

# **Analysis of an Electric-Field Gradient (EFG): the EFG-switch in LAPW2**

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## 0.1 In brief: the EFG and how it is obtained in LAPW

The EFG is a traceless symmetric tensor of rank 2, defined as the second derivative (with respect to spatial coordinates) evaluated at the position of the nucleus ( $\vec{r} = \vec{0}$ ):

$$V_{ij} = \left. \frac{\partial^2 V(\vec{r})}{\partial x_i \partial x_j} \right|_{r=0} \quad (0.1)$$

Five independent quantities have to be provided in order to determine the tensor unambiguously <sup>1</sup>. This can be done either in cartesian notation as a traceless symmetric 3x3-matrix, or in spherical coordinates by 5 ‘angular momentum’ components of rank 2 (L=2, M=-2, -1, 0, 1, 2).

In WIEN2k the 5 spherical components of the EFG tensor are calculated (since the potential is calculated using a spherical notation) and the cartesian components of the EFG tensor are obtained by evaluating:

$$V_{ij} = \sqrt{\frac{15}{16\pi}} \lim_{r \rightarrow 0} \frac{1}{r^2} \cdot \begin{pmatrix} V_{22}(r) - \frac{1}{\sqrt{3}}V_{20}(r) & V_{2,-2}(r) & V_{21}(r) \\ V_{2,-2}(r) & -V_{22}(r) - \frac{1}{\sqrt{3}}V_{20}(r) & V_{2,-1}(r) \\ V_{21}(r) & V_{2,-1}(r) & \frac{2}{\sqrt{3}}V_{20}(r) \end{pmatrix}. \quad (0.2)$$

In either notation, one is most interested in the principal component, which is  $V_{zz}$  (cartesian) or  $V_{20}$  (spherical). <sup>2</sup>

$V_{zz}$  can be obtained from the charge density  $\rho(\vec{r})$  in the following way:

$$V_{zz} = \int \rho(r) \frac{2P_2(\cos \vartheta)}{r^3} dr \quad (0.3)$$

In the LAPW method,  $\rho(\vec{r})$  is expressed by lattice harmonics, i.e. under an LM-form:

$$\rho_{LM}(r) = \sum_{E < E_F} \sum_{lm} \sum_{l'm'} R_{lm}(r) R_{l'm'}(r) G_{LL'}^{Mmm'} \quad (0.4)$$

The  $R_{lm}$  are radial functions with angular momentum  $l$  or  $l'$ , and the  $G$  are the so-called Gaunt numbers (an integral over a product of spherical harmonics). Because of the product with  $P_2 \propto Y_{20}$  in the expression of  $V_{zz}$  (Eq. 0.3), only the component  $\rho_{20}$  will be important. After this, the Gaunt numbers further limit the number of contributions: for L=2 and M=0, only  $l=l'=1$  and  $l=l'=2$  (and to a minor extent  $l=0$ ,  $l'=2$  and  $l=1$ ,  $l'=3$ ) give non-zero Gaunt numbers. We call this p-p, d-d (s-d and p-f) contributions to the EFG.

<sup>1</sup>Due to the permutation of partial derivatives the tensor has to be symmetric and due to the Poisson equation ( $\sum_i V_{ii} = \rho(0) = 0$ ) the tensor has to be traceless  $\Rightarrow$  5 degrees of freedom.

<sup>2</sup>In the code the potential is stored as  $r^2 v_{LM}(r)$  and the  $LM$ -components are given in  $\frac{15}{16\pi}$  which is why this prefactor is omitted in the outputfiles (see page 7 and 11).

## 0.2 Example: body-centered tetragonal In

These are the input files:

case.struct:

```
In
B LATTICE,NONEQUIV.ATOMS: 1139_I4/mmm
MODE OF CALC=RELA unit=ang
  6.145960 6.145960 9.346780 90.000000 90.000000 90.000000
ATOM -1: X=0.00000000 Y=0.00000000 Z=0.00000000
        MULT= 1          ISPLIT= 8
In      NPT= 781  R0=0.00001000 RMT= 2.5000    Z: 49.0
LOCAL ROT MATRIX: 1.0000000 0.0000000 0.0000000
                  0.0000000 1.0000000 0.0000000
                  0.0000000 0.0000000 1.0000000
  0      NUMBER OF SYMMETRY OPERATIONS
```

case.inst:

```
In 1
Kr 4 5
4, 2,2.0 N
4, 2,2.0 N
4,-3,3.0 N
4,-3,3.0 N
5,-1,1.0 N
5,-1,1.0 N
5, 1,1.0 N
5, 1,0.0 N
*** End of Input
*** End of Input
```

Run this case to self consistency using GGA (PBE) and with a separation energy of  $-6.5$  Ry in `lstart`. Use e.g.  $R_{mt} * K_{max} = 7$  and 40 k-points in the IBZ (=400 points as input for `kgen`), which is not too accurate but very fast for a try-out. With these settings and an energy convergence criterion of  $10^{-6}$  Ry, you will end up with `:EFG001` =  $3.74 \cdot 10^{21}$  V/m<sup>2</sup>. Inspection of the following part of `case.scf` learns that there are six 4p-electrons at  $-5.02$  Ry, 10 4d-electrons at about  $-0.65$  Ry and some tendency to localize s-electrons at  $-0.24$  Ry (the Fermi energy `:FER` = 0.41):

ATOMIC SPHERE DEPENDENT PARAMETERS FOR ATOM In

OVERALL ENERGY PARAMETER IS 0.3000

OVERALL BASIS SET ON ATOM IS LAPW

E( 1)= 0.3000

APW+lo

E( 1)= -5.0225 E(BOTTOM)= -5.040 E(TOP)= -5.005

LOCAL ORBITAL

E( 2)= -0.680 E(BOTTOM)= -0.850 E(TOP)= -0.510

APW+lo

E( 2)= 0.3000

LOCAL ORBITAL

E( 0)= 0.3000

APW+lo

K= 0.14286 0.14286 0.14286 1

:RKM : MATRIX SIZE 79LOs: 17 RKM= 6.98 WEIGHT= 8.00 PGR:

EIGENVALUES ARE:

-5.0217440 -5.0205144 -5.0204366 -0.6625649 -0.6594197

-0.6558732 -0.6524609 -0.6454063 -0.2362241 0.9171429

0.9306819 1.1476094 1.2111875 1.3829636 1.4540965

\*\*\*\*\*

Before proceeding, it is instructive to produce a Density of States (DOS) over a wide energy region first. Use the following case.int:

In

-5.50 0.0001 2.000 0.0002 EMIN, DE, EMAX Gauss-broadening(>;de)

6 NUMBER OF DOS-CASES

0 1 tot atom,case=column in qtl-header, label

1 2 In-s

1 3 In-p

1 4 In-pz

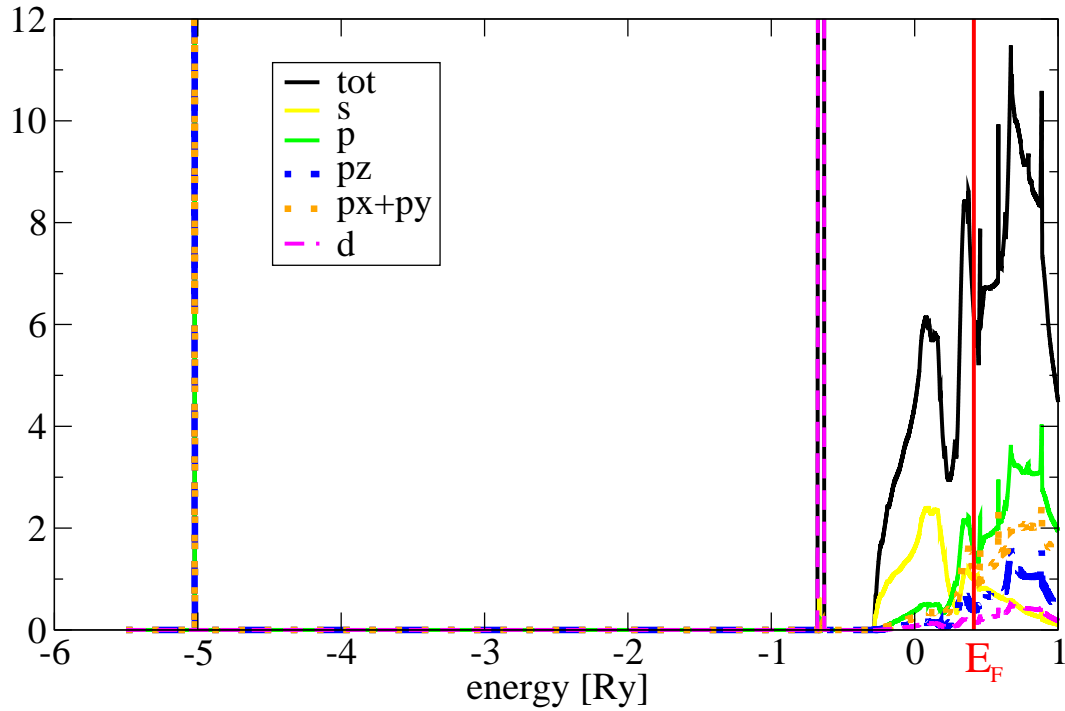
1 5 In-pxy

1 6 In-d

It starts deep down in energy (-5.50), in order to show the 4p-states. You will have to adapt the Y-scale in your plot if you want to see the valence region, which is invisible due to the huge semi-core peaks (normally, you use e.g. -0.70 as starting energy, which is just deep enough to see the 4d).

(For later comparison, use the file case.dos1 (and not case.dos1ev) to plot the density of states, which gives the DOS in Ry with the Fermi energy at 0.41 Ry (instead of 0 Ry).)

# DOS



Now run lapw2, with 'EFG' instead of 'TOT' in case.in2 (do not change anything else for now, also leave EMIN at the default  $-9.5$ ). Here are some comments on the case.output2 file:

LL is what is called L in the Gaunt number defined above, MM=M, L=l, LP=l', M=m, MP=m'

L	LL	LP	M	MM	MP	CONTRIB TO EFG
0	2	2	0	0	0	-0.007
1	2	1	-1	0	-1	991.477
1	2	1	0	0	0	-1979.704
1	2	1	1	0	1	991.477
1	2	3	-1	0	-1	0.000
1	2	3	0	0	0	0.001
1	2	3	1	0	1	0.000
2	2	0	0	0	0	-0.007
2	2	2	-2	0	-2	118.671
2	2	2	-1	0	-1	-59.306
2	2	2	0	0	0	-118.609
2	2	2	1	0	1	-59.306

2	2	2	2	0	2	118.671
3	2	1	-1	0	-1	0.000
3	2	1	0	0	0	0.001
3	2	1	1	0	1	0.000
3	2	3	-3	0	-3	0.001
3	2	3	-2	0	-2	0.000
3	2	3	-1	0	-1	-0.001
3	2	3	0	0	0	0.000
3	2	3	1	0	1	-0.001
3	2	3	2	0	2	0.000
3	2	3	3	0	3	0.001

You see that with our above notation, only (L=2, M=0) combinations appear here (LL-column and MM-column). Each of these lines is related to a charge density component, and gives the contribution of this component to the EFG. E.g., the first line has  $l=0$  and  $l'=2$ , which is an s-d contribution of -0.007. You can now add the different contributions into:

```
s-d : -0.014
p-p : 3.250
p-f : 0.002
d-d : 0.013
f-f : 0.000
total: 3.251
```

This tells you that in the energy window  $E_{MIN} - E_{Fermi}$  (here  $-9.0 \rightarrow 0.41$ , which is actually from minus infinity to  $E_{Fermi}$ ) the dominant contribution to the EFG comes from electrons with strong p-character (you have twice p (or p-p) because this comes from *wave-functions* with p-character, that combine to give a *density* with p-p character, which is a 'pure' p-electron density).

(Warning: note once more that  $E_{Fermi}$  is at 0.41 Ry and not at 0.00 Ry. Also  $E_{MIN}$  is expressed with respect to the same zero-energy. If in the following chapters we will start to change  $E_{MIN}$ , we will not stop at 0.00 but continue up to 0.41 Ry: only for  $E_{MIN} > 0.41$  the EFG due to the 'remaining states' will be zero.)

```
TOTAL VCOUL 20 = 3.247
TOTAL VCOUL 22 = 0.000
TOTAL VCOUL 22M= 0.000
TOTAL VCOUL 21 = 0.000
TOTAL VCOUL 21M= 0.000
CARTH. TENSOR:
V_xx=V_22-V_20/sqrt3; V_yy=-V_22-V_20/sqrt3; V_zz=2*V_20/sqrt3
V_xy=V_22M; V_xz=V_21; V_yz=V_21M
```

```

-1.87467    0.00000    0.00000
 0.00000   -1.87467    0.00000
 0.00000    0.00000    3.74935

```

```

Eigenvalues      Eigen vectors (rows)
  -1.8747         1.0000 0.0000 0.0000
  -1.8747         0.0000 1.0000 0.0000
   3.7493         0.0000 0.0000 1.0000

```

Indeed, we found above that the principal component of the EFG tensor in Cartesian notation is 3.74 (which is  $(2/\sqrt{3}) 3.247$ ). Because of the symmetry of our crystal and the type of atoms involved (p-block of the periodic table), there are no other contributions here. (The small deviation is due to numerical rounding.)

The EFG is specified always in its Principal Axis System (PAS), i.e. an axis system where the matrix is diagonal. Here the diagonalization was trivial, it was already diagonal.

Then the different l and l' contributions are given in detail (which means that you don't have to add the different lines with L and LP yourself to get the total s-d, p-p, ... contributions):

```

----- pp -----
-1.87596  0.00000  0.00000
 0.00000 -1.87596  0.00000
 0.00000  0.00000  3.75193

```

```

Eigenvalues Eigen vectors (rows)
-1.8760 1.0000 0.0000 0.0000
-1.8760 0.0000 1.0000 0.0000
 3.7519 0.0000 0.0000 1.0000

```

partial QMAT projection on eigenvectors of total tensor

```

-1.87596  0.00000  0.00000
 0.00000 -1.87596  0.00000
 0.00000  0.00000  3.75193

```

```

----- sd -----
 0.00838  0.00000  0.00000
 0.00000  0.00838  0.00000
 0.00000  0.00000 -0.01676

```

...

```

----- dd -----
-0.00719  0.00000  0.00000
 0.00000 -0.00719  0.00000
 0.00000  0.00000  0.01438
...

```

```

----- pf -----
 0.00010  0.00000  0.00000
 0.00000  0.00010  0.00000
 0.00000  0.00000 -0.00019
...

```

```

----- ff -----
 0.00000  0.00000  0.00000
 0.00000  0.00000  0.00000
 0.00000  0.00000 -0.00001

```

Except for slight numerical noise these  $V_{zz}$  contributions agree with the ones calculated on page 6.

Finally the spatial dependence is printed:

```

EFG INSIDE SPHERE 1:  3.749388 UP TO R = 2.5000000
EFG INSIDE SPHERE 1:  3.742326 UP TO R = 2.1317469
EFG INSIDE SPHERE 1:  3.736701 UP TO R = 1.8177380
EFG INSIDE SPHERE 1:  3.733681 UP TO R = 1.5499830
EFG INSIDE SPHERE 1:  3.733771 UP TO R = 1.3216686
:
:
EFG INSIDE SPHERE 1:  3.680746 UP TO R = 0.5080383
:
:

```

Here you see how the EFG is dominated by the region very close to the nucleus: even at only 20% of  $R_{MT}$ , almost the full EFG is reached already.

Further analysis can be done. In case.scf, you will see :EFG001= $3.74472 \cdot 10^{21}$  V/m<sup>2</sup>, which is slightly different from  $V_{zz}=3.74935$  here. The latter value is also printed as :VZZ001 in case.scf. This is the EFG inside the muffin tin sphere only. This is sometimes called the ‘valence EFG’ (not to be confused with a quantity with the same name in the old point charge EFG model). The difference of both ( $3.74935-3.74472=0.00463$ ) is the contribution from the interstitial region, and is sometimes called the ‘lattice EFG’ (again, not related to a quantity with that name in the point charge model). The lattice EFG is usually very small, except for very light elements (with very extended wave functions).



Another step in the analysis is to look at the DOS you produced earlier. Consider the 4p-states at  $-5.02$  Ry. They are taken into account in our EFG-analysis with  $\text{EMIN}=-9.5$  Ry. Now set  $\text{EMIN}=-4.0$ , and run lapw2 (with EFG) again. This will be the result:

```
-1.85322  0.00000  0.00000
 0.00000 -1.85322  0.00000
 0.00000  0.00000  3.70644
```

This is almost - but not exactly - the same as the previous result. The conclusion must be that all the state between  $-9.0$  and  $-4.0$  Ry contribute  $3.7519 - 3.70644 = 0.05$  (which is only 1%) to the EFG. Hence, the 4p-electrons do not contribute, which is what you could expect from semi-core states. There is also a d-peak at  $-0.65$ . Put  $\text{EMIN}=-0.4$ , and rerun lapw2. You find:

```
-1.90667  0.00000  0.00000
 0.00000 -1.90667  0.00000
 0.00000  0.00000  3.81335
```

The contribution from states between  $-4.0$  and  $-0.4$  Ry is therefore  $3.70644 - 3.81335 = -0.11$ . This analysis cannot pin down from which electrons this contribution is, as the DOS for s, p and d is nonzero at about  $-0.65$  Ry: hybridization.

It will be clear now that the EFG is made by the p-electrons in the valence region ( $> -0.4$  Ry), which are the 5p electrons. In order to visualize their contribution, make with your DOS-output the following function as a function of energy:

$$\frac{1}{2}p_{xy} - p_z \quad (0.5)$$

(preferably use a DOS produced with  $-0.7$  as starting energy). Now integrate this function from  $-0.7$  Ry up to  $E$ , and plot it as a function of  $E$ . The value of this integral at the Fermi energy is roughly proportional to the EFG by p-electrons (if this integral-function would be very steep at the Fermi energy, it means that the EFG is very sensitive to small changes in e.g. the number of electrons, or the temperature, or whatever else that can change either the position of the Fermi energy or the DOS at the Fermi energy.). Published examples on the analysis of this  $p$ -anisotropy function can be found e.g. in PRB 66 (2002) 195103 and in PRB 70 (2004) 155418. For d-electrons, the relevant function is (PRB 42 (1990) 2051):

$$d_{xy} + d_{x^2-y^2} - \frac{1}{2}(d_{xz} + d_{yz}) - d_{z^2}. \quad (0.6)$$

Remark I: the value for the calculated EFG (resp.  $V_{zz}$ ) depends on:

- the basis set size (RKMAX)
- the number of irreducible k-points
- the accuracy of your convergence criteria
- the XC-functional (LDA or GGA)
- the structure (i.e. portion of atoms, ratio of lattice constants)  
(sometimes an optimization can help)

The first three criteria should always be tested for convergence (try with this In example: how much larger does the k-mesh has to be to provide a really converged result?). The EFG might be very sensitive to small changes in the structure (lattice constants, c/a ratio, internal positions). Comparing the EFG for the experimental structure and a fully optimized structure is recommended. In very sensitive cases, it might depend on the XC-functional as well (it cannot be said in general which choice to make then).

Remark II:

If the EFG for one (or more) atom(s) of a compound is zero *by symmetry*, it will not be printed in the case.scf or case.output2 out files. Instead of printing EFG00x =  $0.0 \cdot 10^{21}$  V/m<sup>2</sup> there will be no EFG00x at all in the output files.

Such symmetry conditions appear if the atom under consideration has cubic symmetry, which means that the point group of this atom is cubic. For crystals, there are 5 such point groups: three tetrahedral ones (23, -43m and m-3) and two octahedral ones (432 and m-3m). Or in Schönflies notation:  $T$ ,  $T_d$ ,  $T_h$ ,  $O$  and  $O_h$ . You can check if this is the case by taking a look into case.outputs or case.outputsgroup, where the point groups for all atom sorts (Wyckoff positions) are printed.

### 0.3 The orientation of the EFG tensor

There are two different coordinate systems to consider: first the global coordinate system  $(x, y, z)$  and second the local coordinate system  $(x', y', z')$  of the atomic site under consideration. The global system is rotated into the local coordinate system with the local rotation matrix  $R$ :  $R\vec{r} = \vec{r}'$ .

This is done for each atomic site. There are two reasons for this procedure: it makes the code numerically more efficient (it minimizes the number of LM combinations in the lattice harmonics) and furthermore it is needed for interpretation. (Check appendix A in the userguide for more information.)

The EFG is calculated in the local coordinate system, and it is printed (in case.scf0 and case.output2) in this one as well as in its PAS (principal axis system) with respect to the local coordinate system. This will be more clear soon.

### 0.3.1 trivial case

Example In (see section 0.2):

the local rotation matrix (check case.struct) is unity:

```
ATOM -1: X=0.00000000 Y=0.00000000 Z=0.00000000
        MULT= 1 ISPLIT=-2
In NPT= 781 R0=0.00001000 RMT= 2.5000 Z: 49.0
LOCAL ROT MATRIX: 1.0000000 0.0000000 0.0000000
                   0.0000000 1.0000000 0.0000000
                   0.0000000 0.0000000 1.0000000
```

the main direction of the EFG (check case.scf0) is unity as well:

```
:EFG001:          EFG = 3.74472 *10**21 V / m**2
                V20 TOT/SRF= 3.24303 0.00307
                V22 TOT/SRF= 0.00000 0.00000
                V22M TOT/SRF= 0.00000 0.00000
                V21 TOT/SRF= 0.00000 0.00000
                V21M TOT/SRF= 0.00000 0.00000

-1.87236  0.00000  0.00000          -1.87236  0.00000  0.00000
 0.00000 -1.87236  0.00000          0.00000 -1.87236  0.00000
 0.00000  0.00000  3.74472          0.00000  0.00000  3.74472

MAIN DIRECTIONS OF THE EFG 1.0000 0.0000 0.0000
                             0.0000 1.0000 0.0000
                             0.0000 0.0000 1.0000
```

Here you see first all contributions in  $lm$  representation. Then the cartesian EFG tensor (left matrix) is calculated (according to (Eq. 0.2)). The EFG has diagonal form if the off-diagonal terms vanish:  $V_{22M}=V_{21}=V_{21M}=0$ . This is the case here, and the EFG tensor in the PAS (right matrix) equals the left matrix. (If additionally  $V_{22}=0$ , then there is no asymmetryparameter  $\eta$ . This is also the case here.)

Since the local rotation matrix is unity, the PAS of the EFG coincides with the global coordinate system. One sees immediately, that the main component  $V_{zz}$  points in  $z$ -direction (parallel to the  $c$ -axis).

### 0.3.2 semi trivial case 1

Example Ca in CaGa<sub>4</sub> (see appendix):

the local rotation matrix (check case.struct) is unity:

```
ATOM -1: X=0.00000000 Y=0.00000000 Z=0.00000000
        MULT= 1 ISPLIT= 8
Ca NPT= 781 RO=0.00005000 RMT= 2.50000 Z: 20.0
LOCAL ROT MATRIX: 1.0000000 0.0000000 0.0000000
                   0.0000000 1.0000000 0.0000000
                   0.0000000 0.0000000 1.0000000
```

the main direction of the EFG (check case.scf0) not:

```
:EFG001:          EFG = 0.65471 *10**21 V / m**2
                 V20 TOT/SRF= -0.30929 -0.00945
                 V22 TOT/SRF= -0.16361 -0.00535
                 V22M TOT/SRF=  0.44715  0.01402
                 V21 TOT/SRF=  0.00000  0.00000
                 V21M TOT/SRF=  0.00000  0.00000

0.01496 0.44715  0.00000          -0.29757 0.00000  0.00000
0.44715 0.34218  0.00000          0.00000 0.65471  0.00000
0.00000 0.00000 -0.35714          0.00000 0.00000 -0.35714

MAIN DIRECTIONS OF THE EFG  1.0000 0.6989 0.0000
                             -0.6989 1.0000 0.0000
                             0.0000 0.0000 1.0000
```

Here the V22M component is nonzero, which yields a non-diagonalized cartesian EFG tensor in the local coordinate system (left matrix,  $M$ ). In order to rotate this into the PAS of the EFG (with respect to the local coordinate system) (right matrix,  $D$ ) it has to be diagonalized. The diagonalization matrix  $U$  consists of the eigenvectors:  $D = U^{-1}MU$ .

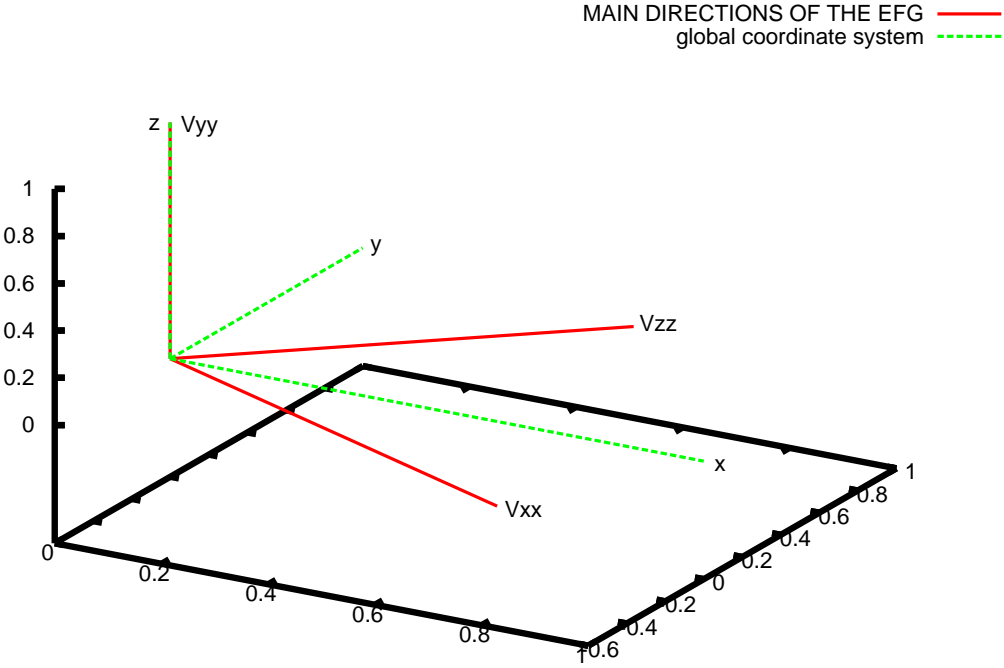
The eigenvectors (columnwise) are printed in the MAIN DIRECTIONS OF THE EFG. WIEN2k has here the less common convention of normalizing the eigenvectors such that the largest component is scaled to one.

If you calculate the eigenvalues of  $M$  yourself you obtain the diagonal elements of  $D$ . As eigenvectors you obtain the unit vectors: (0.81964, -0.57288, 0) (for  $V_{xx} = -0.298$ ), (0.57288, 0.819639, 0) (for  $V_{zz} = 0.655$ ) and (0, 0, 1) (for  $V_{yy} = -0.357$ ). These vectors have the same directions as the vectors in MAIN DIRECTIONS OF THE EFG, but different

lengths. This is allowed, as an eigenvector is not uniquely defined: multiply it by whatever scalar, and it's still an eigenvector.

You can check this and calculate  $U^{-1}MU$  using the MAIN DIRECTION for  $U$  and the normed eigenvectors for  $U$ , in both cases you will end up with  $D$ .

In this case (local rotation matrix is unity) the eigenvectors (MAIN DIRECTIONS) give you the orientations of the  $V_{xx}$ ,  $V_{yy}$  and  $V_{zz}$  in the global coordinate system (there is no other transformation necessary). You can also see immediately, that the main component  $V_{zz}$  does not point along one axis of the global coordinate system like in the trivial case:



### 0.3.3 semi trivial case 2

Example Ga4 in  $\text{Sr}_{1-x}\text{Ga}_{2+3x}$  (see appendix):

the local rotation matrix (check case.struct) is not unity:

```

ATOM -4: X=0.10000000 Y=0.90000000 Z=0.50000000
        MULT= 3 ISPLIT= 8
      -4: X=0.10000000 Y=0.20000000 Z=0.50000000
      -4: X=0.80000000 Y=0.90000000 Z=0.50000000
Ga4 NPT= 781 R0=0.00005000 RMT= 2.3000 Z: 31.0
LOCAL ROT MATRIX: 0.0000000 0.5000000 0.8660254
                   0.0000000-0.8660254 0.5000000
                   1.0000000 0.0000000 0.0000000

```

the main direction of the EFG (check case.scf0) is unity:

```

:EFG004:                EFG = -5.59592 *10**21 V / m**2
                        V20 TOT/SRF=  4.23714 -0.02839
                        V22 TOT/SRF=  3.14960 -0.00808
                        V22M TOT/SRF= -0.00002  0.00000
                        V21 TOT/SRF=  0.00000  0.00000
                        V21M TOT/SRF=  0.00000  0.00000

                        0.70329 -0.00002 0.00000          0.70329  0.00000 0.00000
                        -0.00002 -5.59592 0.00000          0.00000 -5.59592 0.00000
                        0.00000  0.00000 4.89263           0.00000  0.00000 4.89263

MAIN DIRECTIONS OF THE EFG 1.0000 0.0000 0.0000
                             0.0000 1.0000 0.0000
                             0.0000 0.0000 1.0000

```

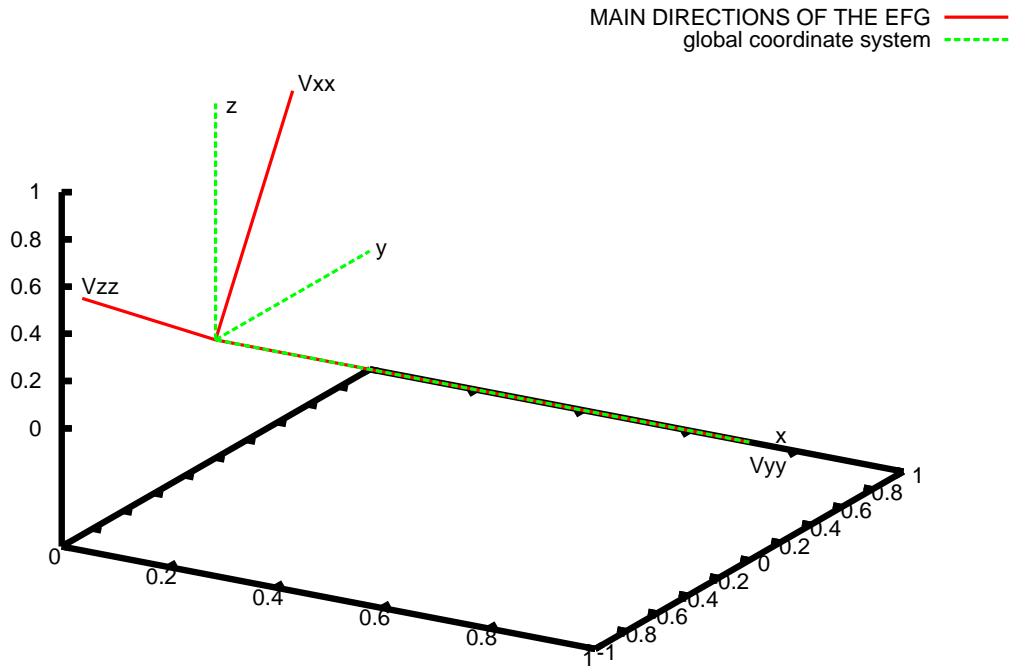
Here the V22M component is almost zero (-0.00002) and therefore the cartesian EFG tensor in the local coordinate system is almost diagonalized ( $M \simeq D$ ). Therefore the MAIN DIRECTIONS are the unit vectors  $\vec{e}_{x'}$ ,  $\vec{e}_{y'}$  and  $\vec{e}_{z'}$  of the local coordinate system of this atomic site.

But since the local rotation matrix is not unity, these directions do not coincide with the unit vectors of the global coordinate system  $\vec{e}_x$ ,  $\vec{e}_y$  and  $\vec{e}_z$ . In order to get the information how  $\vec{e}_{x'}$ ,  $\vec{e}_{y'}$  and  $\vec{e}_{z'}$  lie in  $(x, y, z)$  we need the local rotation matrix:

$$R\vec{r} = \vec{r}' \Rightarrow \vec{r} = R^{-1}\vec{r}'$$

By multiplying every unit vector  $\vec{e}_{x'}$ ,  $\vec{e}_{y'}$  and  $\vec{e}_{z'}$  from the left with the inverse local rotation matrix  $R^{-1}$  one obtains:

$V_{xx}$  in  $(x, y, z)$ :  $\vec{e}_{x'} = (0, 0.5, 0.866025)$ ,  
 $V_{zz}$  in  $(x, y, z)$ :  $\vec{e}_{y'} = (0, -0.866025, 0.5)$  and  
 $V_{yy}$  in  $(x, y, z)$ :  $\vec{e}_{z'} = (1, 0, 0)$



### 0.3.4 non-trivial case

Example Ga8 in  $\text{Sr}_{1-x}\text{Ga}_{2+3x}$  (see appendix):

the local rotation matrix is not unity:

```
ATOM -8: X=0.83333333 Y=0.16666667 Z=0.75000000
        MULT= 3 ISPLIT= 8
      -8: X=0.83333333 Y=0.66666666 Z=0.75000000
      -8: X=0.33333334 Y=0.16666667 Z=0.75000000
Ga8 NPT= 781 R0=0.00005000 RMT= 2.3000 Z: 31.0
LOCAL ROT MATRIX: 0.0000000 0.5000000 0.8660254
                   0.0000000-0.8660254 0.5000000
                   1.0000000 0.0000000 0.0000000
```

and neither are the main directions of the EFG:

```
:EFG008:          EFG = 7.98776 *10**21 V / m**2
                V20 TOT/SRF= -3.31709  0.03286
                V22 TOT/SRF=  5.13044 -0.03923
                V22M TOT/SRF= -3.24893 -0.01261
                V21 TOT/SRF=  0.00000  0.00000
                V21M TOT/SRF=  0.00000  0.00000

    7.04556 -3.24893  0.00000          7.98776 0.00000 0.00000
   -3.24893 -3.21532  0.00000          0.00000 -4.15752 0.00000
    0.00000  0.00000 -3.83025          0.00000 0.00000 -3.83025

MAIN DIRECTIONS OF THE EFG  1.0000 0.2900 0.0000
                             -0.2900 1.0000 0.0000
                             0.0000 0.0000 1.0000
```

Here the same things are true as discussed before: the left matrix is the cartesian EFG tensor in the local coordinate system, the right matrix contains the eigenvalues of the left one; it is the EFG in the PAS.

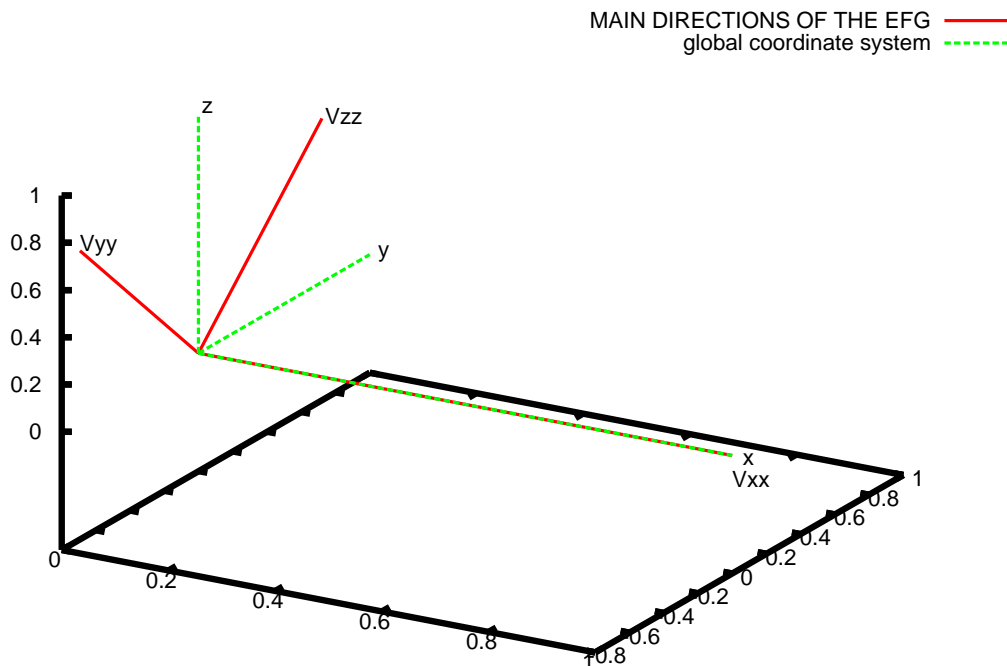
In the MAIN DIRECTIONS you see the (WIEN scaled) eigenvectors (again columnwise). The unit vectors of these are: (0.960428, -0.278527, 0), (0.278527, 0.960428, 0) and (0, 0, 1).

In order to visualize the directions of the  $V_{ii}$  components in the global coordinate system (remember: the PAS is also in the local coordinate system) you have to use the (inverse) local rotation matrix  $\vec{r} = R^{-1}\vec{r}'$  and obtain:

$V_{zz}$  in  $(x, y, z)$ :  $\vec{e}_x = (0, 0.721425, 0.692492)$



$V_{yy}$  in  $(x, y, z)$ :  $\vec{e}_y = (0, -0.692492, 0.721425)$  and  
 $V_{xx}$  in  $(x, y, z)$ :  $\vec{e}_z = (1, 0, 0)$



### Remark

If the crystal structure is orthogonal and primitive, the axes of the global coordinate system are parallel to the lattice sides:  $(a,0,0)$ ,  $(0,b,0)$  and  $(0,0,c)$ .

If the crystal structure is hexagonal, you have to consider the  $120^\circ$  angle between the  $a$  and  $b$ . In this case the  $x$ -axis is not parallel to the lattice vector  $a$ . In the global axis system, the lattice vector  $a$  is given by  $(\sqrt{3}a/2, -a/2, 0)$ ,  $b$  by  $(0,a,0)$  and  $c$  by  $(0,0,c)$ .

Check the userguide (table 4.4 in section 4.3.) for more information (also about more complicated structures): the table gives the components of the lattice vectors  $a$ ,  $b$  and  $c$  (primitive unit cell) in the global axis system. (Note that in some cases these do not coincide at first sight with the information given at the top of case.struct, where the lattice vectors for the conventional unit cell are given).

# Appendix

A published EFG analysis of the ordered and disordered digallides and tetragallides that are used as examples in this document can be found in Chem. Eur. J. **15** (2009) 1673-1684 and Chem. Eur. J. **17** (2011) 7560-7568).

## CaGa<sub>4</sub>

The input data is:

```
spacegroup 12_B2/m
a=6.039309243165Å, b= 6.028190176041Å, c=6.01398547783Å
α = 90°, β = 90°, γ = 118.922°
ATOM 1 Ca: X=0.00000000 Y=0.00000000 Z=0.00000000
ATOM 2 Ga: X=0.40419184 Y=0.77126531 Z=0.00000000
ATOM 3 Ca: X=0.00000000 Y=0.50000000 Z=0.23446389
RMT(Ca)=2.5 au, RMT(Ga)=2.27 au
LDA with separation energy -6.0Ry
2500 kpoints (582 irreducible kpoints)
RMTKmax = 7.0, l=10
convergence criteria: energy 0.000001 and charge 0.000001
```

## Sr<sub>1-x</sub>Ga<sub>2+3x</sub>

the input data is:

```
spacegroup: 156_P3m1
a=8.696800153129Å, b=8.696800153129Å, c=9.472200036167Å
α = 90° β = 90°, γ = 120°
ATOM 1 Sr1: X=0.00000000 Y=0.00000000 Z=0.00000000
ATOM 2 Sr2: X=0.50000000 Y=0.50000000 Z=0.00000000
ATOM 3 Sr3: X=0.50000000 Y=0.50000000 Z=0.50000000
ATOM 4 Ga4: X=0.10000000 Y=0.90000000 Z=0.50000000
ATOM 5 Ga5: X=0.33333333 Y=0.66666667 Z=0.75000000
ATOM 6 Ga6: X=0.66666667 Y=0.33333333 Z=0.25000000
ATOM 7 Ga7: X=0.16666667 Y=0.83333333 Z=0.25000000
ATOM 8 Ga8: X=0.83333333 Y=0.16666667 Z=0.75000000
ATOM 9 Ga9: X=0.33333333 Y=0.66666667 Z=0.25000000
ATOM 10 Ga10: X=0.66666667 Y=0.33333333 Z=0.75000000
ATOM 11 Ga11: X=0.83333333 Y=0.16666667 Z=0.25000000
ATOM 12 Ga12: X=0.16666667 Y=0.83333333 Z=0.75000000
RMT(Sr)=2.6 au, RMT(Ga)=2.3 au
LDA with separation energy -6.0Ry
2000 kpoints (350 irreducible kpoints)
```

$R_{MT}K_{max} = 7.0, l=10$

convergence criteria: energy 0.000001 and charge 0.000001