

Electronic Supporting information

Delta-Augmented Subsystem Density Functional Theory: A Study Across Diverse Systems

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A. Machine learning training

In this section we are going to give the ‘input.nn’ required by the n2p2 code for the machine learning training. Useful information such as the number of layers, the percentage of structure used for testing and the Atom-centered Symmetry Functions can be found here for ammonia:

```
#####  
# GENERAL NNP SETTINGS  
#####  
number_of_elements          2  
elements                    H N  
cutoff_type                 2 0.0  
scale_symmetry_functions  
#scale_symmetry_functions_sigma  
scale_min_short             0.0  
scale_max_short             1.0  
center_symmetry_functions  
global_hidden_layers_short  2  
global_nodes_short          25 25  
global_activation_short     t t 1  
#normalize_nodes  
  
#####  
# ADDITIONAL SETTINGS FOR TRAINING  
#####  
epochs                      150  
updater_type                1  
parallel_mode               1  
jacobian_mode               1  
task_batch_size_energy      1  
task_batch_size_force       1
```

```

update_strategy          0
selection_mode           0
memorize_symfunc_results
random_seed              123456
test_fraction            0.10
use_short_forces
force_weight             10.0
short_energy_fraction    1.00
short_force_fraction     0.10
short_energy_error_threshold 1.00
short_force_error_threshold 1.00
rmse_threshold_trials    3
weights_min              -1.0
weights_max              1.0
write_trainpoints        1
write_trainforces        1
write_weights_epoch      1
write_neuronstats        1
write_trainlog
#####
# KALMAN FILTER (STANDARD) #
#####
kalman_type              0
kalman_epsilon           1.0E-2
kalman_q0                0.01
kalman_qtau              2.302
kalman_qmin              1.0E-6
kalman_eta               0.01
kalman_etatau            2.302
kalman_etamax            1.0

#####

```

SYMMETRY FUNCTIONS

#####

symfunction_short H 2 H 0.001 0.0 12.00
symfunction_short H 2 H 0.01 0.0 12.00
symfunction_short H 2 H 0.03 0.0 12.00
symfunction_short H 2 H 0.06 0.0 12.00
symfunction_short H 2 H 0.15 1.9 12.00
symfunction_short H 2 H 0.30 1.9 12.00
symfunction_short H 2 H 0.60 1.9 12.00
symfunction_short H 2 H 1.50 1.9 12.00

#

symfunction_short H 2 N 0.001 0.0 12.00
symfunction_short H 2 N 0.01 0.0 12.00
symfunction_short H 2 N 0.03 0.0 12.00
symfunction_short H 2 N 0.06 0.0 12.00
symfunction_short H 2 N 0.15 0.9 12.00
symfunction_short H 2 N 0.30 0.9 12.00
symfunction_short H 2 N 0.60 0.9 12.00
symfunction_short H 2 N 1.50 0.9 12.00

#

symfunction_short N 2 H 0.001 0.0 12.00
symfunction_short N 2 H 0.01 0.0 12.00
symfunction_short N 2 H 0.03 0.0 12.00
symfunction_short N 2 H 0.06 0.0 12.00
symfunction_short N 2 H 0.15 0.9 12.00
symfunction_short N 2 H 0.30 0.9 12.00
symfunction_short N 2 H 0.60 0.9 12.00
symfunction_short N 2 H 1.50 0.9 12.00

#

symfunction_short N 2 N 0.001 0.0 12.00
symfunction_short N 2 N 0.01 0.0 12.00

```

symfunction_short N 2 N 0.03 0.0 12.00
symfunction_short N 2 N 0.06 0.0 12.00
symfunction_short N 2 N 0.15 4.0 12.00
symfunction_short N 2 N 0.30 4.0 12.00
symfunction_short N 2 N 0.60 4.0 12.00
symfunction_short N 2 N 1.50 4.0 12.00
#
symfunction_short H 3 N H 0.2 1.0 1.0 12.00000

symfunction_short N 3 H H 0.07 1.0 1.0 12.00000
symfunction_short H 3 N H 0.07 1.0 1.0 12.00000
symfunction_short N 3 H H 0.07 -1.0 1.0 12.00000
symfunction_short H 3 N H 0.07 -1.0 1.0 12.00000

symfunction_short N 3 H H 0.03 1.0 1.0 12.00000
symfunction_short H 3 N H 0.03 1.0 1.0 12.00000
symfunction_short N 3 H H 0.03 -1.0 1.0 12.00000
symfunction_short H 3 N H 0.03 -1.0 1.0 12.00000

symfunction_short N 3 H H 0.01 1.0 4.0 12.00000
symfunction_short H 3 N H 0.01 1.0 4.0 12.00000
symfunction_short N 3 H H 0.01 -1.0 4.0 12.00000
symfunction_short H 3 N H 0.01 -1.0 4.0 12.00000

symfunction_short N 3 N H 0.03 1.0 1.0 12.00000
symfunction_short N 3 N H 0.03 -1.0 1.0 12.00000
symfunction_short N 3 N H 0.001 1.0 4.0 12.00000
symfunction_short N 3 N H 0.001 -1.0 4.0 12.00000

symfunction_short H 3 N N 0.03 1.0 1.0 12.00000
symfunction_short H 3 N N 0.03 -1.0 1.0 12.00000
symfunction_short H 3 N N 0.001 1.0 4.0 12.00000

```

```

symfunction_short H 3 N N 0.001 -1.0 4.0 12.00000
symfunction_short N 3 N N 0.03 1.0 1.0 12.00000
symfunction_short N 3 N N 0.03 -1.0 1.0 12.00000
symfunction_short N 3 N N 0.001 1.0 4.0 12.00000
symfunction_short N 3 N N 0.001 -1.0 4.0 12.00000

```

Symmetry functions for methanol can be found here:

```

#####
# GENERAL NNP SETTINGS
#####
number_of_elements          3
elements                    H O C
cutoff_type                 2 0.0
scale_symmetry_functions
#scale_symmetry_functions_sigma
scale_min_short             0.0
scale_max_short             1.0
center_symmetry_functions
global_hidden_layers_short  2
global_nodes_short          25 25
global_activation_short     t t l
#normalize_nodes

#####
# ADDITIONAL SETTINGS FOR TRAINING
#####
epochs                      150
updater_type                1

```

```

parallel_mode          1
jacobian_mode         1
task_batch_size_energy 1
task_batch_size_force  1
update_strategy       0
selection_mode        0
memorize_symfunc_results
random_seed           123456
test_fraction         0.10
use_short_forces
force_weight          10.0
short_energy_fraction 1.00
short_force_fraction  0.10
short_energy_error_threshold 1.00
short_force_error_threshold 1.00
rmse_threshold_trials 3
weights_min           -1.0
weights_max           1.0
write_trainpoints     1
write_trainforces     1
write_weights_epoch   1
write_neuronstats     1
write_trainlog

#####
# KALMAN FILTER (STANDARD) #
#####
kalman_type           0
kalman_epsilon        1.0E-2
kalman_q0             0.01
kalman_qtau           2.302
kalman_qmin           1.0E-6

```

```
kalman_eta          0.01
kalman_etatau       2.302
kalman_etamax       1.0
```

```
#####
```

```
# SYMMETRY FUNCTIONS
```

```
#####
```

```
# radial H H
```

```
symfunction_short H 2 H 0.001 0.0 12.00
symfunction_short H 2 H 0.01  0.0 12.00
symfunction_short H 2 H 0.03  0.0 12.00
symfunction_short H 2 H 0.06  0.0 12.00
symfunction_short H 2 H 0.15  1.9 12.00
symfunction_short H 2 H 0.30  1.9 12.00
symfunction_short H 2 H 0.60  1.9 12.00
symfunction_short H 2 H 1.50  1.9 12.00
```

```
#
```

```
# radial H 0 / 0 H
```

```
symfunction_short H 2 0 0.001 0.0 12.00
symfunction_short H 2 0 0.01  0.0 12.00
symfunction_short H 2 0 0.03  0.0 12.00
symfunction_short H 2 0 0.06  0.0 12.00
symfunction_short H 2 0 0.15  0.9 12.00
symfunction_short H 2 0 0.30  0.9 12.00
symfunction_short H 2 0 0.60  0.9 12.00
symfunction_short H 2 0 1.50  0.9 12.00
```

```
#
```

```
symfunction_short 0 2 H 0.001 0.0 12.00
symfunction_short 0 2 H 0.01  0.0 12.00
symfunction_short 0 2 H 0.03  0.0 12.00
symfunction_short 0 2 H 0.06  0.0 12.00
```

```

symfunction_short 0 2 H 0.15 0.9 12.00
symfunction_short 0 2 H 0.30 0.9 12.00
symfunction_short 0 2 H 0.60 0.9 12.00
symfunction_short 0 2 H 1.50 0.9 12.00
#
# radial 0 0
symfunction_short 0 2 0 0.001 0.0 12.00
symfunction_short 0 2 0 0.01 0.0 12.00
symfunction_short 0 2 0 0.03 0.0 12.00
symfunction_short 0 2 0 0.06 0.0 12.00
symfunction_short 0 2 0 0.15 4.0 12.00
symfunction_short 0 2 0 0.30 4.0 12.00
symfunction_short 0 2 0 0.60 4.0 12.00
symfunction_short 0 2 0 1.50 4.0 12.00
#
# radial H C / C H
symfunction_short H 2 C 0.001 0.0 12.00
symfunction_short H 2 C 0.01 0.0 12.00
symfunction_short H 2 C 0.03 0.0 12.00
symfunction_short H 2 C 0.06 0.0 12.00
symfunction_short H 2 C 0.15 0.9 12.00
symfunction_short H 2 C 0.30 0.9 12.00
symfunction_short H 2 C 0.60 0.9 12.00
symfunction_short H 2 C 1.50 0.9 12.00
#
symfunction_short C 2 H 0.001 0.0 12.00
symfunction_short C 2 H 0.01 0.0 12.00
symfunction_short C 2 H 0.03 0.0 12.00
symfunction_short C 2 H 0.06 0.0 12.00
symfunction_short C 2 H 0.15 0.9 12.00
symfunction_short C 2 H 0.30 0.9 12.00
symfunction_short C 2 H 0.60 0.9 12.00

```

```

symfunction_short C 2 H 1.50 0.9 12.00
#
# radial 0 C / C 0
symfunction_short 0 2 C 0.001 0.0 12.00
symfunction_short 0 2 C 0.01 0.0 12.00
symfunction_short 0 2 C 0.03 0.0 12.00
symfunction_short 0 2 C 0.06 0.0 12.00
symfunction_short 0 2 C 0.15 0.9 12.00
symfunction_short 0 2 C 0.30 0.9 12.00
symfunction_short 0 2 C 0.60 0.9 12.00
symfunction_short 0 2 C 1.50 0.9 12.00
#
symfunction_short C 2 0 0.001 0.0 12.00
symfunction_short C 2 0 0.01 0.0 12.00
symfunction_short C 2 0 0.03 0.0 12.00
symfunction_short C 2 0 0.06 0.0 12.00
symfunction_short C 2 0 0.15 0.9 12.00
symfunction_short C 2 0 0.30 0.9 12.00
symfunction_short C 2 0 0.60 0.9 12.00
symfunction_short C 2 0 1.50 0.9 12.00
#
# radial C C
symfunction_short C 2 C 0.001 0.0 12.00
symfunction_short C 2 C 0.01 0.0 12.00
symfunction_short C 2 C 0.03 0.0 12.00
symfunction_short C 2 C 0.06 0.0 12.00
symfunction_short C 2 C 0.15 4.0 12.00
symfunction_short C 2 C 0.30 4.0 12.00
symfunction_short C 2 C 0.60 4.0 12.00
symfunction_short C 2 C 1.50 4.0 12.00
# angular
symfunction_short H 3 0 H 0.2 1.0 1.0 12.00000

```

```

symfunction_short 0 3 H H 0.07 1.0 1.0 12.00000
symfunction_short H 3 0 H 0.07 1.0 1.0 12.00000
symfunction_short 0 3 H H 0.07 -1.0 1.0 12.00000
symfunction_short H 3 0 H 0.07 -1.0 1.0 12.00000

symfunction_short 0 3 H H 0.03 1.0 1.0 12.00000
symfunction_short H 3 0 H 0.03 1.0 1.0 12.00000
symfunction_short 0 3 H H 0.03 -1.0 1.0 12.00000
symfunction_short H 3 0 H 0.03 -1.0 1.0 12.00000

symfunction_short 0 3 H H 0.01 1.0 4.0 12.00000
symfunction_short H 3 0 H 0.01 1.0 4.0 12.00000
symfunction_short 0 3 H H 0.01 -1.0 4.0 12.00000
symfunction_short H 3 0 H 0.01 -1.0 4.0 12.00000

symfunction_short 0 3 0 H 0.03 1.0 1.0 12.00000
symfunction_short 0 3 0 H 0.03 -1.0 1.0 12.00000
symfunction_short 0 3 0 H 0.001 1.0 4.0 12.00000
symfunction_short 0 3 0 H 0.001 -1.0 4.0 12.00000

symfunction_short H 3 0 0 0.03 1.0 1.0 12.00000
symfunction_short H 3 0 0 0.03 -1.0 1.0 12.00000
symfunction_short H 3 0 0 0.001 1.0 4.0 12.00000
symfunction_short H 3 0 0 0.001 -1.0 4.0 12.00000

symfunction_short 0 3 0 0 0.03 1.0 1.0 12.00000
symfunction_short 0 3 0 0 0.03 -1.0 1.0 12.00000
symfunction_short 0 3 0 0 0.001 1.0 4.0 12.00000
symfunction_short 0 3 0 0 0.001 -1.0 4.0 12.00000

symfunction_short C 3 C C 0.03 1.0 1.0 12.00000

```

```

symfunction_short C 3 C C 0.03 -1.0 1.0 12.00000
symfunction_short C 3 C C 0.001 1.0 4.0 12.00000
symfunction_short C 3 C C 0.001 -1.0 4.0 12.00000

symfunction_short C 3 C 0 0.0010 1.000 1.000 12.000
symfunction_short C 3 C 0 0.0010 -1.000 1.000 12.000
symfunction_short C 3 C 0 0.0010 1.000 4.000 12.000
symfunction_short C 3 C 0 0.0010 -1.000 4.000 12.000
symfunction_short C 3 C 0 0.0316 1.000 1.000 12.000
symfunction_short C 3 C 0 0.0316 -1.000 1.000 12.000
symfunction_short C 3 C 0 0.0316 1.000 4.000 12.000
symfunction_short C 3 C 0 0.0316 -1.000 4.000 12.000

symfunction_short C 3 C H 0.0010 1.000 1.000 12.000
symfunction_short C 3 C H 0.0010 -1.000 1.000 12.000
symfunction_short C 3 C H 0.0010 1.000 4.000 12.000
symfunction_short C 3 C H 0.0010 -1.000 4.000 12.000
symfunction_short C 3 C H 0.0316 1.000 1.000 12.000
symfunction_short C 3 C H 0.0316 -1.000 1.000 12.000
symfunction_short C 3 C H 0.0316 1.000 4.000 12.000
symfunction_short C 3 C H 0.0316 -1.000 4.000 12.000

symfunction_short C 3 0 0 0.0010 1.000 1.000 12.000
symfunction_short C 3 0 0 0.0010 -1.000 1.000 12.000
symfunction_short C 3 0 0 0.0010 1.000 4.000 12.000
symfunction_short C 3 0 0 0.0010 -1.000 4.000 12.000
symfunction_short C 3 0 0 0.0316 1.000 1.000 12.000
symfunction_short C 3 0 0 0.0316 -1.000 1.000 12.000
symfunction_short C 3 0 0 0.0316 1.000 4.000 12.000
symfunction_short C 3 0 0 0.0316 -1.000 4.000 12.000

symfunction_short C 3 0 H 0.0010 1.000 1.000 12.000

```

symfunction_short C 3 0 H 0.0010 -1.000 1.000 12.000
symfunction_short C 3 0 H 0.0010 1.000 4.000 12.000
symfunction_short C 3 0 H 0.0010 -1.000 4.000 12.000
symfunction_short C 3 0 H 0.0316 1.000 1.000 12.000
symfunction_short C 3 0 H 0.0316 -1.000 1.000 12.000
symfunction_short C 3 0 H 0.0316 1.000 4.000 12.000
symfunction_short C 3 0 H 0.0316 -1.000 4.000 12.000

symfunction_short C 3 H H 0.0010 1.000 1.000 12.000
symfunction_short C 3 H H 0.0010 -1.000 1.000 12.000
symfunction_short C 3 H H 0.0010 1.000 4.000 12.000
symfunction_short C 3 H H 0.0010 -1.000 4.000 12.000
symfunction_short C 3 H H 0.0316 1.000 1.000 12.000
symfunction_short C 3 H H 0.0316 -1.000 1.000 12.000
symfunction_short C 3 H H 0.0316 1.000 4.000 12.000
symfunction_short C 3 H H 0.0316 -1.000 4.000 12.000

symfunction_short 0 3 C C 0.0010 1.000 1.000 12.000
symfunction_short 0 3 C C 0.0010 -1.000 1.000 12.000
symfunction_short 0 3 C C 0.0010 1.000 4.000 12.000
symfunction_short 0 3 C C 0.0010 -1.000 4.000 12.000
symfunction_short 0 3 C C 0.0316 1.000 1.000 12.000
symfunction_short 0 3 C C 0.0316 -1.000 1.000 12.000
symfunction_short 0 3 C C 0.0316 1.000 4.000 12.000
symfunction_short 0 3 C C 0.0316 -1.000 4.000 12.000

symfunction_short 0 3 C 0 0.0010 1.000 1.000 12.000
symfunction_short 0 3 C 0 0.0010 -1.000 1.000 12.000
symfunction_short 0 3 C 0 0.0010 1.000 4.000 12.000
symfunction_short 0 3 C 0 0.0010 -1.000 4.000 12.000
symfunction_short 0 3 C 0 0.0316 1.000 1.000 12.000
symfunction_short 0 3 C 0 0.0316 -1.000 1.000 12.000

symfunction_short 0 3 C 0 0.0316 1.000 4.000 12.000
symfunction_short 0 3 C 0 0.0316 -1.000 4.000 12.000

symfunction_short 0 3 C H 0.0010 1.000 1.000 12.000
symfunction_short 0 3 C H 0.0010 -1.000 1.000 12.000
symfunction_short 0 3 C H 0.0010 1.000 4.000 12.000
symfunction_short 0 3 C H 0.0010 -1.000 4.000 12.000
symfunction_short 0 3 C H 0.0316 1.000 1.000 12.000
symfunction_short 0 3 C H 0.0316 -1.000 1.000 12.000
symfunction_short 0 3 C H 0.0316 1.000 4.000 12.000
symfunction_short 0 3 C H 0.0316 -1.000 4.000 12.000

symfunction_short H 3 C C 0.0010 1.000 1.000 12.000
symfunction_short H 3 C C 0.0010 -1.000 1.000 12.000
symfunction_short H 3 C C 0.0010 1.000 4.000 12.000
symfunction_short H 3 C C 0.0010 -1.000 4.000 12.000
symfunction_short H 3 C C 0.0316 1.000 1.000 12.000
symfunction_short H 3 C C 0.0316 -1.000 1.000 12.000
symfunction_short H 3 C C 0.0316 1.000 4.000 12.000
symfunction_short H 3 C C 0.0316 -1.000 4.000 12.000

symfunction_short H 3 C 0 0.0010 1.000 1.000 12.000
symfunction_short H 3 C 0 0.0010 -1.000 1.000 12.000
symfunction_short H 3 C 0 0.0010 1.000 4.000 12.000
symfunction_short H 3 C 0 0.0010 -1.000 4.000 12.000
symfunction_short H 3 C 0 0.0316 1.000 1.000 12.000
symfunction_short H 3 C 0 0.0316 -1.000 1.000 12.000
symfunction_short H 3 C 0 0.0316 1.000 4.000 12.000
symfunction_short H 3 C 0 0.0316 -1.000 4.000 12.000

symfunction_short H 3 C H 0.0010 1.000 1.000 12.000
symfunction_short H 3 C H 0.0010 -1.000 1.000 12.000

```

symfunction_short H 3 C H 0.0010 1.000 4.000 12.000
symfunction_short H 3 C H 0.0010 -1.000 4.000 12.000
symfunction_short H 3 C H 0.0316 1.000 1.000 12.000
symfunction_short H 3 C H 0.0316 -1.000 1.000 12.000
symfunction_short H 3 C H 0.0316 1.000 4.000 12.000
symfunction_short H 3 C H 0.0316 -1.000 4.000 12.000

```

B. KG input details

In this section we are going to give some part of our cp2k input for the ML-P-KG calculation. For the general parts regarding the DFT section we want to recall the setup presented in previous KG works [us], however parameters have been changed according to what we have showed in the main text of this work and to the test we have made.

The ‘TNADD-PBE’ for ammonia corresponds to:

```

N      TNADD-PBE
      3          2
      0.3061      0.0000      0.7200
      0.5358      0.0000      0.7116
      0.9080      0.4393      0.2517
#
H TNADD-PBE
      2          1
      0.3167      0.4717
      0.7540      0.7444

```

The ‘TNADD-PBE’ for methanol corresponds to:

```

O      TNADD-PBE
      3          2

```

		0.4703	0.0000	0.9708
		0.2646	0.0000	1.1115
		0.8690	0.7697	0.2317
#				
H	TNADD-PBE			
		2	1	
		0.3167	0.4717	
		0.7540	0.7444	
#				
C	TNADD-PBE			
		3	2	
		0.9886	0.2149	0.2158
		0.3652	0.0000	0.4184
		0.6238	0.0000	0.4817

C. cross-validation - ammonia and methanol

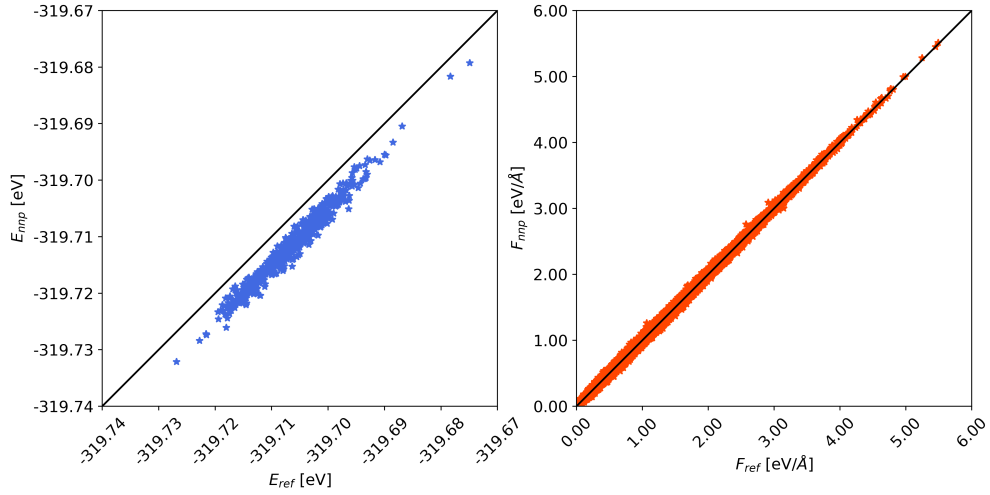


FIG. 1. On the left, reference potential energy (eV) vs NNP potential energy (eV) per molecule extracted during the cross-validation of ammonia. On the right, reference forces ($\text{eV}/\text{\AA}$) vs NNP forces ($\text{eV}/\text{\AA}$) per atom extracted during the cross-validation of ammonia. The configurations used for the checking come from a ML-P-KG simulation of liquid ammonia performed.

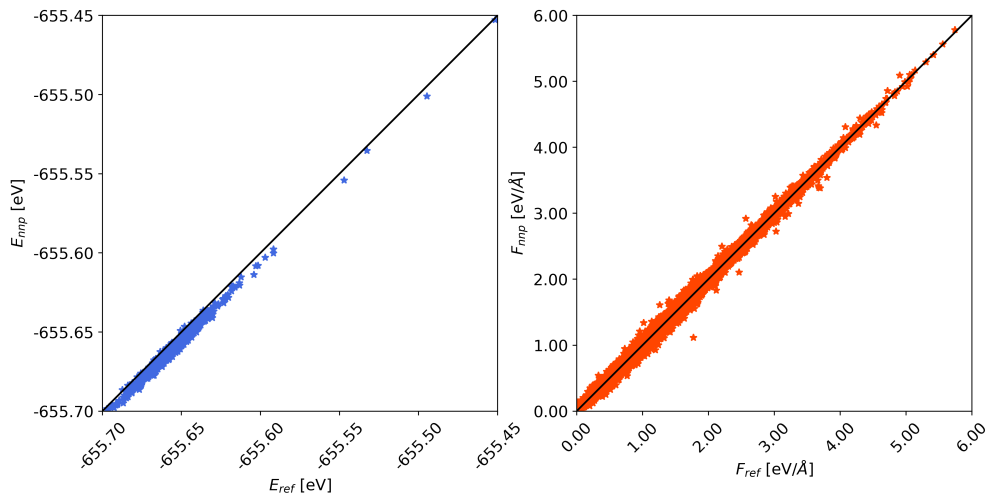


FIG. 2. On the left, reference potential energy (eV) vs NNP potential energy (eV) per molecule extracted during the cross-validation of methanol. On the right, reference forces ($\text{eV}/\text{\AA}$) vs NNP forces ($\text{eV}/\text{\AA}$) per atom extracted during the cross-validation of methanol. The configurations used for the checking come from a ML-P-KG simulation of liquid methanol performed.

D. Other results

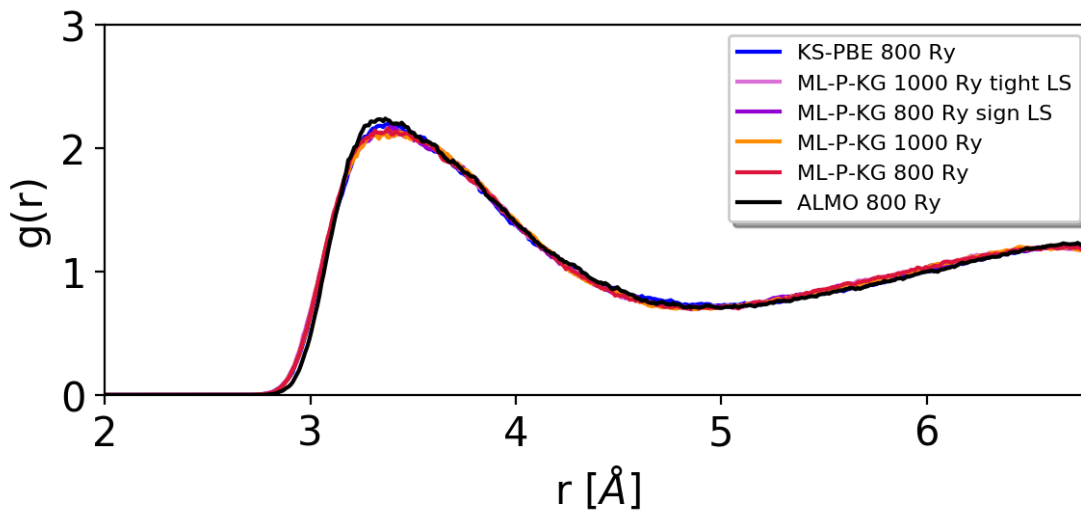


FIG. 3. N-N pair distribution function calculated for KS with cutoff 800 Ry (blue line), ML-P-KG with cutoff equal to 800 Ry (red line), ML-P-KG with cutoff equal to 1000 Ry (orange line), ML-P-KG with cutoff equal to 1000 Ry using a tight LS filter (pink line), ML-P-KG with cutoff equal to 800 Ry using a different LS algorithm (violet line) and ALMO SCF with cutoff equal to 800 Ry (black line). The MD sampling has been carried out at 230 K.

E. Cluster results

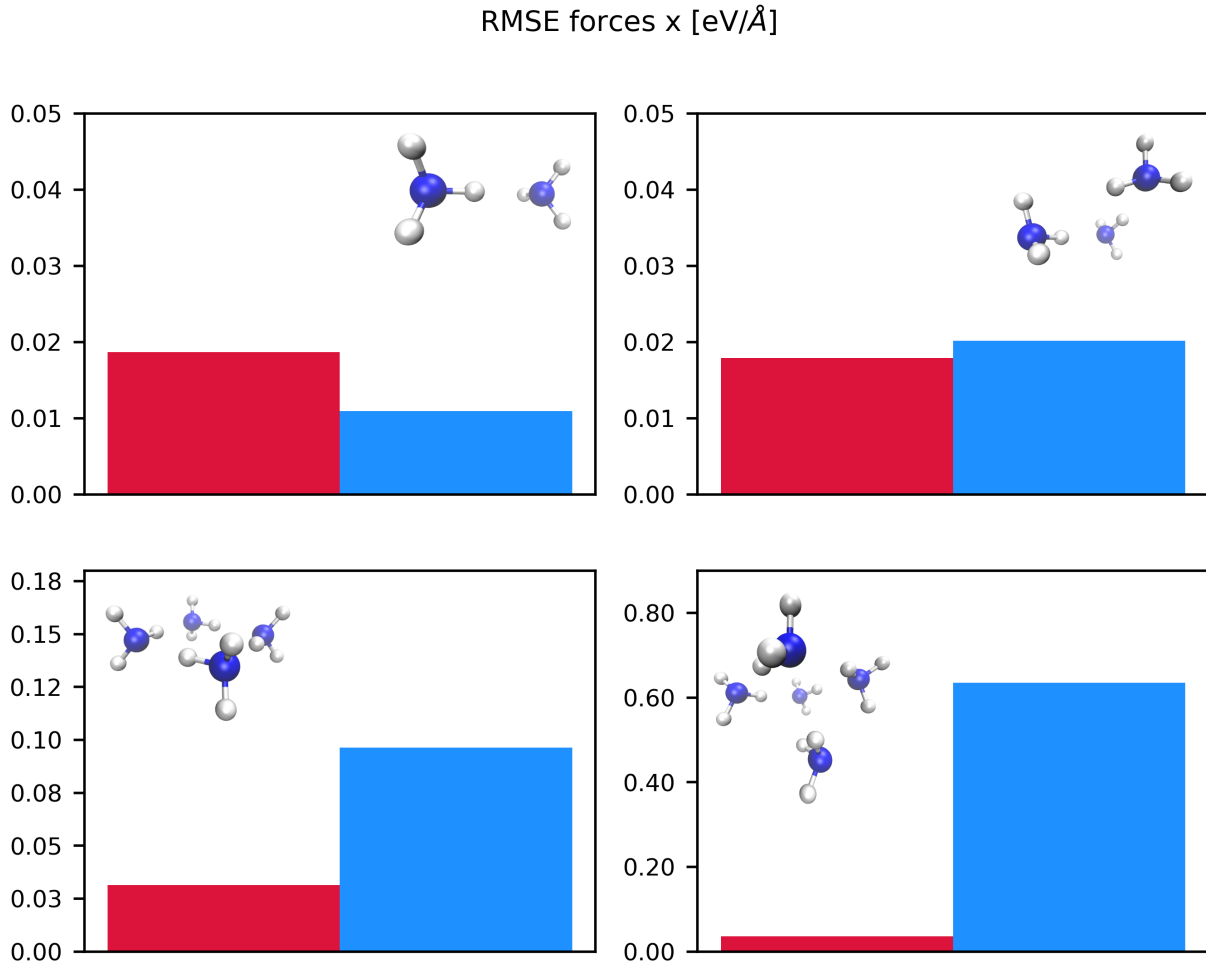


FIG. 4. RMSE of x component of forces per atom in eV/Å of four different cluster systems (dimer, trimer, tetramer and pentamer). All the structures have been previously optimized at Kohn-Sham level. The red bars represent the RMSE calculated comparing KS and KG corrected by the bulk potential, whereas the blue bars comparing KS and KG corrected by the cluster potential.

RMSE forces y [eV/Å]

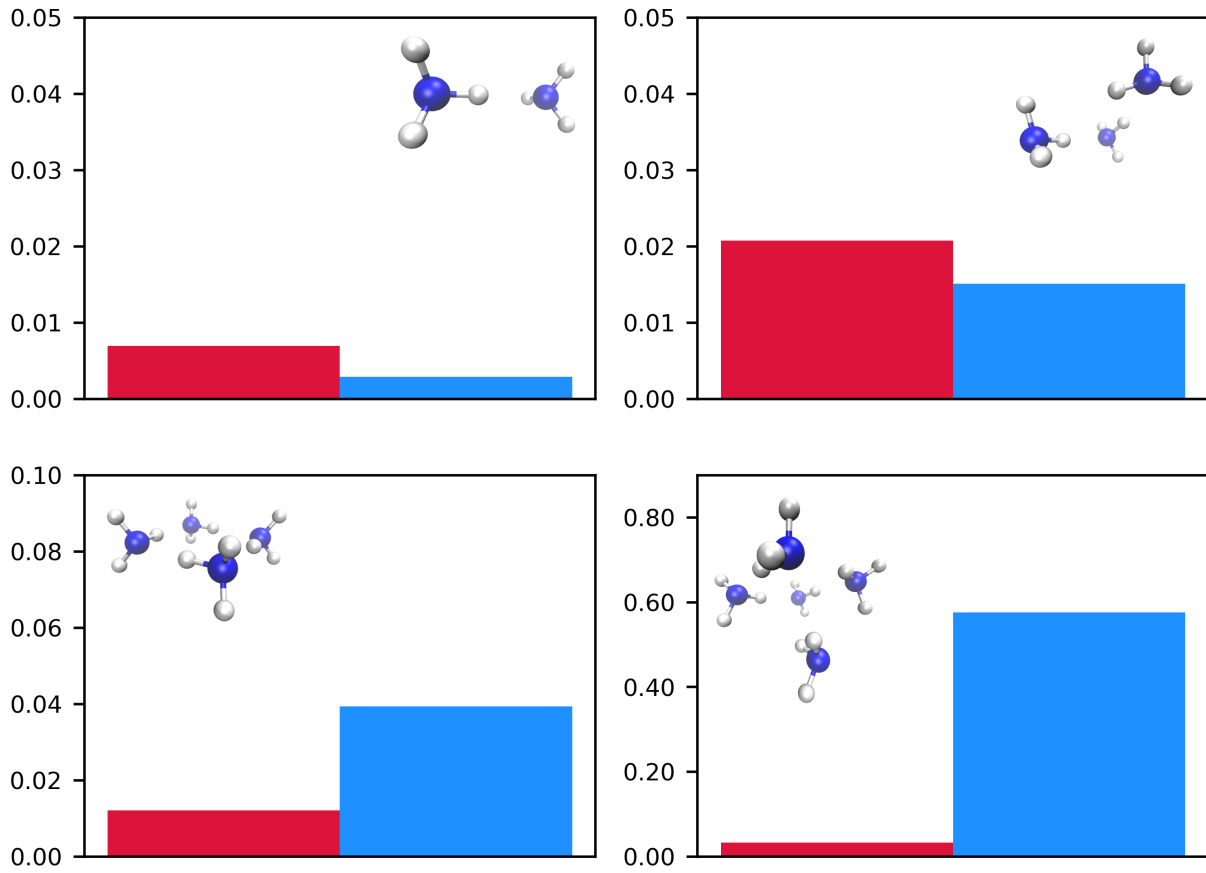


FIG. 5. RMSE of y component of forces per atom in eV/Å of four different cluster systems (dimer, trimer, tetramer and pentamer). All the structures have been previously optimized at Kohn-Sham level. The red bars represent the RMSE calculated comparing KS and KG corrected by the bulk potential, whereas the blue bars comparing KS and KG corrected by the cluster potential.

RMSE forces z [eV/Å]

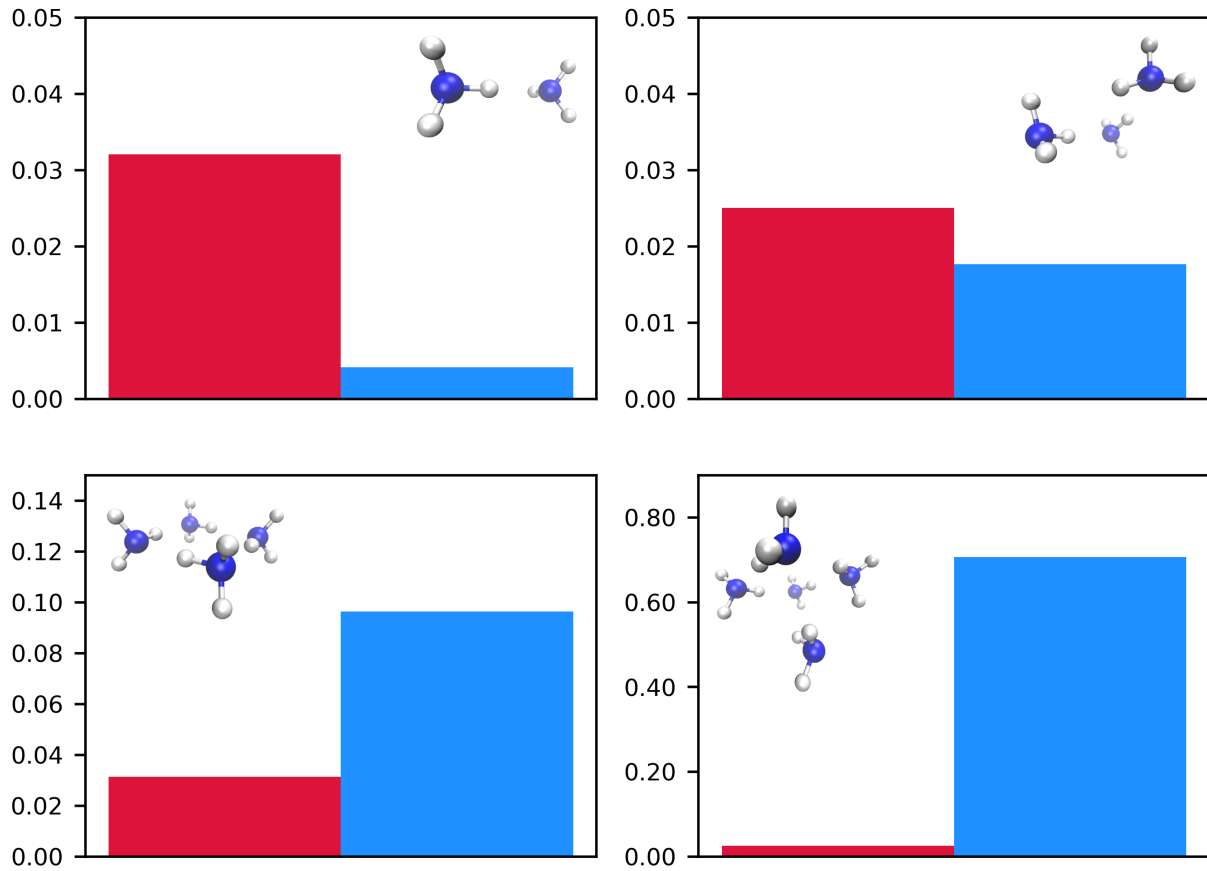


FIG. 6. RMSE of z component of forces per atom in eV/Å of four different cluster systems (dimer, trimer, tetramer and pentamer). All the structures have been previously optimized at Kohn-Sham level. The red bars represent the RMSE calculated comparing KS and KG corrected by the bulk potential, whereas the blue bars comparing KS and KG corrected by the cluster potential.