Occupation matrix control in VASP

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Version History

Version 1	9th May 2014. Initial release with occupation control and input through OCCDIR keyword in INCAR
Version 1.01	Not released. Tidied up syntax and code to allow compilation with gfortran
Version 1.02	Not released. Added support for direct input of the occupation matrix from an external file – alpha test version
Version 1.1	Input / output modified to be compatible with the code when compiled for non-collinear / spin orbit. In this case the occupation matrix is complex, however the input only allows the real part to be specified. In principle the complex part could be added but this is not currently implemented.
	External file input of occupation matrix – documentation update
Version 1.2	26th June 2019. Add support for vasp.5.4.4
Version 1.3	Not released. Tidy up code.
Version 1.4	4th Sept 2019. Extended to include spin orbit fully with external input of the full matrix.

Occupation matrix control in VASP

Occupation matrix control sets the occupations used when calculating the DFT+U corrections. It does not directly change the electron distribution. In this way it will effectively encourage the occupations entered. This has two direct uses

1) To set a specific occupation.

In this case the electron occupations are set and the structure relaxed. It is usually best in the first step to ensure localisation on the site of choice as the initial localisation will direct the associated polaronic distortion at the site during relaxation. Once the relaxation is complete (to some degree) the occupation control should be switched off and the calculation restarted. The occupation can be picked up from the WAVECAR and the system is allowed to relax. The system may or may not retain the occupation originally intended and this will need to be checked. LDAUPRINT=2 is useful for this.

The reason for this is that using the occupation matrix causes shifts in the energy as you are setting (integer) occupations - which even for the specific electron configuration you are looking at is never correct (there is always some mixing of orbitals). Hence the need to restart with the occupation matrix switched off.

2) To obtain localisation at a specific site and look for the minimum energy occupation.

This is slightly easier as essentially you are attempting to create a polaronic distortion. In simple systems like TiO_2 and CeO_2 this can be done by setting a single electron occupation (usually use one of the low energy orbitals for the crystal field) and relaxing the system. Again it is usually best in the first step to ensure localisation on the site of choice as the initial localisation will direct the associated polaronic distortion at the site during relaxation. Once it has relaxed and created the distortion (do not usually need it that well converged) you can switch the occupation matrix control off. Generally we have found (especially for f orbitals) that the occupation becomes trapped in a specific orbital while in some d electron systems the electron can sometimes switch orbitals.

For d orbitals, if you want the lowest energy it is usually best to delete the WAVECAR and allow VASP to search for the lowest electronic structure for the given distortion . It is also advised to perform a single SCF initially and ensure reasonable localisation before relaxing the structure.

For f orbitals we have sometimes found that the distortions for different orbitals can be sufficiently different that it can direct the occupation even with the WAVECAR deleted. Hence, you have to search (or at least guess) which orbital should be occupied in the initial optimisation (i.e. choose a low energy orbital for the crystal field splitting).

Obtaining the Occupation matrix code

The occupation matrix control code is available from

The code is provided as patch files (stored in separate directories for different version of VASP and which can be applied to the specific version of VASP.

The patch files can then be applied to the VASP files in the source code directly and compile VASP normally.

```
patch < mods_main.F_vasp.5.4.4_spin_orbit.diff
```

and

```
patch < mods_LDApU.F_vasp_5.4.4_spin_orbit.diff
```

Note.

     Patch files are provided for the latest version of vasp as development to the code are made.

Conditions

If you use the occupation matrix control please cite

Allen J.P. and Watson G.W., Occupation Matrix Control of d and f electron localisation using DFT+U, Physical Chemistry Chemical Physics DOI: 10.1039/c4cp01083c

The code is provided under an MIT license. New versions of the patch will be provided to users as new versions of VASP are released or as modification / new features are implemented.

Occupation matrices within VASP

Occupation matrix control can be used for any orbital - s, p, d or f - although VASP only allows *U* to be applied to a single set of orbitals (s, p, d or f) for a given atom. Each atom essentially has a matrix of orbital occupations - VASP defines this with respect to the Cartesian coordinates. This can make getting specific occupation (or orbitals) difficult if the local structure of the atom does not correspond to the x, y and z axes.

In principle there is one element for s, a 3x3 matrix for p, a 5x5 matrix for d and a 7x7 matrix for f. This is stored in one matrix with indexes sequentially from 1 to 16. 1:s, 2-4:p, 5-9:d, 10-16:f. The f-orbitals are the general set (10 = f_{-3} to 16 = f_3). So for standard f-orbitals in a cubic crystal field off diagonal elements and non-integer occupations need to be set. See below for examples.

Input of Occupation Matrix

The method of inputting the occupation matrix is in the INCAR using the keyword **OCCDIRX** (where **X** is a number from 1-999)

OCCDIRX   No of atoms, No * (ATOM, LDAUL, No of elements, No of E *(i, j, spin, occ))

No of atoms	-	number of atoms specified on this line
Atom	-	atom number in POSCAR
LDAUL	-	orbital type (0-s, 1-p, 2-d, 3-f)
No of elements	-	Number of occupation matrix elements set for this atom
i,j	-	matrix element (1-16,1-16)
spin	-	which spin the occupation is for (1-up, 2-down)
occ	-	the occupation (up to 1.0)

NOTE - Anything not set by the **OCCDIRX** lines will automatically be set to zero.

e.g. **OCCDIR1 = 2 1 3 1 13 13 1 1.0 2 3 1 13 13 1 1.0**

Occupations are set on two atoms:

Atom 1 in POSCAR - f orbital, 1 element to set: 13-13 (f_{-3}) up spin occupation set to 1.0

Atom 2 in POSCAR - f orbital, 1 element to set: 13-13 (f_{-3}) up spin occupation set to 1.0

Note of Non-collinear / spin orbit calculations.

This method has not been fully implemented for occupation matrices for non-collinear / spin orbit calculations and these should be done through the external matrix input.

Cubic f orbitals

For the unique cubic orbital (f_{-2}, f_0 and f_2 are in both the general and cubic sets), the following can be used for an approximate occupation (once occupation matrix control is released the correct cubic orbital typically results):

Note - The lines below miss out the atoms specification / orbital type and starts with the number of matrix elements to set i.e. 4

```
fy³:       4 10 10 1 0.6 10 12 1  0.43 12 10 1  0.43 12 12 1 0.4

fy(z²-x²): 4 10 10 1 0.4 10 12 1 -0.46 12 10 1 -0.46 12 12 1 0.6

fx(z²-y²): 4 14 14 1 0.6 14 16 1  0.46 16 14 1  0.46 16 16 1 0.4

fx³:       4 14 14 1 0.4 14 16 1 -0.43 16 14 1 -0.43 16 16 1 0.6
```

Direct Input of the occupation Matrix

We have implemented a direct occupation matrix input for atoms through an external file. This greatly helps when

- the crystal field is not aligned with the axis of the structure (in which case a number of off diagonal elements are required)
- dealing with atoms with large numbers of d and f electrons
- there is a specific orbital distortion (e.g. due to vacancies or at surfaces)
- there is significant co-valent interactions resulting in more d occupation than simply the filling of specific orbitals.

To use this you need a good guess of the occupation matrix appropriate for the environment. This can often be achieve by using OCCDIR on a simple unit cell or taken from another crystal structure (e.g. for a particular oxidation state)

Reading in from an external file (OCCMATRIX) is specified in the INCAR by the tag OCCEXT = 1.

The format of the file is similar to the output when LDAUPRINT = 2 is specified (see example below). The top line has the number of atoms which have their occupations set in the external file. There are then this number of blocks on input with the following format. The first line of each block has the atom number (in the POSCAR), the angular momentum of the orbitals in question and whether there is spin(2) or not(1). Following this is a line which I usually just use to label the spin component (which is not actually taken notice of). Following this is the spin up occupation matrix (size appropriate for the angular momentum). If spin polarization was requested this is followed by another line for comment and a second occupation matrix. There is a blank line between the end of one block and the start of the next.

For example the occupations of Fe^{3+} (d^5) taken from a FM calculation can be used to specific an AFM arrangement with the matrices for the spin up and spin down reversed for the second atom (I left the spin label to remind me a reversed them). These can also be used to generate the spin for supercells containing many Fe atoms and arranging the spin. In this case VASP often has more trouble in relaxing all of the metals atoms to the appropriate spin.

```
2                              No of atoms to be specified
3   2 2                        Atom No (in POSCAR),  L,  spin(2) or not (1)
spin component  1              Not really important what is here !
   0.7997  0.3554 -0.0000 -0.0000 -0.0000
   0.3554  0.5269 -0.0000 -0.0000 -0.0000
  -0.0000 -0.0000  1.0225  0.0653  0.0575
  -0.0000 -0.0000  0.0653  0.7468 -0.3435
  -0.0000 -0.0000  0.0575 -0.3435  0.6179
spin component  2
   0.9057 -0.3651  0.0000 -0.0000  0.0000
  -0.3651  0.3291  0.0000 -0.0000  0.0000
   0.0000  0.0000  0.5578  0.4221  0.0993
  -0.0000 -0.0000  0.4221  0.5288  0.2056
   0.0000  0.0000  0.0993  0.2056  0.2269
                               Blank line between atoms
4   2 2                        Atom No (in POSCAR),  L,  spin(2) or not (1)
spin component  2                Spins switched to give the AFM arrangmnet
   0.9057 -0.3651  0.0000 -0.0000  0.0000
  -0.3651  0.3291  0.0000 -0.0000  0.0000
   0.0000  0.0000  0.5578  0.4221  0.0993
  -0.0000 -0.0000  0.4221  0.5288  0.2056
   0.0000  0.0000  0.0993  0.2056  0.2269
spin component  1
   0.7997  0.3554 -0.0000 -0.0000 -0.0000
   0.3554  0.5269 -0.0000 -0.0000 -0.0000
  -0.0000 -0.0000  1.0225  0.0653  0.0575
  -0.0000 -0.0000  0.0653  0.7468 -0.3435
  -0.0000 -0.0000  0.0575 -0.3435  0.6179
                                Blank line
```

Direct Input of the occupation Matrix for Non-collinear / spin orbit

In the case of non-collinear / spin orbit the occupation matrix is now twice as large as the number of atomic orbital involved. In addition, the matrix is complex. VASP handles this by having 4 complex n x n matrices, where n is the number of atomic orbital relevant for the given L. e.g. a four 5x5 matrices for d orbitals or four 7x7 matrices for f orbitals.

The matrix input follows the same format as for spin polarised calculation except instead of two spins the spin tag is used to select the four matrices input. In addition there are two matrices side by side which are the real and complex parts of the occupation matrix.

The example below shows the occupation matrix for the 3K magnetic structure of UO2. There are four atoms in the cubic unit cell with each with 4 "spin components" which represent the different parts of the single occupation matrix.

```
4
1 3 4
spin component  1
  0.2942   0.0147   0.0789   0.0078   0.0297  -0.0015  -0.0876      -0.0000   0.0006   0.0021   0.0039   0.0215  -0.2219  -0.0922
  0.0147   0.1290   0.0137   0.0186   0.0035   0.0020  -0.0045      -0.0006   0.0000   0.0188  -0.0116  -0.0147  -0.0165  -0.0121
  0.0789   0.0137   0.3010   0.0060  -0.0652   0.0030  -0.0285      -0.0021  -0.0188  -0.0000  -0.2886  -0.0733  -0.0890  -0.0242
  0.0078   0.0186   0.0060   0.3732   0.0933   0.0226  -0.0062      -0.0039   0.0116   0.2886   0.0000  -0.0864  -0.0013  -0.0048
  0.0297   0.0035  -0.0652   0.0933   0.0832  -0.0134  -0.0212      -0.0215   0.0147   0.0733   0.0864   0.0000  -0.0168  -0.0044
 -0.0015   0.0020   0.0030   0.0226  -0.0134   0.2214   0.0798       0.2219   0.0165   0.0890   0.0013   0.0168  -0.0000  -0.0738
 -0.0876  -0.0045  -0.0285  -0.0062  -0.0212   0.0798   0.0945       0.0922   0.0121   0.0242   0.0048   0.0044   0.0738  -0.0000
spin component  2
  0.1042   0.0116   0.0345   0.0033   0.0022   0.0827  -0.0006       0.0966   0.0055   0.0302  -0.0023   0.0168  -0.0904  -0.0713
  0.0049   0.0041   0.0264   0.0051  -0.0025  -0.0068  -0.0065      -0.0083  -0.0040   0.0020  -0.0210  -0.0073  -0.0166  -0.0005
  0.0015   0.0017   0.0585   0.0809   0.0042   0.0178   0.0030       0.0130   0.0001   0.0717  -0.0663  -0.0359  -0.0047  -0.0048
 -0.0115  -0.0043   0.0799  -0.1147  -0.0596  -0.0018   0.0066       0.0060  -0.0097  -0.0976  -0.0983   0.0025   0.0007   0.0037
 -0.0095   0.0152   0.0134   0.2741   0.0759  -0.0437  -0.0251      -0.0758   0.0038   0.2104  -0.0165  -0.0836   0.0118   0.0259
  0.0673   0.0033  -0.0087   0.0162   0.0278  -0.0635  -0.0477      -0.0757   0.0048  -0.0094   0.0316   0.0030  -0.0544   0.0013
 -0.0186  -0.0002  -0.0053  -0.0007  -0.0237   0.2309   0.1020       0.2714   0.0163   0.0829   0.0056   0.0266   0.0147  -0.0837
spin component  3
  0.1042   0.0049   0.0015  -0.0115  -0.0095   0.0673  -0.0186      -0.0966   0.0083  -0.0130  -0.0060   0.0758   0.0757  -0.2714
  0.0116   0.0041   0.0017  -0.0043   0.0152   0.0033  -0.0002      -0.0055   0.0040  -0.0001   0.0097  -0.0038  -0.0048  -0.0163
  0.0345   0.0264   0.0585   0.0799   0.0134  -0.0087  -0.0053      -0.0302  -0.0020  -0.0717   0.0976  -0.2104   0.0094  -0.0829
  0.0033   0.0051   0.0809  -0.1147   0.2741   0.0162  -0.0007       0.0023   0.0210   0.0663   0.0983   0.0165  -0.0316  -0.0056
  0.0022  -0.0025   0.0042  -0.0596   0.0759   0.0278  -0.0237      -0.0168   0.0073   0.0359  -0.0025   0.0836  -0.0030  -0.0266
  0.0827  -0.0068   0.0178  -0.0018  -0.0437  -0.0635   0.2309       0.0904   0.0166   0.0047  -0.0007  -0.0118   0.0544  -0.0147
 -0.0006  -0.0065   0.0030   0.0066  -0.0251  -0.0477   0.1020       0.0713   0.0005   0.0048  -0.0037  -0.0259  -0.0013   0.0837
spin component  4
  0.1086  -0.0001   0.0115  -0.0011  -0.0299  -0.0017   0.0924      -0.0000   0.0079  -0.0058  -0.0025   0.0204   0.0545  -0.1132
 -0.0001   0.1230   0.0030   0.0019   0.0071   0.0021  -0.0093      -0.0079  -0.0000  -0.0026   0.0083  -0.0101  -0.0031  -0.0066
  0.0115   0.0030   0.0625  -0.0078   0.0650  -0.0067   0.0148       0.0058   0.0026  -0.0000   0.0480  -0.0495  -0.0054  -0.0027
 -0.0011   0.0019  -0.0078   0.1029  -0.0894  -0.0185   0.0053       0.0025  -0.0083  -0.0480  -0.0000  -0.0867   0.0057   0.0087
 -0.0299   0.0071   0.0650  -0.0894   0.2707   0.0281  -0.0766      -0.0204   0.0101   0.0495   0.0867   0.0000  -0.0489   0.0163
 -0.0017   0.0021  -0.0067  -0.0185   0.0281   0.0682  -0.0829      -0.0545   0.0031   0.0054  -0.0057   0.0489   0.0000  -0.0621
  0.0924  -0.0093   0.0148   0.0053  -0.0766  -0.0829   0.3109       0.1132   0.0066   0.0027  -0.0087  -0.0163   0.0621  -0.0000

2 3 4
spin component  1
  0.2942  -0.0147   0.0789   0.0078  -0.0297  -0.0015   0.0876      -0.0000  -0.0006   0.0021   0.0039  -0.0215  -0.2219   0.0922
 -0.0147   0.1290  -0.0137  -0.0186   0.0035  -0.0020  -0.0045       0.0006   0.0000  -0.0188   0.0116  -0.0147   0.0165  -0.0121
```

```
    0.0789 -0.0137  0.3010  0.0060  0.0652  0.0030  0.0285    -0.0021  0.0188  0.0000 -0.2886  0.0733 -0.0890  0.0242
    0.0078 -0.0186  0.0060  0.3732 -0.0933  0.0226  0.0062    -0.0039 -0.0116  0.2886  0.0000  0.0864 -0.0013  0.0048
   -0.0297  0.0035  0.0652 -0.0933  0.0832  0.0134 -0.0212     0.0215  0.0147 -0.0733 -0.0864 -0.0000  0.0168 -0.0044
   -0.0015 -0.0020  0.0030  0.0226  0.0134  0.2214 -0.0798     0.2219 -0.0165  0.0890  0.0013 -0.0168 -0.0000  0.0738
    0.0876 -0.0045  0.0285  0.0062 -0.0212 -0.0798  0.0945    -0.0922  0.0121 -0.0242 -0.0048  0.0044 -0.0738 -0.0000
 spin component  2
   -0.1042  0.0116 -0.0345 -0.0033  0.0022 -0.0827 -0.0006    -0.0966  0.0055 -0.0302  0.0023  0.0168  0.0904 -0.0713
    0.0049 -0.0041  0.0264  0.0051  0.0025 -0.0068  0.0065    -0.0083  0.0040  0.0020 -0.0210  0.0073 -0.0166  0.0005
   -0.0015  0.0017 -0.0585 -0.0809  0.0042 -0.0178  0.0030    -0.0130  0.0001 -0.0717  0.0663 -0.0359  0.0047 -0.0048
    0.0115 -0.0043 -0.0799  0.1147 -0.0596  0.0018  0.0066    -0.0060 -0.0097  0.0976  0.0983  0.0025 -0.0007  0.0037
   -0.0095 -0.0152  0.0134  0.2741 -0.0759 -0.0437  0.0251    -0.0758 -0.0038  0.2104 -0.0165  0.0836  0.0118 -0.0259
   -0.0673  0.0033  0.0087 -0.0162  0.0278  0.0635 -0.0477     0.0757  0.0048  0.0094 -0.0316  0.0030  0.0544  0.0013
   -0.0186  0.0002 -0.0053 -0.0007  0.0237  0.2309 -0.1020     0.2714 -0.0163  0.0829  0.0056 -0.0266  0.0147  0.0837
 spin component  3
   -0.1042  0.0049 -0.0015  0.0115 -0.0095 -0.0673 -0.0186     0.0966  0.0083  0.0130  0.0060  0.0758 -0.0757 -0.2714
    0.0116 -0.0041  0.0017 -0.0043 -0.0152  0.0033  0.0002    -0.0055 -0.0040 -0.0001  0.0097  0.0038 -0.0048  0.0163
   -0.0345  0.0264 -0.0585 -0.0799  0.0134  0.0087 -0.0053     0.0302 -0.0020  0.0717 -0.0976 -0.2104 -0.0094 -0.0829
   -0.0033  0.0051 -0.0809  0.1147  0.2741 -0.0162 -0.0007    -0.0023  0.0210 -0.0663 -0.0983  0.0165  0.0316 -0.0056
    0.0022  0.0025  0.0042 -0.0596 -0.0759  0.0278  0.0237    -0.0168 -0.0073  0.0359 -0.0025 -0.0836 -0.0030  0.0266
   -0.0827 -0.0068 -0.0178  0.0018 -0.0437  0.0635  0.2309    -0.0904  0.0166 -0.0047  0.0007 -0.0118 -0.0544 -0.0147
   -0.0006  0.0065  0.0030  0.0066  0.0251 -0.0477 -0.1020     0.0713 -0.0005  0.0048 -0.0037  0.0259 -0.0013 -0.0837
 spin component  4
    0.1086  0.0001  0.0115 -0.0011  0.0299 -0.0017 -0.0924    -0.0000 -0.0079 -0.0058 -0.0025 -0.0204  0.0545  0.1132
    0.0001  0.1230 -0.0030 -0.0019  0.0071 -0.0021 -0.0093     0.0079 -0.0000  0.0026 -0.0083 -0.0101  0.0031 -0.0066
    0.0115 -0.0030  0.0625 -0.0078 -0.0650 -0.0067 -0.0148     0.0058 -0.0026 -0.0000  0.0480  0.0495 -0.0054  0.0027
   -0.0011 -0.0019 -0.0078  0.1029  0.0894 -0.0185 -0.0053     0.0025  0.0083 -0.0480 -0.0000  0.0867  0.0057 -0.0087
    0.0299  0.0071 -0.0650  0.0894  0.2707 -0.0281 -0.0766     0.0204  0.0101 -0.0495 -0.0867  0.0000  0.0489  0.0163
   -0.0017 -0.0021 -0.0067 -0.0185 -0.0281  0.0682  0.0829    -0.0545 -0.0031  0.0054 -0.0057 -0.0489  0.0000  0.0621
   -0.0924 -0.0093 -0.0148 -0.0053 -0.0766  0.0829  0.3109    -0.1132  0.0066 -0.0027  0.0087 -0.0163 -0.0621 -0.0000


 3 3 4
 spin component  1
    0.1086  0.0001  0.0115  0.0011 -0.0299  0.0017  0.0924    -0.0000 -0.0079 -0.0058  0.0025  0.0204 -0.0545 -0.1132
    0.0001  0.1230 -0.0030  0.0019 -0.0071  0.0021  0.0093     0.0079 -0.0000  0.0026  0.0083  0.0101 -0.0031  0.0066
    0.0115 -0.0030  0.0625  0.0078  0.0650  0.0067  0.0148     0.0058 -0.0026 -0.0000 -0.0480 -0.0495  0.0054 -0.0027
    0.0011  0.0019  0.0078  0.1029  0.0894 -0.0185 -0.0053    -0.0025 -0.0083  0.0480 -0.0000  0.0867  0.0057 -0.0087
   -0.0299 -0.0071  0.0650  0.0894  0.2707 -0.0281 -0.0766    -0.0204 -0.0101  0.0495 -0.0867  0.0000  0.0489  0.0163
    0.0017  0.0021  0.0067 -0.0185 -0.0281  0.0682  0.0829     0.0545  0.0031 -0.0054 -0.0057 -0.0489  0.0000  0.0621
    0.0924  0.0093  0.0148 -0.0053 -0.0766  0.0829  0.3109     0.1132 -0.0066  0.0027  0.0087 -0.0163 -0.0621 -0.0000
```

```
spin component  2
  0.1042 -0.0049  0.0015  0.0115 -0.0095 -0.0673 -0.0186    -0.0966 -0.0083 -0.0130  0.0060  0.0758 -0.0757 -0.2714
 -0.0116  0.0041 -0.0017 -0.0043 -0.0152  0.0033  0.0002     0.0055  0.0040  0.0001  0.0097  0.0038 -0.0048  0.0163
  0.0345 -0.0264  0.0585 -0.0799  0.0134  0.0087 -0.0053    -0.0302  0.0020 -0.0717 -0.0976 -0.2104 -0.0094 -0.0829
 -0.0033  0.0051 -0.0809 -0.1147 -0.2741  0.0162  0.0007    -0.0023  0.0210 -0.0663  0.0983 -0.0165 -0.0316  0.0056
  0.0022  0.0025  0.0042  0.0596  0.0759 -0.0278 -0.0237    -0.0168 -0.0073  0.0359  0.0025  0.0836  0.0030 -0.0266
 -0.0827 -0.0068 -0.0178 -0.0018  0.0437 -0.0635 -0.2309    -0.0904  0.0166 -0.0047 -0.0007  0.0118  0.0544  0.0147
 -0.0006  0.0065  0.0030 -0.0066 -0.0251  0.0477  0.1020     0.0713 -0.0005  0.0048  0.0037 -0.0259  0.0013  0.0837
spin component  3
  0.1042 -0.0116  0.0345 -0.0033  0.0022 -0.0827 -0.0006     0.0966 -0.0055  0.0302  0.0023  0.0168  0.0904 -0.0713
 -0.0049  0.0041 -0.0264  0.0051  0.0025 -0.0068  0.0065     0.0083 -0.0040 -0.0020 -0.0210  0.0073 -0.0166  0.0005
  0.0015 -0.0017  0.0585 -0.0809  0.0042 -0.0178  0.0030     0.0130 -0.0001  0.0717  0.0663 -0.0359  0.0047 -0.0048
  0.0115 -0.0043 -0.0799 -0.1147  0.0596 -0.0018 -0.0066    -0.0060 -0.0097  0.0976 -0.0983 -0.0025  0.0007 -0.0037
 -0.0095 -0.0152  0.0134 -0.2741  0.0759  0.0437 -0.0251    -0.0758 -0.0038  0.2104  0.0165 -0.0836 -0.0118  0.0259
 -0.0673  0.0033  0.0087  0.0162 -0.0278 -0.0635  0.0477     0.0757  0.0048  0.0094  0.0316 -0.0030 -0.0544 -0.0013
 -0.0186  0.0002 -0.0053  0.0007 -0.0237 -0.2309  0.1020     0.2714 -0.0163  0.0829 -0.0056  0.0266 -0.0147 -0.0837
spin component  4
  0.2942 -0.0147  0.0789 -0.0078  0.0297  0.0015 -0.0876    -0.0000 -0.0006  0.0021 -0.0039  0.0215  0.2219 -0.0922
 -0.0147  0.1290 -0.0137  0.0186 -0.0035  0.0020  0.0045     0.0006  0.0000 -0.0188 -0.0116  0.0147 -0.0165  0.0121
  0.0789 -0.0137  0.3010 -0.0060 -0.0652 -0.0030 -0.0285    -0.0021  0.0188 -0.0000  0.2886 -0.0733  0.0890 -0.0242
 -0.0078  0.0186 -0.0060  0.3732 -0.0933  0.0226  0.0062     0.0039  0.0116 -0.2886  0.0000  0.0864 -0.0013  0.0048
  0.0297 -0.0035 -0.0652 -0.0933  0.0832  0.0134 -0.0212    -0.0215 -0.0147  0.0733 -0.0864  0.0000  0.0168 -0.0044
  0.0015  0.0020 -0.0030  0.0226  0.0134  0.2214 -0.0798    -0.2219  0.0165 -0.0890  0.0013 -0.0168 -0.0000  0.0738
 -0.0876  0.0045 -0.0285  0.0062 -0.0212 -0.0798  0.0945     0.0922 -0.0121  0.0242 -0.0048  0.0044 -0.0738 -0.0000


4 3 4
spin component  1
  0.1086 -0.0001  0.0115  0.0011  0.0299  0.0017 -0.0924    -0.0000  0.0079 -0.0058  0.0025 -0.0204 -0.0545  0.1132
 -0.0001  0.1230  0.0030 -0.0019 -0.0071 -0.0021  0.0093    -0.0079 -0.0000 -0.0026 -0.0083  0.0101  0.0031  0.0066
  0.0115  0.0030  0.0625  0.0078 -0.0650  0.0067 -0.0148     0.0058  0.0026 -0.0000 -0.0480  0.0495  0.0054  0.0027
  0.0011 -0.0019  0.0078  0.1029 -0.0894 -0.0185  0.0053    -0.0025  0.0083  0.0480 -0.0000 -0.0867  0.0057  0.0087
  0.0299 -0.0071 -0.0650 -0.0894  0.2707  0.0281 -0.0766     0.0204 -0.0101 -0.0495  0.0867  0.0000 -0.0489  0.0163
  0.0017 -0.0021  0.0067 -0.0185  0.0281  0.0682 -0.0829     0.0545 -0.0031 -0.0054 -0.0057  0.0489  0.0000 -0.0621
 -0.0924  0.0093 -0.0148  0.0053 -0.0766 -0.0829  0.3109    -0.1132 -0.0066 -0.0027 -0.0087 -0.0163  0.0621 -0.0000
spin component  2
 -0.1042 -0.0049 -0.0015 -0.0115 -0.0095  0.0673 -0.0186     0.0966 -0.0083  0.0130 -0.0060  0.0758  0.0757 -0.2714
 -0.0116 -0.0041 -0.0017 -0.0043  0.0152  0.0033 -0.0002     0.0055 -0.0040  0.0001  0.0097 -0.0038 -0.0048 -0.0163
 -0.0345 -0.0264 -0.0585  0.0799  0.0134 -0.0087 -0.0053     0.0302  0.0020  0.0717  0.0976 -0.2104  0.0094 -0.0829
  0.0033  0.0051  0.0809  0.1147 -0.2741 -0.0162  0.0007     0.0023  0.0210  0.0663 -0.0983 -0.0165  0.0316  0.0056
```

```
    0.0022 -0.0025  0.0042  0.0596 -0.0759 -0.0278  0.0237    -0.0168  0.0073  0.0359  0.0025 -0.0836  0.0030  0.0266
    0.0827 -0.0068  0.0178  0.0018  0.0437  0.0635 -0.2309     0.0904  0.0166  0.0047  0.0007  0.0118 -0.0544  0.0147
   -0.0006 -0.0065  0.0030 -0.0066  0.0251  0.0477 -0.1020     0.0713  0.0005  0.0048  0.0037  0.0259  0.0013 -0.0837
spin component  3
   -0.1042 -0.0116 -0.0345  0.0033  0.0022  0.0827 -0.0006    -0.0966 -0.0055 -0.0302 -0.0023  0.0168 -0.0904 -0.0713
   -0.0049 -0.0041 -0.0264  0.0051 -0.0025 -0.0068 -0.0065     0.0083  0.0040 -0.0020 -0.0210 -0.0073 -0.0166 -0.0005
   -0.0015 -0.0017 -0.0585  0.0809  0.0042  0.0178  0.0030    -0.0130 -0.0001 -0.0717 -0.0663 -0.0359 -0.0047 -0.0048
   -0.0115 -0.0043  0.0799  0.1147  0.0596  0.0018 -0.0066     0.0060 -0.0097 -0.0976  0.0983 -0.0025 -0.0007 -0.0037
   -0.0095  0.0152  0.0134 -0.2741 -0.0759  0.0437  0.0251    -0.0758  0.0038  0.2104  0.0165  0.0836 -0.0118 -0.0259
    0.0673  0.0033 -0.0087 -0.0162 -0.0278  0.0635  0.0477    -0.0757  0.0048 -0.0094 -0.0316 -0.0030  0.0544 -0.0013
   -0.0186 -0.0002 -0.0053  0.0007  0.0237 -0.2309 -0.1020     0.2714  0.0163  0.0829 -0.0056 -0.0266 -0.0147  0.0837
spin component  4
    0.2942  0.0147  0.0789 -0.0078 -0.0297  0.0015  0.0876    -0.0000  0.0006  0.0021 -0.0039 -0.0215  0.2219  0.0922
    0.0147  0.1290  0.0137 -0.0186 -0.0035 -0.0020  0.0045    -0.0006  0.0000  0.0188  0.0116  0.0147  0.0165  0.0121
    0.0789  0.0137  0.3010 -0.0060  0.0652 -0.0030  0.0285    -0.0021 -0.0188 -0.0000  0.2886  0.0733  0.0890  0.0242
   -0.0078 -0.0186 -0.0060  0.3732  0.0933  0.0226 -0.0062     0.0039 -0.0116 -0.2886  0.0000 -0.0864 -0.0013 -0.0048
   -0.0297 -0.0035  0.0652  0.0933  0.0832 -0.0134 -0.0212     0.0215 -0.0147 -0.0733  0.0864  0.0000 -0.0168 -0.0044
    0.0015 -0.0020 -0.0030  0.0226 -0.0134  0.2214  0.0798    -0.2219 -0.0165 -0.0890  0.0013  0.0168 -0.0000 -0.0738
    0.0876  0.0045  0.0285 -0.0062 -0.0212  0.0798  0.0945    -0.0922 -0.0121 -0.0242  0.0048  0.0044  0.0738 -0.0000
```

Output

When the program reads a occupation control directive it will acknowledge this in the OUTCAR. Once all the occupations are read it will then print out the occupations matrices for those atoms that they have been set for.

For example for a spin polarised calculation involving the setting of the first two atoms occupations using OCCDIR the output will be. This allows the user to check that the input was successfully read.

```
OCCDIR1    found

OCCDIR2    found

Occupation matrix control coded by Prof. Graeme Watson
at Trinity College Dublin

Occupation set for the following atoms


ATOM            1  Spin            1
       10      11      12      13      14      15      16
10   0.6000  0.0000  0.4300  0.0000  0.0000  0.0000  0.0000    10
11   0.0000  0.0000  0.0000  0.0000  0.0000  0.0000  0.0000    11
12   0.4300  0.0000  0.4000  0.0000  0.0000  0.0000  0.0000    12
13   0.0000  0.0000  0.0000  0.0000  0.0000  0.0000  0.0000    13
14   0.0000  0.0000  0.0000  0.0000  0.0000  0.0000  0.0000    14
15   0.0000  0.0000  0.0000  0.0000  0.0000  0.0000  0.0000    15
16   0.0000  0.0000  0.0000  0.0000  0.0000  0.0000  0.0000    16

ATOM            1  Spin            2
       10      11      12      13      14      15      16
10   0.0000  0.0000  0.0000  0.0000  0.0000  0.0000  0.0000    10
11   0.0000  0.0000  0.0000  0.0000  0.0000  0.0000  0.0000    11
12   0.0000  0.0000  0.0000  0.0000  0.0000  0.0000  0.0000    12
13   0.0000  0.0000  0.0000  0.0000  0.0000  0.0000  0.0000    13
14   0.0000  0.0000  0.0000  0.0000  0.0000  0.0000  0.0000    14
15   0.0000  0.0000  0.0000  0.0000  0.0000  0.0000  0.0000    15
16   0.0000  0.0000  0.0000  0.0000  0.0000  0.0000  0.0000    16

ATOM            2  Spin            1
       10      11      12      13      14      15      16
10   0.6000  0.0000  0.4300  0.0000  0.0000  0.0000  0.0000    10
11   0.0000  0.0000  0.0000  0.0000  0.0000  0.0000  0.0000    11
12   0.4300  0.0000  0.4000  0.0000  0.0000  0.0000  0.0000    12
13   0.0000  0.0000  0.0000  0.0000  0.0000  0.0000  0.0000    13
14   0.0000  0.0000  0.0000  0.0000  0.0000  0.0000  0.0000    14
15   0.0000  0.0000  0.0000  0.0000  0.0000  0.0000  0.0000    15
16   0.0000  0.0000  0.0000  0.0000  0.0000  0.0000  0.0000    16

ATOM            2  Spin            2
       10      11      12      13      14      15      16
10   0.0000  0.0000  0.0000  0.0000  0.0000  0.0000  0.0000    10
11   0.0000  0.0000  0.0000  0.0000  0.0000  0.0000  0.0000    11
12   0.0000  0.0000  0.0000  0.0000  0.0000  0.0000  0.0000    12
13   0.0000  0.0000  0.0000  0.0000  0.0000  0.0000  0.0000    13
14   0.0000  0.0000  0.0000  0.0000  0.0000  0.0000  0.0000    14
15   0.0000  0.0000  0.0000  0.0000  0.0000  0.0000  0.0000    15
16   0.0000  0.0000  0.0000  0.0000  0.0000  0.0000  0.0000    16
```

What to do if localisation does not occur

Most defect calculations start from an idealised structure without distortion and hence the initial localisation of an electron or hole onto the site of choice may not occur in the first SCF step and hence the relaxation will not be directed to create the distortion that will stabilize it. It is very important to get this initial localisation otherwise the approach is likely to fail. The localisation required in the first step, however, is not full localisation. As long as there is significant charge associated with the site (easiest to see in the spin density projections at the end of a run with LORBIT = 11) above 0.5 then the relaxation should reinforce the localisation.

In bulk materials this is not usually a problem as all of the potential sites have similar energies and the occupation matrix approach can overcome the energetic preference of one site over another. It can become more problematic if the site energies are quite different (e.g. at a surface) or if there are more than one ion that could be oxidized or reduced (e.g. Ti doped CeO_2). In these cases, additional measures may have to be taken to obtain the initial localisation.

An obvious approach is to temporarily increase the U value. This increases the push of the electrons and hence increases the encouragement of the occupation matrix control on the electron density. This can be useful to assist in the initial localisation and relaxation. Once sufficient distortion of the structure has occurred the U value should be returned to its original value and the normal procedure followed.

An additional approach is to set the occupations of the sites to which electrons / holes are incorrectly localising to to 0.00. This can be done using the normal occupation matrix control and only requires a single element to be set to 0.00 as the default action is to set all of the occupations left unset to 0.00. This can work with formally unoccupied ions (e.g. Ce^{4+} or Ti^{4+}) but will not work for ions which have occupations in both charge states (e.g. Mn^{2+} vs Mn^{3+}). This can cause some issues where there is significant mixing with the anions in the pure material (e.g. it works better for TiO_2 than V_2O_5). In this case the direct specification of the occupation matrix through the externals input may prove more useful (see below)

Finally, if there is a very large energy difference between the localisation being attempted and the lowest energy configuration it may simply not be possible to force the localisation. This is more likely in d electron systems where the electrons can more easily move from one orbital to another.

VASP

VASP (Vienna Ab-initio Simulation Package) is a software package created, distributed, and maintained by the Hafner Research Group at the University of Vienna.