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Rare events

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NEB: input variables

To perform a NEB calculation, in additional to variables for a SCF run, specify: (details in the file `Doc/INPUT_PW`)

```
&CONTROL
  calculation = “neb”      <=  mandatory
  ...
  nstep                    <=  optional (0)
  ...
/
...
...
&IONS
  num_of_images            <=  mandatory
  CI_scheme                <=  optional (no-CI)
  opt_scheme               <=  optional (quick-min)
  ds                       <=  optional (1.0)
  first_last_opt           <=  optional (.FALSE.)
  k_max                    <=  optional (0.1)
  k_min                    <=  optional (0.1)
  path_thr                 <=  optional (0.05)
  ...
/
```

And ...

NEB: input variables

To perform a NEB calculation, in additional to variables for a SCF run, specify:
(details in the file `Doc/INPUT_PW`)

```
first_image                                                    <= mandatory
   X 0.0  0.0  0.0  { if_pos(1) if_pos(2) if_pos(3) }
   Y 0.5  0.0  0.0  { if_pos(1) if_pos(2) if_pos(3) }
   Z 0.0  0.2  0.2  { if_pos(1) if_pos(2) if_pos(3) }
intermediate_image 1                                           <= optional
   X 0.0  0.0  0.0
   Y 0.9  0.0  0.0
   Z 0.0  0.2  0.2
intermediate_image ...                                         <= optional
   X 0.0  0.0  0.0
   Y 0.9  0.0  0.0
   Z 0.0  0.2  0.2
last_image                                                     <= mandatory
   X 0.0  0.0  0.0
   Y 0.7  0.0  0.0
   Z 0.0  0.5  0.2
```

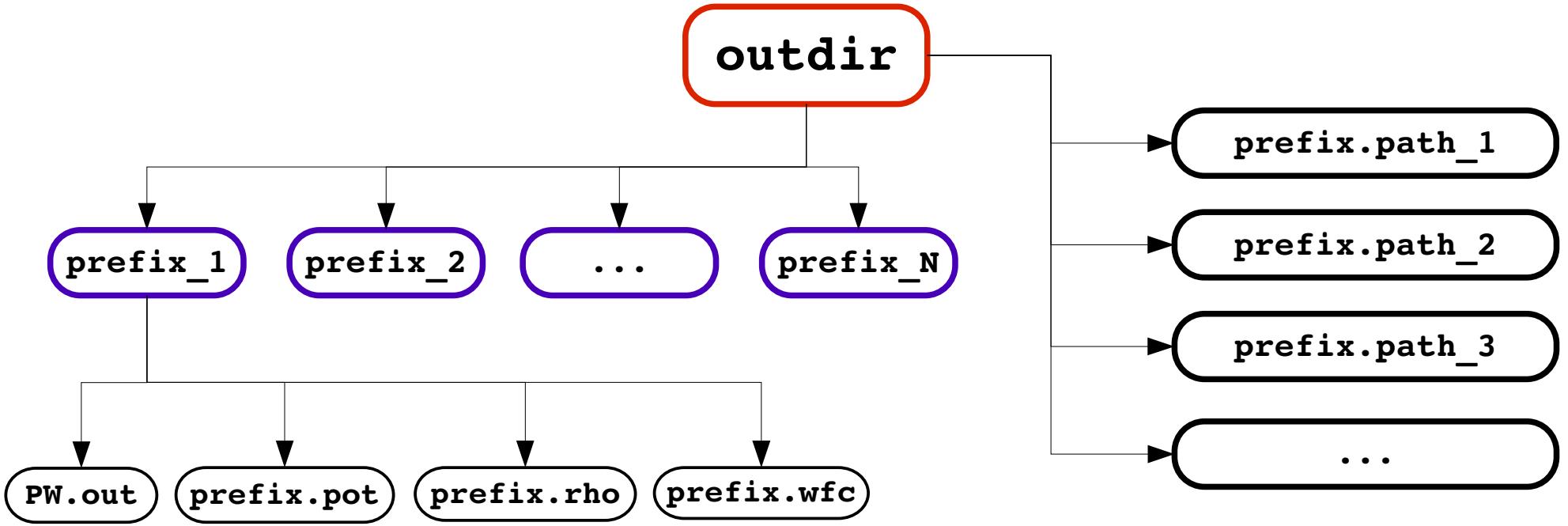
The nudged elastic band will connect `first_image` to `last_image`, passing *close* to `intermediate_image`s, if specified. Otherwise starts with a linear interpolation.

NEB: output

Files in the working directory (./):

- `prefix.path` <= file containing data required to restart a NEB calculation
- `prefix.axsf` <= file containing the path in *xcrysden* format
- `prefix.xyz` <= file containing the path in *xyz* format
- `prefix.dat` <= file containing the reaction coordinate, the energy and the error of each image
- `prefix.int` <= file containing a cubic interpolation for the energy profile

Files in the temporary directory (`outdir`/):



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Collinear proton transfer

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Purpose: study the reaction H_2+H to H+H_2 with NEB.

1) Take a look at the input file for SCF calculation for H_2+H (`H2+H.scf.in`, provided).

Atomic coordinates:

```
ATOMIC_POSITIONS bohr
     H      -4.566700090     0.000000000     0.000000000     1   0   0
     H       0.000000000     0.000000000     0.000000000     0   0   0
     H       1.557766760     0.000000000     0.000000000     1   0   0
```

Those are optimized coordinates, and will be the `first_image`.

Coordinates for the `last_image` will be:

```
ATOMIC_POSITIONS bohr
     H      -1.557766760     0.000000000     0.000000000
     H       0.000000000     0.000000000     0.000000000
     H       4.566700090     0.000000000     0.000000000
```

2) Take a look at the input file for NEB calculation with 7 images (`H2+H.neb.in`):

```
diff H2+H.neb.in H2+H.scf.in
```

`less H2+H.neb.in` (type `q` to exit)

3) Run the calculation:

```
pw.x < H2+H.neb.in > H2+H.neb.out
```

pw.x will stop immediately (`nstep`=0), but gives us several informations. This is good for checking before running long calculations.

Collinear proton transfer

4) Check that you are starting with a reasonable path.
In the output file:

```
     initial path length           =   4.2553 bohr
     initial inter-image distance  =   0.7092 bohr
```

(should not be too large, if this is the case increase the number of images)
Look at the path, either directly (`less H2+H.xyz`) or with XCrySDen:

```
xcrysden --axsf H2+H.axsf
```

5) If everything is fine, increase `nstep` to 1 and rerun the calculation.

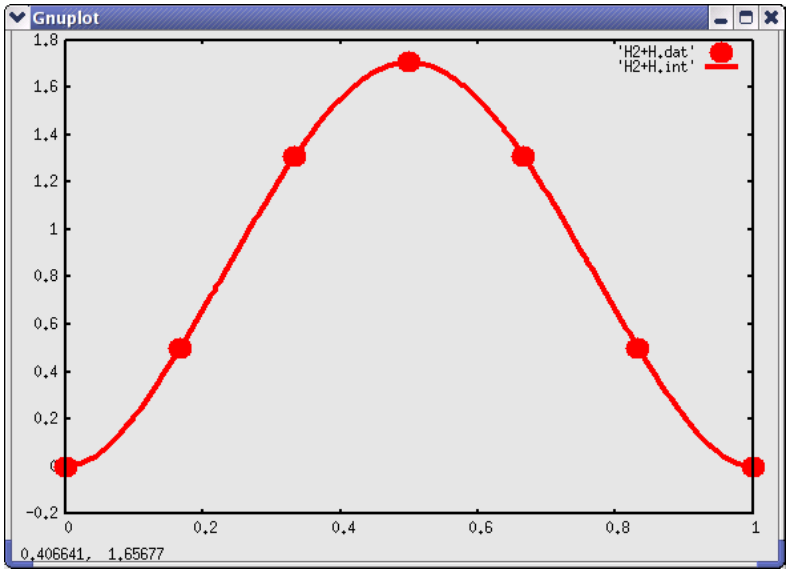
```
pw.x < H2+H.neb.in > H2.H.neb.out
less H2-H.neb.out
```

```
     ------------------------------ iteration   1 -------------
     tcpu =       0.0    self-consistency for image   1
[...]
     tcpu =      15.6    self-consistency for image   7

     activation energy (->) =   1.705781 eV
     activation energy (<-) =   1.705781 eV

     image        energy (eV)         error (eV/A)         frozen
         1        -49.5020596             0.018535              T
         2        -49.0015164             2.084107              F
[...]
     path length           =  4.255 bohr
     inter-image distance  =  0.709 bohr
```

Collinear proton transfer

6) Plot the energy profile along the path, and save it for future use:

```
gnuplot
  > plot 'H2+H.dat' w p, 'H2+H.int' w l
  > quit

cp H2+H.dat linear.dat
cp H2+H.int linear.int
```



7) Finally, increase `nstep` (say, 50), and rerun the calculation:

```
pw.x < H2+H.neb.in > H2.H.neb.out &
```

8) Look at the activation energy:

```
grep "activation energy" H2+H.neb.out
 activation energy (->) =   1.705781 eV
 activation energy (<-) =   1.705781 eV
 [...]
 activation energy (->) =   0.204270 eV
 activation energy (<-) =   0.204270 eV
```

Collinear proton transfer

9) The path length increases:

```
grep length H2+H.neb.out
 initial path length               =  4.2553 bohr
 path length           =  4.255 bohr
 path length           =  4.293 bohr
 [...]
 path length           =  5.293 bohr
 path length           =  5.312 bohr
```

10) Plot the energy profile along the path, and compare with the linear interpolation:

```
gnuplot
  > plot 'H2+H.dat' w p, 'H2+H.int' w l, 'linear.int' w l
  > quit
```

IMPORTANT: In this specific case, the forces on image 4 are automatically small.
Forces are written in the PW.out file of the image 4:

```
less [outdir]/H2+H_4/PW.out
```

Hence, at convergence, image 4 is at the transition state of the reaction.
This is a very special case (due to the special symmetry of the path). In general we will have to use Climbing-Image-NEB.

Let us see a specific example (it is sufficient to have an even number of images)

Necessity of climbing-image

1) Copy the input file:

```
cp H2+H.neb.in H2+H.neb8.in
```

2) Increase the number of images to 8:

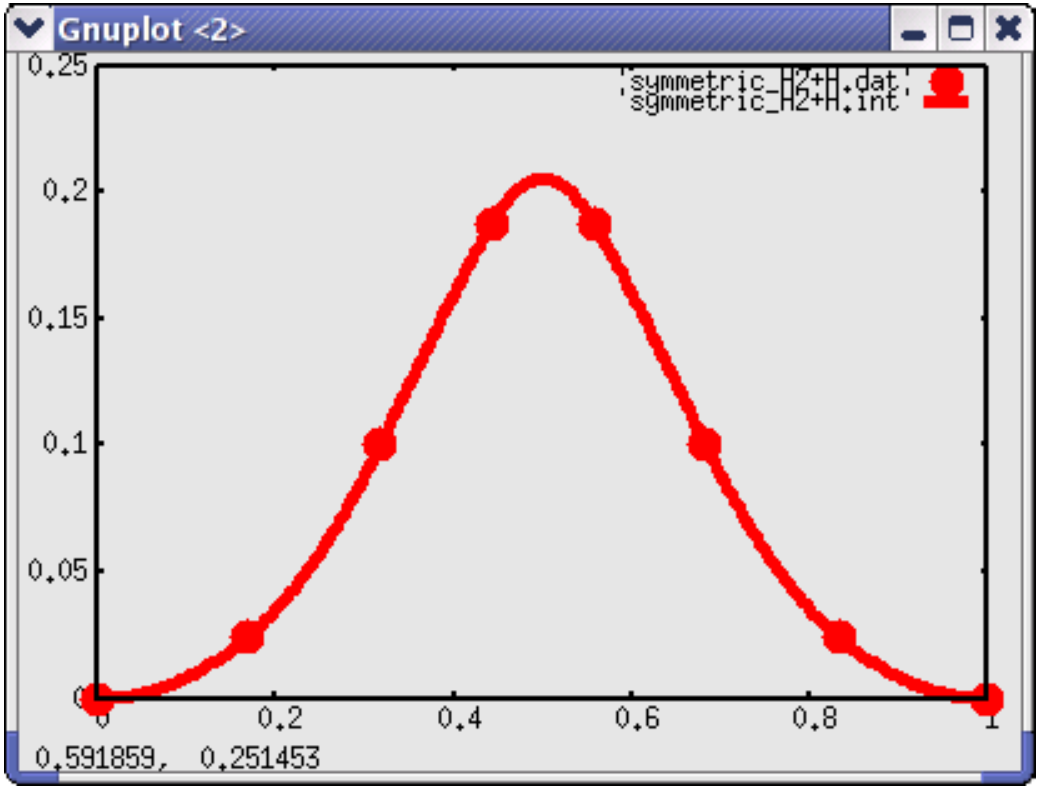
```
num_of_images = 8
```

3) Set `nstep`=50 and run the calculation:

```
pw.x < H2+H.neb8.in > H2+H.neb8.out
```

4) At convergence, none of the images is now at the transition state:

```
gnuplot
  > plot 'H2+H.dat' w p,
                 'H2+H.int' w l
  > quit
```



CI-NEB is necessary!

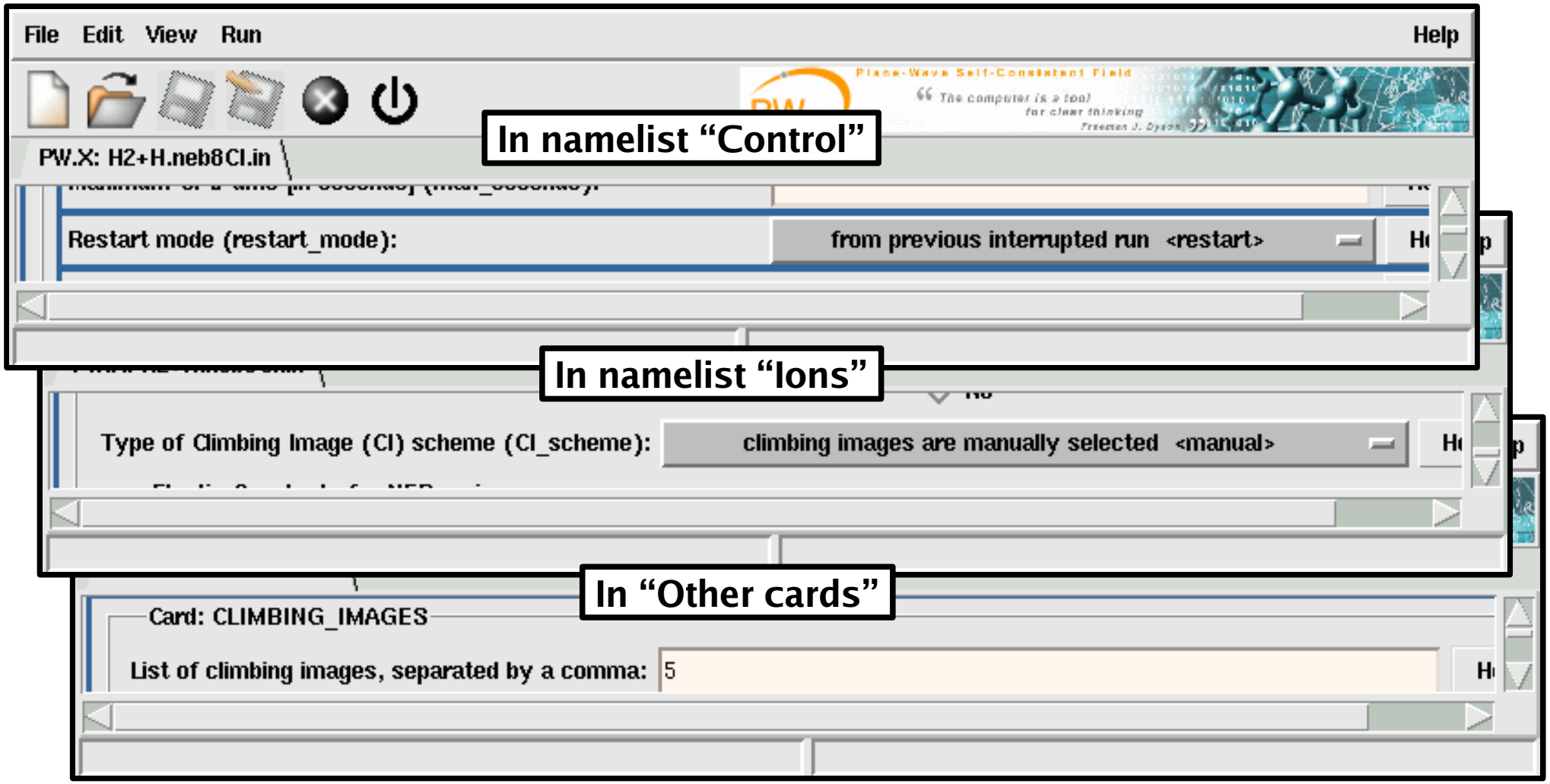
Use of climbing-image

We now restart the calculation, by selecting that image 5 should "climb":

1) Copy the input file:

```
cp H2+H.neb8.in H2+H.neb8CI.in
```

2) Select to restart, to use manual CI, to let image 5 climb (here with PWgui):



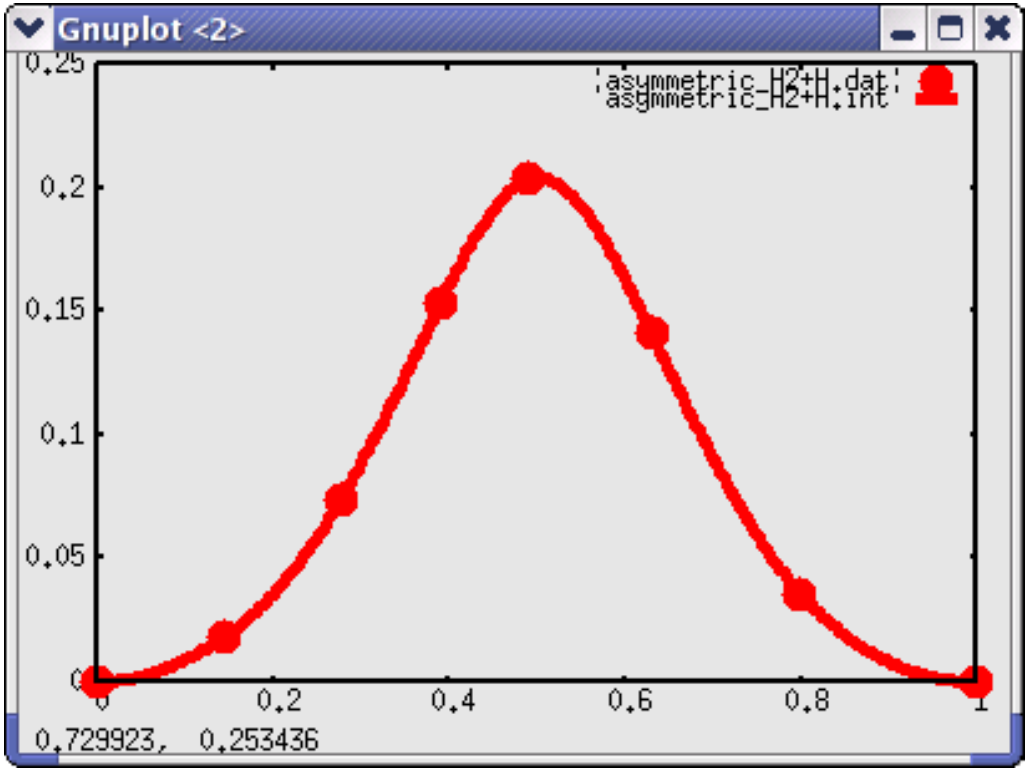
Use of climbing-image

3) Rerun the calculation:

```
pw.x < H2+H.neb8CI.in > H2+H.neb8CI.out
```

4) At convergence, image 5 is now at the transition state:

```
gnuplot
  > plot 'H2+H.dat' w p, 'H2+H.int' w l
  > quit
```



5) Remember to check forces at the transition state (here image 5, written in the PW.out file for image 5):

```
less [outdir]/H2+H_5/PW.out
```

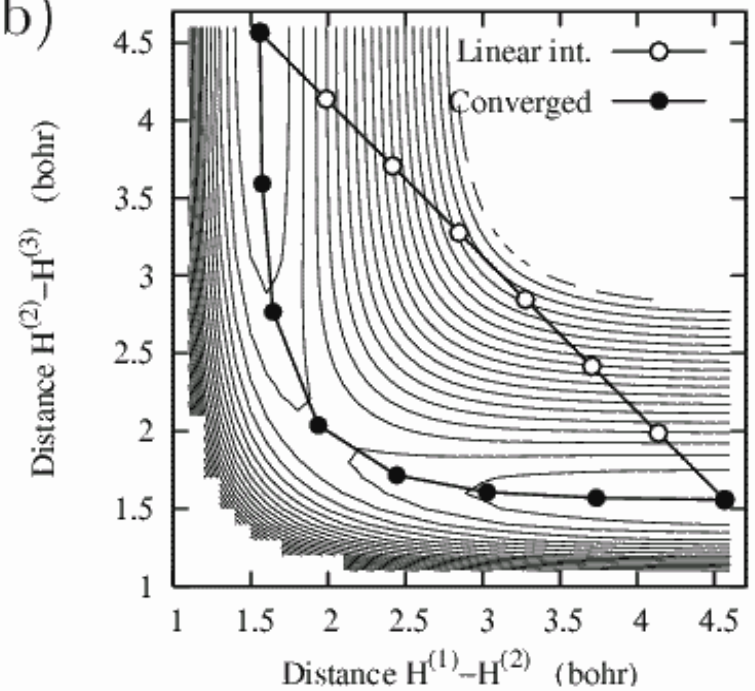
Summary

The reaction:

a) IS: H H + H ⇢ TS: H···H···H ⇢ FS: H + H H

The Potential Energy Surface:

b)



The energy profile:

c)