

Occupation matrix control in VASP

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Version History

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|--------------|--|
| Version 1 | 9 th 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

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

<https://github.com/WatsonGroupTCD>

The code is provided as patch files which can be applied to a 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.5.3.5.diff
```

and

```
patch < mods_LDAPU.F_vasp_5.3.5.diff
```

Note

The patch files will work with vasp.5.4.1. The LDAPU.F routine from 5.3.5 and 5.4.1 are identical. The main.F routine has changed but the patch application finds the correct part of the code issuing a warning that the line numbers are different. This is OK and the resulting code works properly.

Conditions

The code is provided as is and should not be distributed. New versions of the patch will be provided to users as new versions of VASP are released or as modification / new features are implemented.

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

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

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

```

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 associate 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 CeO₂). 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 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. Ce⁴⁺ or Ti⁴⁺) but will not work for ions which have occupations in both charge states (e.g. Mn²⁺ vs Mn³⁺). This can cause some issues where there is significant mixing with the anions in the pure material (e.g. it works better for TiO₂ than V₂O₅). 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.

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 achieved 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 specify 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
  0.7997  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 1
  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

```

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.