Implementation of the calculation of NMR parameters in PWSCF

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1 Introduction

Nuclear Magnetic Resonance (NMR) spectroscopy is widely used in structural chemistry and in solid states studies. Experimental spectra can often be difficult to analyse due to the overlap of the contribution of the different atoms and the poor signal/noise ratio. Thanks to the work of C.J. Pickard and F. Mauri [1], it is possible to calculate the NMR parameters thanks to a DFT calculation with pseudopotentials.

One of the main issue of this calculation is the determination of the 'all-electron' response through a pseudopential calculation. NMR parameters are seen on the position of the nuclei. In a pseudopotential calculation, the potential in this region, close to the nuclei, are modified to decrease the number of plane waves used to converge the calculation. In order to obtain the 'all-electron' response, it is necessary to reconstruct the results from the pseudopotential calculation. For the calculation of the electric field gradient (efg) tensor, we use the PAW method of Blöchl [2] to reconstruct the 'all-electron' results, whereas in the case of the chemical shift tensor, it is necessary to use an extension of the previous method due to the presence of the magnetic field, the GIPAW method[1].

The goal of this work is to implement the calculation of the efg and the chemical shift tensor with the appropriate reconstruction in PWSCF. This can be separated in three parts:

- The atomic part: In order to calculate the reconstruction element, it is necessary to have the 'all-electron' and pseudo-wavefunction of each atom in the structure. I then modify the *atomic* code in PWSCF to produce a reconstruction file with the necessary informations.

- The calculation of the efg tensor: In order to have the quadrupolar parameters of the NMR spectra of nuclei of spin over 1/2, I implement the calculation of the electric field gradient tensor with the reconstruction of the all-electron response using the PAW method. This is done as a post-processing program, after a scf calculation, in the `efg.x` program.

- The calculation of the chemical shift tensor: I implement the calculation of the chemical shift tensor with the GIPAW reconstruction. This calculation is divided in three parts: After a SCF calculation, it is necessary to do a non-SCF calculation to calculate the wavefunction on the k-point k+q, where q is a little displacement in the three cartesian directions. The third part is the calculation of the induced current which leads to the chemical shift tensor, including the GIPAW reconstruction. This is done in the program `nmr.x` in the directory Nmr of the PWSCF distribution.

2 Atomic part

In order to reconstruct the 'all-electron' response from a pseudopotential calculation, we use the projected augmented wave method (PAW) of Blöchl. This projectors are constructed with the pseudo and all-electron atomic wavefunctions corresponding to each pseudopotentials. It is then necessary to generate these wavefunctions during the generation of the pseudopotentials. At the present state, only norm conserving pseudopotentials are considered.

For an atom, and for each atomic momentum, it is necessary to have two projectors. Thus we must produce two 'all-electron' and pseudo wavefunctions for each orbital momentum. To do that, we use the valence and the first excited wavefunction of each orbital momentum (for example $2s$ and $3s$ for the s orbital momentum of oxygen). If necessary, it is possible to use ionised configuration of the atom in order to have the excited states still bounded.

To produce these wavefunctions, we use the 'test' part of the atomic code which can generate the needed wavefunctions. An extra flag "`file_recon`" was added in the input file. When present, the name of the file after "`file_recon`" is used to write the all-electron and pseudo wavefunctions in a format close to the UPF format. The subroutine in charge of the generation of the "`file_recon`" file is `write_paw_recon.f90` in the atomic directory. Notice that we check that the maximum of the all-electron and pseudo wavefunction are positives.

Structure of the "Recon"file:

```
<PP_PAW>
  4 ! Number of the wavefunctions (couple all-electron/pseudo) in the file
</PP_PAW>

<PP_REC>
<PP_kbeta>
  929      ! Number of point in the radial grid
</PP_kbeta>
<PP_L>
  0        ! Value of l
</PP_L>
<PP_REC_AE>
0.0 0.0 0.0 0.0  ! The all-electron wavefunction ...
</PP_REC_AE>
<PP_REC_PS>
0.0 0.0
0.0 0.0    ! The pseudo wavefunction ...
</PP_REC_PS>
</PP_REC>

<PP_REC> ...
```

To produce the pseudopotential and the reconstruction, it is advised to proceed in two steps:

- first produce the pseudopotential;

```
    &input
          title='O',
```

```
zed=8.0,
        rel=0,
        beta=0.5,
        rlderiv=1.5,
        eminld=-4.0,
        emaxld=4.0,
        deld=0.02d0,
        nld=3,
        iswitch=3,
        dft='PBE',
 /
3
1S  1  0  2.0  1
2S  2  0  2.0  1
2P  2  1  3.0  1
 &test
  pseudotype=1,
  nconf=1,
 /
2
2S  1  0  2.00  0.00  1.30  1.30  1
2P  2  1  3.00  0.00  1.40  1.40  1
 &inputp
   lloc=1,
   file_pseudopw='OPBE_nc.RRKJ3',
   zval=6.d0,
 /
2
2S  1  0  2.00  0.00  1.30  1.30
2P  2  1  3.00  0.00  1.40  1.40
```

- then produce the `recon_file` with the same configuration and cutoff radii, but with the excited states in the all-electron and test part.

```
 &input
        title='O',
zed=8.0,
        rel=0,
        beta=0.5,
        rlderiv=1.5,
        eminld=-4.0,
        emaxld=4.0,
        deld=0.02d0,
        nld=3,
        iswitch=3,
        dft='PBE',
 /
5
```

```
1S   1   0   2.0   1
2S   2   0   2.0   1
2P   2   1   3.0   1
3S   3   0   0.0   1
3P   3   1   0.0   1
 &test
  pseudotype=1,
  file_recon='O.recon',
  nconf=1,
 /
4
2S   1   0   2.00   0.00   1.30   1.30   1
2P   2   1   3.00   0.00   1.40   1.40   1
3S   3   0   0.0    0.00   1.30   1.30   1
3P   3   1   0.0    0.00   1.40   1.40   1
 &inputp
   lloc=1,
   file_pseudopw='OPBE_nc.RRKJ3.bad',
   zval=6.d0,
 /
2
2S   1   0   2.00   0.00   1.30   1.30
2P   2   1   3.00   0.00   1.40   1.40
```

3 efg tensor

Nuclei with spin greater than 1/2 have a quadrupolar contribution in NMR spectra. This interaction is responsible for the shape and the enlargement of the NMR signal of these nuclei. This quadrupolar interaction is directly related with the electric field gradient (efg) tensor on the nuclei. Thus in order to calculate these quadrupolar parameters, we should calculate the efg tensor.

The electric field gradient tensor $\overset{\leftrightarrow}{G}$ is calculated as the second derivative of the charge density in respect to the position:

$$G_{\alpha\beta}(\mathbf{r}) = \int d^3 r' \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|^3} \left[\delta_{\alpha\beta} - 3 \frac{(r_\alpha - r'_\alpha)(r_\beta - r'_\beta)}{|\mathbf{r} - \mathbf{r}'|^2} \right]. \tag{1}$$

This tensor can be divided in three contribution:

- The ionic contribution: Contribution of the charge of the frozen ion, considered as point charge and calculated thanks to an ewald sum.

- The pseudopotenital contribution: The scf calculation compute the charge density corresponding to the pseudopotential calculation. This charge density leads to an efg tensor thanks to equation (1) where $n(\mathbf{r})$ is replaced by the charge computed by the scf calculation.

- The reconstruction contribution: Thanks to PAW method, we can calculate the contribution of the core region and reconstruct tha all-electron calculation.

3.1 The ionic contribution

The contribution of the frozen ions (charge of the nuclei + core electrons = valence charge) considered as point charge, is calculated thanks to an ewald sum in the subroutine /PW/ewald_dipole.f90.

- In the real space:

$$
\begin{aligned}
G(\alpha,\beta,at) \;=\; & e^2 \sum_{at'} Z_{at'} \left[\frac{3}{\Delta r^3} \, \mathrm{erfc}(\eta\Delta r) + \right. \\
& \left. \left(\frac{6\eta}{\sqrt{\pi}} \frac{1}{\Delta r^2} + \frac{4\eta^3}{\sqrt{\pi}} \right) \mathrm{e}^{-(\eta\Delta r)^2} \right] \left(\frac{(r_{at'_\alpha} - r_{at_\alpha})(r_{at'_\beta} - r_{at_\beta})}{\Delta r^2} - \frac{1}{3}\delta_{\alpha\beta} \right) \quad (2)
\end{aligned}
$$

  where at and at' are for the atomic sites, $\Delta r = |\mathbf{r}_{at'} - \mathbf{r}_{at}|$.

- In the reciprocal space:

$$
G(\alpha,\beta,at) \;=\; e^2 \frac{4\pi}{V} \sum_{G\neq 0} -\frac{G_\alpha G_\beta}{G^2} \mathrm{e}^{\frac{-G^2}{4\eta^2}} \left(\sum_{at'} Z_{at'} \, \mathrm{e}^{-i\mathbf{G}\cdot\mathbf{r}_{at'}} \right) \mathrm{e}^{-i\mathbf{G}\cdot\mathbf{r}_{at}} \quad (3)
$$

3.2 The pseudopotentiel contribution

The electronic charge density is calculated in a SCF calculation. In order to get the contribution of this charge density to the efg tensor

- the charge density is transformed in the reciprocal space thanks to a FFT

- it is multiply by $(G_\alpha G_\beta)/G^2$

- fourier transformed on the atomic position

This is the main part of the subroutine do_efg in the file /PP/efg.f90.

3.3 The reconstruction part

The PAW method is based on projectors constructed from the atomic pseudo and all-electron wavefunctions. Their use is very similar to the treatment of ultrasoft(US) pseudopotential, and I copy the structure used to deal with US pseudopotentials for the PAW projectors.

- The module paw in the file /PW/paw.f90 regroups the necessary variables for the paw reconstruction. Each variable is prefixed with paw_ .

- This module contains two subroutines paw_wfc_init which initializes the default values for wavefunction structure and read_recon which reads the reconstruction file, given in the input file, for each atom.

- The subroutine /PW/init_paw_1.f90 initializes the projectors and construct the part which does not depend on k-point. In particular, when there is more than one wavefuntion for a value of ℓ, the wavefunctions are orthogonalised. Then, each wavefunction are multiply by a "step function" which goes smoothly to zero from r_s to r_c, where r_c is the core region, usually chosen slightly bigger than the position of the maximum of the wavefunction, and r_s is here chosen to be equal to $2/3 r_c$.

- The subroutine /PW/init_paw_2.f90 is very similar to /PW/init_us_2.f90, the only difference is that one acts on US projectors, the other on PAW.

- The subroutine efg_correction in the file PP/efg.f90 is the one in charge of the calculation of the reconstruction term.

The reconstruction term to be calculated is:

$$
\begin{aligned}
G_{\alpha\beta}^{\mathrm{El,corr}}(\mathbf{R}) &= 2\sum_{o,J,J'} \langle\tilde\psi_o^{(0)}|\tilde p_{\mathbf{R},J}\rangle[\langle\phi_{\mathbf{R},J}|\frac{1}{r^3}[\delta_{\alpha\beta}-3\frac{r_\alpha r_\beta}{r^2}]|\phi_{\mathbf{R},J'}\rangle \\
&\quad -\langle\tilde\phi_{\mathbf{R},J}|\frac{1}{r^3}[\delta_{\alpha\beta}-3\frac{r_\alpha r_\beta}{r^2}]|\tilde\phi_{\mathbf{R},J'}\rangle]\langle\tilde p_{\mathbf{R},J'}|\tilde\psi_o^{(0)}\rangle.
\end{aligned}
\tag{4}
$$

where $|\tilde\psi_o^{(0)}\rangle$ is the wavefunction found in the SCF calculation, $|\tilde p_{\mathbf{R},J}\rangle$ is the PAW projector for the atom in position R and quantum number J (J stands for the orbital momentum, and an extra number in the case there is more than one atomic wavefunction by value of ℓ). $|\phi_{\mathbf{R},J'}\rangle$ is the atomic all-electron wavefunction, and $|\tilde\phi_{\mathbf{R},J'}\rangle$ the pseudo atomic wavefunction.

It can be separated into two parts, a term which depend only on the radial term and can be computed for each atom

$$
\langle R_{\mathbf{R},J}|\frac{1}{r^3}|R_{\mathbf{R},J'}\rangle - \langle\tilde R_{\mathbf{R},J}|\frac{1}{r^3}|\tilde R_{\mathbf{R},J'}\rangle
\tag{5}
$$

and a term with the spherical harmonics, the central operator can be written as Y_{2m}.

We obtain the terms for the different values of $m = -2, -1, 0, 1, 2$. Linear combination can be done to obtain the tensor with matrix element $G_{\alpha\beta}^{\mathrm{El,corr}}$ (α, β are the cartesian coordinates.

The efg tensor is the sum of these three contributions. It is then symmetrize according to the symmetry of the system.

The tensor obtained, is the all-electron electric field gradient tensor. If we call V_{xx}, V_{yy} and V_{zz} the three eigenvalues of this tensor, $|V_{xx}| < |V_{yy}| < |V_{zz}|$ we can calculate the quadrupolar parameters of the NMR spectroscopy:

$$
Cq = \frac{e\,Q\,V_{zz}}{h}
$$

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

where e is the electron charge, h the Planck constant and Q the quadrupolar momentum of the nuclei.

Example of input file for the efg.x program:

```
&inputpp
  filerec(1)='/u/cm/profeta/PW/O-sesame/pseudo/Si.recon'
  filerec(2)='/u/cm/profeta/PW/O-sesame/pseudo/O.recon'
  prefix='quartz'
  outdir='/u/cm/profeta/tmp/'
  Q(1)=0.0
  Q(2)=2.55
/
```

An example of calculation of the efg tensor is in example24 of PWSCF distribution.

4 chemical shift tensor

A uniform external magnetic field **B** applied to a sample induces an electric current. This current is proportionnal to the external field **B** and is the first ordered-induced current $\mathbf{j}^{(1)}(\mathbf{r})$. This current produces a non uniform magnetic field $\mathbf{B}^{(1)}_{in}$:

$$\mathbf{B}^{(1)}_{in}(\mathbf{r}) = \frac{1}{c} \int d^3r' \, \mathbf{j}^{(1)}(\mathbf{r}') \frac{\mathbf{r} - \mathbf{r}'}{|\mathbf{r} - \mathbf{r}'|^3} \tag{6}$$

The chemical shift tensor is defined as the ratio between the induces magnetic field and the external uniform magnetic field:

$$\mathbf{B}^{(1)}_{in}(\mathbf{r}) = -\overset{\leftrightarrow}{\sigma}(\mathbf{r})\mathbf{B} \tag{7}$$

The isotropic chemical shift is one third af the trace of the chemical shift tensor.

The goal of the calculation is to calculate the all-electron current, in order to deduce the chemical shift tensor from eq (6).

4.1 bare current

In opposition with the diamagnetic and paramagnetic reconstruction term, the bare current is the term directly formed by the pseudopotential wavefunction.

As explained in reference [1], in the case of infinitely periodic system, the bare induced field can be computed in the reciprocal space:

$$\mathbf{B}^{(1)}_{bare}(\mathbf{G}) = \frac{4\pi}{c} \frac{i\mathbf{G} \times \mathbf{j}^{(1)}_{bare}(\mathbf{G})}{G^2} \tag{8}$$

equation (61) of reference [1].

For $\mathbf{G} = 0$ previous equation can not be applied, the $\mathbf{G} = 0$ component is:

$$\mathbf{B}^{(1)}_{in}(\mathbf{G} = 0) = \frac{8\pi}{3} \overset{\leftrightarrow}{\chi} \mathbf{B} \tag{9}$$

equation (62) of reference [1]. Where χ is macroscopic magnetic susceptibility. We do not take into account the contribution of the correction current for the evaluation of χ which is the contribution from $\mathbf{j}^{(1)}_{bare}$.

An approximation of the evaluation of this susceptibility is:

$$\overset{\leftrightarrow}{\chi} = \frac{\overset{\leftrightarrow}{F}(q) - 2\overset{\leftrightarrow}{F}(0) + \overset{\leftrightarrow}{F}(-q)}{q^2} \tag{10}$$

equation (64) of reference [1].

where q is a little displacement of the k-point in the 3 cartesian directions, and $F_{ij}(q) = (2 - \delta_{ij})Q_{ij}(q)$

$$\overset{\leftrightarrow}{Q}(q) = -\sum_{i=x,y,z} \sum_{o,k} \mathrm{Re}\left[\frac{1}{c^2 N_k V_c} \langle u^{(0)}_{0,k} | \mathbf{e}_i \times (-i\nabla + k)\mathcal{G}_{k+q}(\epsilon_{o,k})\mathbf{e}_i \times v_{k+q,k} | u^{(0)}_{0,k} \rangle \right] \tag{11}$$

equation (65) of reference [1].

V_c is the unit cell volume N_k the number of k-points and $\mathbf{e}_i$ are unit vectors in the three cartesian directions.

$|u^{(0)}_{0,k}\rangle$ is the ground state electronic Bloch wavefunction of occupied state o and k-point k.

$v_{k+q,k} = -i\nabla + k + \frac{1}{i}[\mathbf{r}, V^{nl}_{k+q,k}]$ where $V^{nl}_{k+q,k}$ is the generalized non local potential

$$V^{nl}_{k+q,k} = \sum_{I,J} D_{I,J} |\beta_I^{k+q}\rangle\langle\beta_J^k| \tag{12}$$

The expression of the bare current is

$$\mathbf{j}^{(1)}_{bare}(\mathbf{r}) = \frac{S_{bare}(\mathbf{r}, q) - S_{bare}(\mathbf{r}, -q)}{2q} \tag{13}$$

Equation (45) of reference [1], where

$$S_{bare}(\mathbf{r}, q) = \frac{2}{cN_k} \sum_{i=x,y,z} \sum_{0,k} \mathrm{Re} \left[\frac{1}{i} \langle u^{(}_{o,k}0)| J^p_{k,k+q}(\mathbf{r}) \mathcal{G}_{k+q}(\epsilon_{o,k})\mathbf{B} \times \mathbf{e}_i \cdot v_{k+q,k} |u^{(}_{o,k}0)\rangle \right] \tag{14}$$

Equation (52) of reference [1], and

$$J^p_{k,k+q}(\mathbf{r}) = \frac{(-i\nabla + k)|\mathbf{f}\rangle\langle\mathbf{r}| + |\mathbf{f}\rangle\langle\mathbf{r}|(-i\nabla + k + q)}{2} \tag{15}$$

Equation (51) of reference [1].

4.2 Description of a nmr calculation

To evaluate the bare contribution to the chemical shift, equation (10) and (13) must be calculated. In those expression appears the Bloch electronic function in the occupied states on k-points $\mathbf{k}$ and $\mathbf{k} + \mathbf{q}$. Indeed the calculation of the nmr tensor is divided in three parts:

- an scf calculation to have the occupied states on k-point $\mathbf{k}$;

- a non-scf calculation to evaluate the occupied states on k-point $\mathbf{k} + \mathbf{q}$. q is a little displacement of the k-point in the three cartesian directions. To perform this calculation, we used a flag created for the raman calculation which generate automatically the different k-point giving the norm of the displacement `b_length`.

Example of input file for the non-scf calculation:

```
HF
HF

 &control
        calculation='raman'
        restart_mode='from_scratch',
        prefix='HF',
        pseudo_dir='./',
 /
 &system
        ibrav=0,
        celldm(1)=10.,
        nat=2, ntyp=2,
        ecutwfc = 80, ecutrho = 320.0
        nspin=1,
```

```
/
&electrons
        conv_thr = 1.0d-8
        mixing_beta=0.1
 /
 &raman
  b_length = 0.001,
lcart = .true
 /
ATOMIC_SPECIES
 F 9.  FPBE.RRKJ3.UPF
 H 1.  HPBE.RRKJ3.UPF
ATOMIC_POSITIONS {bohr}
H 0.0 0.0 0.0
F 1.732 0.0 0.0
CELL_PARAMETERS {cubic}
1.0 0.0 0.0
0.0 1.0 0.0
0.0 0.0 1.0
K_POINTS {automatic}
1 1 1   1 1 1
```

the wavefunctions are stored in the .wfc file in this order:

```
    k(   1) = (  -0.5000000  -0.5000000  -0.5000000), wk =   2.0000000
    k(   2) = (  -0.4990000  -0.5000000  -0.5000000), wk =   0.0000000
    k(   3) = (  -0.5000000  -0.4990000  -0.5000000), wk =   0.0000000
    k(   4) = (  -0.5000000  -0.5000000  -0.4990000), wk =   0.0000000
    k(   5) = (  -0.5010000  -0.5000000  -0.5000000), wk =   0.0000000
    k(   6) = (  -0.5000000  -0.5010000  -0.5000000), wk =   0.0000000
    k(   7) = (  -0.5000000  -0.5000000  -0.5010000), wk =   0.0000000
```

- the nmr calculation in itself. All the subroutines are in a directory `Nmr` of the pwscf CVS. The main program is `nmr.f90`. In order to compile it, you should do a `make all` in this directory.

  Example of input for the nmr calculation:

```
&inputnmr
   filerec(1)='F.recon'
   filerec(2)='H.recon'
   prefix='HF'
/
```

4.3   description of the code

- $|\tilde{u}_{o,k}^{(0)}\rangle = v_{k+q,k}|u_{o,k}^{(0)}\rangle$ is calculated in subroutine `take_nloc_k_kq`

  $\frac{1}{i}[\mathbf{r}, V_{k+q,k}^{nl}]$ is calculated as the derivative of the non-local potential with respect to k.

9

$$\frac{1}{i}[\mathbf{r}, V_{k+q,k}^{nl}|u_{o,k}^{(0)}\rangle = \sum_{I,J} D_{I,J}\left[|\beta_I^{k+q}\rangle\frac{\mathrm{d}}{\mathrm{d}k}\langle\beta_J^k|u_{o,k}^{(0)}\rangle + \frac{\mathrm{d}}{\mathrm{d}k}|\beta_I^{k+q}\rangle\langle\beta_J^k|u_{o,k}^{(0)}\rangle\right] \qquad (16)$$

In the original code (`paratec`) it was calculated by a numerical difference, whereas here we try to use an analytical expression as in `PH/dvpsi_e.f90`.

- The subroutine `grad.f90` simply multiply the wavefunction by $\mathbf{k} + \mathbf{G}$.

- The linear response $\mathcal{G}_{k+q}(\epsilon_{o,k})|\tilde{u}_{o,k}^{(0)}\rangle$ is calculated in subroutine `solve_cg.f90` using the conjugate gradient in `PH/cgsolve_all.f90`.

- The subroutine `add_j_bare.f90` apply the operator $|\mathbf{r}\rangle\langle\mathbf{r}|$ used in (13) thanks to a FFT.

- The subroutine `magnetic_kkterm.f90` calculate $Q(0)$ in (11).

Each k-points are calculated separately in the most external loop.

At present time, the calculation with k-point k (`magnetic_kkterm`) seem to give resonnable output, but the calculation of χ with $F(q)$ and $F(-q)$ does not works properly when generalized with $k + q$. It seems that `take_nloc_k_kq` has some bugs, but I can not discover it yet....

References

[1] Chris J. Pickard and Francesco Mauri. All-electron magnetic response with pseudopotentials: Nmr chemical shifts. *Phys. Rev. B*, 63:245101, 2001.

[2] M. Profeta, F. Mauri, and C.J. Pickard. Accurate first principles prediction of ^{17}o nmr parameters in sio$_2$: assignment of the zeolite ferrierite spectrum. *J. Am. Chem. Soc.*, 125:541, 2003.