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Hands-on Tutorial on Electronic Structure Computations

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Calculations with GIPAW in QE

Stefano de Gironcoli
SISSA and CNR-IOM DEMOCRITOS
Trieste
Italy

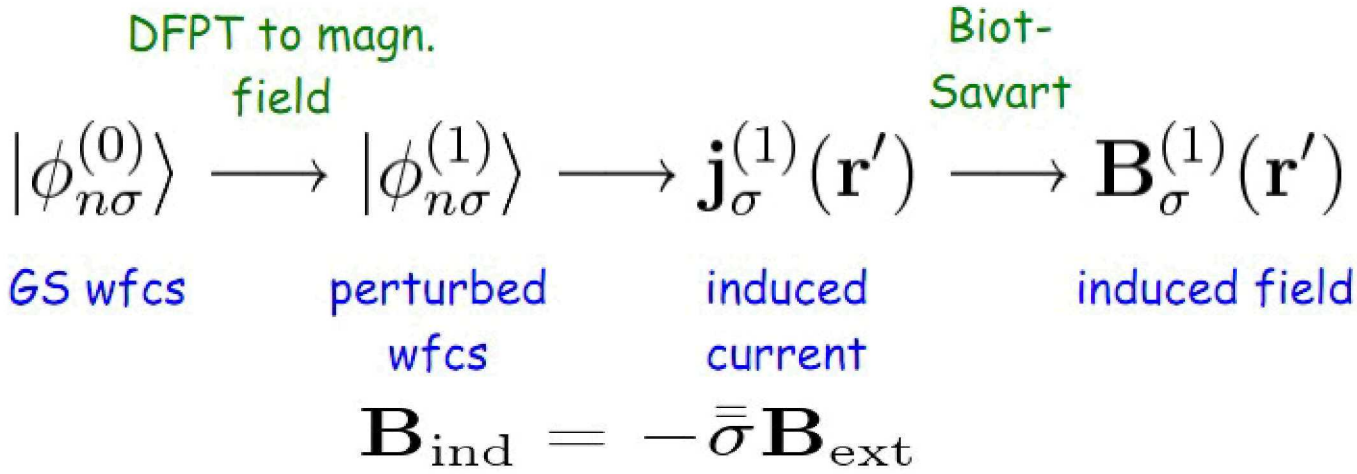
Strada Costiera 11, 34151 Trieste, Italy - Tel.+39 040 2240 111; Fax +39 040 224 163 - sci_info@ictp.it

Calculations with GIPAW in QE

- What can GIPAW do for you?
  - NMR
    - Chemical shieldings
    - Electric Field Gradients
  - EPR
    - Determining change in g tensor
    - Hyperfine coefficients
- Installation & Setup
  - How to get the GIPAW module
  - SCF run and what to watch out for
  - Pseudopotentials (or what you can do for GIPAW :)
- Running GIPAW & Output files

NMR with GIPAW in QE

- Chemical Shieldings:



  - Diamagnetic insulators
  - Core contribution is constant
  - Restart option
  - Norm-conserving / Ultrasoft / PAW Pseudopotentials
  - Gamma-specific algorithms are not allowed.
  - Perturbation is done in nscf fashion.
  - Works in parallel
  - Scales like pw.x , but memory demanding.

NMR with GIPAW in QE

- Electric Field Gradient (EFG)

$$\bar{\bar{\mathbf{Q}}}^{I}_{\alpha\beta} = \frac{eQ}{h} \langle \psi_0 | \frac{\delta \mathbf{E}_\alpha}{\delta \mathbf{r}_\beta} | \psi_0 \rangle = \frac{eQ}{h} \bar{\bar{\mathbf{V}}}_{\alpha\beta}$$

$\mathbf{E}$ = electric field ; eQ = electric quadrupole moment

Observables:

- Quadrupolar coupling constant $Cq = \frac{eQ\,V_{zz}}{h}$
- Asymmetry parameter $\eta = \frac{V_{xx} - V_{yy}}{V_{zz}}$

Principal axis system: Eigenvectors and -values of $\bar{\bar{\mathbf{V}}}_{\alpha\beta}$

Convention: $|V_{zz}| \geq |V_{yy}| \geq |V_{xx}|$

- Easy to calculate (GS density) (bare+paw reconstruction+ionic)
- Requires EQM (in e x 10^-30 m^2)
- Output QCC in MHz

EPR with GIPAW in QE

- Hyperfine coupling

$$\overleftrightarrow{A}_R = \left\langle \frac{\partial^2 \mathcal{H}}{\partial \mathbf{S}\, \partial \boldsymbol{I}_R} \right\rangle = A_{\mathrm{iso,R}} \overleftrightarrow{1} + \overleftrightarrow{A}_{\mathrm{dip,R}}$$

Isotropic (Fermi-contact)

$$A_{\mathrm{iso}} = \frac{4\pi}{3} \frac{g_e\, \mu_e\, g_N\, \mu_N}{S} \int d^3\mathbf{r}\, n_s(\mathbf{r}) \underline{\delta(\mathbf{r})}$$

$\mathbf{r} \equiv \mathbf{r} - \mathbf{R}$

Dipolar (traceless)

$$A^{\alpha\beta}_{\mathrm{dip}} = \frac{1}{2} \frac{g_e\, \mu_e\, g_N\, \mu_N}{S} \int d^3\mathbf{r}\, n_s(\mathbf{r}) \frac{3 r_\alpha r_\beta - \delta_{\alpha\beta} r^2}{r^5}$$

- Should input nuclear g factors
- Easy to calculate (GS density)
- ZORA : in experimental stage (not reported)
- Core relaxation (experimental – reported)
- Not throughly tested with ultrasoft/PAW pseudopotentials.

EPR with GIPAW in QE

- Determining g tensor

$$\overleftrightarrow{g} = \frac{2}{\alpha}\frac{\partial^2 \mathcal{H}}{\partial \mathbf{S} \partial \mathbf{B}}$$

$$\begin{aligned}
\overleftrightarrow{g}_{\mathrm{Z}} &= g_e \overleftrightarrow{1} \\
\Delta\overleftrightarrow{g}_{\mathrm{Z-KE}} &= -\frac{g_e \alpha^2}{2}\left(\sum_{S=\pm 1/2} S\, T_S\right)\overleftrightarrow{1} \\
\Delta\overleftrightarrow{g}_{\mathrm{SO}} &= \alpha^2 g' \sum_{S=\pm 1/2} S \int d^3\mathbf{r}'\, \nabla V(\mathbf{r}') \times \overleftrightarrow{j}_S^{(1)}(\mathbf{r}') \\
\Delta\overleftrightarrow{g}_{\mathrm{SOO}} &\simeq \alpha \sum_{S=\pm 1/2} S \int d^3\mathbf{r}'\, \overleftrightarrow{B}_S^{(1)}(\mathbf{r}')\rho_S(\mathbf{r}')
\end{aligned}$$

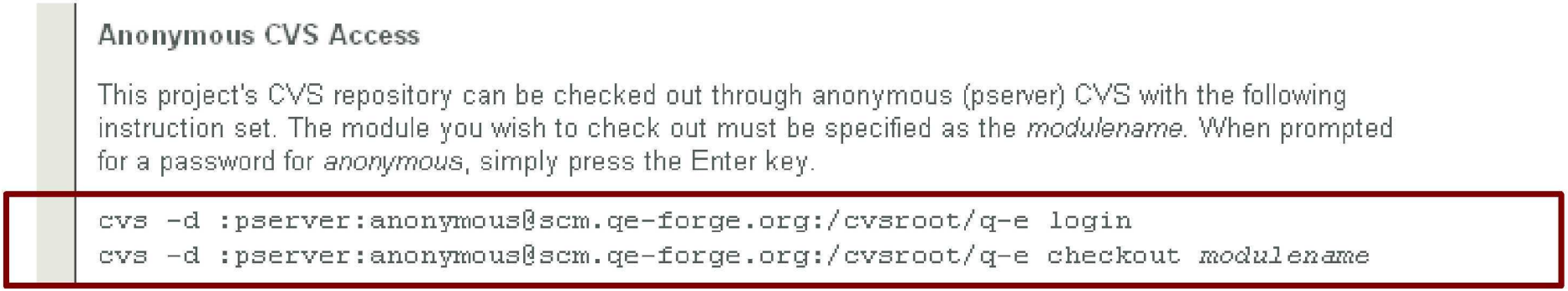
- Requires Linear Response (like chemical shieldings)
- Not working with Ultrasoft/PAW yet
- Gamma-specific algorithms are not allowed.
- Perturbation is done in nscf fashion.
- Works in parallel etc.

Installation & Setup

- How to get:

Right now, you can only get the older version within QE dist.

But next week: Try qe-forge.org



Installation & Setup

- What to watch for during SCF run:
  - You need to do one (GS wavefunctions)
  - You need to do a good enough one:

  Well converged (cut off, k point sampling, conv_thr)

  - Symmetry:

  GIPAW works only with symmetry operations that map the axes on to themselves (use nosym=.true. in doubt)

  - For EPR, nspin=2
  - Same “outdir” and “prefix” for both SCF and GIPAW calculations
  - Relax the structure when necessary (celebrate vdW in QE :)

GIPAW Pseudopotentials

- PAW

Starting from next week, cvs version of ld1.x would produce every PAW pseudopotential suitable for GIPAW.

- NC/US (UPF version 1)
  - Contains extra datasets
    - Core electron wavefunction
    - Valance AE and PS partial waves, 2x angular momentum
    - AE and PS potential
  - Can be generated using ld1.x code..

...How ?

GIPAW Pseudopotentials

```
&input
title = 'O'
prefix = 'O'
zed = 8.0
rel = 1
config = '1s2 2s2 2p4 3s-1 3p-1 3d-1
iswitch = 3
dft = 'PBE'
/
&inputp
pseudotype = 1
tm = .true.
lloc = 2
file_pseudopw = 'O.pbe-tm-gipaw.UPF'
lgipaw_reconstruction = .true.
/
3
2S 1 0 2.00 0.00 1.45 1.45
2P 2 1 4.00 0.00 1.40 1.40
3D 3 2 -1.00 -0.30 1.40 1.40
&test
/
4
2S 1 0 2.00 0.00 1.45 1.45
2P 2 1 4.00 0.00 1.40 1.40
3S 2 0 0.00 0.00 1.45 1.45
3P 3 1 0.00 -0.10 1.40 1.40
```

States that will be used for PAW reconsruction should be added to the configuration

Norm-conserving, Semilocal,lmax=2

Generates PAW dataset to be used in GIPAW

PAW dataset is generated using these energy and cut off radii. (in Rydberg and bohr)

$$|\psi^{\mathrm{AE}}\rangle = |\psi^{\mathrm{PS}}\rangle + \sum_{R,n} \left(|\phi^{\mathrm{AE}}_{r,n}\rangle - |\phi^{\mathrm{PS}}_{R,n}\rangle\right) \langle p_{R,n}|\psi^{\mathrm{PS}}\rangle$$

GIPAW Input/Output

➔Types of 'job's

- 'nmr' : Magnetic susceptibility & shielding tensors
- 'efg' : Electric Field Gradients (EFGs)
- 'g_tensor' : EPR g-tensor
- 'hyperfine' : Hyperfine couplings

➔Similar input files, SCF calculation required

GIPAW Module: NMR

- **mysystem.scf.in**

```
&control
prefix='name'
outdir='./scratch/'
…
/
&system
nosym=.true.
…
/
&electrons
conv_thr = 1.0d-14
..
/
ATOMIC_SPECIES
H 1.000 H.pbe-tm-gipaw.UPF
C …
K_POINTS automatic
1 1 1 0 0 0
```

- **mysystem.nmr.in**

```
&inputgipaw
job='nmr'
prefix= 'name'
tmp_dir = './scratch/'
!iverbosity = 0
!isolve=0  (0 davidson, 1 cg)
! use_nmr_macroscopic_shape=.true.
!  q_gipaw = 0.01
!  isolve = 0
!   conv_threshold =.1.0d-14
```

- **mysystem.efg.in**

```
&inputgipaw
job='efg'
prefix= 'name'
tmp_dir = './scratch/'
q_efg(1)=1.0 , q_efg(2),  ...
```

$$Cq = \frac{eQ\,V_{zz}}{h}$$

GIPAW Module: NMR

mysystem.nmr.out

```
Program GIPAW v.> 4.2      starts on  8Dec2010 at 18:12:41

This program is part of the open-source Quantum ESPRESSO suite
for quantum simulation of materials; please cite
    "P. Giannozzi et al., J. Phys.:Condens. Matter 21 395502 (2009);
     URL http://www.quantum-espresso.org",
in publications or presentations arising from this work. More details at
http://www.quantum-espresso.org/wiki/index.php/Citing_Quantum-ESPRESSO

Parallel version (MPI), running on   128 processors
R & G space division:  proc/pool =  128

Planes per process (thick) : nr3 = 110 npp =    1 ncplane = 50688

Proc/  planes cols     G    planes cols    G      columns  G
Pool       (dense grid)       (smooth grid)      (wavefct grid)
   1     1    299    20992    1    257    16661     64     2083
   2     1    299    20992    1    257    16668     64     2083
   3     1    299    20992    1    257    16668     64     2083
   4     1    299    20992    1    257    16664     64     2083

 init_gipaw_1: projectors nearly linearly dependent:
 ntyp =  3, l/n1/n2 =  0 2 1  0.99609069
```

GIPAW Module: NMR

mysystem.nmr.out

```
f-sum rule (should be -1268.7943):
    -1268.6930          0.0005          0.0081
        0.0020      -1268.8319          0.0758
       -0.0142          0.0705      -1269.7387
-------------------------------------------------------------

chi_bare pGv (HH) in 10^{-6} cm^3/mol:
    -2169.2892         19.6299         20.0379
       15.8248      -2266.5085         -6.8170
       19.7302         -6.2021      -2225.3303

chi_bare vGv (VV) in 10^{-6} cm^3/mol:
    -2232.6153         12.1138         19.3819
       12.1129      -2317.7319         -1.9445
       19.3747         -1.9465      -2299.7079

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

Contributions to the NMR chemical shifts: ------------------------------

Core contribution in ppm:

Atom   1   H    pos: (   3.982630 11.194231   5.088020)   sigma:          0.00
Atom   2   C    pos: (   4.525000 11.806911   5.792070)   sigma:        200.33
Atom   3   O    pos: (   3.749640 12.976041   6.094290)   sigma:        270.64
Atom   4   H    pos: (   3.750800 13.430031   5.243950)   sigma:          0.00
```

GIPAW Module: NMR

mysystem.nmr.out

```
Total NMR chemical shifts in ppm: ------------------------------------

Atom   1  H   pos: (  3.982630 11.194231  5.088020)  sigma:          27.73
H    1    anisotropy:      1.89    eta:     2.1243
H    1    sigma_xx=    24.7803    axis=( -0.479988 -0.621869  0.618782)
H    1    sigma_yy=    28.7948    axis=( -0.680708  0.708950  0.184462)
H    1    sigma_zz=    29.6223    axis=( -0.553397 -0.332671 -0.763598)

Atom   2  C   pos: (  4.525000 11.806911  5.792070)  sigma:          90.54
C    2    anisotropy:     35.97    eta:     0.4568
C    2    sigma_xx=    64.3409    axis=( -0.577455 -0.023790 -0.816076)
C    2    sigma_yy=    80.7737    axis=(  0.706264  0.486878 -0.513946)
C    2    sigma_zz=   126.5132    axis=( -0.409556  0.873146  0.264348)

Atom   3  O   pos: (  3.749640 12.976041  6.094290)  sigma:         242.51
O    3    anisotropy:     24.85    eta:     0.6034
O    3    sigma_xx=   222.5877    axis=(  0.814800  0.496331  0.299594)
O    3    sigma_yy=   237.5844    axis=(  0.543913 -0.475605 -0.691346)
O    3    sigma_zz=   267.3662    axis=(  0.200648 -0.726261  0.657484)

Atom   4  H   pos: (  3.750800 13.430031  5.243950)  sigma:          27.09
H    4    anisotropy:     17.55    eta:     0.3448
H    4    sigma_xx=    15.2885    axis=(  0.723599  0.638482  0.262192)
H    4    sigma_yy=    21.3405    axis=(  0.676632 -0.581176 -0.452110)
H    4    sigma_zz=    44.6404    axis=(  0.136284 -0.504554  0.852556)
```

GIPAW Module: NMR

mysystem.efg.out

```
NQR/NMR SPECTROSCOPIC PARAMETERS:
Ca   1    Vxx=   -0.0989    axis=(  0.000000  1.000000  0.000000)
Ca   1    Vyy=   -0.1114    axis=( -0.999870  0.000000 -0.016136)
Ca   1    Vzz=    0.2103    axis=( -0.016136  0.000000  0.999870)
Ca   1    Q=-4.44 1e-30 m^2    Cq=  -2.1939 MHz    eta= 0.05958

O    2    Vxx=   -0.6964    axis=(  0.591482 -0.806161 -0.015948)
O    2    Vyy=   -0.7087    axis=(  0.806304  0.591239  0.017603)
O    2    Vzz=    1.4052    axis=( -0.004762 -0.023271  0.999718)
O    2    Q=-2.55 1e-30 m^2    Cq=  -8.4191 MHz    eta= 0.00875
```

Observables:

- Quadrupolar coupling constant

$$Cq = \frac{eQ\,V_{zz}}{h}$$

- Asymmetry parameter

$$\eta = \frac{V_{xx} - V_{yy}}{V_{zz}}$$

GIPAW Module: EPR

- **mysystem.scf.in**

```
&control
prefix='name'
…
/
&system
nspin = 2
…
/
&electrons
..
/
ATOMIC_SPECIES
H 1.000 H.pbe-tm-gipaw.UPF
C …
K_POINTS automatic
1 1 1 0 0 0
```

- **mysystem.epr.in**

```
&inputgipaw
job='g_tensor'
prefix= 'name'
...
```

- **mysystem.hyperfine.in**

$$\overleftrightarrow{A}_R = \left\langle \frac{\partial^2 \mathcal{H}}{\partial \mathbf{S}\, \partial \boldsymbol{I}_R} \right\rangle$$

```
&inputgipaw
job='hyperfine'
prefix= 'name'
tmp_dir = './scratch/'
hfi_nuclear_g_factor (1)=5.5
hfi_nuclear_g_factor (2)=...
hfi_output_unit= 'MHz' ! mT, G,
                       !10e-4cm^-1
```

Isotropic (Fermi-cont

$$A_{\text{iso}} = \frac{4\pi}{3} \frac{g_e\, \mu_e\, g_N}{S}$$

Dipolar (traceless)

$$A^{\alpha\beta}_{\text{dip}} = \frac{1}{2} \frac{g_e\, \mu_e\, g_N}{S}$$

./pw.x < mysystem.scf.in > mysyste.scf.out
./gipaw.x <mysystem.*.in > mysystem.*.out

GIPAW Module: EPR

mysystem.epr.out

```
 ***********************************************
 Delta g - relativistic-mass-correction                    -181.8418
 Delta g - relativistic-mass-correction gipaw               -22.0214
   ***********************************************
 Delta g - spin-orbit-bare
           58.4845       0.0000       0.0000
           0.0000     -528.6593       0.0000
           0.0000       0.0000    1030.3405
 Delta g - spin-orbit diamagnetic correction (GIPAW)
           4.1945       0.0000       0.0000
           0.0000       7.3901       0.0000
           0.0000       0.0000       7.2626
 Delta g - spin-orbit paramagnetic correction (GIPAW)
           81.1631       0.0000       0.0000
           0.0000    -1700.5893      -0.0001
           0.0000       0.0000    2562.6578
 Delta g - spin-other-orbit
          -48.7107       0.0000       0.0000
           0.0000      10.4777       0.0000
           0.0000       0.0000     -98.7437
Delta g - total
          -108.7318         0.0000         0.0000
             0.0000     -2415.2440        -0.0001
             0.0000         0.0000      3297.6540
```

GIPAW Module: EPR

mysystem.hyperfine.out

```
********************************* HFI ****************************

 C    1: g_n =  1.404844                        MHz
 C    1  hfi_dipole        2.845759        0.000000        0.000000
 C    1  hfi_dipole        0.000000       15.908649        0.000000
 C    1  hfi_dipole        0.000000        0.000000      -18.754409

 C    1  hfi_dipole       15.908649        2.845759      -18.754409

Fermi contact term:           bare     reconstruction       total
                          0.000000      -67.134569     -67.134569
 **** ZORA ****
                          0.000000      -66.455587     -66.455587
```