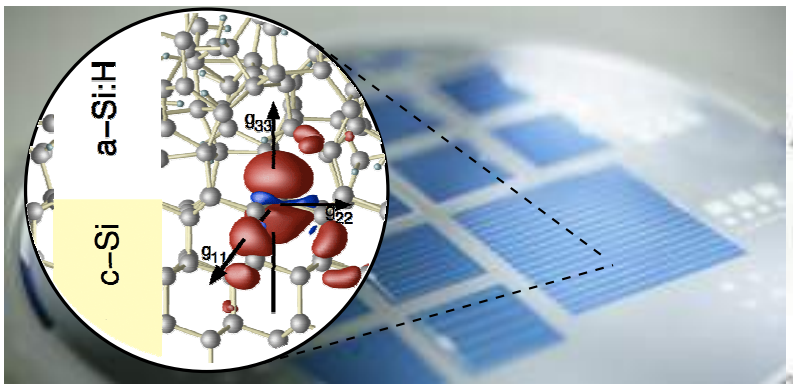
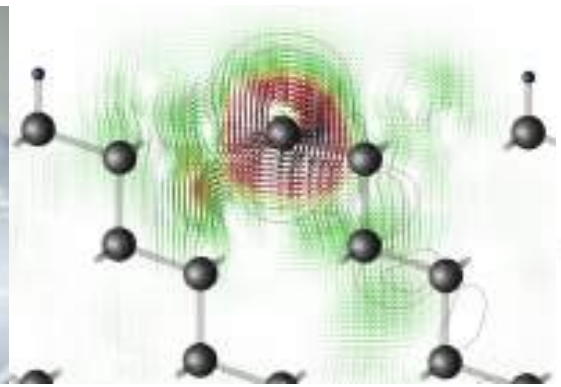
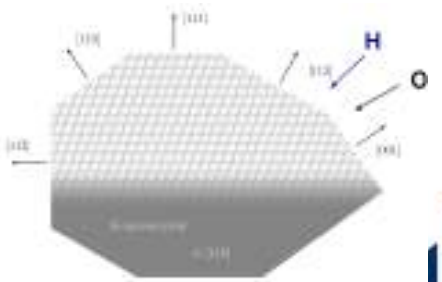
New development in spin-orbit calculations with (GI)PAW pseudopotentials

U. Gerstmann, University of Paderborn

QE developers meeting, Lausanne 08.01.2014







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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**

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

- g-tensors:
  microscopic spins are aligned along the magnetic field $\vec{B}$

  $\rightsquigarrow$ collinear relativistic desription 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

$$\mathcal{H} = \left(\frac{1}{2}(\mathbf{p}+\alpha\vec{A})^2 - \frac{1}{2}\mathbf{p}^4 + \ldots\right) + V_{\mathrm{scf}} + \frac{\alpha}{2}\vec{\sigma}\cdot\vec{B} + \mathcal{H}_{SO} - \frac{\alpha^2}{4}\nabla\cdot\vec{E}$$

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

  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 $\vec{e}_\nu$

$$\mathcal{H} = \mathcal{H}_0 + \mathcal{H}_Z + \mathcal{H}_{SO}$$

with $\mathcal{H}_{SO} = \frac{\alpha^2}{4}\,\vec{\sigma}\cdot\nabla V^{\sigma}_{\text{eff}} \times \left(\vec{\mathbf{p}} + \alpha\vec{A}\right)$

and (GI)PAW reconstruction $\overline{\mathcal{H}}_{\text{SO}} = \mathcal{T}_0^{+}\,\mathcal{H}_{\text{SO}}\,\mathcal{T}_0$

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.

g-tensors via $\Delta g_{\mu\nu} = -\frac{2}{\alpha S}\vec{e}_\mu \cdot \vec{M}^{\mathrm{orb}}(\vec{e}_\nu)$

	[ppm]	Lin.Resp.	MTM
H_2^+	$\Delta g_\parallel$	−39.3	−39.3
	$\Delta g_\perp$	−41.7	−41.7
CN	$\Delta g_\parallel$	−141	−139
	$\Delta g_\perp$	−2600	−2603
CO^+	$\Delta g_\parallel$	−136	−134
	$\Delta g_\perp$	−3229	−3231
BO	$\Delta g_\parallel$	−70	−75
	$\Delta g_\perp$	−2384	−2384
BS	$\Delta g_\parallel$	−81	−82
	$\Delta g_\perp$	−9990	−10001
AlO	$\Delta g_\parallel$	−149	−149
	$\Delta g_\perp$	−1834	−1842

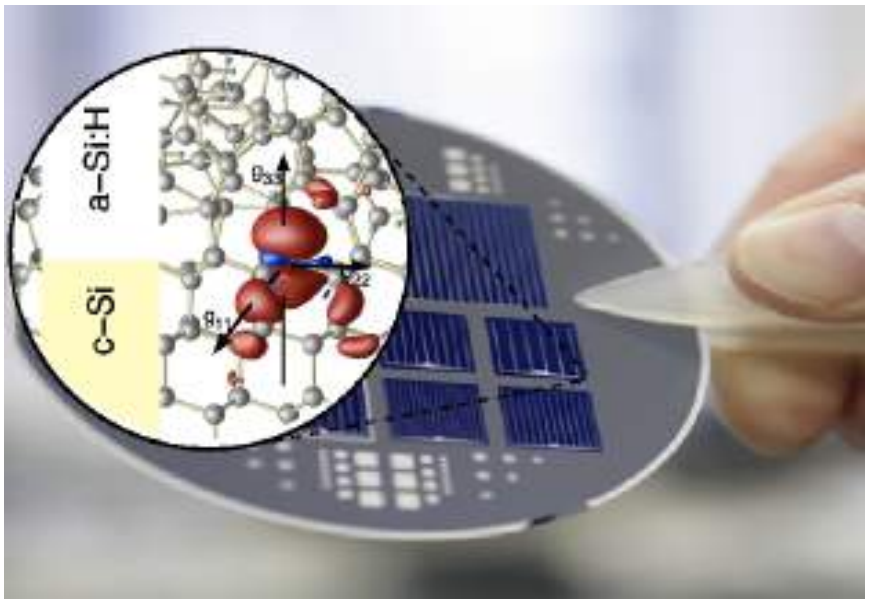
	[ppm]	Linear Response	MTM
CF	$\Delta g_\parallel$	$-\infty$	−1999719
	$\Delta g_\perp$	1920	−553
SiF	$\Delta g_\parallel$	$-\infty$	−1995202
	$\Delta g_\perp$	−480	−2470
GeF	$\Delta g_\parallel$	$-\infty$	−1998078
	$\Delta g_\perp$	−15505	−39101
SnF	$\Delta g_\parallel$	$-\infty$	−1996561
	$\Delta g_\perp$	−64997	−142687
PbF	$\Delta g_\parallel$	$-\infty$	−1999244
	$\Delta g_\perp$	−288383	−556326

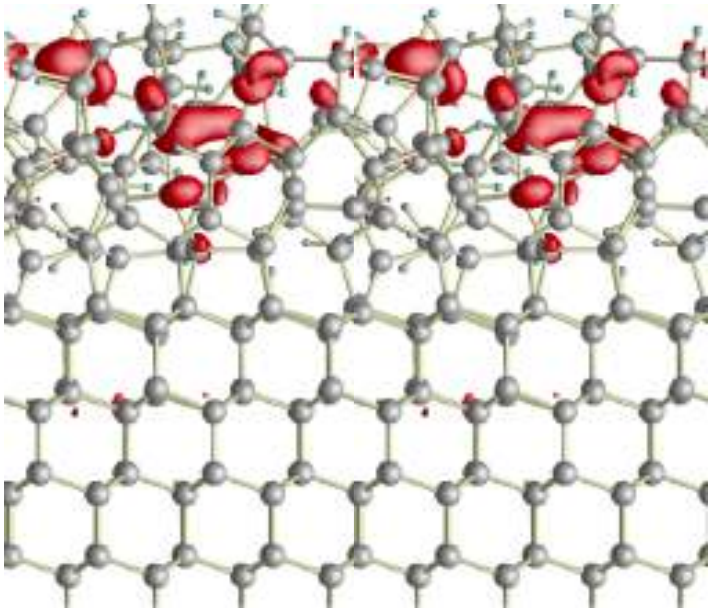
Ceresoli, Gerstmann, Seitsonen, Mauri, Phys. Rev. B **81**, 060409(R) (2010).

- circumvents perturbation theory
- works for **any** DFT functional and also for **metallic** systems

Example: *c*-Si/*a*-Si:H heterojunctions

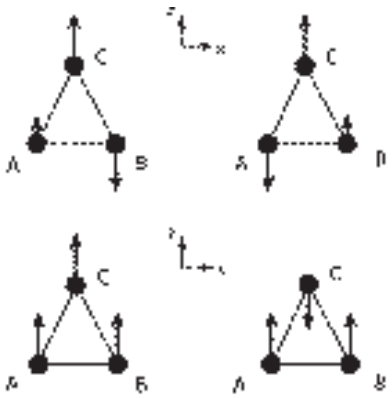
EDMR of a working device (solar cell):

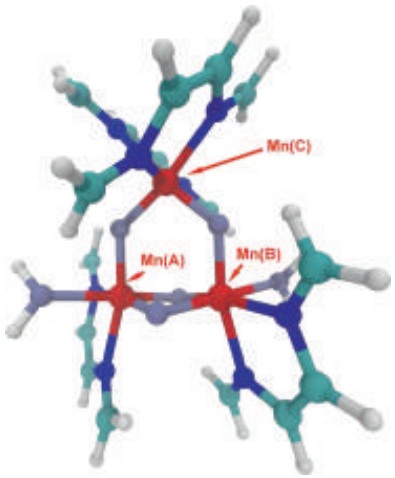


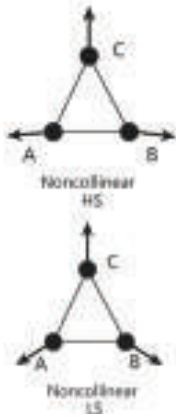


George, Schnegg, Lips, Gerstmann, *et al.*, PRL **110**, 13680 (2013).

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







software	method	ΔE
ADF	collinear weighted-average BS	-1.5
Quantum Espresso	collinear weighted-average BS	-1.6
Quantum Espresso	noncollinear	-0.2
experiment		-0.2

model trimer $[(Mn^{IV})_3O_4L_4(H^2O)]$, Luo, Batista, Truhlar, J. Phys. Chem. Lett. **2**, 2692 (2011).

$\rightsquigarrow$ **noncollinear spin-polarization** becomes important:
relativistic two-componenent description (**spinors**)!

Efficient PAW pseudopotential implementation

By the PAW transformation $\overline{\Delta\mathcal{H}_{\mathrm{SO}}} = \mathcal{T}_0^{+}\,\Delta\mathcal{H}_{\mathrm{SO}}\,\mathcal{T}_0$,

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

with $f_{\mathbf{R},nm} = \langle\phi_{\mathbf{R},n}|\,\vec{\sigma}\cdot\nabla V\times\vec{p}\,|\phi_{\mathbf{R},m}\rangle - \langle\overline{\phi_{\mathbf{R},n}}|\,\vec{\sigma}\cdot\nabla V_{\mathrm{ps}}\times\vec{p}\,|\overline{\phi_{\mathbf{R},m}}\rangle$

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

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

Saves a factor-of-10 ... 20 in computational time!

Spin-orbit coupling in a "*reconstruction-only*" way

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

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

$$\vec{\sigma} = \sigma_z \, \vec{e}_\nu = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \vec{e}_\nu$$

as well as non-collinear way:

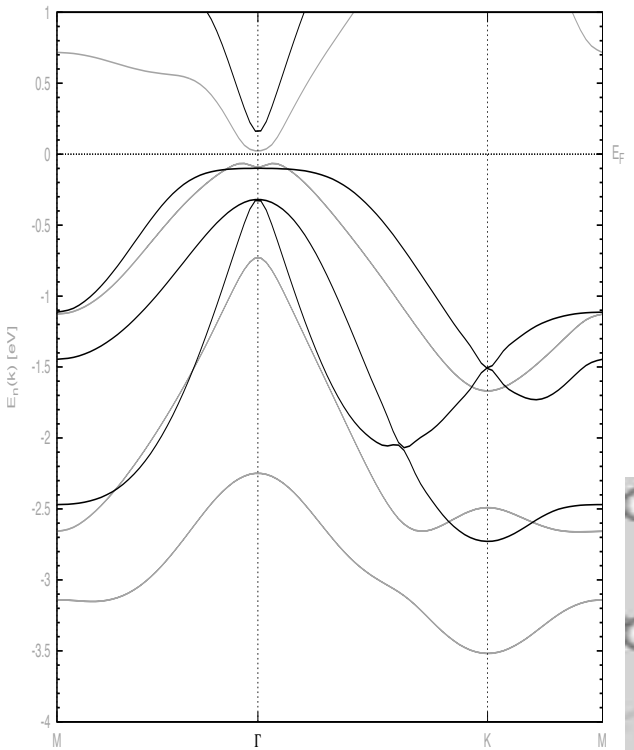
$$\vec{\sigma} \cdot \vec{L} = \begin{pmatrix} L_z & L_x - iL_y \\ L_x + iL_y & -L_z \end{pmatrix}$$

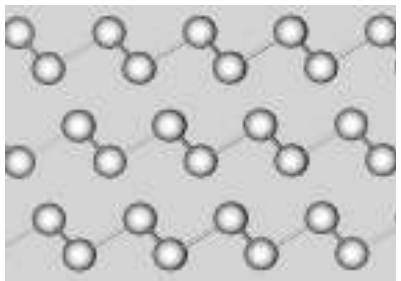
Spin-orbit coupling in a "*reconstruction-only*" way

Correct description of expectation values in spin-aligned cases.

What about relativistic band structures?

Bi(111) surface as an example:

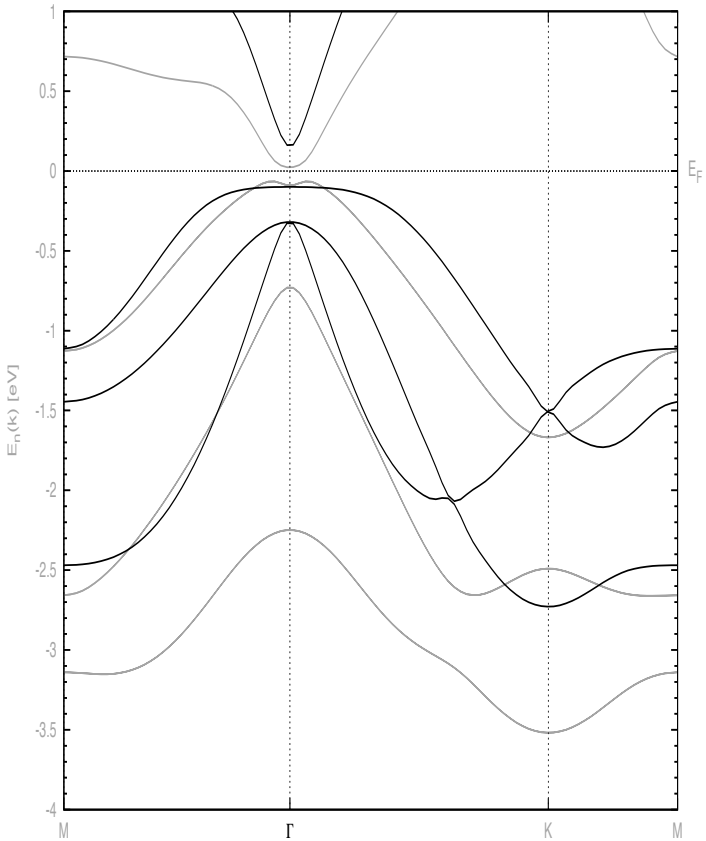




Spin-orbit coupling in a "*reconstruction-only*" way

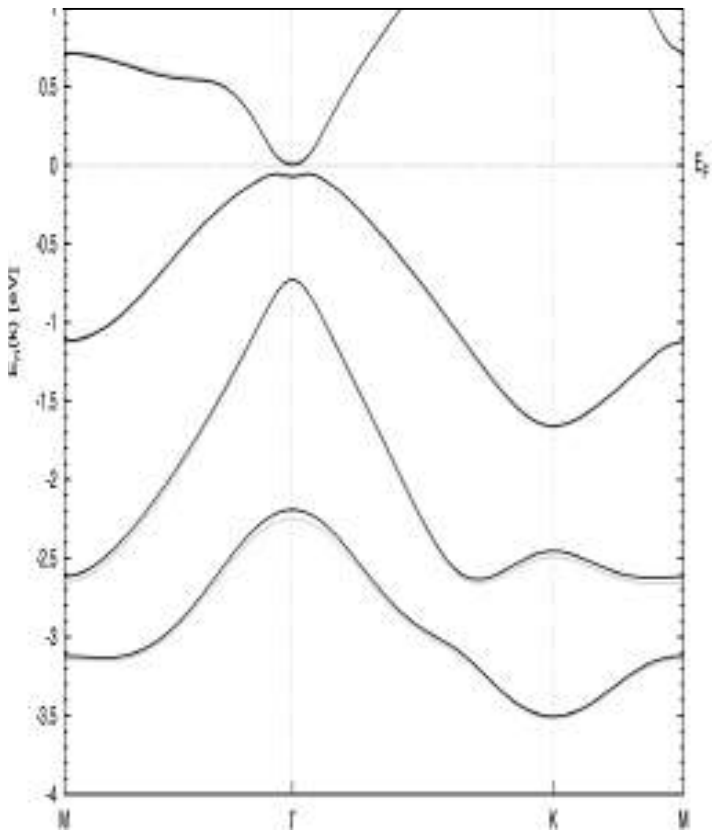
grey: full-relativistic bandstructure

no spin-orbit coupling



15 min → 10 h

"*reconstruction-only*" spin-orbit



50 min

Required changes in the code

```
<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 c_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!

Paderborn:
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