any other point of the PES, and a local minimum otherwise (if we are in a minimum). In addition, we have found the true transition state if there is no lower first-order saddle point between the two minima it connects.

Let us optimize a geometry. Obviously we can reach the closest minimum by simply following the gradient where it *descends steepest*. This is the simple equation

$$(7) \quad \mathbf{R}^{(k+1)} = \mathbf{R}^{(k)} - \mathbf{g}^{(k+1)}$$

Unfortunately we are lacking second derivatives, so we cannot say for sure what kind of extremal point we reached. In addition, this simple algorithm tends to oscillate. We can improve this applying a weighted gradient, where we weight by *conjugate gradients*, i.e. according to Fletcher and Reeves

$$(8) \quad \mathbf{R}^{(k+1)} = \mathbf{R}^{(k)} - \frac{\mathbf{g}^{(k+1)T} \mathbf{g}^{(k+1)}}{\mathbf{g}^{(k)T} \mathbf{g}^{(k)}} \mathbf{g}^{(k+1)}$$

or as proposed by Polak and Ribière

$$(9) \quad \mathbf{R}^{(k+1)} = \mathbf{R}^{(k)} - \frac{\mathbf{g}^{(k+1)T} (\mathbf{g}^{(k+1)} - \mathbf{g}^{(k)})}{\mathbf{g}^{(k)T} \mathbf{g}^{(k)}} \mathbf{g}^{(k+1)}$$



Beyond its vastly improved stability the conjugate gradients (CG) method has the advantage that it converges to a minimum within a maximum of  $k = N$  steps, where  $N$  is the dimension of the problem. Linear convergence is guaranteed. But maybe we can go with superlinear convergence. Let us take second derivatives, in a *Newton-like* method:

$$(10) \quad \mathbf{R}^{(k+1)} = \mathbf{R}^{(k)} - \mathbf{G}^{(k+1)^{-1}} \mathbf{g}^{(k+1)}$$

This is not only stable, it yields especially in proximity to the minimum superlinear convergence. Plus we automatically move towards a minimum, as the sign of the Hessian pushes us in the right direction. Furthermore we can select one eigenvalue of the Hessian to run into the opposite direction. This directly leads us to a transition state.

Finally, we may want to optimize our cell parameters. This yields 6 additional degrees of freedom from the stress tensor

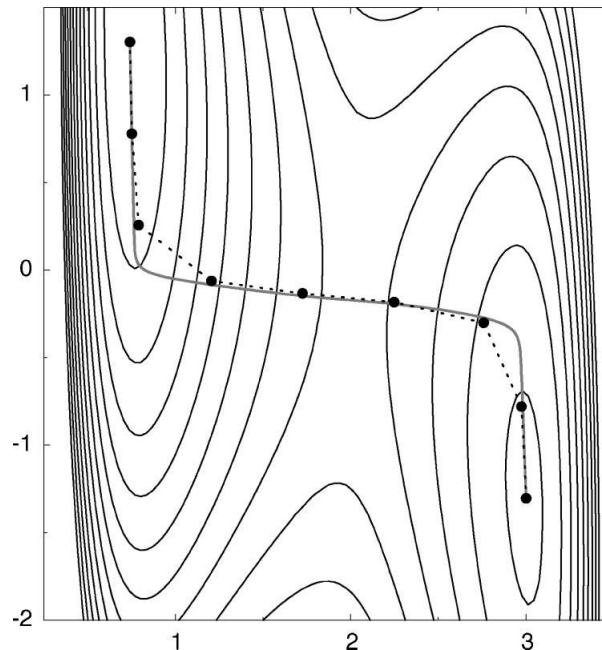
$$(11) \quad \boldsymbol{\sigma} = \begin{pmatrix} \sigma_{xx} & \tau_{xy} & \tau_{xz} \\ \tau_{yx} & \sigma_{yy} & \tau_{yz} \\ \tau_{zx} & \tau_{zy} & \sigma_{zz} \end{pmatrix}$$

We have reached a minimum if our PES is minimal under the constraints of the pressure tensor, i.e. when all forces are zero. This means that we derive forces on the cell, typically as sum of atomic forces.

We can apply the aforementioned optimization algorithms to cell optimization as well, and we can optimize molecular geometries and cell parameters synchronously.

Sometimes we want to keep some parts of our ensemble fixed. This yields *constrained optimization*, which is a widely used tool. There are many different constraints, i.e. fixed distances, added forces, fixed chemical potential etc.

One example of constrained optimization are nudged elastic band (NEB) methods. Here, a series of geometrical interpolations, called images, between reactant and products structures are constructed and constrained by a spring force so they form a chain.



Optimizing the images now yields the minima for the two final images, but all images in between are experiencing a harmonic force by both neighbors. This means that they cannot proceed to their closest minimum, as in this case the additional force from the constraint rises quadratically. This optimizes them (ideally) so that all images are on the minimum energy path (MEP), hence the reaction path. The images highest in energy can serve as an approximation to the transition state.

Why do we need a transition state?

According to transition state theory (TST) we can obtain the rate constant from it as

$$(12) \quad k = \frac{k_B T}{h} \exp\left(-\frac{E^{TS} - E^{init}}{k_B T}\right)$$

or, more precise

$$(13) \quad k = \frac{k_B T}{h} \frac{\prod_i^{3N} \nu_i^{init}}{\prod_i^{3N-1} \nu_i^{TS}} \exp\left(-\frac{E^{TS} - E^{init}}{k_B T}\right)$$

## Optimization of your batch script (UCI HPC)

```
#!/bin/bash
#$ -N test
#$ -q free32i
#$ -pe one-node-mpi 32
#$ -R y
#$ -m beas
module load espresso/5.3.0
export StartDir=$PWD
export WorkDir=/scratch/$JOB_ID
mkdir $WorkDir
cp * $WorkDir
cd $WorkDir
mpirun -np $CORES pw.x -i pyrope.in > pyrope.out
cp -r * $StartDir
rm -rf $WorkDir
```