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 ($\vec{r} = \vec{0}$):

$$V_{ij} = \frac{\partial^2 V(0)}{\partial x_i \, \partial x_j} \tag{1}$$

Five independent quantities have to be provided in order to determine the tensor unambiguously [1]. 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 either notation, one is most interested in the principal component, which is V_{zz} (cartesian) or V_{20} (spherical) ($V_{zz} = 2 \cdot V_{20}/\sqrt{3}$). V_{zz} can be obtained from the charge density $\rho(\vec{r})$ in the following way:

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

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

$$\rho_{LM}(r) = \sum_{E<E_F} \sum_{lm} \sum l'm' R_{lm}(r) R_{l'm'}(r) G_{Ll'}^{Mmm'} \tag{3}$$

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. 2), only the component ρ_{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.

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

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^2. 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 0.00250 2.000 0.003 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).

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 EMIN - 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).*

```
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
```

Indeed, we found above that the principal component of the EFG tensor in Cartesian notation is 3.74 (which is $\left(2/\sqrt{3}\right) 3.247$). 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 diagonalisation 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 5.

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^2, which is slightly different from V_{zz}=3.74935 here. The latter value 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 EMIN$=-9.5$ Ry. Now set 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 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:

$$\frac{1}{2}p_{xy} - p_z \tag{4}$$

(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.). For d-electrons, the relevant function is

$$d_{xy} + d_{x^2-y^2} - \frac{1}{2}(d_{xz} + d_{yz}) - d_{z^2}. \tag{5}$$

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 large 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^2 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 Schönfliess 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.