New development in spin-orbit calculations with (GI)PAW pseudopotentials

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Motivation – spin-orbit coupling in spectroscopy

spectroscopical data for large systems (> 300 atoms), e.g. interfaces, functionalized surfaces, molecular crystals, ...

- Electron Paramagnetic Resonance (EPR): non-perturbative calculation of $g$-tensor calculation as an alternative to linear magnetic response (GIPAW)
- Zero Field splitting (ZFS)
- Magnetic Circular Dichroism of X-ray adsorbtion (XMCD)

All these quantities require spin-orbit (SO) coupling
We need an efficient (non-) collinear relativistic treatment!
Electron Paramagnetic Resonance

- **Experimental Spin-Hamiltonian**

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

- **g-tensors:**
  microscopic spins are aligned along the magnetic field \( \vec{B} \)
  \( \sim \) collinear relativistic description sufficient,

  but to get the full tensor (all matrix elements),
  three independent calculations necessary!
Choice of the relativistic Hamiltonian

- **basic idea:**
  Foldy-Wouthuysen (FW) transformation onto Dirac’s equation

\[
\mathcal{H} = \left( \frac{1}{2} \mathbf{p}^2 + \alpha \mathbf{A} \right)^2 - \frac{1}{2} \mathbf{p}^4 + ... + V_{\text{scf}} + \frac{\alpha}{2} \sigma \cdot \mathbf{B} + \mathcal{H}_{\text{SO}} - \frac{\alpha^2}{4} \nabla \cdot \mathbf{E}
\]

\[
\mathcal{H}_{\text{SO}} = - \frac{\alpha^2}{4} \sigma \cdot \left[ \mathbf{E} \times (\mathbf{p} + \alpha \mathbf{A}) \right] - \frac{i \alpha^2}{8} \sigma \cdot \left[ \nabla \times \mathbf{E} \right]
\]

small component reduced by six orders in $1/c$!

- remaining problem of the resulting FW-Hamiltonian
  (*ill defined expansion of the kinetic part*)
  is coped by using the *scalar-relativistic approximation*.

- **important advantage:** we can use *scalar-relativistic pseudos"
Choice of the relativistic Hamiltonian

- **1st step:** collinear spin-polarisation along $\vec{e}_\nu$

\[ H = H_0 + H_Z + H_{SO} \]

with \( H_{SO} = \frac{\alpha^2}{4} \vec{\sigma} \cdot \nabla V_{\text{eff}}^\sigma \times \left( \vec{p} + \alpha \vec{A} \right) \)

and (GI)PAW reconstruction \( H_{SO}^\text{flip} = T_0^+ H_{SO} T_0 \)

with \( \vec{\sigma} = \sigma_z \vec{e}_\nu = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \vec{e}_\nu \)

**advantage:** spin remains a “good” quantum number, spin channels remain decoupled.
Spin-orbit coupling in spectroscopy

Conclusions

\[ g\text{-tensors via } \Delta g_{\mu\nu} = -\frac{2}{\alpha S} \bar{e}_{\mu} \cdot \vec{M}_{\text{orb}}(\vec{e}_{\nu}) \]

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- circumvents perturbation theory
- works for any DFT functional and also for metallic systems
Example: $c$-Si/$a$-Si:H heterojunctions

**EDMR of a working device (solar cell):**

in the 'Zero-field': spins are not necessarily aligned

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noncollinear spin-polarization becomes important: relativistic two-component description (spinors)!
Efficient PAW pseudopotential implementation

By the PAW transformation

\[ \Delta \mathcal{H}_{SO} = T_0^+ \Delta \mathcal{H}_{SO} T_0, \]

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

with

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

can be very accurately computed in a "reconstruction-only" way:

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

Saves a factor-of-10 ... 20 in computational time!
Spin-orbit coupling in spectroscopy

Conclusions

Spin-orbit coupling in a “reconstruction-only” way

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

- applicable to scalar-relativistic (GI)-PAW pseudo-potentials
- implemented in collinear way

\[ \mathbf{\vec{\sigma}} = \sigma_z \mathbf{\vec{e}}_\nu = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \mathbf{\vec{e}}_\nu \]

as well as non-collinear way:

\[ \mathbf{\vec{\sigma}} \cdot \mathbf{\vec{L}} = \begin{pmatrix} L_z & L_x - iL_y \\ L_x + iL_y & -L_z \end{pmatrix} \]

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New development in spin-orbit calculations with (GI)PAW pseudopotentials
Spin-orbit coupling in a “reconstruction-only” way

Correct description of expectation values in spin-aligned cases.

What about relativistic band structures?

Bi(111) surface as an example:
Spin-orbit coupling in a “reconstruction-only” way

grey: full-relativistic bandstructure

no spin-orbit coupling

“reconstruction-only” spin-orbit

15 min → 10 h

50 min

New development in spin-orbit calculations with (GI)PAW pseudopotentials
Required changes in the code

```plaintext
<gipaw_module> to be put into PW (or Modules);
also needed for 'the XMCD extension of the XSpectra code,
the 'orbital magnetization' PRB 81, 060409 (2010);
in slightly modified form also for 'converse-NMR' (Emine)

including:

init_gipaw_1  basic initialization of GIPAW data
init_gipaw_2  paw_beta functions, called by e_bands.f90 etc.
paw_gipaw    UPF read-in, paw_becp, paw_becp_nc,...
gipaw_setup  called by hinit0.f90
             includes the additional terms to
             h_psi (collinear) and h_psi_nc:
             ------------------------  ------------------------
             add_so_bare    add_so_bare_nc
             add_so_Fnl    add_so_Fnl_nc
             deeq_so substitutes deeq, deeq_nc.

essential:

update set_vrs: calculation of dvrs
             (gradient of the total potential in real space,
              to be stored in scf_mod, allocated in allocate_fft)

update force_us AND stress_us nonlocal contributions from deeq_so and paw_becp(_nc).
```
conclusions – approximated SO-coupling

“reconstruction-only” scheme for scalar-relativistic pseudos:

- SO-including spinor good enough to compute reliable expectations values (spectroscopical data)

- relativistic bandstructures of the full-relativistic approach are precisely reproduced (e.g. Bi(111) bilayer)

- forces and even stress (!!!) can be calculated straightforward.

- user-friendly (standard PAW pseudos), fast converging.

- improved results if using relativistic ZORA for the SO-part, many-body effects (spin-other orbit contributions?)
Thanks for your attention!

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