**LookForMECP 2.0 Manual.**

**A brief introduction:**

LookForMECP 2.0 is a program mainly designed to locating MECP.

**Operating system:**

Linux (64 bits). Test calculation is completed under fedora 23.

**Environmental requirements:**

Gaussian 09 or Gaussian 16 is installed on the computer.

**Input File:**

The input file of LookForMECP 2.0 is like the input file of the Guassian program, which was changed in three parts.

1. % Section:

If .chk files need to be read in the calculation process, the following commands are given in the %Section part.

%chk=state1.chk state2.chk

“state1.chk” and “state2.chk” are chk file names corresponding to two states respectively, and the two filenames are separated by spaces.

1. Route Section:

The key words related to MECP calculation are added in braces. For details, see list of keywords.

1. Charge & Multipl.:

The charge, the spin multiplicity of the first state and the spin multiplicity of the second state are given respectively, and they are separated by spaces.

A typical LookForMECP input file:

%chk=State1.chk State2.chk

%mem=60gb

%nprocshared=16

#p b3lyp/aug-cc-pvtz scf=maxcycle=999 {task=mecp method=ln hessianN=5 stepSize=0.1 Lambda=1.17 mecpFreq=liu}

MECP

0 1 3

H

N 1 B1

C 2 B2 1 A1

O 3 B3 2 A2 1 D1 0

B1 = 1.03289

B2 = 1.609249

B3 = 1.13

A1 = 103.080264

A2 = 113.938387

D1 = 179.998702

**List of keywords:**

All keywords and parameters are not case sensitive, and they are separated by “=”.

## **task**: Computational tasks.

= mecp: Optimizing MECP.

## **cmd**: Command of external *ab initio* program.

= g16: gaussian 16.

= g09: gaussian 09.

## **method**: Methods for optimizing MECP.

= ln: Lagrange-Newton method. This is the default.

## **cyc**: The maximum number of optimization steps.

## **stepSize**: The maximum size for an optimization step.

## **hessianN**: Hessian matrix is calculated every N step. If Hessian matrix is not calculated, it will be guessed.

= N: Setting the N value.

## **guessHessian**: Method for guessing Hessian matrix

= bfgs: Broyden–Fletcher–Goldfarb–Shanno algorithm. This is the default.

= powell: Powell algorithm.

## **energyCon**: Specifies the convergence criteria derived from the energy difference. The default value is 0.00001 hartree.

## **maxCon**: Specifies the convergence criteria of maximum force. The default value is 0.001 a.u..

## **rmsCon**: Specifies the convergence criteria of root mean square force. The default value is 0.0005 a.u..

## **Lambda**: The initial value of Lagrange multiplier.

## **mecpFreq**: Check the sufficient condition of MECP.

= liu: Constrained frequency analysis using the above-mentioned method. This is the default.

= simple: Check sufficient conditions without constrained frequency analysis.

**Output File:**

There are three important information in the output file, as follows.

(1) Necessary condition.

Item Value Threshold Converged?

Delta Energy -9.30000E-006 1E-05 Yes

Maximum KKT Force 0.000377 0.001 Yes

RMS KKT Force 0.000155 0.0005 Yes

“Delta Energy” gives the energy difference between the two states. “Maximum KKT Force” and “RMS KKT Force” are the maximum KKT force and the root-mean-square KKT force respectively.

(2) *KKT* point information

bnulk@foxmail.com-MECP Result

\*\*\*\*\*\*\*\*\*\*\*\*\*\*\*\*\*\*\*\*\*\*\*\*\*\*\*\*\*\*\*\*\*\*\*\*\*\*\*\*\*\*\*\*\*

Energy = -168.6070306

Lambda = 1.4178592621661

-Lambda/(1-Lambda) = 3.39315025546209

Gradient ratio between two states:

B1 = smallGradient

B2 = 3.4

B3 = 3.47

A1 = smallGradient

A2 = 3.39

D1 = smallGradient

“Energy” is the average energy of the two states at *KKT* point. “Lambda” is Lagrange multiplier. “The gradients of two state are proportional at MECP” is another expression of the necessary condition for MECP points. For details, please refer to “Koga, N.; Morokuma, K. *Chem. Phys. Lett.* **1985**, *119*, 371.” and “Liu, K.; Li, Y.; Su, J.; Wang, B. *J. Comput. Chem.* **2014**, *35*, 703.”.