Orbital magnetism

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Two ways of looking at chemical shielding

Total energy:

$$E = \overbrace{-\mu \cdot \mathbf{B}}^{\text{Zeeman}} + \overbrace{\mu \cdot \overleftrightarrow{\sigma} \cdot \mathbf{B}}^{\text{shielding}}$$

$$\mu \cdot \underbrace{\overleftrightarrow{\sigma} \cdot \mathbf{B}}_{\text{induced field}}$$

- Standard approach
- As done by GIPAW: estimate current due to external **B**, use Biot-Savart law to compute induced **B**

$$\underbrace{\mu \cdot \overleftrightarrow{\sigma}}_{\text{induced dipole}} \cdot \mathbf{B}$$

- "Converse" method
- Apply nuclear magnetic dipole by hand
- Compute orbital magnetization to determine induced dipole

Converse method strategies

$$\mu \cdot \overleftrightarrow{\sigma} = M_\alpha = \frac{i}{2}\epsilon_{\alpha\beta\gamma}\sum_n^{\text{occ}} \int d\mathbf{k} \langle \partial_\beta u_{n\mathbf{k}} | H^0_{\mathbf{k}} + E_{n\mathbf{k}} | \partial_\gamma u_{n\mathbf{k}} \rangle$$

Approach 1 (Ceresoli, Vanderbilt):

- Apply nuclear dipole, compute with above formula directly
- However, the above is an "all-electron" formula, and it's not strictly clear what the proper PAW objects are, due to overlap operator and nonlocality
- Not obviously extensible to higher order interactions

Approach 2 (this work):

- Compute

$$\frac{\partial E}{\partial B} = \frac{\partial \mu \cdot \overleftrightarrow{\sigma} \cdot \mathbf{B}}{\partial B} = \mu \cdot \overleftrightarrow{\sigma}$$

- Requires more elaborate theory to construct E in finite B field and then take limit appropriately, but all PAW objects including overlap treated rigorously
- Much more extensible
- Implementation actually *much* simpler than approach 1!!

Step 1: Energy as a constrained minimization problem

We think of the energy as a functional of the Hamiltonian and the wavefunction overlap (generalized eigenstates!)

$$E[H,S] = \min_\rho \mathrm{Tr}[\rho H - \Lambda(\rho - \rho S \rho)] - \mu\left(\frac{1}{2}\mathrm{Tr}[\rho S + S\rho] - N\right),$$

with two constraints:

$$\begin{aligned} \mathrm{Tr}[\rho S] &= N \\ \rho &= \rho S \rho \end{aligned}$$

These mean that the total number of electrons is conserved, and the density operator acts like a density operator (i.e., idempotent)

Step 2: Magnetic translation group

The magnetic field appears in the Hamiltonian as a vector potential $\mathbf{A}$:

$$H = \frac{1}{2}(\mathbf{p} - q\mathbf{A})^2 + V$$

which generally breaks periodicity. But working in the symmetric gauge $\mathbf{A} = \frac{1}{2}\mathbf{B} \times \mathbf{r}$ allows definition of a translation group, such that

$$O_{\mathbf{r_1},\mathbf{r_2}} = \bar{O}_{\mathbf{r_1},\mathbf{r_2}} e^{\frac{i}{2}\mathbf{B}\cdot(\mathbf{r_1}\times\mathbf{r_2})},$$

where

$$\bar{O}_{\mathbf{r_1}+\mathbf{R},\mathbf{r_2}+\mathbf{R}} = \bar{O}_{\mathbf{r_1},\mathbf{r_2}}.$$

Nontrivially,

$$\overline{U_{\mathbf{k}} V_{\mathbf{k}}} = \bar{U}_{\mathbf{k}} \bar{V}_{\mathbf{k}} - \frac{i}{2}\epsilon_{\alpha\beta\gamma} B_\alpha (\partial_\beta \bar{U}_{\mathbf{k}})(\partial_\gamma \bar{V}_{\mathbf{k}}) + \ldots$$

Step 3: Treat the above framework perturbatively in magnetic field

$$E^{(1)} = \frac{\partial E}{\partial B_\alpha} = -M_\alpha = \int \frac{d^3k}{(2\pi)^3} \Bigg[\frac{i}{2}\epsilon_{\alpha\beta\gamma} \sum_n^{\text{occ}} \langle P_c \partial_\beta \bar{u}^{(0)}_{n\mathbf{k}} | \bar{H}^{(0)}_{\mathbf{k}} + \epsilon_{n\mathbf{k}} \bar{S}^{(0)}_{\mathbf{k}} - 2\mu^{(0)} \bar{S}^{(0)}_{\mathbf{k}} | P_c \partial_\gamma \bar{u}^{(0)}_{n\mathbf{k}} \rangle$$
$$+ \frac{i}{2}\epsilon_{\alpha\beta\gamma} \sum_n^{\text{occ}} (\epsilon_{n\mathbf{k}} - \mu^{(0)}) \left(\langle \bar{u}^{(0)}_{n,\mathbf{k}} | \partial_\beta \bar{S}^{(0)}_{\mathbf{k}} | P_c \partial_\gamma \bar{u}^{(0)}_{n\mathbf{k}} \rangle + \langle P_c \partial_\beta \bar{u}^{(0)}_{n\mathbf{k}} | \partial_\gamma \bar{S}^{(0)}_{\mathbf{k}} | \bar{u}^{(0)}_{n,\mathbf{k}} \rangle \right)$$
$$- \frac{i}{2}\epsilon_{\alpha\beta\gamma} \sum_{n,n'}^{\text{occ}} (\epsilon_{n\mathbf{k}} - \mu^{(0)}) \langle \bar{u}^{(0)}_{n,\mathbf{k}} | \partial_\beta \bar{S}^{(0)}_{\mathbf{k}} | \bar{u}^{(0)}_{n',\mathbf{k}} \rangle \langle \bar{u}^{(0)}_{n',\mathbf{k}} | \partial_\gamma \bar{S}^{(0)}_{\mathbf{k}} | \bar{u}^{(0)}_{n,\mathbf{k}} \rangle$$
$$+ \sum_n^{\text{occ}} \langle \bar{u}^{(0)}_{n,\mathbf{k}} | \bar{H}^{(1)}_{\mathbf{k}} - \epsilon_{n\mathbf{k}} \bar{S}^{(1)}_{\mathbf{k}} | \bar{u}^{(0)}_{n,\mathbf{k}} \rangle \Bigg] .$$

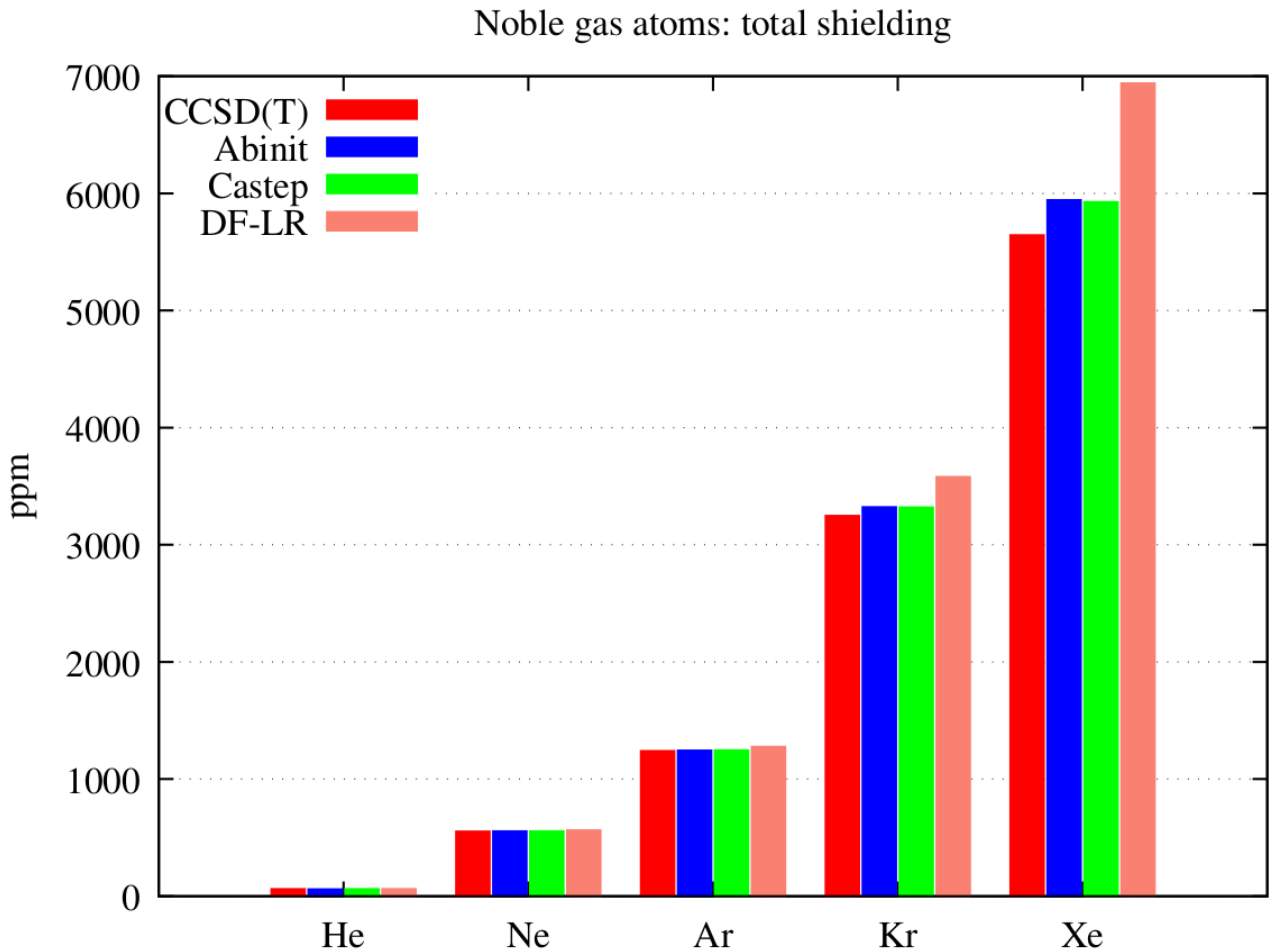
Zwanziger, Torrent, and Gonze, Phys. Rev. B **107**, 165157 (2023). See `m_orbmag.F90`.

How do you actually run it?

1. Run a ground state calculation, with a dipole on the atom of interest. This yields $|\bar{u}^{(0)}_{n,\mathbf{k}}\rangle$.
2. Run a second calculation, which uses $|\bar{u}^{(0)}_{n,\mathbf{k}}\rangle$ to find $|\partial_\alpha \bar{u}^{(0)}_{n\mathbf{k}}\rangle$. At the end of this calculation, assembly of the above formula is triggered to give $-M_\alpha$.
3. Obtain shielding as

$$\sigma_{ij} = \frac{\Omega}{|\mathbf{m}_i|}\frac{\partial E}{\partial B_j} = -\frac{\Omega}{|\mathbf{m}_i|}\mathbf{M}_j.$$

Results: atomic benchmarks

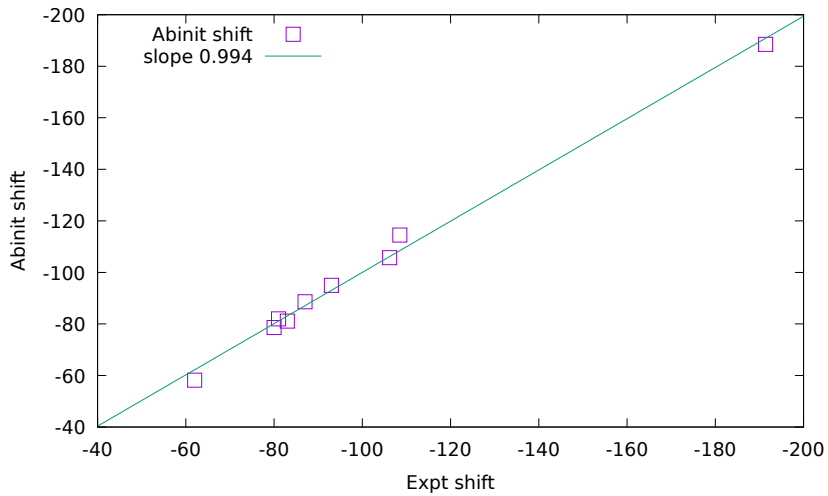


Vaara and Pyykkö, *J. Chem. Phys.* **118**, 2973 (2003)

Results: selected solids

^{29}Si shifts compared to experiment

Formula	Compound	ABINIT	Experiment
Si	Silicon	-82.0	-81
SiO_2	α-Quartz	-105.7	-106.2
	Cristobalite	-114.5	-108.5
	Stishovite	-188.5	-191.4
$Li_2Si_2O_5$	Lithium disilicate	-95.0	-93
Mg_2SiO_4	Forsterite	-58.2	-62
Al_2SiO_5	Andalusite	-78.6	-80
	Sillimanite	-88.6	-87
	Kyanite	-81.1	-83

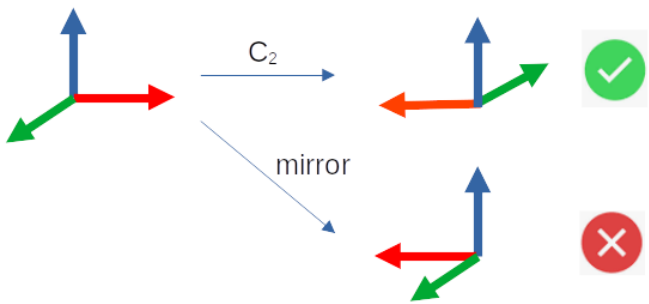


Updates: Spin Orbit Coupling

- The ZORA Hamiltonian $\sigma \cdot \mathbf{p} K \sigma \cdot \mathbf{p} + V$ leads to the SO term in atomic units
$$\frac{1}{2}\alpha^2 K \frac{1}{r}\frac{dV}{dr}\mathbf{L}\cdot\mathbf{S},$$
for a spherical potential near an atom. This term is present in in ABINIT in PAW.
- Need this term to first order in B: $\mathbf{p} \rightarrow \mathbf{\Pi} = \mathbf{p} - q\mathbf{A}$ for the vector potential.
- This leads to an additional term in the induced orbital moment:
$$\frac{1}{2}\alpha^2 K \frac{1}{r}\frac{dV}{dr}(\mathbf{r}\times\mathbf{A_0})\cdot\mathbf{S}$$
- Has been included and tested in `m_orbmag.F90`

Updates: Symmetry of nuclear dipoles

- Adding a nuclear dipole to a single site in the unit cell lowers the symmetry a lot.
- Time reversal always broken.
- Most spatial symmetries broken.
- But can use `kptopt 4`, I've added code to preserve placement and handedness of dipole.



Updates: PEAD

- The formula for the orbital moment relies on $|P_c \partial_\gamma \tilde{u}^{(0)}_{n\mathbf{k}}\rangle$.
- This derivative can be realized using the DDK functionality of DFPT.
- It can also be realized by finite differences, using `berryopt -2`:

$$|\partial_\gamma \tilde{u}_{n\mathbf{k}}\rangle = \frac{1}{2}(|\tilde{u}_{n\mathbf{k}+\mathbf{b}_\gamma}\rangle - |\tilde{u}_{n\mathbf{k}-\mathbf{b}_\gamma}\rangle)$$

where

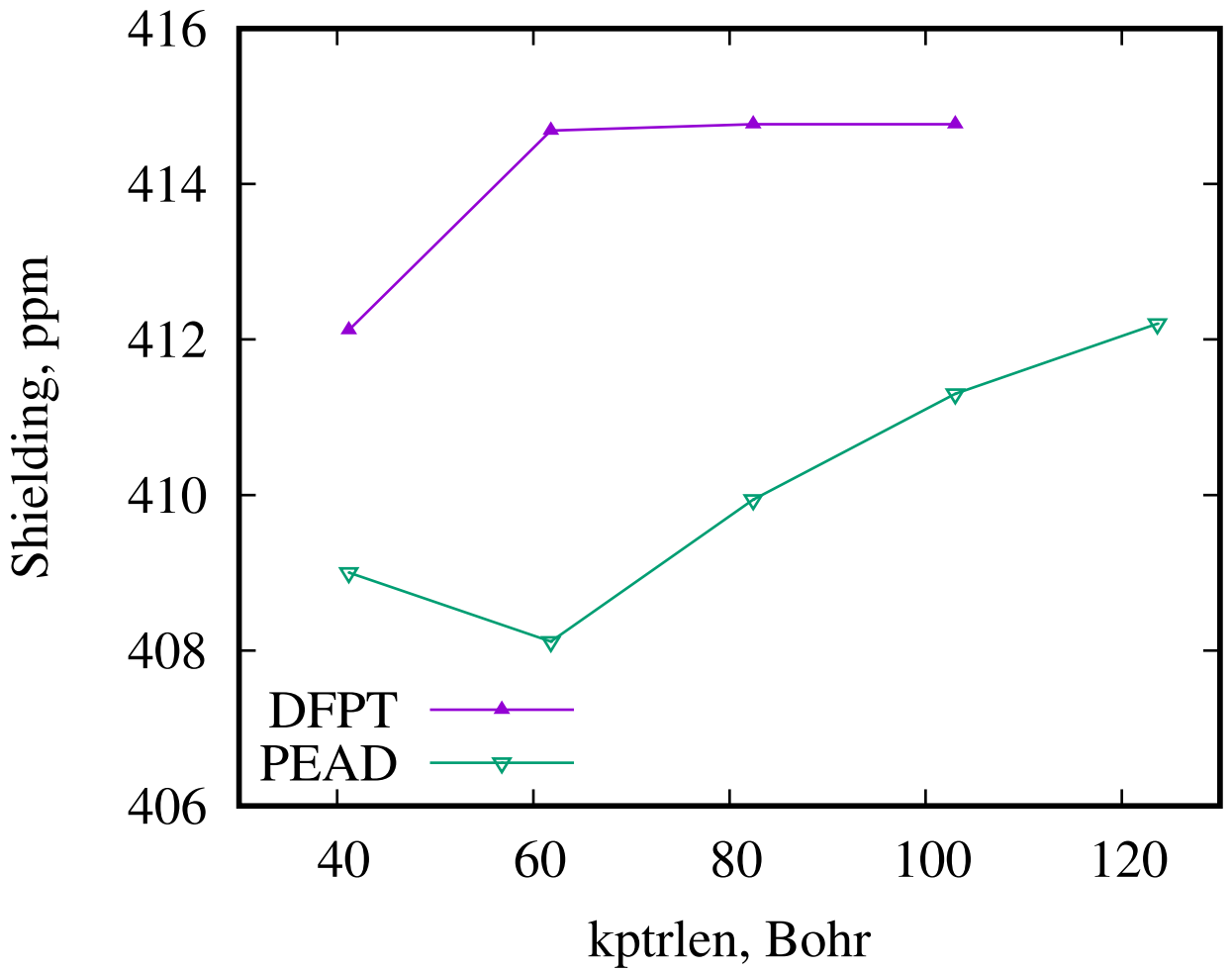
$$|\tilde{u}_{n\mathbf{k}+\mathbf{b}_\gamma}\rangle = \sum_{n'} (S^{-1}_{\mathbf{k},\mathbf{k}+\mathbf{q}})_{n'n} |u_{n'\mathbf{k}+\mathbf{b}_\gamma}\rangle$$

and

$$(S_{\mathbf{k},\mathbf{k}+\mathbf{q}})_{nn'} = \langle u_{n\mathbf{k}} | u_{n'\mathbf{k}+\mathbf{q}} \rangle .$$

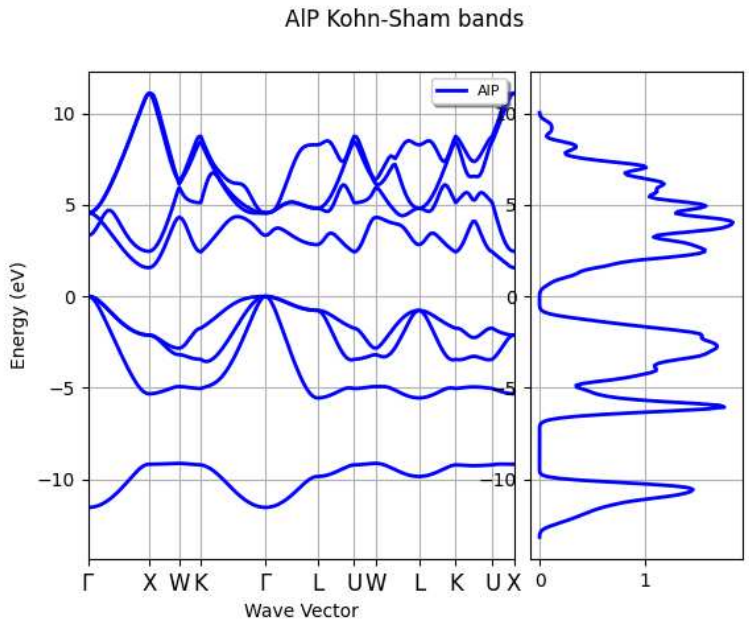
- I have added this functionality, as it allows the code to run using *only* a ground state calculation (hence checking, and more functionals available). Run a ground state calculation using a dipole, `berryopt -2`, and `orbmag 2`.

DFPT versus PEAD convergence

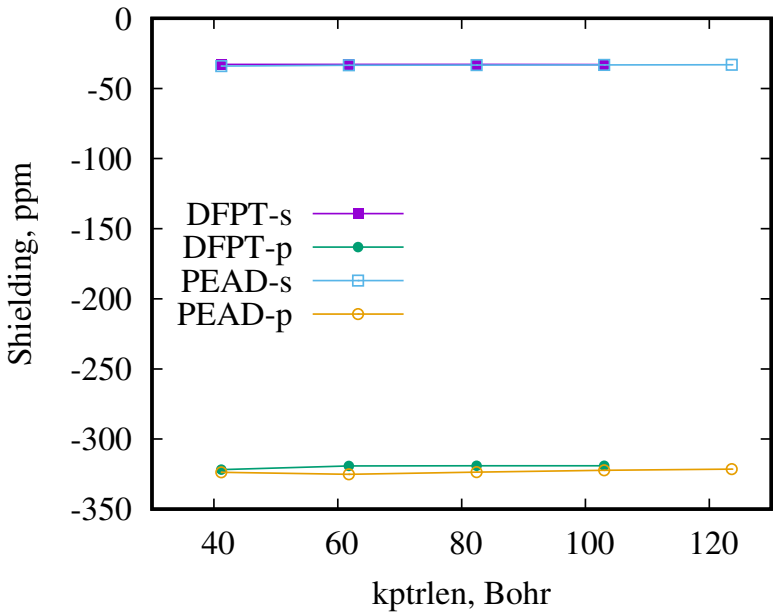


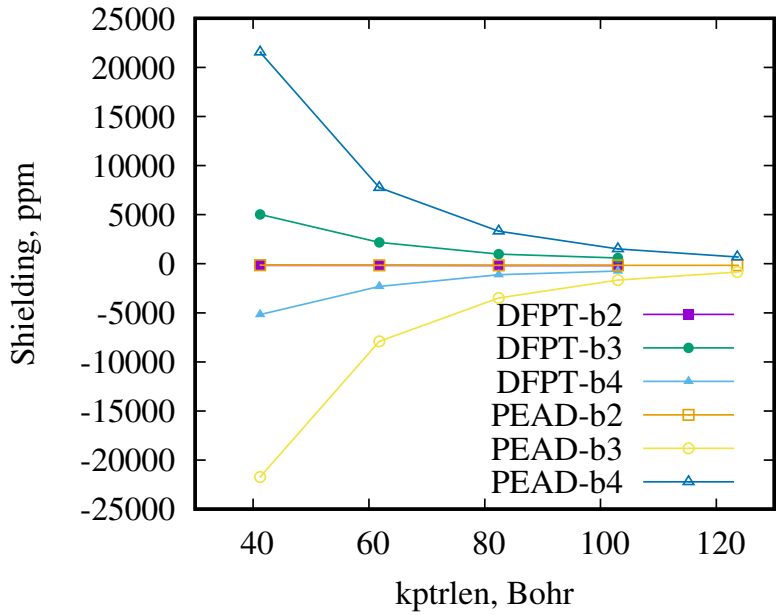
AlP band structure

For AlP, have filled, isolated *s*-character band, three filled *p*-character bands



DFPT versus PEAD bands



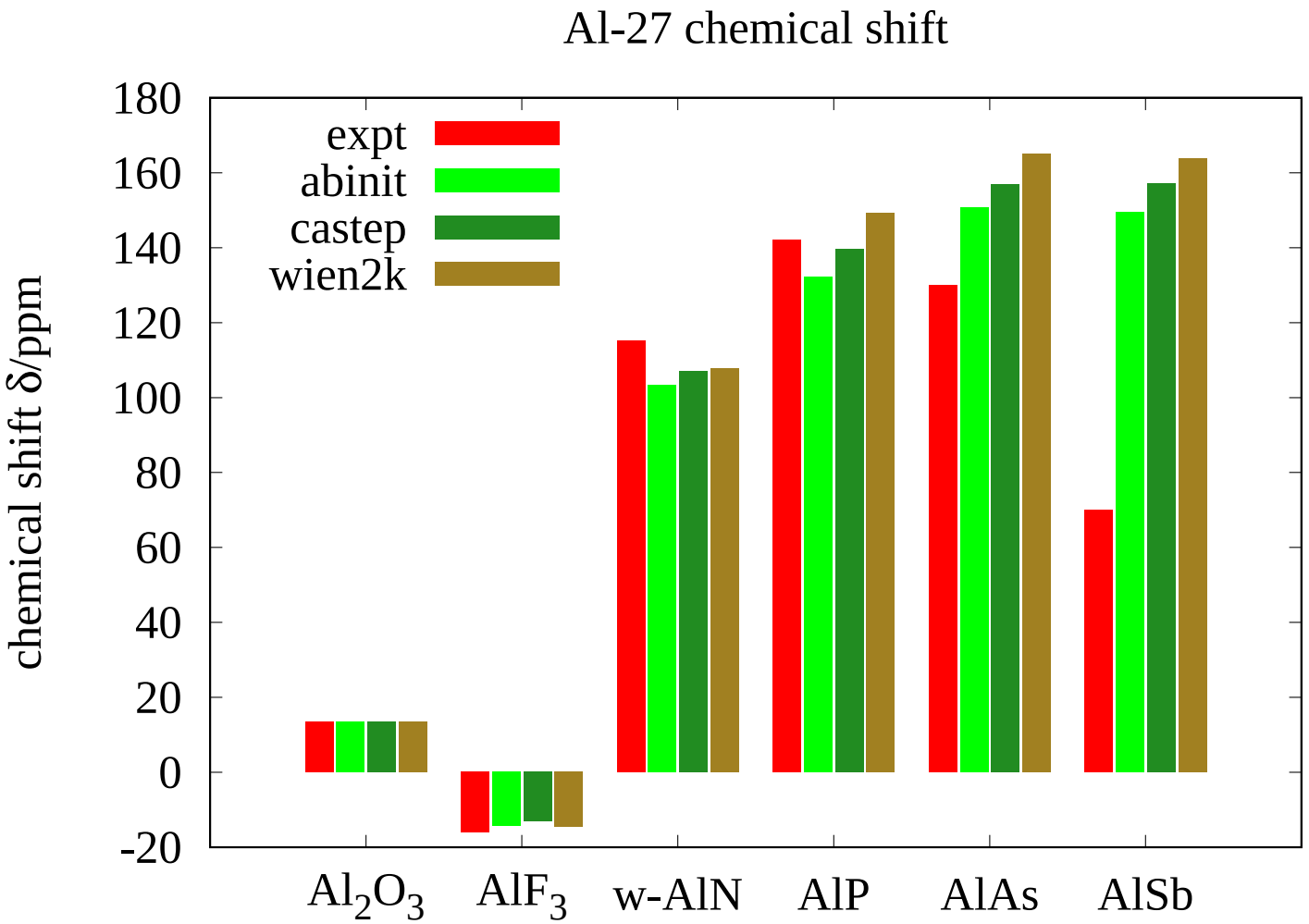


This bodes well for band-by-band decomposition as *connected groups* of bands.

Updates: mGGA and hybrid functionals

- For mGGA, ground state already working with PEAD.
- For DDK in DFPT, TB09 (potential, no energy) works thanks to Marc Torrent but other mGGA's not yet
- For hybrid functionals, should work in ground state with PEAD but nuclear dipole causing problems

Current open problem



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