Tutorial: Fix-DE Method

Since the **2024**Oct version (kst48_2024Oct.py), a new function named "Fix-DE" has been added. It does not optimize an MECP; instead, it locates the lowest-energy structure for state A, while its energy difference between state B is constrained to be the value set by *fix_dE* option. It is useful for searching for a structure with an IP or EA exactly controlled.

In this example, we are going to find the lowest-energy structure of 2,2',2''-(cyclopropane-1,2,3-triylidene)trimalononitrile dianion with the constraint that its redox potential should be 0.4 V versus NHE. Although redox potential is a concept related to free energy, by taking an approximation, we could expect that locating a structure with the first ionization energy (IP) of 4.68 eV (the absolute level of NHE is 4.28 eV) would be interesting. The corresponding input file is shown as below and unrelevant options are omitted:

```
nprocs = 28
mem = 48GB # change this into the maxcore value for orca
method = wb97xd def2svp scrf=(smd,solvent=acetonitrile) g09default scf=
(xqc,maxcycle=64)
charge = -2
mult1 = 1
mult2 = 2
mode = normal #normal; stable; read; inter_read; noread
fix_dE = -4.68 # fix-dE opt: set the value to be the target dE (eV). When it is zero,
a normal MECP optimization will be performed.
charge2 = -1
program = gaussian  #gaussian, orca, xtb
gau_comm = 'g16'

*geom
@C6CN6_vertRed.log
*
```

The key point is to set *fix_dE* to be -4.68 eV: the target *E*(state A) - *E*(state B) value. By setting *charge2* (which is only useful in fix-dE calculations), the charge and spin multiplicity is set to be -2/1 and -1/2 for the two states, respectively. In gometry part, an external file for the optimized dianion is included.

After 60 iterations, the convergence is achieved. The outputted information is slightly different from a common MECP calculation:

```
Now Entering GDIIS Step 59
The current multiplier for fix-dE optimization is [1.7553588432420713]
0.005840734526385636
E1 = -785.032607425
E2 = -784.860703739
deltaE  (eV)              -4.677758
deviation of dE (a.u.)    0.000082     0.000050     NO
RMS Gradient              0.000143     0.000500     YES
Maximium Gradient         0.000450     0.000700     YES
RMS Displacement          0.000795     0.002500     YES
Maximium Displacement     0.002273     0.004000     YES

Now Entering GDIIS Step 60
The current multiplier for fix-dE optimization is [1.7590554857255418]
0.007965048544876348
E1 = -785.032634508
E2 = -784.86069464
deltaE  (eV)              -4.678742
deviation of dE (a.u.)    0.000046     0.000050     YES
RMS Gradient              0.000160     0.000500     YES
Maximium Gradient         0.000431     0.000700     YES
RMS Displacement          0.001084     0.002500     YES
Maximium Displacement     0.003486     0.004000     YES
****Congrats! MECP has converged****
```