Orbital magnetism in the projector-augmented wave formalism

J. W. Zwanziger

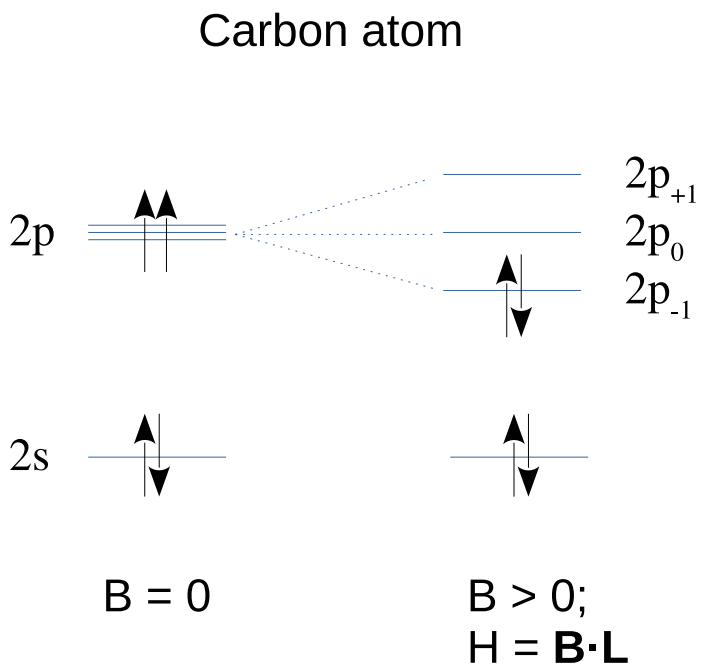
Dept of Chemistry, Dalhousie University, Halifax, Nova Scotia

June 2021

What's the basic problem?

How does a solid react to a homogeneous magnetic field?

- Spinless electrons, in a solid, in an external magnetic field.
- *Classically*, no magnetization could result (Bohr-Van Leeuwen theorem)
- *Quantum mechanically*, angular momentum states can be stabilized that lead to currents, and changes in the energy.



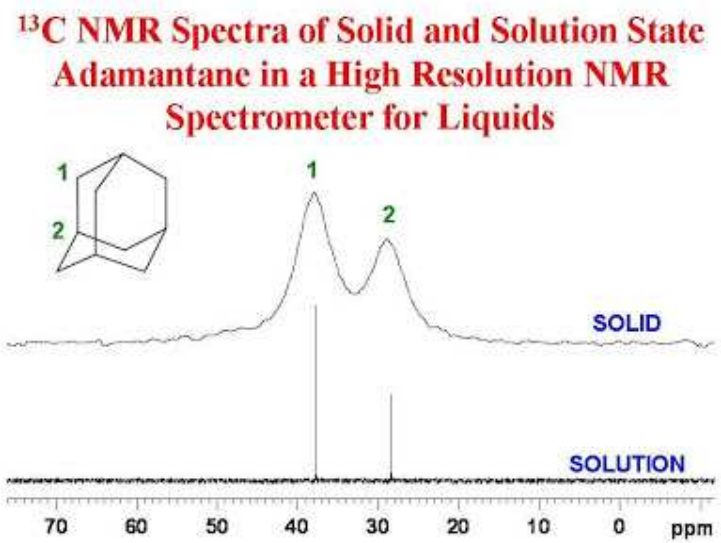
Why is it a hard problem?

- Basic interaction is $\mathbf{B} \cdot \mathbf{L} = \mathbf{B} \cdot \mathbf{r} \times \mathbf{p}$ which is NOT periodic.
- Hamiltonian is $\frac{1}{2}(\mathbf{p} - q\mathbf{A})^2 + V$, where $\mathbf{B} = \nabla \times \mathbf{A}$ so must cope with gauge variance issues.

What's to be gained?

- Energy derivatives:
  - Magnetization: $\partial E/\partial B$
  - Susceptibility: $\partial^2 E/\partial B^2$
- Mixed derivatives
  - Chemical shielding: $\partial^2 E/\partial \mu \partial B$
  - Magneto-electric response: $\partial^2 E/\partial \mathcal{E} \partial B$

and doubtless others



Plan of attack

- Account for vector potential to obtain cell periodic PAW transform and operators

Plan of attack

- Account for vector potential to obtain cell periodic PAW transform and operators
- Construct total energy, in presence of magnetic field, using these PAW and operator objects

Plan of attack

- Account for vector potential to obtain cell periodic PAW transform and operators
- Construct total energy, in presence of magnetic field, using these PAW and operator objects
- Functional differentiation to obtain magnetic field dependent Hamiltonian, to first order

Plan of attack

- Account for vector potential to obtain cell periodic PAW transform and operators
- Construct total energy, in presence of magnetic field, using these PAW and operator objects
- Functional differentiation to obtain magnetic field dependent Hamiltonian, to first order
- Also, use idempotency condition $\rho = \rho S \rho$ and magnetic translation invariance to find expression for density operator to first order in magnetic field.

Plan of attack

- Account for vector potential to obtain cell periodic PAW transform and operators
- Construct total energy, in presence of magnetic field, using these PAW and operator objects
- Functional differentiation to obtain magnetic field dependent Hamiltonian, to first order
- Also, use idempotency condition $\rho = \rho S \rho$ and magnetic translation invariance to find expression for density operator to first order in magnetic field.
- Find energy to first order in magnetic field through

$$\mathrm{Tr}[\rho H] \approx \mathrm{Tr}[\rho^0 H^0] + \mathrm{Tr}[\rho^1 H^0] + \mathrm{Tr}[\rho^0 H^1]$$

Translation in a vector potential

One ingredient we use in our treatment is the Gauge Including PAW transformation.
The usual generator of translations, $\mathbf{p}$, becomes the canonical momentum $\mathbf{p} - q\mathbf{A}$. This leads to

$$\langle \mathbf{r} | \Psi \rangle = e^{\frac{i}{2}\mathbf{B}\cdot\mathbf{r}\times\mathbf{t}} \langle \mathbf{r} - \mathbf{t} | \Psi \rangle$$

for translation by $\mathbf{t}$.
This leads to a modified PAW transform, where the on-site projectors and wavefunctions located at ionic site $\mathbf{R}$ acquire the phase factor $\mathcal{G} = e^{\frac{i}{2}\mathbf{B}\cdot\mathbf{r}\times\mathbf{R}}$:

$$T = 1 + \sum \mathcal{G}(|\phi_{Ri}\rangle - |\tilde{\phi}_{Ri}\rangle)\langle \tilde{p}_{Ri}|\mathcal{G}^{\dagger}.$$

Magnetic translation symmetry

The second, related ingredient applies to general operators, again where $\mathbf{A} = \frac{1}{2}\mathbf{B} \times \mathbf{r}$:

$$\mathcal{O}_{\mathbf{r_1},\mathbf{r_2}} = \overline{\mathcal{O}_{\mathbf{r_1},\mathbf{r_2}}} e^{\frac{i}{2}\mathbf{B}\cdot\mathbf{r_1}\times\mathbf{r_2}},$$

where $\overline{\mathcal{O}}$ is cell-periodic.

The result are various modified PAW objects:

$$\begin{aligned}
\overline{\mathrm{KE}} &= -\frac{1}{2}\nabla^2; \\
\overline{S} &= 1 + \sum_{Rij} e^{\frac{i}{2}\mathbf{B}\cdot(\mathbf{r_1}-\mathbf{R})\times(\mathbf{r_2}-\mathbf{R})} |\tilde{p}_{iR}\rangle q_{Rij} \langle\tilde{p}_{jR}|; \\
\overline{\rho_{ijR}} &= \sum_{nk} e^{\frac{i}{2}\mathbf{B}\cdot(\mathbf{r_1}-\mathbf{R})\times(\mathbf{r_2}-\mathbf{R})} \langle\tilde{\psi}_{nk}|\tilde{p}_{iR}\rangle\langle\tilde{p}_{jR}|\tilde{\psi}_{nk}\rangle.
\end{aligned}$$

We can now develop H^0 and H^1.

Perturbing the density operator

The idempotency condition $\rho = \rho S \rho$ yields in a perturbation expansion:

$$
\begin{aligned}
\overline{\rho}^0_{\mathbf{k}} &= \overline{\rho}^0_{\mathbf{k}} \overline{S}^0_{\mathbf{k}} \overline{\rho}^0_{\mathbf{k}} \\
\overline{\rho}^1_{\mathbf{k}} &= \overline{\rho}^1_{\mathbf{k}} \overline{S}^0_{\mathbf{k}} \overline{\rho}^0_{\mathbf{k}} + \overline{\rho}^0_{\mathbf{k}} \overline{S}^1_{\mathbf{k}} \overline{\rho}^0_{\mathbf{k}} + \overline{\rho}^0_{\mathbf{k}} \overline{S}^0_{\mathbf{k}} \overline{\rho}^1_{\mathbf{k}} - \frac{i}{2} \epsilon_{\alpha\beta\gamma} B_\alpha \times \\
&\qquad \left[(\partial_\beta \overline{\rho}^0_{\mathbf{k}})(\partial_\gamma \overline{S}^0_{\mathbf{k}}) \overline{\rho}^0_{\mathbf{k}} + (\partial_\beta \overline{\rho}^0_{\mathbf{k}}) \overline{S}^0_{\mathbf{k}} (\partial_\gamma \overline{\rho}^0_{\mathbf{k}}) + \overline{\rho}^0_{\mathbf{k}} (\partial_\beta \overline{S}^0_{\mathbf{k}})(\partial_\gamma \overline{\rho}^0_{\mathbf{k}}) \right]
\end{aligned}
$$

Because the energy term depends only on $\mathrm{Tr}[\overline{\rho}^{(1)}_{\mathbf{k}} \, \overline{H}^{(0)}_{\mathbf{k}}]$, we need these expressions projected only in the unperturbed valence and conduction subspaces.

Subspace projections

Valence subspace:

$$(\overline{\rho}^0_{\mathbf{k}}\overline{S}^0_{\mathbf{k}})\overline{\rho}^1_{\mathbf{k}}(\overline{S}^0_{\mathbf{k}}\overline{\rho}^0_{\mathbf{k}}) = -\overline{\rho}^0_{\mathbf{k}}\overline{S}^1_{\mathbf{k}}\overline{\rho}^0_{\mathbf{k}} + \frac{i}{2}\epsilon_{\alpha\beta\gamma}B_\alpha(\overline{\rho}^0_{\mathbf{k}}\overline{S}^0_{\mathbf{k}})\,[\ldots]\,(\overline{S}^0_{\mathbf{k}}\overline{\rho}^0_{\mathbf{k}})$$

Conduction subspace:

$$\left(1-\overline{\rho}^0_{\mathbf{k}}\overline{S}^0_{\mathbf{k}}\right)\overline{\rho}^1_{\mathbf{k}}\left(1-\overline{S}^0_{\mathbf{k}}\overline{\rho}^0_{\mathbf{k}}\right) = - \frac{i}{2}\epsilon_{\alpha\beta\gamma}B_\alpha\left(1-\overline{\rho}^0_{\mathbf{k}}\overline{S}^0_{\mathbf{k}}\right)[\ldots]\left(1-\overline{S}^0_{\mathbf{k}}\overline{\rho}^0_{\mathbf{k}}\right)$$

where $[\ldots]$ are the three partial derivative terms.

Finally, key terms

Main contribution from ρ^1:

$$\frac{i}{2(2\pi)^2}\epsilon_{\alpha\beta\gamma}\sum_{n}^{\mathrm{occ}}\langle P_c\left(\partial_\beta \bar{u}^{(0)}_{n\mathbf{k}}\right)|\bar{H}^{(0)}_{\mathbf{k}}+E^{(0)}_{n\mathbf{k}}|P_c\left(\partial_\gamma \bar{u}^{(0)}_{n\mathbf{k}}\right)\rangle.$$

Main contribution from H^1:

$$-\frac{i}{2(2\pi)^2}\epsilon_{\alpha\beta\gamma}\sum_{Rijn}\langle \bar{u}^{(0)}_{n,\mathbf{k}}|\partial_\beta \tilde{p}_{Rik}\rangle(\hat{D}^{(0)}_{ij}+D^{1,(0)}_{ij}-\tilde{D}^{1,(0)}_{ij})\langle\partial_\gamma \tilde{p}_{Rjk}|\bar{u}^{(0)}_{n,\mathbf{k}}\rangle$$

Remarks

- Final resulting quantity: $\partial E/\partial \mathbf{B}|_{B=0}$.

Remarks

- Final resulting quantity: $\partial E/\partial \mathbf{B}|_{B=0}$.
- Our development is identical to "modern theory of magnetization" at first order/all electron level.

Remarks

- Final resulting quantity: $\partial E/\partial \mathbf{B}|_{B=0}$.
- Our development is identical to "modern theory of magnetization" at first order/all electron level.
- But our treatment is extensible to all orders, also treats PAW fully.

Remarks

- Final resulting quantity: $\partial E/\partial \mathbf{B}|_{B=0}$.
- Our development is identical to "modern theory of magnetization" at first order/all electron level.
- But our treatment is extensible to all orders, also treats PAW fully.
- Work flow: compute ground state wavefunctions, DDK wavefunctions, then assemble terms.

Remarks

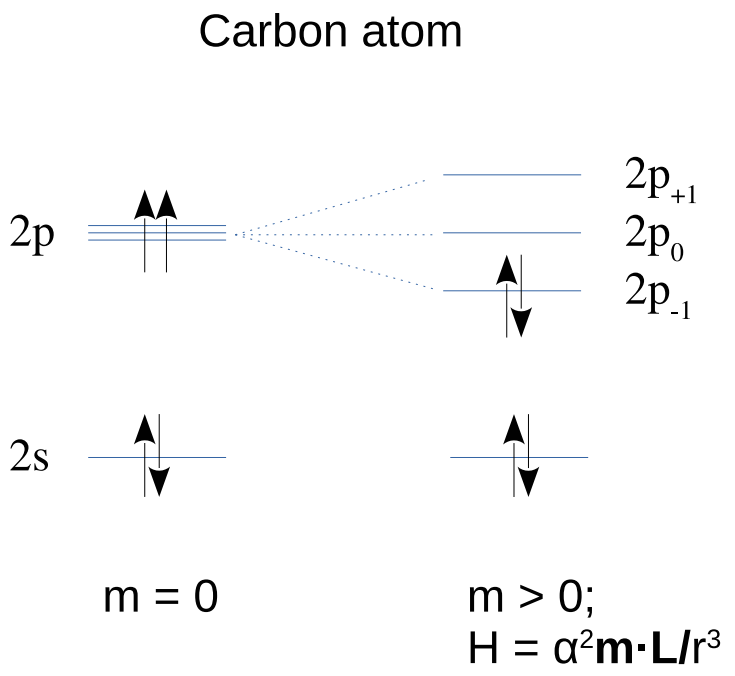
- Final resulting quantity: $\partial E/\partial \mathbf{B}|_{B=0}$.
- Our development is identical to "modern theory of magnetization" at first order/all electron level.
- But our treatment is extensible to all orders, also treats PAW fully.
- Work flow: compute ground state wavefunctions, DDK wavefunctions, then assemble terms.
- For insulators, result is zero. . . so break that by applying a fixed nuclear magnetic dipole at the site of interest.

Nuclear magnetic dipole

In atomic units the first order nuclear dipole Hamiltonian is

$$\alpha^2 \frac{\mathbf{m} \times (\mathbf{r} - \mathbf{R}) \cdot \mathbf{p}}{|\mathbf{r} - \mathbf{R}|^3} \equiv \alpha^2 \frac{\mathbf{L_R} \cdot \mathbf{m}}{|\mathbf{r} - \mathbf{R}|^3}$$

where α is the fine structure constant, and $\mathbf{L_R} = (\mathbf{r} - \mathbf{R}) \times \mathbf{p}$. This term has lattice periodicity. Applied with `nucdipmom` input variable (turn off symmetry).



Gauge Invariance

- Electric field problems: Berry phase

$$i \oint dk \langle u_{n\mathbf{k}} | \nabla | u_{n\mathbf{k}} \rangle$$

Integrand *is not* gauge invariant but integral is; discretization of the wavefunction and finite differences is *required* to enforce gauge choice locally.

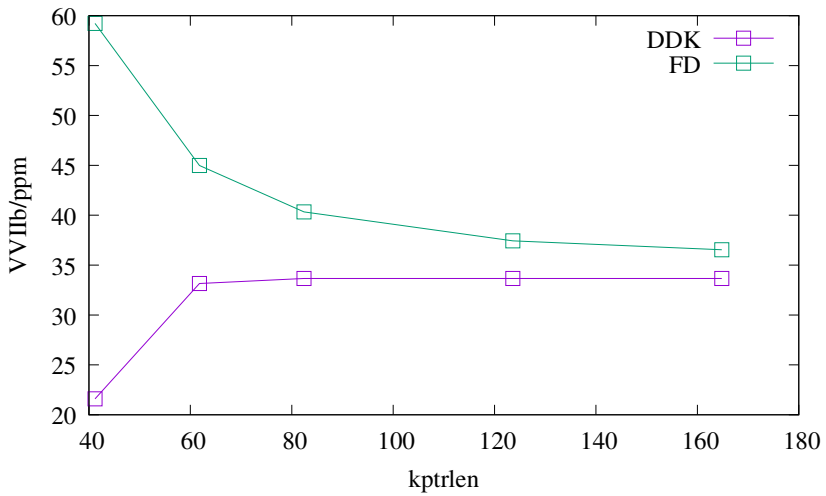
- Magnetic field problems: Berry curvature

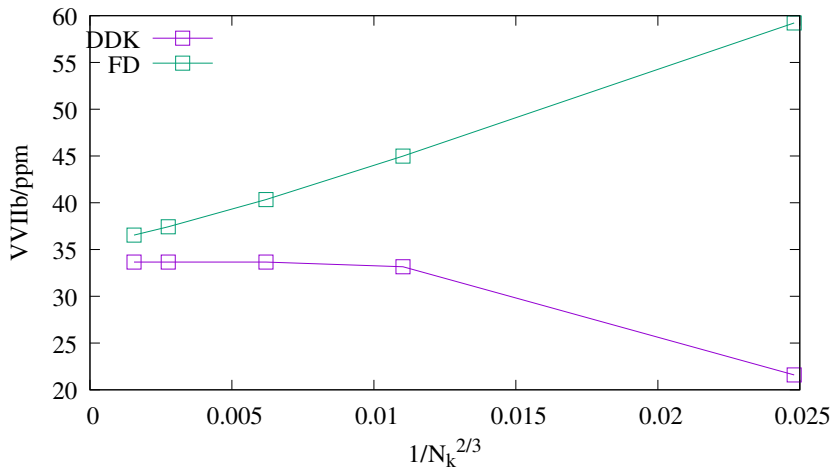
$$i \int d\mathbf{k} \langle \nabla u_{n\mathbf{k}} | \times | \nabla u_{n\mathbf{k}} \rangle$$

Integrand *itself* is gauge invariant, no discretization necessary, can use DDK wavefunctions computed from DFPT!

Convergence comparison

Comparing the $\langle \partial_\beta u | E | \partial_\gamma u \rangle$ term, with discretized derivatives and DDK derivatives





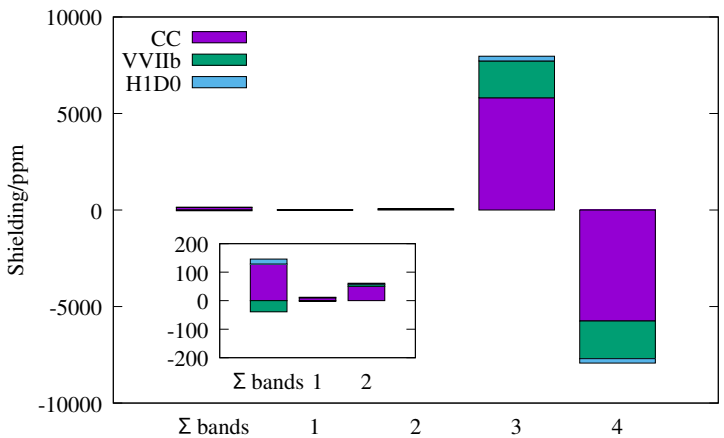
Preliminary Results

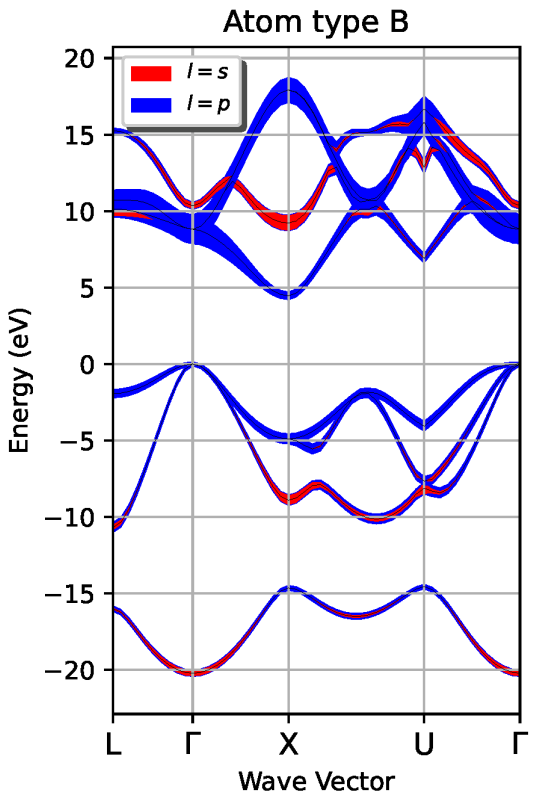
Boron chemical shieldings: $\sigma = -\frac{\partial^2 E}{\partial B \partial \mu}$ where μ is nuclear dipole applied to B site of interest.

Compound	This work	QE
BN	0	0
BP	-48	-30
$B_2O_3(1)$	16	15.0
$B_2O_3(2)$	17	15.4
high pressure B_2O_3	-4	-1
$\alpha-$B(1)	7	2
$\alpha-$B(2)	9	5

Band-by-band decomposition aids interpretation

Main terms by band for boron shielding in BN, compared to fat bands at B

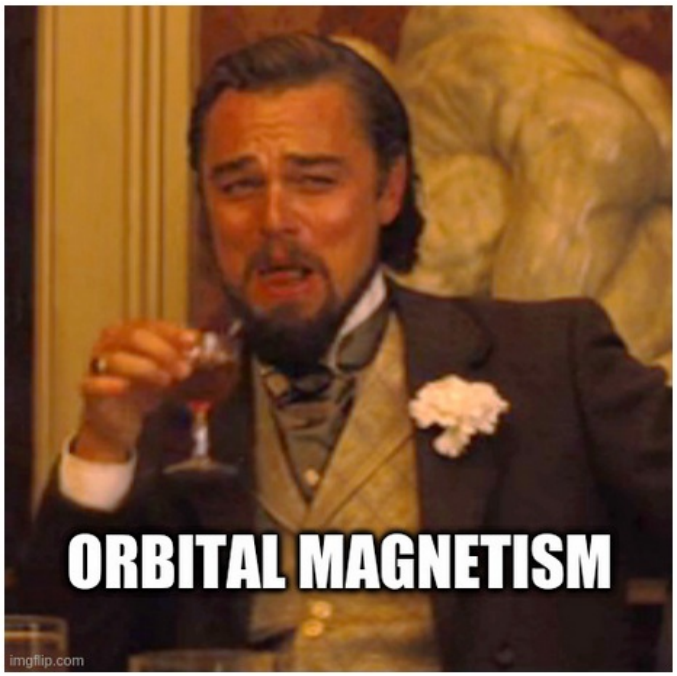




Next steps

- ρ^1 (the conduction and valence space parts) seem to be complete, but H^1 is "mostly" complete.
- Agreement with reference cases (for example, Quantum Espresso chemical shielding) is not as close as it should be.

Every time I think I'm done...



Summary

- Orbital magnetism coded for insulators (see `m_orbmag.F90`), currently in extensive tests
- Requires PAW
- Parallelized over k pts
- So grateful to Xavier Gonze and Marc Torrent for much help and advice

Some references

- Perturbation approach: Gonze and Zwanziger, PRB **84** 064445 (2011).
- GIPAW: Pickard and Mauri, PRB **63**, 245101 (2001).
- Magnetic translation symmetry: Essin, Turner, Moore, and Vanderbilt, PRB **81** 205104 (2010).
- Orbital magnetism: Ceresoli, Thonhauser, Vanderbilt, and Resta, PRB **74** 024408 (2006).
- Shielding: Thonhauser, Ceresoli, Mostofi, Marzari, Resta, and Vanderbilt, JCP **131** 101101 (2009).