GIPAW – Linear response in the presence of magnetic fields

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Originally aimed to calculate NMR chemical shifts, later also the EPR electronic g-tensor, ...

Standard version: qe-gipaw-5.3.tar @ qe-forge
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GIPAW – Linear Magnetic Response

Originally aimed to calculate **NMR chemical shifts**, later also the **EPR electronic $g$-tensor**, ...

**GIPAW routines/pseudopotentials** are also used for

- X-ray spectra (Xspectra): XANES, (XMCD)
- orbital magnetization, converse NMR-approach
- SOC including two component noncolinear scheme using scalar-relativistic GIPAW pseudos
Essential: \( B \)-field brings the phase of the wfc into play

\[
\tilde{\psi}_{n,k}(\mathbf{r}) \rightarrow e^{(ie/\hbar c)A_0(t)\cdot \mathbf{r}} \tilde{\psi}_{n,k}(\mathbf{r} - \mathbf{t})
\]

(to insure translational invariance within PBC)

The \textbf{PAW} augmentation scheme has to be extended in a \textbf{Gauge Including way}: \( \rightarrow \textbf{GIPAW} \)

\[
\tilde{O} = O + \sum_{ij} |\tilde{p}_i\rangle(\tilde{D}^{1}_{ij}[O] - \tilde{D}^{1}_{ij}[O])\langle \tilde{p}_j|
\]

\[
\tilde{D}^{1}_{ij}[O] = \langle \phi_i | e^{(-ie/\hbar c)A_0(\mathbf{R})\cdot \mathbf{r}} O e^{(ie/\hbar c)A_0(\mathbf{R})\cdot \mathbf{r}} | \phi_j \rangle
\]
Basic quantity for NMR (EPR): **(spin) currents** induced by the B-field

**EPR:**

\[ g_{\mu\nu} = g_e \cdot \delta_{\mu\nu} + \frac{\alpha^2}{2S_{\text{eff}}} \left[ \sum_{\sigma} \int \nabla V_{\text{eff}}^\sigma \times \vec{j}^{(1),\sigma}_{\mu}(\vec{r}) d^3r \right]_\nu \]

\[ g_e = \begin{cases} 2.002 \, 319 \, 278 & \text{spin-currents} \\ \vec{j}^{(1),\sigma}_{\mu} : = & \text{spin-currents induced by } \vec{B} \end{cases} \]


\[ \vec{j}^{(1),\mu}_{\sigma}(\vec{r}) = \sum_{\sigma} \text{Re} \left\langle \psi_{(0),0}^\sigma \right| \mathcal{J}^p G_{\sigma}^\sigma (\epsilon_o) \mathcal{H}_{(1)} \left| \psi_{(0),0}^\sigma \right\rangle - \frac{1}{2} n_{\sigma}(\vec{r}) \cdot B_0 \vec{e}_\mu \times \vec{r} = \left| \psi_{(1),\sigma}^\sigma \right\rangle \]

\[ \Rightarrow \text{Green's function required} \]
Basic quantity for NMR (EPR): **(spin) currents** induced by the B-field

\[ \text{NMR: } B_{\text{ind}}(r') = \ldots \frac{r'-r}{|r'-r|^3} \ldots \]

\[ \text{EPR: } g_{\mu\nu} = g_e \cdot \delta_{\mu\nu} + \frac{\alpha^2}{2 S_{\text{eff}}} \left[ \sum_\sigma \int \nabla V_{\text{eff}}^\sigma \times \vec{j}_{(1),\sigma}^\mu(\vec{r}) d^3 r \right]_{\nu} \]

\[ g_e = 2.002 \ 319 \ 278 \ldots \]

Spin-currents induced by \( \vec{B} \)

\[ \vec{j}_{(1),\mu}^\sigma(\vec{r}) = \sum_{\sigma} \text{Re} \left\langle \psi_{(0),\sigma} \left| J^\mu \ G^\sigma(\epsilon^\sigma_0) \ H_{(1)} \right| \psi_{(0),\sigma} \right\rangle \]

\[ - \frac{1}{2} n^\sigma(\vec{r}) \cdot B_0 \vec{\epsilon}_\mu \times \vec{r} = \left| \psi_{(1),\sigma} \right\rangle \]

\( \Rightarrow \) Green’s function required
Central routine: `greenfunction.f90`

Green’s function@\( k+q \) to be applied on a modified version of the unperturbed wfc:

\[
G_{k+q} |\psi> = G_{k+q} \{ V_{k+q,k} |\text{evc}> \}; \quad q = \{0, \pm \Delta q \ e^i \text{ with } i=x,y,z\}
\]

Similar to `solve_linter.f90` in PH, it calls:

- `cgsolve_all.f90` iterative solver of linear systems
- `cg_psi.f90` for (simple) preconditioning (via diagonals of H),
- `ch_psi_all.f90` for application of H-eS+P_cv
- `orthogonalize.f90` for computing P_cv
- `(h_psi_q.f90` for BAND parallelization only;
  otherwise: `h_psi, calbec, s_psi` )
Central routine: greenfunction.f90

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\[ G_{k+q} |\psi > = G_{k+q} \{ V_{k+q,k} |\text{evc}\}; \quad q = \{0, \pm \Delta q \ e_i \text{ with } i=x,y,z\} \]

in addition: `apply_operators.f90` , e.g. apply \( V_{k+q,k} \) to \( \text{rhs} \)

`compute_u_kq.f90` prepares unperturbed \( \text{wfc}@k+q \)

**NEW:** Speed-up for small \( \Delta q \):

resuse \( G_{k+q} |\psi > \) from previous \( q \),

`ch_psi.f90` only for \( q=0 \).

Includes all things for preconditioning, e.g. also

small parts from `phq_init.f90`: 

\[ \text{eprec} = 1.35*\text{zdotc}(\text{evq},\text{work}) \]
Central routine: `greenfunction.f90`

\[
G_{k+q} \mid \psi \rangle = G_{k+q} \{ V_{k+q,k} \mid \text{evc}\}; \quad q = \{0, \pm \Delta q e_i\} \text{ with } i=x,y,z
\]

in addition: `apply_operators.f90`\(^\star\), e.g. apply \(V_{k+q,k}\) to rhs

`compute_u_kq.f90`\(\star\) prepares unperturbed \(\text{wfc}@k+q\)

Specific topics:

- quantities at \(k\) and \(k+q\) must have the same G-vector ordering; we call \(gk\_sort\) only for \(k\), not for \(k+q\).

- symmetry operations that do not map cartesian axes might be – in principle – removed (as done in 5.3.0), but:

  **NEW:** it works also with full symmetry, if symmetrization is applied at the very end (onto the full tensors) excusively.
**LR related routines** *(as a general observation)*:

**LR in GIPAW** has very few dependencies, can be easily decoupled from the code, and can be „librarized“ away (into **LR_Modules**).

**As my present personal opinion:**

- `greenfunction.f90` (or something like that) should be either kept GIPAW-specific
- or
- `solve_linter.f90` should be reorganized, split-up into less PH-specific logical subroutines, may be all of them kept within the same file.

*interface between GIPAW/LR_Modules* can be changed accordingly.
Open Question (loosely related to LR):

- Where to put the Berry-phase routines applicable onto NMR/EPR, GIPAW-tree or (partially) PW-core?
- Orbital magnetization as a more general quantity (MTM analogue to MTM, suggesting PW), but to compute accurate $du/dk$: greenfunction.f90

Proposal: keep it close to “NMR/EPR“, should be found in GIPAW, e.g.:

$$\Delta g_{\mu\nu} = \frac{2}{\alpha} \left. \frac{\partial^2 E_{\text{tot}}}{\partial S_\nu \partial B_\mu} \right|_{\vec{B}=0} = -\frac{2}{\alpha} \frac{\partial M^\text{orb}_\mu}{\partial S_\nu}$$

Work in progress, perspectives:

- Zero-Field Splitting (ZFS) of EPR, both $D_{s-s}$ and $D_{SO}$!
- NMR/EPR for hybrid functionals
- NMR with spin-orbit coupling, colinear & non-collinear based on relativistic & scalar relativistic (GI)PAW pseudos
- Circular Dichroism of X-ray Adsorption (XMCD)  (Matteo Calandra, UG)
Thanks for your attention!
2\textsuperscript{nd} method: beyond perturbation theory

\begin{equation}
H_{\text{spin}} = \frac{\alpha}{2} \vec{B} \cdot \vec{g} \cdot \vec{S} + \sum_{N} \vec{I}_{N} \cdot \vec{A}_{N} \cdot \vec{S} + \vec{S} \cdot \vec{D} \cdot \vec{S}
\end{equation}

basic idea: \[ \Delta g_{\mu\nu} = \left. \frac{2}{\alpha} \frac{\partial^2 E_{\text{tot}}}{\partial S_{\nu} \partial B_{\mu}} \right|_{\vec{B}=0} = -\frac{2}{\alpha} \frac{\partial M_{\mu}^{\text{orb}}}{\partial S_{\nu}} \]


How to calculate the derivative \( \partial / \partial S_{\nu} \)?

1. B-field induced spin alignment along \( \vec{e}_{\nu} \):
   \[ H_{\text{so}} = \frac{\alpha^2}{4} \vec{\sigma} \cdot (\nabla V_{\text{eff}} \times \vec{p}) \] with \( \vec{\sigma} = \sigma_{z} \vec{e}_{\nu} \)
   \[ \Delta g_{\mu\nu} = -\frac{2}{\alpha} \vec{e}_{\mu} \cdot \frac{\partial \tilde{M}_{\mu}^{\text{orb}}(\vec{e}_{\nu}) - \tilde{M}_{\mu}^{\text{orb}}(-\vec{e}_{\nu})}{S - (-S)} \]

2. spin flip
2\textsuperscript{nd} method: beyond perturbation theory

EPR

\[ H_{\text{spin}} = \frac{\alpha}{2} \vec{B} \cdot \vec{g} \cdot \vec{S} + \sum_{N} \vec{l}_N \cdot \vec{A}_N \cdot \vec{S} + \vec{S} \cdot \vec{D} \cdot \vec{S} \]

- well defined in finite systems: \( \vec{M}^{\text{orb}} = \frac{\alpha}{2} \langle \vec{r} \times i [\vec{r}, \mathcal{H}] \rangle_{B=0} \)
- periodic systems: **Berry phase formula**

\[ \vec{M}^{\text{orb}} = -\frac{\alpha}{2} \text{Im} \sum_{n,k} f_{n,k} \langle \partial_k u_{nk} | \times (\mathcal{H}_k + \epsilon_{nk} - 2\epsilon_F) | \partial_k u_{nk} \rangle \]


\[ \Delta g_{\mu\nu} = \frac{2}{\alpha} \frac{\partial^2 E_{\text{tot}}}{\partial S_\nu \partial B_\mu} = -\frac{2}{\alpha S} \vec{e}_\mu \cdot \vec{M}^{\text{orb}}(\vec{e}_\nu) \]

Both methods are now applicable also on metallic systems, e.g. electrons trapped by the conduction band minimum in Si bulk:

Strongly delocalized states:
conduction band electrons in Si: $g_{\text{exp}} = 1.9995$
cc unit cell (2 atoms),
(24 × 24 × 24) MP k-point set:

$g_{\text{DFT} 1} = 1.9991$ (Berry phase)
$g_{\text{DFT} 2} = 1.9990$ (non-eq. GIPAW)

Young et al., PRB 55, 16245 (1997)
Efficient relativistic DFT calculations

**scalar-relativistic pseudopotentials:**
- Relativistic kinetic energy
- spin-orbit (SO) coupling neglected
**Efficient relativistic DFT calculations**

*scalar-relativistic pseudopotentials:*  
- Relativistic kinetic energy  
- spin-orbit (SO) coupling neglected

**full-relativistic approach:**  
large SO coupling effects, but:  
factor-of-40 more computational costs
**Efficient relativistic DFT calculations**

**scalar-relativistic pseudopotentials:**
- Relativistic kinetic energy
- spin-orbit (SO) coupling neglected

**alternative relativistic approach:**
PAW-reconstruction of SO coupling

\[
\Delta \hat{H}_{\text{SO}} = \hat{T}^+ \Delta \hat{H}_{\text{SO}} \hat{T} \\
= \frac{\alpha^2}{4} \left\{ \hat{\sigma} \cdot \left( \nabla V_{ps}(\vec{r}) \times \hat{p} \right) \right\} \\
+ \sum_{\mathbf{R}} \sum_{n,m} |p_{\mathbf{R},n}\rangle f_{\mathbf{R},nm} \langle p_{\mathbf{R},m}| \\
\]

\[
f_{\mathbf{R},nm} = \langle \phi_{\mathbf{R},n} | \hat{\sigma} \cdot \nabla V \times \hat{p} | \phi_{\mathbf{R},m} \rangle \\
- \langle \phi_{\mathbf{R},n} | \hat{\sigma} \cdot \nabla V_{ps} \times \hat{p} | \phi_{\mathbf{R},m} \rangle
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+ \sum_{\vec{R}} \sum_{n,m} |p_{\vec{R},n}\rangle f_{\vec{R},nm} \langle p_{\vec{R},m}|}
\]

**ZORA:**
\[
\tilde{\nabla} V = \nabla \left( \frac{2c^2}{1 - V/(2c^2)} \right) = \frac{1}{(1 - \frac{V}{2c^2})^2} \cdot \nabla V
\]
**Efficient relativistic DFT calculations**

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+ \sum_{R} \sum_{n,m} |p_{R,n}\rangle f_{R,nm} \langle p_{R,m}| \\
\]

\[
f_{R,nm} = \langle \phi_{R,n} | \hat{\sigma} \cdot \nabla V \times \hat{p} | \phi_{R,m} \rangle \\
- \langle \phi_{R,m} | \hat{\sigma} \cdot \nabla V_{ps} \times \hat{p} | \phi_{R,n} \rangle
\]

**identical results !**
Efficient „reconstruction-only“ approach:

\[ \Delta \hat{H}_{\text{SO}} = \frac{\alpha^2}{4} \sum_{R,n,m} |p_{R,n}\rangle \langle \phi_{R,n}| \frac{1}{r} \frac{\partial V(r)}{\partial r} \hat{\sigma} \cdot \hat{L} |\phi_{R,m}\rangle \langle p_{R,m}| \]

relativistic calculations for large systems (500 atoms) possible: