Contents

NfO-TEMPO-Me parameters

The complete sets of parameters for the NfO-TEMPO-Me (4-naphthoyloxy-1-methoxy-2,2,6,6-tetramethylpiperidine) ground and electronically excited state are reported.
The topologies are specified in the Gromacs 4.5.4 "`.top`" format[1] and they can be used directly for MD simulations in gas phase. The atomic charges were obtained through the CM5 procedure[2] from the equilibrium geometries, while the *sigma* and *epsilon* values are taken from similar atomtypes in the OPLS AA force field[3,4].
All the parameters are obtained and written directly in the Gromacs format by the Joyce 2.0 package[5,6].

Atom numbering

See Fig. 1 for the atom numbers and the paper for the atomtype definitions.

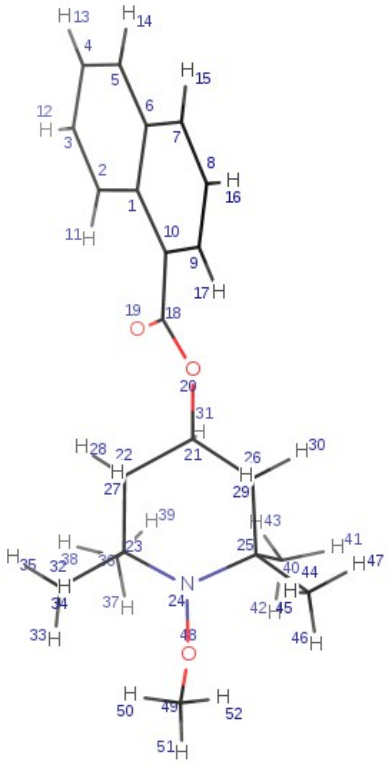

Fig. 1: The NfO-TEMPO-Me molecule and the atom numbers used in the topology files.

Ground state GROMACS topology

```
[ defaults ]
 ; nbfunc   comb-rule   gen-pairs  fudgeLJ  fudgeQQ
     1        3          no         1.0        1.0

 [ atomtypes ]
 ; name   mass       charge ptype   sigma       espilon
   C1     12.0110    0.000  A    3.55000e-01  2.92880e-01
   C2     12.0110    0.000  A    3.55000e-01  2.92880e-01
   C3     12.0110    0.000  A    3.55000e-01  2.92880e-01
   Cc     12.0110    0.000  A    3.55000e-01  3.17984e-01
   Ct1    12.0110    0.000  A    3.50000e-01  2.76144e-01
   Ct2    12.0110    0.000  A    3.50000e-01  2.76144e-01
   Ctn    12.0110    0.000  A    3.50000e-01  2.76144e-01
   Ct     12.0110    0.000  A    3.50000e-01  2.76144e-01
   Co     12.0110    0.000  A    3.75000e-01  4.39320e-01
   O      15.9994    0.000  A    2.90000e-01  5.85760e-01
   Oc     15.9994    0.000  A    2.96000e-01  8.78640e-01
   On     15.9994    0.000  A    2.96000e-01  8.78640e-01
   Nt     14.0070    0.000  A    3.25000e-01  7.11280e-01
   H2      1.0079    0.000  A    2.42000e-01  1.25520e-01
   H3      1.0079    0.000  A    2.42000e-01  1.25520e-01
   Ha      1.0079    0.000  A    2.42000e-01  1.25520e-01
   Ht      1.0079    0.000  A    2.50000e-01  1.25520e-01
   Ht1     1.0079    0.000  A    2.50000e-01  1.25520e-01
   Ht2     1.0079    0.000  A    2.50000e-01  1.25520e-01

 [ moleculetype ]
 ; Name            nrexcl
nft         3

 [ atoms ]
 ; nr  type resnr res  atom  cgnr     charge     mass
   1   C1     1   nft   C1     1     0.000982  12.01100
   2   C2     1   nft   C2     2    -0.099993  12.01100
   3   C3     1   nft   C3     3    -0.101094  12.01100
   4   C3     1   nft   C3     4    -0.105663  12.01100
   5   C2     1   nft   C2     5    -0.101451  12.01100
   6   C1     1   nft   C1     6    -0.011475  12.01100
   7   C2     1   nft   C2     7    -0.086975  12.01100
   8   C3     1   nft   C3     8    -0.107463  12.01100
   9   C3     1   nft   C3     9    -0.088407  12.01100
  10   Cc     1   nft   Cc    10    -0.018322  12.01100
  11   H2     1   nft   H2    11     0.110523  1.00790
  12   Ha     1   nft   Ha    12     0.109367  1.00790
  13   Ha     1   nft   Ha    13     0.108965  1.00790
  14   Ha     1   nft   Ha    14     0.107837  1.00790
  15   Ha     1   nft   Ha    15     0.111799  1.00790
  16   Ha     1   nft   Ha    16     0.110430  1.00790
  17   H3     1   nft   H3    17     0.114614  1.00790
  18   Co     1   nft   Co    18     0.279924  12.01100
  19   O      1   nft   O     19    -0.320576  15.99940
  20   Oc     1   nft   Oc    20    -0.200854  15.99940
  21   Ct1    1   nft   Ct1   21     0.006497  12.01100
  22   Ct2    1   nft   Ct2   22    -0.166489  12.01100
  23   Ctn    1   nft   Ctn   23     0.080752  12.01100
```

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  24   Nt     1   nft   Nt    24    -0.274850  14.00700
  25   Ctn    1   nft   Ctn   25     0.080579  12.01100
  26   Ct2    1   nft   Ct2   26    -0.163912  12.01100
  27   Ht2    1   nft   Ht2   27     0.101499  1.00790
  28   Ht2    1   nft   Ht2   28     0.105740  1.00790
  29   Ht2    1   nft   Ht2   29     0.102898  1.00790
  30   Ht2    1   nft   Ht2   30     0.104054  1.00790
  31   Ht1    1   nft   Ht1   31     0.113649  1.00790
  32   Ct     1   nft   Ct    37    -0.251421  12.01100
  33   Ht     1   nft   Ht    38     0.095145  1.00790
  34   Ht     1   nft   Ht    39     0.092548  1.00790
  35   Ht     1   nft   Ht    40     0.092732  1.00790
  36   Ct     1   nft   Ct    41    -0.258818  12.01100
  37   Ht     1   nft   Ht    42     0.096106  1.00790
  38   Ht     1   nft   Ht    43     0.092560  1.00790
  39   Ht     1   nft   Ht    44     0.090623  1.00790
  40   Ct     1   nft   Ct    45    -0.259616  12.01100
  41   Ht     1   nft   Ht    46     0.090612  1.00790
  42   Ht     1   nft   Ht    47     0.097137  1.00790
  43   Ht     1   nft   Ht    48     0.089517  1.00790
  44   Ct     1   nft   Ct    49    -0.251666  12.01100
  45   Ht     1   nft   Ht    50     0.092806  1.00790
  46   Ht     1   nft   Ht    51     0.095466  1.00790
  47   Ht     1   nft   Ht    52     0.091722  1.00790
  48   On     1   nft   On    32    -0.157050  15.99940
  49   Ct     1   nft   Ct    33    -0.145314  12.01100
  50   Ht     1   nft   Ht    34     0.098255  1.00790
  51   Ht     1   nft   Ht    35     0.108139  1.00790
  52   Ht     1   nft   Ht    36     0.097932  1.00790

; Stretchings
[ bonds ]
      1     2   1     0.1421     295428.277
      2     3   1     0.1376     389704.417
      3     4   1     0.1411     334055.220
      4     5   1     0.1373     389704.417
      1     6   1     0.1433     214674.769
      5     6   1     0.1418     295428.277
      6     7   1     0.1417     295428.277
      7     8   1     0.1373     389704.417
      8     9   1     0.1407     334055.220
      1    10   1     0.1437     255388.900
      9    10   1     0.1384     350687.318
      2    11   1     0.1083     348251.793
      3    12   1     0.1088     336716.460
      4    13   1     0.1087     336716.460
      5    14   1     0.1089     331717.248
      7    15   1     0.1089     331717.248
      8    16   1     0.1087     336716.460
      9    17   1     0.1085     343833.699
     10    18   1     0.1492     203433.885
     18    19   1     0.1212     670324.835
     18    20   1     0.1345     293586.495
     20    21   1     0.1439     238984.170
     21    22   1     0.1516     227593.665
     22    23   1     0.1535     193608.595
     23    24   1     0.1485     205311.077
     24    25   1     0.1484     205311.077
     21    26   1     0.1513     227593.665
```

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      25    26   1      0.1535     193608.595
      22    27   1      0.1098     312688.400
      22    28   1      0.1095     312688.400
      26    29   1      0.1098     312688.400
      26    30   1      0.1096     312688.400
      21    31   1      0.1094     313756.075
      23    32   1      0.1532     187859.978
      32    33   1      0.1094     317872.889
      32    34   1      0.1095     317872.889
      32    35   1      0.1096     317872.889
      23    36   1      0.1539     187859.978
      36    37   1      0.1094     317872.889
      36    38   1      0.1096     317872.889
      36    39   1      0.1092     317872.889
      25    40   1      0.1539     187859.978
      40    41   1      0.1096     317872.889
      40    42   1      0.1094     317872.889
      40    43   1      0.1092     317872.889
      25    44   1      0.1532     187859.978
      44    45   1      0.1095     317872.889
      44    46   1      0.1094     317872.889
      44    47   1      0.1096     317872.889
      24    48   1      0.1417     244404.989
      48    49   1      0.1413     249065.487
      49    50   1      0.1096     317872.889
      49    51   1      0.1095     317872.889
      49    52   1      0.1096     317872.889

; Bendings
[ angles ]
       1    2    3   1    120.94     462.7985
       2    1    6   1    117.73     580.7412
       2    1   10   1    124.36     804.8759
       1    2   11   1    118.76     276.2565
       2    3    4   1    121.13     647.7019
       3    2   11   1    120.30     340.6464
       2    3   12   1    119.29     291.3257
       3    4    5   1    119.51     647.7019
       4    3   12   1    119.58     349.9091
       3    4   13   1    120.10     349.9091
       4    5    6   1    120.94     462.7985
       5    4   13   1    120.40     291.3257
       4    5   14   1    120.61     358.0181
       1    6    5   1    119.75     580.7412
       1    6    7   1    120.01     580.7412
       6    1   10   1    117.90     408.1189
       5    6    7   1    120.24     753.6716
       6    5   14   1    118.45     282.6840
       6    7    8   1    120.86     462.7985
       6    7   15   1    118.60     282.6840
       7    8    9   1    119.72     647.7019
       8    7   15   1    120.54     358.0181
       7    8   16   1    120.61     291.3257
       8    9   10   1    121.69     613.2843
       9    8   16   1    119.67     349.9091
       8    9   17   1    119.51     386.8791
       1   10    9   1    119.81     463.9117
       1   10   18   1    121.88     419.8719
      10    9   17   1    118.80     266.9345
```

9	10	18	1	118.30	575.1678
10	18	19	1	125.77	346.4522
10	18	20	1	111.84	194.3096
19	18	20	1	122.39	968.4915
18	20	21	1	117.04	726.7427
20	21	22	1	110.20	760.0122
20	21	26	1	106.82	760.0122
20	21	31	1	107.41	422.9746
21	22	23	1	112.58	594.8864
22	21	26	1	109.89	616.3931
21	22	27	1	108.08	404.5906
21	22	28	1	110.23	404.5906
22	21	31	1	110.70	352.3422
22	23	24	1	107.24	444.4157
23	22	27	1	109.03	378.2445
23	22	28	1	108.79	378.2445
22	23	32	1	107.79	543.0843
22	23	36	1	111.30	543.0843
23	24	25	1	118.91	626.2965
24	23	32	1	107.35	692.1551
24	23	36	1	115.20	692.1551
23	24	48	1	108.00	880.1386
24	25	26	1	107.23	444.4157
24	25	40	1	115.15	692.1551
24	25	44	1	107.40	692.1551
25	24	48	1	107.91	880.1386
21	26	25	1	112.53	594.8864
21	26	29	1	108.40	404.5906
21	26	30	1	110.38	404.5906
26	21	31	1	111.71	352.3422
25	26	29	1	108.97	378.2445
25	26	30	1	108.86	378.2445
26	25	40	1	111.37	543.0843
26	25	44	1	107.75	543.0843
27	22	28	1	108.03	332.6699
29	26	30	1	107.56	332.6699
23	32	33	1	111.02	364.1370
23	32	34	1	110.69	364.1370
23	32	35	1	109.71	364.1370
32	23	36	1	107.68	546.9719
33	32	34	1	109.05	311.1554
33	32	35	1	107.79	311.1554
34	32	35	1	108.50	311.1554
23	36	37	1	110.08	364.1370
23	36	38	1	109.30	364.1370
23	36	39	1	113.55	364.1370
37	36	38	1	108.10	311.1554
37	36	39	1	108.58	311.1554
38	36	39	1	107.06	311.1554
25	40	41	1	109.37	364.1370
25	40	42	1	110.03	364.1370
25	40	43	1	113.53	364.1370
40	25	44	1	107.64	546.9719
41	40	42	1	108.03	311.1554
41	40	43	1	107.32	311.1554
42	40	43	1	108.39	311.1554
25	44	45	1	110.67	364.1370
25	44	46	1	111.02	364.1370
25	44	47	1	109.75	364.1370

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     45   44   46   1    109.03     311.1554
     45   44   47   1    108.50     311.1554
     46   44   47   1    107.79     311.1554
     24   48   49   1    111.10     714.1289
     48   49   50   1    111.80     486.8403
     48   49   51   1    105.45     486.8403
     48   49   52   1    111.79     486.8403
     50   49   51   1    109.41     311.1554
     50   49   52   1    108.88     311.1554
     51   49   52   1    109.42     311.1554

; Torsions
[ dihedrals ]
;   napthalene harmonic
      1   2   3   4   2      0.0     53.573
      2   3   4   5   2      0.0     53.573
      3   4   5   6   2      0.0     53.573
      4   5   6   1   2      0.0     53.573
      2   1   6   5   2      0.0     53.573
      6   1   2   3   2      0.0     53.573
      6   7   8   9   2      0.0     53.573
      7   8   9  10   2      0.0     53.573
      8   9  10   1   2      0.0     53.573
      6   1  10   9   2      0.0     53.573
      1   6   7   8   2      0.0     53.573
     10   1   6   7   2      0.0     53.573
     10   1   6   5   2    180.0     53.573
      2   1   6   7   2    180.0     53.573
;   napthalene harmonic o.o.p.
     12   2   4   3   2      0.0    554.247
     13   3   5   4   2      0.0    554.247
     14   4   6   5   2      0.0    554.247
     15   6   8   7   2      0.0    554.247
     16   7   9   8   2      0.0    554.247
     17   8  10   9   2      0.0    554.247
     11   1   3   2   2      0.0    554.247
     10   1   9  18   2      0.0    583.337
;   d2 dihedral (harm)
     19  18  20  21   2      0.0     30.340
;   o.o.p. COO-nfo
     10  19  20  18   2      0.0    928.593
;   TEMPO ring
     20  21  22  23   1      0.00       8.953   3
     20  21  26  25   1      0.00       8.953   3
     26  21  22  23   1      0.00       0.980   3
     22  21  26  25   1      0.00       0.980   3
     22  23  24  25   1      0.00       0.980   3
     23  24  25  26   1      0.00       0.980   3
     21  22  23  24   1      0.00       0.980   3
     24  25  26  21   1      0.00       0.980   3
;   OCH3@TEMPO
     32  23  24  48   1      0.00       5.611   3
     36  23  24  48   1      0.00       5.611   3
     22  23  24  48   1      0.00      20.229   3
     48  24  25  26   1      0.00      20.229   3
;   CH3@TEMPO
     21  22  23  32   1      0.00       6.026   3
     32  23  24  25   1      0.00       0.980   3
     21  22  23  36   1      0.00       0.980   3
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     36  23  24  25   1      0.00       0.980   3
     40  25  26  21   1      0.00       0.980   3
     23  24  25  40   1      0.00       0.980   3
     44  25  26  21   1      0.00       0.980   3
     23  24  25  44   1      0.00       0.980   3
; -CH3@C24
     22  23  32  33   1      0.00       3.371   3
     22  23  32  34   1      0.00       3.371   3
     22  23  32  35   1      0.00       3.371   3
     24  23  32  33   1      0.00       3.801   3
     24  23  32  34   1      0.00       3.801   3
     24  23  32  35   1      0.00       3.801   3
     24  23  36  37   1      0.00       3.801   3
     24  23  36  38   1      0.00       3.801   3
     24  23  36  39   1      0.00       3.801   3
     22  23  36  37   1      0.00       3.371   3
     22  23  36  38   1      0.00       3.371   3
     22  23  36  39   1      0.00       3.371   3
; -CH3@C26
     24  25  40  41   1      0.00       3.801   3
     24  25  40  42   1      0.00       3.801   3
     24  25  40  43   1      0.00       3.801   3
     26  25  40  41   1      0.00       3.371   3
     26  25  40  42   1      0.00       3.371   3
     26  25  40  43   1      0.00       3.371   3
     24  25  44  45   1      0.00       3.801   3
     24  25  44  46   1      0.00       3.801   3
     24  25  44  47   1      0.00       3.801   3
     26  25  44  45   1      0.00       3.371   3
     26  25  44  46   1      0.00       3.371   3
     26  25  44  47   1      0.00       3.371   3
; CH3@NO
     24  48  49  50   1      0.00       4.391   3
     24  48  49  51   1      0.00       4.391   3
     24  48  49  52   1      0.00       4.391   3
;  d1 dihedral
      1  10  18  19   1      0.00      -1.374   1
      1  10  18  19   1      0.00      -3.513   2
      1  10  18  19   1      0.00      -0.136   3
      1  10  18  19   1      0.00       1.021   4
      9  10  18  20   1      0.00      -1.374   1
      9  10  18  20   1      0.00      -3.513   2
      9  10  18  20   1      0.00      -0.136   3
      9  10  18  20   1      0.00       1.021   4
;  d3 dihedral
     18  20  21  22   1      0.00      16.795   1
     18  20  21  22   1      0.00       7.218   2
     18  20  21  22   1      0.00       3.362   3
     18  20  21  22   1      0.00      -0.184   4
     18  20  21  26   1      0.00      16.795   1
     18  20  21  26   1      0.00       7.218   2
     18  20  21  26   1      0.00       3.362   3
     18  20  21  26   1      0.00      -0.184   4
;  d4 dihedral
     23  24  48  49   1      0.00      23.126   1
     23  24  48  49   1      0.00      22.487   2
     23  24  48  49   1      0.00       4.000   3
     23  24  48  49   1      0.00      13.548   4
     25  24  48  49   1      0.00      23.126   1
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     25   24   48   49    1      0.00      22.487   2
     25   24   48   49    1      0.00       4.000   3
     25   24   48   49    1      0.00      13.548   4

; Nonbonded terms
[ pairs ]
; other nb interactions
 18    23    2    1.000     0.280     0.081      0.3625       0.3483000
 18    24    2    1.000     0.280    -0.275      0.3500       0.5590000
 18    25    2    1.000     0.280     0.081      0.3625       0.3483000
 18    32    2    1.000     0.280    -0.251      0.3625       0.3483000
 18    36    2    1.000     0.280    -0.259      0.3625       0.3483000
 18    40    2    1.000     0.280    -0.260      0.3625       0.3483000
 18    44    2    1.000     0.280    -0.252      0.3625       0.3483000
 20    24    2    1.000    -0.201    -0.275      0.3105       0.7905400
 20    48    2    1.000    -0.201    -0.157      0.2960       0.8786400
 20    32    2    1.000    -0.201    -0.251      0.3230       0.4925800
 20    36    2    1.000    -0.201    -0.259      0.3230       0.4925800
 20    40    2    1.000    -0.201    -0.260      0.3230       0.4925800
 20    44    2    1.000    -0.201    -0.252      0.3230       0.4925800
 21    48    2    1.000     0.006    -0.157      0.3230       0.4925800
 22    40    2    1.000    -0.166    -0.260      0.3500       0.2761400
 22    44    2    1.000    -0.166    -0.252      0.3500       0.2761400
 26    32    2    1.000    -0.164    -0.251      0.3500       0.2761400
 26    36    2    1.000    -0.164    -0.259      0.3500       0.2761400
 32    40    2    1.000    -0.251    -0.260      0.3500       0.2761400
 32    44    2    1.000    -0.251    -0.252      0.3500       0.2761400
 36    40    2    1.000    -0.259    -0.260      0.3500       0.2761400
 36    44    2    1.000    -0.259    -0.252      0.3500       0.2761400

 [ system ]
 ; Name
 NfO-TEMPO-ME GS (nft) Joyce

 [ molecules ]
 ; Compound        #mols
nft              1
```

Excited state GROMACS topology

```
 [ defaults ]
 ; nbfunc   comb-rule   gen-pairs  fudgeLJ  fudgeQQ
     1        3          no         1.0        1.0

 [ atomtypes ]
 ; name   mass       charge ptype   sigma       espilon
   C1     12.0110    0.000  A    3.55000e-01  2.92880e-01
   C2     12.0110    0.000  A    3.55000e-01  2.92880e-01
   C3     12.0110    0.000  A    3.55000e-01  2.92880e-01
   Cc     12.0110    0.000  A    3.55000e-01  3.17984e-01
   Ct1    12.0110    0.000  A    3.50000e-01  2.76144e-01
   Ct2    12.0110    0.000  A    3.50000e-01  2.76144e-01
   Ctn    12.0110    0.000  A    3.50000e-01  2.76144e-01
   Ct     12.0110    0.000  A    3.50000e-01  2.76144e-01
   Co     12.0110    0.000  A    3.75000e-01  4.39320e-01
   O      15.9994    0.000  A    2.90000e-01  5.85760e-01
```

```
   Oc     15.9994    0.000  A    2.96000e-01  8.78640e-01
   On     15.9994    0.000  A    2.96000e-01  8.78640e-01
   Nt     14.0070    0.000  A    3.25000e-01  7.11280e-01
   H2      1.0079    0.000  A    2.42000e-01  1.25520e-01
   H3      1.0079    0.000  A    2.42000e-01  1.25520e-01
   Ha      1.0079    0.000  A    2.42000e-01  1.25520e-01
   Ht      1.0079    0.000  A    2.50000e-01  1.25520e-01
   Ht1     1.0079    0.000  A    2.50000e-01  1.25520e-01
   Ht2     1.0079    0.000  A    2.50000e-01  1.25520e-01

 [ moleculetype ]
 ; Name            nrexcl
nft

 [ atoms ]
 ; nr type  resnr residue  atom  cgnr    charge      mass
   1   C1     1    nft      C1     1    -0.003118   12.01100
   2   C2     1    nft      C2     2    -0.021678   12.01100
   3   C3     1    nft      C3     3    -0.085175   12.01100
   4   C3     1    nft      C3     4    -0.087572   12.01100
   5   C2     1    nft      C2     5    -0.032532   12.01100
   6   C1     1    nft      C1     6    -0.016571   12.01100
   7   C2     1    nft      C2     7    -0.129469   12.01100
   8   C3     1    nft      C3     8    -0.105161   12.01100
   9   C3     1    nft      C3     9    -0.108548   12.01100
  10   Cc     1    nft      Cc    10    -0.030973   12.01100
  11   H2     1    nft      H2    11     0.124927   1.00790
  12   Ha     1    nft      Ha    12     0.119511   1.00790
  13   Ha     1    nft      Ha    13     0.118770   1.00790
  14   Ha     1    nft      Ha    14     0.121784   1.00790
  15   Ha     1    nft      Ha    15     0.098526   1.00790
  16   Ha     1    nft      Ha    16     0.108384   1.00790
  17   H3     1    nft      H3    17     0.107775   1.00790
  18   Co     1    nft      Co    18     0.228264   12.01100
  19   O      1    nft      O     19    -0.359447   15.99940
  20   Oc     1    nft      Oc    20    -0.208081   15.99940
  21   Ct1    1    nft      Ct1   21     0.004542   12.01100
  22   Ct2    1    nft      Ct2   22    -0.166937   12.01100
  23   Ctn    1    nft      Ctn   23     0.080483   12.01100
  24   Nt     1    nft      Nt    24    -0.274441   14.00700
  25   Ctn    1    nft      Ctn   25     0.080431   12.01100
  26   Ct2    1    nft      Ct2   26    -0.164583   12.01100
  27   Ht2    1    nft      Ht2   27     0.100281   1.00790
  28   Ht2    1    nft      Ht2   28     0.103949   1.00790
  29   Ht2    1    nft      Ht2   29     0.101905   1.00790
  30   Ht2    1    nft      Ht2   30     0.102543   1.00790
  31   Ht1    1    nft      Ht1   31     0.111486   1.00790
  32   Ct     1    nft      Ct    32    -0.252112   12.01100
  33   Ht     1    nft      Ht    33     0.093826   1.00790
  34   Ht     1    nft      Ht    34     0.092003   1.00790
  35   Ht     1    nft      Ht    35     0.091648   1.00790
  36   Ct     1    nft      Ct    36    -0.259341   12.01100
  37   Ht     1    nft      Ht    37     0.094686   1.00790
  38   Ht     1    nft      Ht    38     0.091241   1.00790
  39   Ht     1    nft      Ht    39     0.090725   1.00790
  40   Ct     1    nft      Ct    40    -0.260077   12.01100
  41   Ht     1    nft      Ht    41     0.089620   1.00790
  42   Ht     1    nft      Ht    42     0.095868   1.00790
  43   Ht     1    nft      Ht    43     0.089519   1.00790
```

```
  44   Ct     1    nft      Ct    44    -0.252227   12.01100
  45   Ht     1    nft      Ht    45     0.092305   1.00790
  46   Ht     1    nft      Ht    46     0.094291   1.00790
  47   Ht     1    nft      Ht    47     0.090923   1.00790
  48   On     1    nft      On    48    -0.157942   15.99940
  49   Ct     1    nft      Ct    49    -0.146219   12.01100
  50   Ht     1    nft      Ht    50     0.097724   1.00790
  51   Ht     1    nft      Ht    51     0.106936   1.00790
  52   Ht     1    nft      Ht    52     0.097330   1.00790

; Stretchings
[ bonds ]
      1     2   1     0.1420     277993.176
      2     3   1     0.1419     303261.801
      3     4   1     0.1377     380047.069
      4     5   1     0.1413     303261.801
      1     6   1     0.1427     232307.908
      5     6   1     0.1416     277993.176
      6     7   1     0.1417     277993.176
      7     8   1     0.1408     303261.801
      8     9   1     0.1379     380047.069
      1    10   1     0.1437     249809.383
      9    10   1     0.1438     276305.657
      2    11   1     0.1086     340901.458
      3    12   1     0.1086     337795.484
      4    13   1     0.1087     337795.484
      5    14   1     0.1089     335396.564
      7    15   1     0.1087     335396.564
      8    16   1     0.1088     337795.484
      9    17   1     0.1084     345920.857
     10    18   1     0.1452     248953.714
     18    19   1     0.1231     568205.204
     18    20   1     0.1362     284823.316
     20    21   1     0.1430     244126.533
     21    22   1     0.1518     222567.704
     22    23   1     0.1535     192388.537
     23    24   1     0.1485     203601.308
     24    25   1     0.1484     203601.308
     21    26   1     0.1514     222567.704
     25    26   1     0.1535     192388.537
     22    27   1     0.1098     312497.237
     22    28   1     0.1095     312497.237
     26    29   1     0.1098     312497.237
     26    30   1     0.1097     312497.237
     21    31   1     0.1095     311819.293
     23    32   1     0.1532     188081.888
     32    33   1     0.1094     317613.282
     32    34   1     0.1095     317613.282
     32    35   1     0.1096     317613.282
     23    36   1     0.1539     188081.888
     36    37   1     0.1094     317613.282
     36    38   1     0.1096     317613.282
     36    39   1     0.1092     317613.282
     25    40   1     0.1539     188081.888
     40    41   1     0.1096     317613.282
     40    42   1     0.1094     317613.282
     40    43   1     0.1092     317613.282
     25    44   1     0.1532     188081.888
     44    45   1     0.1095     317613.282
```

```
     44    46   1      0.1094     317613.282
     44    47   1      0.1096     317613.282
     24    48   1      0.1418     241617.085
     48    49   1      0.1413     250283.138
     49    50   1      0.1096     317613.282
     49    51   1      0.1095     317613.282
     49    52   1      0.1096     317613.282

; Bendings
[ angles ]
      1    2    3    1    122.70     591.6013
      2    1    6    1    117.56     383.0370
      2    1   10    1    123.03     709.0996
      1    2   11    1    117.22     293.1945
      2    3    4    1    119.48     581.3579
      3    2   11    1    120.07     323.9958
      2    3   12    1    119.26     327.5501
      3    4    5    1    118.79     581.3579
      4    3   12    1    121.25     292.5916
      3    4   13    1    121.41     292.5916
      4    5    6    1    123.04     591.6013
      5    4   13    1    119.80     327.5501
      4    5   14    1    118.93     370.1059
      1    6    5    1    118.33     383.0370
      1    6    7    1    120.89     383.0370
      6    1   10    1    119.40     334.2226
      5    6    7    1    120.77     749.5227
      6    5   14    1    118.02     279.8123
      6    7    8    1    119.02     591.6013
      6    7   15    1    119.86     279.8123
      7    8    9    1    121.23     581.3579
      8    7   15    1    121.09     370.1059
      7    8   16    1    119.41     327.5501
      8    9   10    1    121.47     477.8969
      9    8   16    1    119.36     292.5916
      8    9   17    1    120.29     315.0007
      1   10    9    1    117.88     572.5763
      1   10   18    1    121.99     234.4201
     10    9   17    1    118.23     324.5450
      9   10   18    1    120.12     615.5611
     10   18   19    1    126.92     341.6443
     10   18   20    1    111.71     286.3415
     19   18   20    1    121.38    1012.9014
     18   20   21    1    116.79     660.6782
     20   21   22    1    110.44     784.8779
     20   21   26    1    107.00     784.8779
     20   21   31    1    107.69     434.4930
     21   22   23    1    112.77     562.9091
     22   21   26    1    109.63     664.7192
     21   22   27    1    107.98     401.2313
     21   22   28    1    109.91     401.2313
     22   21   31    1    110.31     349.5285
     22   23   24    1    107.28     464.7117
     23   22   27    1    109.13     381.9184
     23   22   28    1    108.89     381.9184
     22   23   32    1    107.85     525.0364
     22   23   36    1    111.27     525.0364
     23   24   25    1    118.87     607.0102
     24   23   32    1    107.33     697.0866
```

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    24   23   36   1    115.14     697.0866
    23   24   48   1    108.03     862.6692
    24   25   26   1    107.29     464.7117
    24   25   40   1    115.11     697.0866
    24   25   44   1    107.38     697.0866
    25   24   48   1    107.94     862.6692
    21   26   25   1    112.74     562.9091
    21   26   29   1    108.35     401.2313
    21   26   30   1    110.28     401.2313
    26   21   31   1    111.71     349.5285
    25   26   29   1    108.99     381.9184
    25   26   30   1    108.83     381.9184
    26   25   40   1    111.33     525.0364
    26   25   44   1    107.81     525.0364
    27   22   28   1    108.04     333.4131
    29   26   30   1    107.50     333.4131
    23   32   33   1    111.08     365.3633
    23   32   34   1    110.66     365.3633
    23   32   35   1    109.67     365.3633
    32   23   36   1    107.69     550.0783
    33   32   34   1    109.06     311.5716
    33   32   35   1    107.81     311.5716
    34   32   35   1    108.48     311.5716
    23   36   37   1    110.14     365.3633
    23   36   38   1    109.27     365.3633
    23   36   39   1    113.43     365.3633
    37   36   38   1    108.12     311.5716
    37   36   39   1    108.66     311.5716
    38   36   39   1    107.04     311.5716
    25   40   41   1    109.35     365.3633
    25   40   42   1    110.09     365.3633
    25   40   43   1    113.43     365.3633
    40   25   44   1    107.63     550.0783
    41   40   42   1    108.04     311.5716
    41   40   43   1    107.31     311.5716
    42   40   43   1    108.46     311.5716
    25   44   45   1    110.64     365.3633
    25   44   46   1    111.06     365.3633
    25   44   47   1    109.72     365.3633
    45   44   46   1    109.05     311.5716
    45   44   47   1    108.49     311.5716
    46   44   47   1    107.80     311.5716
    24   48   49   1    111.05     720.8339
    48   49   50   1    111.80     485.3804
    48   49   51   1    105.49     485.3804
    48   49   52   1    111.82     485.3804
    50   49   51   1    109.41     311.5716
    50   49   52   1    108.85     311.5716
    51   49   52   1    109.40     311.5716

; Torsions
[ dihedrals ]
;   napthalene harmonic
      1   2   3   4   2      0.0     47.600
      2   3   4   5   2      0.0     47.600
      3   4   5   6   2      0.0     47.600
      4   5   6   1   2      0.0     47.600
      2   1   6   5   2      0.0     47.600
      6   1   2   3   2      0.0     47.600
```

```
      6   7   8   9   2      0.0     47.600
      7   8   9  10   2      0.0     47.600
      8   9  10   1   2      0.0     47.600
      6   1  10   9   2      0.0     47.600
      1   6   7   8   2      0.0     47.600
     10   1   6   7   2      0.0     47.600
     10   1   6   5   2    180.0     47.600
      2   1   6   7   2    180.0     47.600
;   napthalene harmonic o.o.p.
     12   2   4   3   2      0.0    490.421
     13   3   5   4   2      0.0    490.421
     14   4   6   5   2      0.0    490.421
     15   6   8   7   2      0.0    490.421
     16   7   9   8   2      0.0    490.421
     17   8  10   9   2      0.0    490.421
     11   1   3   2   2      0.0    490.421
     10   1   9  18   2      0.0    401.265
;   d2 dihedral (harm)
     19  18  20  21   2      0.0     30.340
; o.o.p. COO-NfO
     10  19  20  18   2      0.0    670.464
;   TEMPO ring
     20  21  22  23   1      0.00       7.769   3
     20  21  26  25   1      0.00       7.769   3
     26  21  22  23   1      0.00       0.554   3
     22  21  26  25   1      0.00       0.554   3
     22  23  24  25   1      0.00       0.554   3
     23  24  25  26   1      0.00       0.554   3
     21  22  23  24   1      0.00       0.554   3
     24  25  26  21   1      0.00       0.554   3
;   OCH3@TEMPO
     32  23  24  48   1      0.00       3.060   3
     36  23  24  48   1      0.00       3.060   3
     22  23  24  48   1      0.00      22.449   3
     48  24  25  26   1      0.00      22.449   3
;   CH3@TEMPO
     21  22  23  32   1      0.00      11.573   3
     32  23  24  25   1      0.00       0.554   3
     21  22  23  36   1      0.00       0.554   3
     36  23  24  25   1      0.00       0.554   3
     40  25  26  21   1      0.00       0.554   3
     23  24  25  40   1      0.00       0.554   3
     44  25  26  21   1      0.00       0.554   3
     23  24  25  44   1      0.00       0.554   3
; -CH3@C24
     22  23  32  33   1      0.00       3.443   3
     22  23  32  34   1      0.00       3.443   3
     22  23  32  35   1      0.00       3.443   3
     24  23  32  33   1      0.00       3.638   3
     24  23  32  34   1      0.00       3.638   3
     24  23  32  35   1      0.00       3.638   3
     24  23  36  37   1      0.00       3.638   3
     24  23  36  38   1      0.00       3.638   3
     24  23  36  39   1      0.00       3.638   3
     22  23  36  37   1      0.00       3.443   3
     22  23  36  38   1      0.00       3.443   3
     22  23  36  39   1      0.00       3.443   3
; -CH3@C26
     24  25  40  41   1      0.00       3.638   3
```

```
     24   25   40   42    1      0.00       3.638    3
     24   25   40   43    1      0.00       3.638    3
     26   25   40   41    1      0.00       3.443    3
     26   25   40   42    1      0.00       3.443    3
     26   25   40   43    1      0.00       3.443    3
     24   25   44   45    1      0.00       3.638    3
     24   25   44   46    1      0.00       3.638    3
     24   25   44   47    1      0.00       3.638    3
     26   25   44   45    1      0.00       3.443    3
     26   25   44   46    1      0.00       3.443    3
     26   25   44   47    1      0.00       3.443    3
; CH3@NO
     24   48   49   50    1      0.00       4.399    3
     24   48   49   51    1      0.00       4.399    3
     24   48   49   52    1      0.00       4.399    3
;  d1 dihedral
      1   10   18   19    1      0.00      -2.277    1
      1   10   18   19    1      0.00     -12.225    2
      1   10   18   19    1      0.00      -0.635    3
      1   10   18   19    1      0.00       1.990    4
      9   10   18   20    1      0.00      -2.277    1
      9   10   18   20    1      0.00     -12.225    2
      9   10   18   20    1      0.00      -0.635    3
      9   10   18   20    1      0.00       1.990    4
;  d3 dihedral
     18   20   21   22    1      0.00      16.742    1
     18   20   21   22    1      0.00       7.465    2
     18   20   21   22    1      0.00       3.699    3
     18   20   21   22    1      0.00       0.170    4
     18   20   21   26    1      0.00      16.742    1
     18   20   21   26    1      0.00       7.465    2
     18   20   21   26    1      0.00       3.699    3
     18   20   21   26    1      0.00       0.170    4
;  d4 dihedral [transferred from GS]
     23   24   48   49    1      0.00      23.126    1
     23   24   48   49    1      0.00      22.487    2
     23   24   48   49    1      0.00       4.000    3
     23   24   48   49    1      0.00      13.548    4
     25   24   48   49    1      0.00      23.126    1
     25   24   48   49    1      0.00      22.487    2
     25   24   48   49    1      0.00       4.000    3
     25   24   48   49    1      0.00      13.548    4

; Nonbonded terms
[ pairs ]
; other nb interactions
 18    23   2    1.000     0.280     0.081      0.3625       0.3483000
 18    24   2    1.000     0.280    -0.275      0.3500       0.5590000
 18    25   2    1.000     0.280     0.081      0.3625       0.3483000
 18    32   2    1.000     0.280    -0.251      0.3625       0.3483000
 18    36   2    1.000     0.280    -0.259      0.3625       0.3483000
 18    40   2    1.000     0.280    -0.260      0.3625       0.3483000
 18    44   2    1.000     0.280    -0.252      0.3625       0.3483000
 20    24   2    1.000    -0.201    -0.275      0.3105       0.7905400
 20    48   2    1.000    -0.201    -0.157      0.2960       0.8786400
 20    32   2    1.000    -0.201    -0.251      0.3230       0.4925800
 20    36   2    1.000    -0.201    -0.259      0.3230       0.4925800
 20    40   2    1.000    -0.201    -0.260      0.3230       0.4925800
 20    44   2    1.000    -0.201    -0.252      0.3230       0.4925800
```

```
 21    48   2    1.000     0.006    -0.157      0.3230       0.4925800
 22    40   2    1.000    -0.166    -0.260      0.3500       0.2761400
 22    44   2    1.000    -0.166    -0.252      0.3500       0.2761400
 26    32   2    1.000    -0.164    -0.251      0.3500       0.2761400
 26    36   2    1.000    -0.164    -0.259      0.3500       0.2761400
 32    40   2    1.000    -0.251    -0.260      0.3500       0.2761400
 32    44   2    1.000    -0.251    -0.252      0.3500       0.2761400
 36    40   2    1.000    -0.259    -0.260      0.3500       0.2761400
 36    44   2    1.000    -0.259    -0.252      0.3500       0.2761400

 [ system ]
 ; Name
 NfO-TEMPO-ME EES (nft) Joyce

 [ molecules ]
 ; Compound        #mols
nft              1
```

Toluene parameters

Parameters from OPLS AA were employed to describe the 991 toluene molecules used for the solvated system. The corresponding lines in the topology files are the following:

· new atomtypes:

```
   CA     12.0110    0.000  A    3.55000e-01  2.92880e-01
   CM     12.0110    0.000  A    3.50000e-01  2.76144e-01
   HA      1.0079    0.000  A    2.42000e-01  1.25520e-01
   HC      1.0079    0.000  A    2.50000e-01  1.25520e-01
```

· new molecule:

```
 [ moleculetype ]
   tol              3

[ atoms ]
      1  CA       1  tol   CA      1  -0.115    12.01100
      2  CA       1  tol   CA      2  -0.115    12.01100
      3  CA       1  tol   CA      3  -0.115    12.01100
      4  CA       1  tol   CA      4  -0.115    12.01100
      5  CA       1  tol   CA      5  -0.115    12.01100
      6  CA       1  tol   CA      6  -0.115    12.01100
      7  CM       1  tol   CM      7  -0.065    12.01100
      8  HA       1  tol   HA      8   0.115     1.00800
      9  HA       1  tol   HA      9   0.115     1.00800
     10  HA       1  tol   HA     10   0.115     1.00800
     11  HA       1  tol   HA     11   0.115     1.00800
     12  HA       1  tol   HA     12   0.115     1.00800
     13  HC       1  tol   HC     13   0.060     1.00800
     14  HC       1  tol   HC     14   0.060     1.00800
     15  HC       1  tol   HC     15   0.060     1.00800
```

```
 [bonds]
        1        2   1      0.1400   392459.20
        2        3   1      0.1400   392459.20
        3        4   1      0.1400   392459.20
        4        5   1      0.1400   392459.20
        1        6   1      0.1400   392459.20
        5        6   1      0.1400   392459.20
        6        7   1      0.1510   265265.60
        1        8   1      0.1080   307105.60
        2        9   1      0.1080   307105.60
        3       10   1      0.1080   307105.60
        4       11   1      0.1080   307105.60
        5       12   1      0.1080   307105.60
        7       13   1      0.1090   284512.00
        7       14   1      0.1090   284512.00
        7       15   1      0.1090   284512.00

[ angles ]
      1       2       3   1     120.0    527.2
      6       1       2   1     120.0    527.2
      8       1       2   1     120.0    292.9
      1       2       9   1     120.0    292.9
      2       3       4   1     120.0    527.2
      9       2       3   1     120.0    292.9
      2       3      10   1     120.0    292.9
      3       4       5   1     120.0    527.2
     10       3       4   1     120.0    292.9
      3       4      11   1     120.0    292.9
      4       5       6   1     120.0    527.2
     11       4       5   1     120.0    292.9
      4       5      12   1     120.0    292.9
      1       6       5   1     120.0    527.2
      1       6       7   1     120.0    585.8
      8       1       6   1     120.0    292.9
      5       6       7   1     120.0    585.8
     12       5       6   1     120.0    292.9
      6       7      13   1     109.5    292.9
      6       7      14   1     109.5    292.9
      6       7      15   1     109.5    292.9
     14       7      13   1     107.8    276.1
     15       7      13   1     107.8    276.1
     15       7      14   1     107.8    276.1

[ dihedrals ]
      1       2       3       4   1       180.0   60.6700   2
      6       1       2       3   1       180.0   60.6700   2
      8       1       2       3   1       180.0   60.6700   2
      1       2       3      10   1       180.0   60.6700   2
      5       6       1       2   1       180.0   60.6700   2
      7       6       1       2   1       180.0   60.6700   2
      6       1       2       9   1       180.0   60.6700   2
      8       1       2       9   1       180.0   60.6700   2
      2       3       4       5   1       180.0   60.6700   2
      9       2       3       4   1       180.0   60.6700   2
      2       3       4      11   1       180.0   60.6700   2
      9       2       3      10   1       180.0   60.6700   2
      3       4       5       6   1       180.0   60.6700   2
     10       3       4       5   1       180.0   60.6700   2
      3       4       5      12   1       180.0   60.6700   2
```

```
 10      3       4      11    1        180.0    60.6700    2
  4      5       6       1    1        180.0    60.6700    2
  4      5       6       7    1        180.0    60.6700    2
 11      4       5       6    1        180.0    60.6700    2
 11      4       5      12    1        180.0    60.6700    2
  8      1       6       5    1        180.0    60.6700    2
  1      6       5      12    1        180.0    60.6700    2
  8      1       6       7    1        180.0    60.6700    2
 12      5       6       7    1          0.0    60.6700    2
```

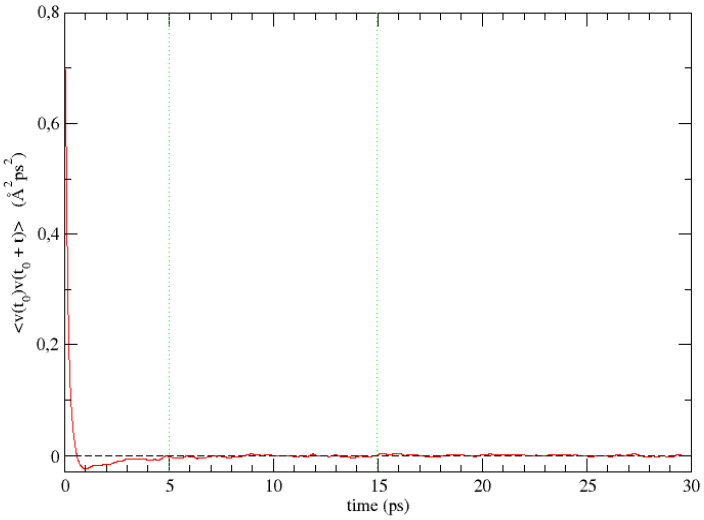
· new “molecules” entry:

```
tol             991
```

Velocity auto-correlation function (acf)

In order to prove that the solute and solute+solvent snapshots, extracted from the MD trajectories, are independent, the solute center of mass velocity acf has been computed. Indeed, given that the vibrational motions take place on a faster time scale with respect to translational ones, sampling the conformational space explored by the MD runs with a time interval larger than that needed to annihilate the correlation of the translational velocity acf should grant also the absence of correlation between two successive snapshots.

The computed velocity acf is reported in red in the figure below.

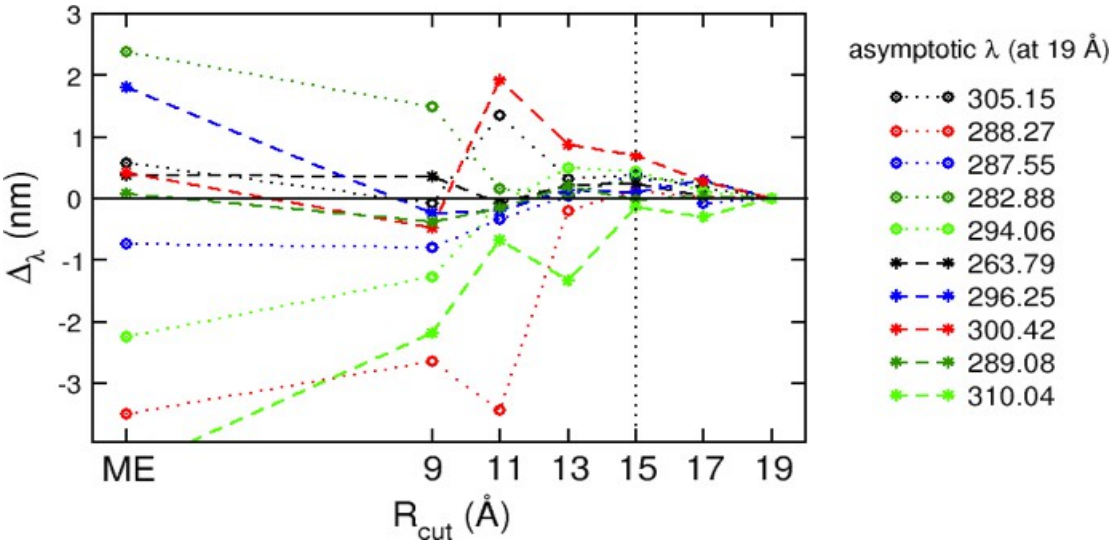


It appears that the correlation breaks down around 5 ps and at 15 ps (the shortest time effectively employed to sample the MD trajectories) the acf is definitively null.

Solvation shell radius

Ten randomly selected snapshots were extracted from the GS dynamics in solvent, including increasingly large explicit solvent spheres and PCM cavities, to assess the convergence behavior on the electronic transition wavelength. As shown in the figure below, for each selected snapshot TDDFT EE transitions were computed for all the considered solvation shell radii (R_{cut}). The

resulting wavelengths are plotted as differences from the "asymptotic value", defined as the result at R_{cut} = 19 Å. The ME values (without charges and PCM, thus R_{cut} = 0) are also reported. For the sake of completeness, the asymptotic values corresponding to each snapshot are listed aside.



It appears that accounting for the first two solvation spheres (*i.e.* R_{cut} < 15 Å) has a not negligible effect on wavelength (which can change more than 3 nm). Nonetheless, a further increase of the solvation sphere beyond 15 Å does not sensibly affect the results, being the variation bound to 0.7 nm.

References

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