Supplementary Information

Bias-Induced NO Adsorption and Configurational Transitions on Cu(110): A Machine Learning enhanced First-Principles Grand Canonical Study

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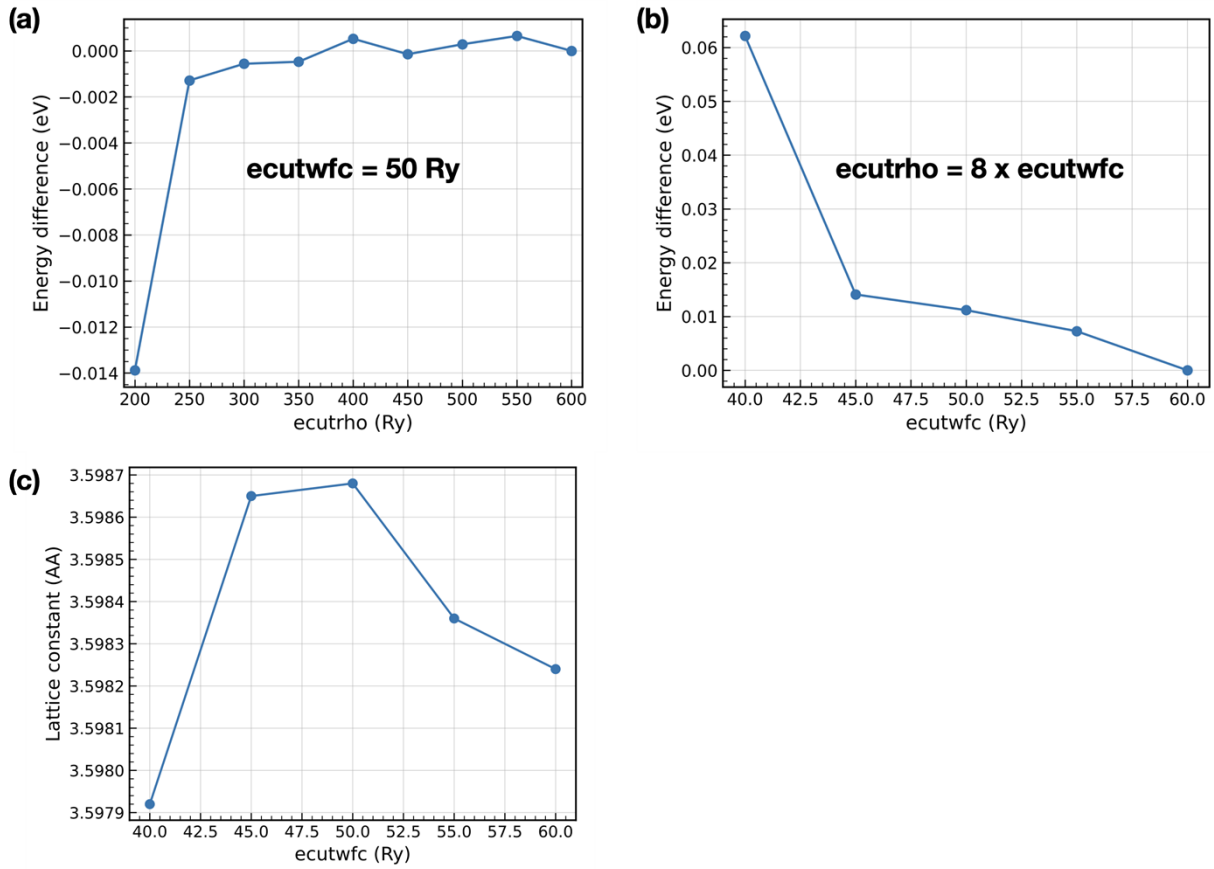

Fig S1. (a) Energy change of isolated NO as a function of the augmented charge density cutoff (ecutrho), with the wave function cutoff fixed at ecutwfc = 50 Ry. (b) Energy change of isolated NO as a function of the wave function cutoff (ecutwfc). (c) Lattice constant of bulk fcc Cu as a function of ecutwfc.

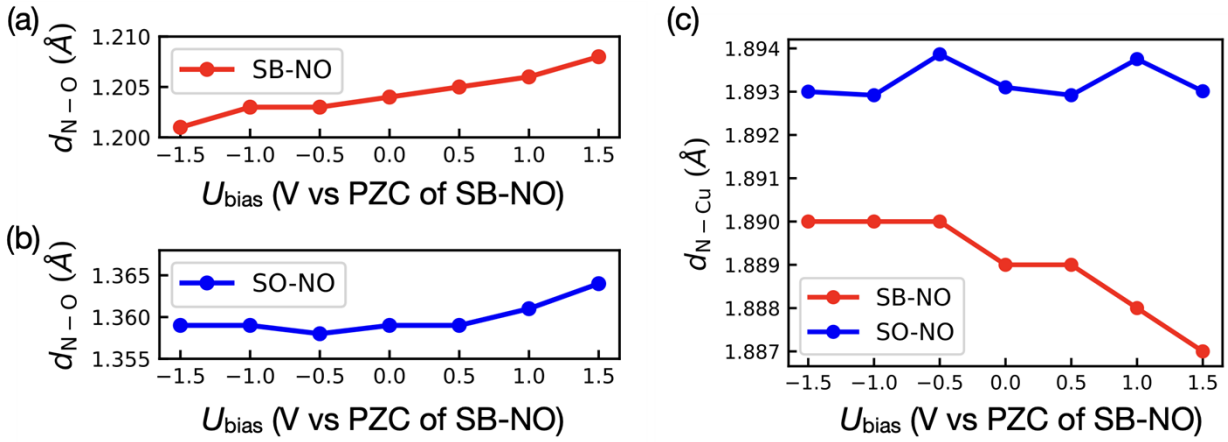

Fig. S2. NO bond length (d_{N-O}) of (a) SB-NO and (b) SO-NO, along with the (c) average bond length between the N atom and the nearest surface Cu atoms (d_{N-Cu}), as a function of the applied GCE bias voltage (U_{bias}) relative to the PZC of SB-NO.

S1. QE input for SB-NO with +1V bias

```
&CONTROL
calculation      = 'relax'
outdir = './out/'
prefix = 'no'
pseudo_dir       = '/home/thanhpn/QE/pslibrary.1.0.0/pbe/PSEUDOPOTENTIALS/'
restart_mode = 'restart'
/
&SYSTEM
ecutwfc          = 50
ecutrho          = 400
occupations      = 'smearing'
degauss          = 0.01
smearing         = 'cold'
nspin            = 1
```

```
input_dft        = 'vdW-DF3-opt1'
assume_isolated  = 'esm'
esm_bc           = 'bc3'
ntyp             = 3
nat              = 44
ibrav            = 0
lgcscf = .TRUE.
gcscf_mu = -4.1454
gcscf_conv_thr = 1.d-3
/
&ELECTRONS
conv_thr         = 1e-07
mixing_mode      = 'local-TF'
mixing_beta      = 0.3
/
&IONS
ion_dynamics     = 'bfgs'
/
&CELL
cell_dynamics    = 'bfgs'
/

ATOMIC_SPECIES
Cu 63.546 Cu.pbe-dn-rrkjus_psl.1.0.0.UPF
O 15.999 O.pbe-n-rrkjus_psl.1.0.0.UPF
N 14.007 N.pbe-n-rrkjus_psl.1.0.0.UPF

K_POINTS automatic
6 6 1  1 1 0

CELL_PARAMETERS angstrom
```

7.15600000000000 0.00000000000000 0.00000000000000

0.00000000000000 7.59008418925640 0.00000000000000

0.00000000000000 0.00000000000000 32.54551370160000

ATOMIC_POSITIONS angstrom

Cu	0.0000000000	0.0000000000	-2.5299579054	0	0	0
Cu	3.5780000000	0.0000000000	-2.5299579054	0	0	0
Cu	0.0000000000	2.5300280631	-2.5299579054	0	0	0
Cu	3.5780000000	2.5300280631	-2.5299579054	0	0	0
Cu	0.0000000000	5.0600561262	-2.5299579054	0	0	0
Cu	3.5780000000	5.0600561262	-2.5299579054	0	0	0
Cu	1.7890000000	1.2650140315	-1.2649438738	0	0	0
Cu	5.3670000000	1.2650140315	-1.2649438738	0	0	0
Cu	1.7890000000	3.7950420946	-1.2649438738	0	0	0
Cu	5.3670000000	3.7950420946	-1.2649438738	0	0	0
Cu	1.7890000000	6.3250701577	-1.2649438738	0	0	0
Cu	5.3670000000	6.3250701577	-1.2649438738	0	0	0
Cu	0.0000000000	0.0000000000	0.0000701577	0	0	0
Cu	3.5780000000	0.0000000000	0.0000701577	0	0	0
Cu	0.0000000000	2.5300280631	0.0000701577	0	0	0
Cu	3.5780000000	2.5300280631	0.0000701577	0	0	0
Cu	0.0000000000	5.0600561262	0.0000701577	0	0	0
Cu	3.5780000000	5.0600561262	0.0000701577	0	0	0
Cu	1.7890000000	1.2650140315	1.2650841893	0	0	0
Cu	5.3670000000	1.2650140315	1.2650841893	0	0	0
Cu	1.7890000000	3.7950420946	1.2650841893	0	0	0
Cu	5.3670000000	3.7950420946	1.2650841893	0	0	0
Cu	1.7890000000	6.3250701577	1.2650841893	0	0	0
Cu	5.3670000000	6.3250701577	1.2650841893	0	0	0
O	0.0007536041	1.2828188262	7.6317980662			
N	0.0062065726	1.2830477445	6.4252411992			

Cu	0.0087087388	-0.0266675301	5.0598083282
Cu	3.5855218221	0.0176779431	4.9491007889
Cu	0.0073611256	2.5914428035	5.0593086152
Cu	3.5856228740	2.5490021771	4.9488036871
Cu	0.0077121465	5.0777059915	4.9720195572
Cu	3.5860280452	5.0781135666	4.9558294991
Cu	1.8164995600	1.2779701112	3.7844531339
Cu	5.3520215647	1.2779225071	3.7841854622
Cu	1.7866995139	3.8017819166	3.8227068973
Cu	5.3825024149	3.8018467166	3.8224445318
Cu	1.7875375531	6.3446713030	3.8227995642
Cu	5.3821814040	6.3452065570	3.8230024487
Cu	0.0036256244	0.0107705275	2.5495158028
Cu	3.5808943035	-0.0048086515	2.5044837162
Cu	0.0035914201	2.5314928533	2.5489822414
Cu	3.5808240913	2.5457928714	2.5042610156
Cu	0.0032199949	5.0660884673	2.5152401044
Cu	3.5811515855	5.0651604847	2.5244624781

S2. QE input for SO-NO with +1V bias

```
&CONTROL
calculation      = 'relax'
outdir = './out/'
prefix = 'no'
pseudo_dir       = '/home/thanhpn/QE/pslibrary.1.0.0/pbe/PSEUDOPOTENTIALS/'
restart_mode = 'restart'
/
&SYSTEM
ecutwfc          = 50
ecutrho          = 400
```

```
occupations      = 'smearing'
degauss          = 0.01
smearing         = 'cold'
nspin            = 1
input_dft        = 'vdW-DF3-opt1'
assume_isolated  = 'esm'
esm_bc           = 'bc3'
ntyp             = 3
nat              = 44
ibrav            = 0
lgcscf = .TRUE.
gcscf_mu = -4.1454
gcscf_conv_thr = 1.d-3
/
&ELECTRONS
conv_thr         = 1e-07
mixing_mode      = 'local-TF'
mixing_beta      = 0.3
/
&IONS
ion_dynamics     = 'bfgs'
/
&CELL
cell_dynamics    = 'bfgs'
/

ATOMIC_SPECIES
Cu 63.546 Cu.pbe-dn-rrkjus_psl.1.0.0.UPF
O 15.999 O.pbe-n-rrkjus_psl.1.0.0.UPF
N 14.007 N.pbe-n-rrkjus_psl.1.0.0.UPF
```

K_POINTS automatic

6 6 1 1 1 0

CELL_PARAMETERS angstrom

7.15600000000000 0.00000000000000 0.00000000000000

0.00000000000000 7.59008418925640 0.00000000000000

0.00000000000000 0.00000000000000 32.54551370160000

ATOMIC_POSITIONS angstrom

Cu	0.0000000000	0.0000000000	-2.5299579054	0	0	0
Cu	3.5780000000	0.0000000000	-2.5299579054	0	0	0
Cu	0.0000000000	2.5300280631	-2.5299579054	0	0	0
Cu	3.5780000000	2.5300280631	-2.5299579054	0	0	0
Cu	0.0000000000	5.0600561262	-2.5299579054	0	0	0
Cu	3.5780000000	5.0600561262	-2.5299579054	0	0	0
Cu	1.7890000000	1.2650140315	-1.2649438738	0	0	0
Cu	5.3670000000	1.2650140315	-1.2649438738	0	0	0
Cu	1.7890000000	3.7950420946	-1.2649438738	0	0	0
Cu	5.3670000000	3.7950420946	-1.2649438738	0	0	0
Cu	1.7890000000	6.3250701577	-1.2649438738	0	0	0
Cu	5.3670000000	6.3250701577	-1.2649438738	0	0	0
Cu	0.0000000000	0.0000000000	0.0000701577	0	0	0
Cu	3.5780000000	0.0000000000	0.0000701577	0	0	0
Cu	0.0000000000	2.5300280631	0.0000701577	0	0	0
Cu	3.5780000000	2.5300280631	0.0000701577	0	0	0
Cu	0.0000000000	5.0600561262	0.0000701577	0	0	0
Cu	3.5780000000	5.0600561262	0.0000701577	0	0	0
Cu	1.7890000000	1.2650140315	1.2650841893	0	0	0
Cu	5.3670000000	1.2650140315	1.2650841893	0	0	0
Cu	1.7890000000	3.7950420946	1.2650841893	0	0	0
Cu	5.3670000000	3.7950420946	1.2650841893	0	0	0

Cu 1.7890000000 6.3250701577 1.2650841893 0 0 0
Cu 5.3670000000 6.3250701577 1.2650841893 0 0 0
O 2.4711251193 1.2831072140 6.1850147707
N 1.1738078374 1.2815034517 5.7470207062
Cu 0.0362430281 -0.0593610299 5.0392235020
Cu 3.6289571152 -0.0005432251 5.0629710777
Cu 0.0340926521 2.6187012281 5.0373180071
Cu 3.6264829885 2.5679578285 5.0612511019
Cu 0.0147718403 5.0755321410 4.9641148940
Cu 3.5884075759 5.0784684338 4.9625667195
Cu 1.7822858682 1.2789393310 3.7359476320
Cu 5.3757389214 1.2778868972 3.8245944471
Cu 1.8108809449 3.8332076758 3.7816214441
Cu 5.3699702856 3.7870688915 3.8541204316
Cu 1.8114589048 6.3152690028 3.7829334346
Cu 5.3707209350 6.3593290390 3.8544143387
Cu -0.0133723937 0.0024504144 2.5322478377
Cu 3.5910621763 0.0090919260 2.5394116621
Cu -0.0138812533 2.5412161075 2.5320613978
Cu 3.5912507473 2.5341035043 2.5394769644
Cu -0.0193474972 5.0664806010 2.5207919019
Cu 3.6010152451 5.0662046488 2.5180035503

S3. QE input for SB-NO with -0.1e

&CONTROL
calculation = 'relax'
disk_io = 'none'
pseudo_dir = '/home/thanhpn/QE/pslibrary.1.0.0/pbe/PSEUDOPOTENTIALS/'
/
&SYSTEM
ecutwfc = 50

```
ecutrho          = 400
occupations      = 'smearing'
degauss          = 0.01
smearing         = 'cold'
nspin            = 1
input_dft        = 'vdW-DF3-opt1'
assume_isolated  = 'esm'
esm_bc           = 'bc3'
tot_charge = -0.1,
ntyp             = 3
nat              = 44
ibrav            = 0
/
&ELECTRONS
conv_thr         = 1e-07
mixing_mode      = 'plain'
mixing_beta      = 0.3
/
&IONS
ion_dynamics     = 'bfgs'
/
&CELL
cell_dynamics    = 'bfgs'
/

ATOMIC_SPECIES
Cu 63.546 Cu.pbe-dn-rrkjus_psl.1.0.0.UPF
O 15.999 O.pbe-n-rrkjus_psl.1.0.0.UPF
N 14.007 N.pbe-n-rrkjus_psl.1.0.0.UPF

K_POINTS automatic
```

6 6 1 1 1 0

CELL_PARAMETERS angstrom

7.15600000000000 0.00000000000000 0.00000000000000

0.00000000000000 7.59008418925640 0.00000000000000

0.00000000000000 0.00000000000000 32.54551370160000

ATOMIC_POSITIONS angstrom

Cu	3.5813351705	5.0650099596	2.5234310854			
Cu	0.0000000000	0.0000000000	-2.5299579054	0	0	0
Cu	3.5780000000	0.0000000000	-2.5299579054	0	0	0
Cu	0.0000000000	2.5300280631	-2.5299579054	0	0	0
Cu	3.5780000000	2.5300280631	-2.5299579054	0	0	0
Cu	0.0000000000	5.0600561262	-2.5299579054	0	0	0
Cu	3.5780000000	5.0600561262	-2.5299579054	0	0	0
Cu	1.7890000000	1.2650140315	-1.2649438738	0	0	0
Cu	5.3670000000	1.2650140315	-1.2649438738	0	0	0
Cu	1.7890000000	3.7950420946	-1.2649438738	0	0	0
Cu	5.3670000000	3.7950420946	-1.2649438738	0	0	0
Cu	1.7890000000	6.3250701577	-1.2649438738	0	0	0
Cu	5.3670000000	6.3250701577	-1.2649438738	0	0	0
Cu	0.0000000000	0.0000000000	0.0000701577	0	0	0
Cu	3.5780000000	0.0000000000	0.0000701577	0	0	0
Cu	0.0000000000	2.5300280631	0.0000701577	0	0	0
Cu	3.5780000000	2.5300280631	0.0000701577	0	0	0
Cu	0.0000000000	5.0600561262	0.0000701577	0	0	0
Cu	3.5780000000	5.0600561262	0.0000701577	0	0	0
Cu	1.7890000000	1.2650140315	1.2650841893	0	0	0
Cu	5.3670000000	1.2650140315	1.2650841893	0	0	0
Cu	1.7890000000	3.7950420946	1.2650841893	0	0	0
Cu	5.3670000000	3.7950420946	1.2650841893	0	0	0

Cu 1.7890000000 6.3250701577 1.2650841893 0 0 0
Cu 5.3670000000 6.3250701577 1.2650841893 0 0 0
O 0.0006506065 1.2827451407 7.6337789574
N 0.0063118993 1.2832083832 6.4226727922
Cu 0.0091239313 -0.0284302821 5.0611039603
Cu 3.5859974526 0.0185139160 4.9486214090
Cu 0.0076942926 2.5933917337 5.0607875660
Cu 3.5861078995 2.5493558810 4.9485783967
Cu 0.0080448563 5.0780795110 4.9712548093
Cu 3.5865255466 5.0787021557 4.9545919333
Cu 1.8163209312 1.2781113194 3.7853563102
Cu 5.3528296127 1.2781143844 3.7848049947
Cu 1.7870465778 3.8019972349 3.8243735911
Cu 5.3830288208 3.8020806301 3.8240930675
Cu 1.7879449712 6.3450166781 3.8246057412
Cu 5.3826643722 6.3456144473 3.8247697065
Cu 0.0037777696 0.0102482205 2.5498667778
Cu 3.5809806244 -0.0052282364 2.5041147179
Cu 0.0037488062 2.5316890074 2.5492641253
Cu 3.5808878887 2.5458843225 2.5040729443
Cu 0.0033938005 5.0660527987 2.5147560183
Cu 3.5813280636 5.0650294817 2.5233597928

S4. QE input for SO-NO with -0.1e

```
&CONTROL
calculation      = 'relax'
disk_io          = 'none'
pseudo_dir       = '/home/thanhpn/QE/pslibrary.1.0.0/pbe/PSEUDOPOTENTIALS/'
/
&SYSTEM
ecutwfc          = 50
ecutrho          = 400
```

```
occupations      = 'smearing'
degauss          = 0.01
smearing         = 'cold'
nspin            = 1
input_dft        = 'vdW-DF3-opt1'
assume_isolated  = 'esm'
esm_bc           = 'bc3'
tot_charge = -0.1,
ntyp             = 3
nat              = 44
ibrav            = 0
/
&ELECTRONS
conv_thr         = 1e-07
mixing_mode      = 'plain'
mixing_beta      = 0.3
/
&IONS
ion_dynamics     = 'bfgs'
/
&CELL
cell_dynamics    = 'bfgs'
/

ATOMIC_SPECIES
Cu 63.546 Cu.pbe-dn-rrkjus_psl.1.0.0.UPF
O 15.999 O.pbe-n-rrkjus_psl.1.0.0.UPF
N 14.007 N.pbe-n-rrkjus_psl.1.0.0.UPF

K_POINTS automatic
6 6 1  1 1 0
```

CELL_PARAMETERS angstrom

7.15600000000000 0.00000000000000 0.00000000000000

0.00000000000000 7.59008418925640 0.00000000000000

0.00000000000000 0.00000000000000 32.54551370160000

ATOMIC_POSITIONS angstrom

O	2.4735216081	1.2830970045	6.1865847184			
N	1.1715853515	1.2814386232	5.7464145984			
Cu	0.0000000000	0.0000000000	-2.5299579054	0	0	0
Cu	3.5780000000	0.0000000000	-2.5299579054	0	0	0
Cu	0.0000000000	2.5300280631	-2.5299579054	0	0	0
Cu	3.5780000000	2.5300280631	-2.5299579054	0	0	0
Cu	0.0000000000	5.0600561262	-2.5299579054	0	0	0
Cu	3.5780000000	5.0600561262	-2.5299579054	0	0	0
Cu	1.7890000000	1.2650140315	-1.2649438738	0	0	0
Cu	5.3670000000	1.2650140315	-1.2649438738	0	0	0
Cu	1.7890000000	3.7950420946	-1.2649438738	0	0	0
Cu	5.3670000000	3.7950420946	-1.2649438738	0	0	0
Cu	1.7890000000	6.3250701577	-1.2649438738	0	0	0
Cu	5.3670000000	6.3250701577	-1.2649438738	0	0	0
Cu	0.0000000000	0.0000000000	0.0000701577	0	0	0
Cu	3.5780000000	0.0000000000	0.0000701577	0	0	0
Cu	0.0000000000	2.5300280631	0.0000701577	0	0	0
Cu	3.5780000000	2.5300280631	0.0000701577	0	0	0
Cu	0.0000000000	5.0600561262	0.0000701577	0	0	0
Cu	3.5780000000	5.0600561262	0.0000701577	0	0	0
Cu	1.7890000000	1.2650140315	1.2650841893	0	0	0
Cu	5.3670000000	1.2650140315	1.2650841893	0	0	0
Cu	1.7890000000	3.7950420946	1.2650841893	0	0	0
Cu	5.3670000000	3.7950420946	1.2650841893	0	0	0

Cu	1.7890000000	6.3250701577	1.2650841893	0	0	0
Cu	5.3670000000	6.3250701577	1.2650841893	0	0	0
Cu	0.0360428514	-0.0596090367	5.0394752108			
Cu	3.6292746586	-0.0011512420	5.0627168942			
Cu	0.0338297467	2.6188338807	5.0375911774			
Cu	3.6268652677	2.5683261327	5.0610426480			
Cu	0.0147086463	5.0754895025	4.9642801909			
Cu	3.5879878330	5.0783973084	4.9626056721			
Cu	1.7820063221	1.2787978950	3.7363503962			
Cu	5.3757151935	1.2777620357	3.8250667006			
Cu	1.8107996475	3.8330168935	3.7822305016			
Cu	5.3700049229	3.7870045343	3.8545230158			
Cu	1.8113444138	6.3152995759	3.7834616654			
Cu	5.3707265743	6.3593483257	3.8548542434			
Cu	-0.0134056468	0.0022588572	2.5322842278			
Cu	3.5907440528	0.0089672231	2.5396234983			
Cu	-0.0138957885	2.5412902155	2.5320018249			
Cu	3.5909096514	2.5341122653	2.5395417041			
Cu	-0.0194670229	5.0665125302	2.5207672206			
Cu	3.6008612161	5.0662297702	2.5176755663			

S5. Catlearn input for NEB

```
from ase.io import read
from ase.neb import NEB
from ase.optimize import MDMin
from ase.calculators.espresso import Espresso
from catlearn.optimize.mlneb import MLNEB
from ase.neb import NEBTools
from ase.parallel import parprint
from catlearn.optimize.tools import plotneb
```

```
import copy


pseudopotentials = {'N': 'N.pbe-n-rrkjus_psl.1.0.0.UPF',
                    'O': 'O.pbe-n-rrkjus_psl.1.0.0.UPF',
                    'Cu': 'Cu.pbe-dn-rrkjus_psl.1.0.0.UPF'}

pseudo_dir='/home/thanhpn/QE/pslibrary.1.0.0/pbe/PSEUDOPOTENTIALS/'

input_data = {
   'system': {
      'ecutwfc': 50,
      'ecutrho': 400,
      'assume_isolated': 'esm',
      'esm_bc':'bc3',
      'tot_charge' : -0.1,
      'input_dft': 'vdW-DF3-opt1',
      'occupations' : 'smearing',
      'degauss': 0.01,
      'smearing': 'cold'},
   'ions': {
      'ion_dynamics': 'bfgs'},
   'cell': {
      'cell_dynamics':'bfgs'}   }

calc = Espresso(calculation = 'scf',input_data=input_data, disk_io = 'none',
                pseudopotentials=pseudopotentials, tprnfor = True,
                kpts = (6,6,1), nspin = 1,koffset = (1, 1,0),
                mixing_mode = 'plain', mixing_beta =0.3, conv_thr =1.0e-7,
                pseudo_dir=pseudo_dir)
```

```
n_images = 7

neb_catlearn = MLNEB(start='sb.traj',
                     end='so.traj',
                     ase_calc=calc,
                     n_images=n_images,
                     interpolation='idpp', restart=False)

neb_catlearn.run(fmax=0.05, trajectory='ML-NEB.traj',  sequential=True, full_output= True)
```