Computational Prediction of Muon Stopping Sites: a Novel Take on the Unperturbed Electrostatic Potential Method - Supplementary Information

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In this document we will show an example of how a search for the muon stopping sites could be carried out in Fe_3O_4.

1 Run `pm-symmetry` using Fe_3O_4's structural file.

This would produce an output, whith the symmetry analysis of the special Wyckoff positions in Fe_3O_4, that is shown below:

Listing 1: Output of `pm-symmetry fe3o4.cell`

```
Wyckoff points symmetry report for fe3o4.cell
Space Group International Symbol: Fd-3m
Space Group Hall Number: 525
Absolute                          Fractional              Hessian constraints
[0.  0.  0.]       [0.  0.  0.]       none
[0.      2.0895  2.0895]   [0.    0.25  0.25]         none
[0.      4.179   4.179 ]   [0.    0.5   0.5 ]   none
[0.      6.2685  6.2685]   [0.    0.75  0.75]         none
[1.04475 1.04475 5.22375]       [0.125 0.125 0.625]     isotropic
[1.04475 5.22375 1.04475]       [0.125 0.625 0.125]     isotropic
[2.0895  0.      2.0895]   [0.25  0.    0.25]         none
[2.0895  2.0895  0.    ]   [0.25  0.25  0.  ]         none
[2.0895  4.179   6.2685]   [0.25  0.5   0.75]         none
[2.0895  6.2685  4.179 ]   [0.25  0.75  0.5 ]         none
[3.13425 3.13425 3.13425]       [0.375 0.375 0.375]     isotropic
[3.13425 7.31325 7.31325]       [0.375 0.875 0.875]     isotropic
[4.179   0.      4.179 ]   [0.5   0.    0.5 ]   none
[4.179   2.0895  6.2685]   [0.5   0.25  0.75]         none
[4.179   4.179   0.    ]   [0.5   0.5   0.  ]   none
[4.179   6.2685  2.0895]   [0.5   0.75  0.25]         none
```

```
[5.22375  1.04475  1.04475]      [0.625  0.125  0.125]     isotropic
[5.22375  5.22375  5.22375]      [0.625  0.625  0.625]     isotropic
[6.2685   0.       6.2685 ]  [0.75   0.     0.75 ]        none
[6.2685   2.0895   4.179  ]  [0.75   0.25   0.5  ]        none
[6.2685   4.179    2.0895 ]  [0.75   0.5    0.25 ]        none
[6.2685   6.2685   0.     ]  [0.75   0.75   0.   ]        none
[7.31325  3.13425  7.31325]      [0.875  0.375  0.875]     isotropic
[7.31325  7.31325  3.13425]      [0.875  0.875  0.375]     isotropic
```

As we can see, the list of unoccupied special Wyckoff positions for Fe_3O_4 is relatively long. Therefore, the symmetry analysis in this case could be useful only if combined with some other piece of known information about the muon stopping site. For instance, we may know that the stopping site is placed somewhere along a Wyckoff *line* (as it is the case for MnSi). Otherwise, we would need to test each one of these positions, which might be impractical because, (as it is the case in Fe_3O_4), the muon stopping site may not be in a Wyckoff position.

So, for cases like this one, we need to continue the search for potential muon stopping sites. The next steps in the procedure include: the generation of muonated structures with muons in random positions; the relaxation of the muon position in each one of this structures and the subsequent performance of a clustering analysis.

2 Generate Structures with Muons in Random Positions

We run `pm-muairss` to generate a set of structure files with muon defects placed in random positions. This is done by running the line:

```
pm-muairss -t w <fe3o4.cell> <fe3o4.yaml>
```

and an example of `fe3o4.yaml` file for running this calculation is:

Listing 2: `fe3o4.yaml`

```
poisson_r: 0.6
name: fe3o4
charged: true
geom_steps: 300
vdw_scale: 0.25
calculator: uep
uep_gw_factor: 4.0
uep_chden: fe3o4.den_fmt
geom_force_tol: 0.05
clustering_method: hier
clustering_hier_t: 0.2
```

The muonated structures generated by this run will be stored in the folders `muon-airss-out/uep/fe3o4_*`, where * is a numerical label that identifies each particular muonated structure. The number of structures generated by this procedure will depend on the values of parameters in the `fe3o4.yaml` file such as `vdw_scale` and `poisson_r`.

The next step is to relax each one of these newly generated muonated structures.

3 Relaxing the Muon Position in each Structure with `pm-uep-opt`

In each one of these newly created `fe3o4_*` folders there will be a new `fe3o4_*.yaml` file, which will contain instructions for relaxing the muon positions in each one of the muonated structures by running the library `pm-uep-opt`. Below there is an example of this `fe3o4_*.yaml` file:

Listing 3: `fe3o4_*.yaml`

```
chden_path: path-to-folder
chden_seed: fe3o4
geom_steps: 300
gw_factor: 6.0
mu_pos:
- 6.6017194506272086
- 3.924221192037714
- 3.8231862749935717
opt_method: trust-exact
opt_tol: 0.05
particle_mass: 1.67382335232e-27
save_pickle: true
```

and we relax each one of these structures by running:

```
pm-uep-opt <fe3o4_*.yaml>
```

for each `fe3o4_*.yaml` in each one of the newly generated folders[1]. The result will be output in a `fe3o4_*.uep` file such as:

[1] If the calculation is being run in Linux, the relaxations could be done, for instance, using a Bash script.

Listing 4: `fe3o4_*.yaml`

```
97
98  ********************************
99  |    UU   UU    EEEEEE     PPPP      |
100 |    UU   UU    EE         PP   PP    |
101 |    UU   UU    EEEEEE     PPPP      |
102 |    UU   UU    EE         PP        |
103 |     UUUU     EEEEEE     PP        |
104 ********************************
105
106 Unperturbed Electrostatic Potential
107 optimiser for mu+ stopping site finding
108
109 by Simone Sturniolo (2018)
110
111 Calculations started on 2019-12-05 15:24:10.820543
112
113 Charge distribution loaded from ~/Calculations/UEP_Paper/Fe3O4/fe3o4
114 Gaussian width factor used: 6.0
115 Particle mass: 1.67382335232e-27 kg
116
117 ----------
118
119 Performing optimisation with method trust-exact
120 Tolerance required for convergence: 0.05 eV
121 Maximum number of steps: 300
122 Defect starting position: 6.6017194506272086 3.924221192037714 3.823186274993571
123
124 ----------
125
126 Optimisation stopped after 8 steps
127
128 Final coordinates: 5.789295137667838 4.670038556634775 2.983741171022327 Ang
129 Final fractional coordinates: 0.6926651277420242 0.5587507246512053 0.3569922434
130 Classical energy: -11.47475742543093 eV
131 Zero-point energy: 0.17842078166219383 eV
132 Quantum total energy: -11.296336643768736 eV
133
134 Calculation time: 64.172284 s
```

135 These relaxations may take some time. If the system is small and simple, the re-
136 laxations will be fast. However, if the system is large and sophisticated and there is a
137 large number of structures, these relaxations could be relatively expensive to run.
138 In any case, once the relaxations are ready, we need to perform the clustering anal-
139 ysis. This is done by running the line

140 `pm-muairss -t r <fe3o4.cell> <fe3o4.yaml>`

from the folder where all the structures were generated[2]. This generates two new files:

- `fe3o4_clusters.text`: This file contains the structures that form each of predicted of the clusters that are associated to potential muon stopping sites. This file also has information about which would be a representative structural file for each stopping site.
- `fe3o4_fe3o4_uep_clusters.dat`: This file has the average energy, minimum structure energy and standard deviation of the energy for each of the clusters.

Examples of this two files are below:

Listing 5: `fe3o4_clusters.text`

```
**************************
|                        |
|         MUAIRSS        |
|    Clustering report   |
|                        |
**************************

Name: fe3o4
Date: 2019-12-05 18:02:33.530251
Structure file(s): fe3o4-out.cell
Parameter file: fe3o4.yaml

Clustering method: Hierarchical
    t = 0.2


******************

Clusters for fe3o4:
CALCULATOR: uep
        2 clusters found


        ___________
        Cluster 1
        ___________
        Structures: 13

        Energy (eV):
        Minimum          Average          StDev
```

[2] In our case, this is the folder from where we can see the `muon-airss-out` folder.

−9.90 −9.90 0.00

Minimum energy structure: fe3o4_29

Structure list:
fe3o4_2 fe3o4_13 fe3o4_14 fe3o4_29
fe3o4_38 fe3o4_57 fe3o4_73 fe3o4_88
fe3o4_115 fe3o4_120 fe3o4_132 fe3o4_137
fe3o4_145

Cluster 2

Structures: 139

Energy (eV):

Minimum	Average	StDev
−11.47	−11.47	0.00

Minimum energy structure: fe3o4_48

Structure list:
fe3o4_1 fe3o4_3 fe3o4_4 fe3o4_5
fe3o4_6 fe3o4_7 fe3o4_8 fe3o4_9
fe3o4_10 fe3o4_11 fe3o4_12 fe3o4_15
fe3o4_16 fe3o4_17 fe3o4_18 fe3o4_19
fe3o4_20 fe3o4_21 fe3o4_22 fe3o4_23
fe3o4_24 fe3o4_25 fe3o4_26 fe3o4_27
fe3o4_28 fe3o4_30 fe3o4_31 fe3o4_32
fe3o4_33 fe3o4_34 fe3o4_35 fe3o4_36
fe3o4_37 fe3o4_39 fe3o4_40 fe3o4_41
fe3o4_42 fe3o4_43 fe3o4_44 fe3o4_45
fe3o4_46 fe3o4_47 fe3o4_48 fe3o4_49
fe3o4_50 fe3o4_51 fe3o4_52 fe3o4_53
fe3o4_54 fe3o4_55 fe3o4_56 fe3o4_58
fe3o4_59 fe3o4_60 fe3o4_61 fe3o4_62
fe3o4_63 fe3o4_64 fe3o4_65 fe3o4_66
fe3o4_67 fe3o4_68 fe3o4_69 fe3o4_70
fe3o4_71 fe3o4_72 fe3o4_74 fe3o4_75
fe3o4_76 fe3o4_77 fe3o4_78 fe3o4_79
fe3o4_80 fe3o4_81 fe3o4_82 fe3o4_83
fe3o4_84 fe3o4_85 fe3o4_86 fe3o4_87
fe3o4_89 fe3o4_90 fe3o4_91 fe3o4_92
fe3o4_93 fe3o4_94 fe3o4_95 fe3o4_96

```
        fe3o4_97        fe3o4_98        fe3o4_99        fe3o4_100
        fe3o4_101       fe3o4_102       fe3o4_103       fe3o4_104
        fe3o4_105       fe3o4_106       fe3o4_107       fe3o4_108
        fe3o4_109       fe3o4_110       fe3o4_111       fe3o4_112
        fe3o4_113       fe3o4_114       fe3o4_116       fe3o4_117
        fe3o4_118       fe3o4_119       fe3o4_121       fe3o4_122
        fe3o4_123       fe3o4_124       fe3o4_125       fe3o4_126
        fe3o4_127       fe3o4_128       fe3o4_129       fe3o4_130
        fe3o4_131       fe3o4_133       fe3o4_134       fe3o4_135
        fe3o4_136       fe3o4_138       fe3o4_139       fe3o4_140
        fe3o4_141       fe3o4_142       fe3o4_143       fe3o4_144
        fe3o4_146       fe3o4_147       fe3o4_148       fe3o4_149
        fe3o4_150       fe3o4_151       fe3o4_152

        ----------

        Similarity (ranked):
        0 <--> 1 (distance = 1.602)

-------------------------------


===========================
```

Listing 6: `fe3o4_fe3o4_uep_clusters.dat`

```
1       13      -9.897753370173747      -9.897721148028158
5.260352456001172e-05
2       139     -11.474801196064512     -11.474700683287459
0.00015287319327130454
```