All-electron magnetic response with pseudopotentials: NMR chemical shifts

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Introduction

- Nuclear Magnetic Resonance widely used
  - structural chemistry
  - increasingly in solid state studies
- Molecular systems
  - frequently use empirical rules
- Solid state
  - often cannot be modelled by chemical analogues or reference compounds
  - use *ab initio* calculations
  - conventional approach is to approximate an infinite solid by a cluster and use quantum chemical approaches

Background

- Mauri, Pfrommer and Louie's solution to the solid state problem (MPL): all-electron only
  - assumed pseudopotential error to be small and controllable
  - worked well for light elements (H,B,C, and N)
- To exploit the pseudopotential approach's ability to tackle large, complex low symmetry systems: *we need a pseudopotential theory*
- The work of Gregor, Mauri and Car suggests that this might be possible
  - contrary to expectations, if core and valence contributions are separated in a gauge-invariant way, the core contribution is essentially rigid
- In this talk, a pseudopotential theory of NMR chemical shifts is presented

NMR chemical shifts

- A uniform magnetic field $\mathbf{B}$ induces an electric current
- Simple case of insulating non-magnetic materials: orbital motion of electrons only
- At field strengths in NMR machines — the current is linear in $\mathbf{B}$, a first order current $\mathbf{j}^{(1)}(\mathbf{r}')$

$$\mathbf{B}^{(1)}_{\text{in}}(\mathbf{r}) = \frac{1}{c}\int d^3r'\mathbf{j}^{(1)}(\mathbf{r}') \times \frac{\mathbf{r}-\mathbf{r}'}{|\mathbf{r}-\mathbf{r}'|^3}$$

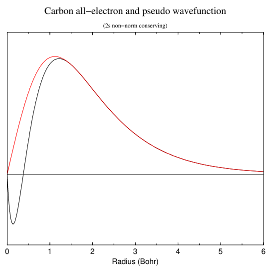
- The chemical shift is the ratio between induced and applied magnetic fields

$$\mathbf{B}^{(1)}_{\text{in}}(\mathbf{r}) = -\sigma(\mathbf{r})\mathbf{B}$$

- We should calculate $\mathbf{j}^{(1)}(\mathbf{r}')$ using perturbation theory

The problem with pseudopotentials

- The form of the wavefunction is explicitly neglected near the nucleus in the interests of computational efficiency
- This is a good approximation for total energies and their derivatives, and properties for which the matrix elements are weighted outside the core
- It is a bad approximation for many other properties
  - hyperfine parameters, core level spectra, EFGs, and NMR chemical shifts



Projector augmented-wave method

- Blöchl solved the problem, introducing a mapping between the all-electron and pseudo wavefunctions, $|\Psi\rangle = \mathcal{T}|\tilde{\Psi}\rangle$, where

$$\mathcal{T} = \mathbf{1} + \sum_{\mathbf{R},n} [|\phi_{\mathbf{R},n}\rangle - |\tilde{\phi}_{\mathbf{R},n}\rangle]\langle \tilde{p}_{\mathbf{R},n}|$$

- This allows the construction of *pseudo*-operators corresponding to the all-electron operators

$$\tilde{O} = O + \sum_{\mathbf{R},n,m} |\tilde{p}_{\mathbf{R},n}\rangle[\langle \phi_{\mathbf{R},n}|O|\phi_{\mathbf{R},m}\rangle - \langle \tilde{\phi}_{\mathbf{R},n}|O|\tilde{\phi}_{\mathbf{R},m}\rangle]\langle \tilde{p}_{\mathbf{R},m}|$$

- This can be applied to the Hamiltonian (no $\mathbf{B}$) to obtain the familiar pseudo-Hamiltonian

$$\tilde{H} = \mathcal{T}^{+} H \mathcal{T} = \frac{1}{2}\mathbf{p}^2 + V^{\mathrm{loc}}(\mathbf{r}) + \sum_{\mathbf{R}} V^{\mathrm{nl}}_{\mathbf{R}}$$

- We have derived pseudopotential theory, where the non-local part of the potential is

$$V^{\mathrm{nl}}_{\mathbf{R}} = \sum_{n,m} |\tilde{p}_{\mathbf{R},n}\rangle a^{\mathbf{R}}_{n,m}\langle \tilde{p}_{\mathbf{R},m}|$$

- The $a^{\mathbf{R}}_{n,m}$ are the strengths of the non-local potential in each channel
- PAW is a significant addition to pseudopotential theory since it allows the evaluation of the expectation values of all-electron operators in terms of pseudo-wavefunctions
- But in practice it doesn't work in the presence of a magnetic field . . .

Wavefunctions in a magnetic field

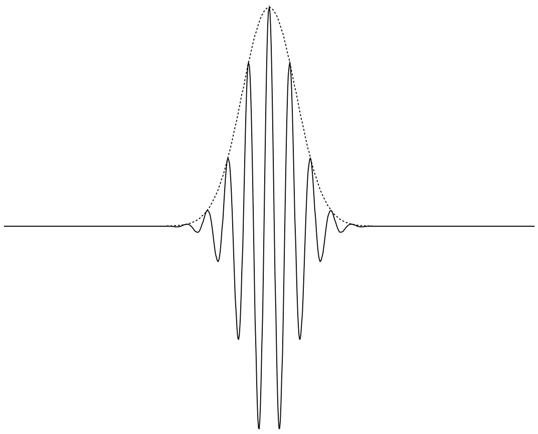
- In a uniform magnetic field, the observables of a system should be invariant following a rigid translation of the atoms by $\mathbf{t}$
- On translation, $V'(\mathbf{r}) = V(\mathbf{r} - \mathbf{t})$
- The Hamiltonian becomes

$$H' = \frac{1}{2}\left(\mathbf{p} + \frac{1}{c}\mathbf{A}(\mathbf{r})\right)^2 + V(\mathbf{r} - \mathbf{t})$$

- Invariance ensures that the eigenvalues are unchanged, but the wavefunctions pick up a phase

$$\langle \mathbf{r}|\Psi'_n\rangle = e^{\frac{i}{2c}\mathbf{r}\cdot\mathbf{t}\times\mathbf{B}}\langle \mathbf{r} - \mathbf{t}|\Psi_n\rangle.$$

Wavefunctions in a magnetic field *continued*



- The PAW transformation will not work unless a large number of projectors are used

Gauge including projector augmented-wave method

- Our novel approach is to introduce a field dependent transformation operator

$$\mathcal{T}_{\mathbf{B}} = \mathbf{1} + \sum_{\mathbf{R},n} e^{\frac{i}{2c}\mathbf{r}\cdot\mathbf{R}\times\mathbf{B}}[|\phi_{\mathbf{R},n}\rangle - |\tilde{\phi}_{\mathbf{R},n}\rangle]\langle\tilde{p}_{\mathbf{R},n}|e^{-\frac{i}{2c}\mathbf{r}\cdot\mathbf{R}\times\mathbf{B}}$$

- Wavefunctions constructed using this operator will transform in the required way in the presence of a magnetic field
- We call this the GIPAW method – The Gauge Including Augmented-wave Method
- Quantum chemical approaches include the gauge phase in their localised basis sets
- There was no need to do this with plane wave basis set, but our operators must carry the phase instead (since we use pseudopotentials)

The GIPAW first order current

- The magnetic pseudo-Hamiltonian is constructed using the GIPAW transformation operator, and perturbation theory (as in MPL) is performed for the first order current
- The first order current now consists of three terms

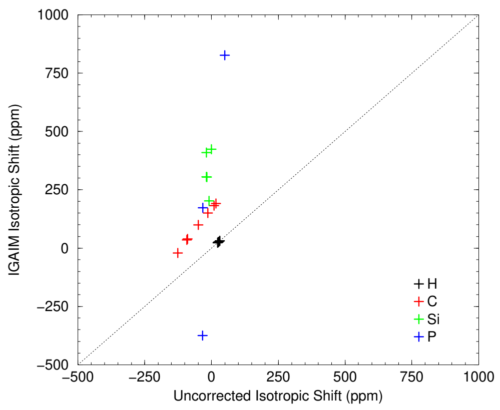
$$\mathbf{j}^{(1)}(\mathbf{r}') = \mathbf{j}^{(1)}_{\mathrm{bare}}(\mathbf{r}') + \mathbf{j}^{(1)}_{\Delta\mathrm{p}}(\mathbf{r}') + \mathbf{j}^{(1)}_{\Delta\mathrm{d}}(\mathbf{r}')$$

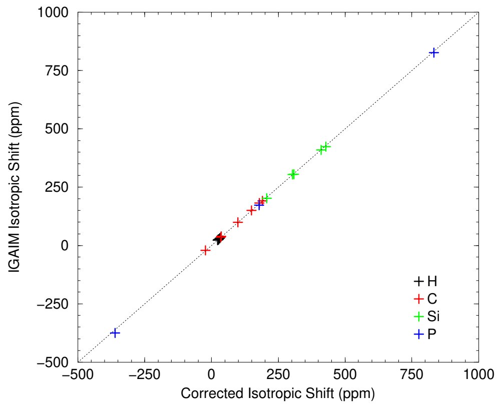
- As does the final chemical shift tensor that we calculate

$$\sigma(\mathbf{R}') = \sigma_{\mathrm{bare}}(\mathbf{R}') + \sigma_{\Delta\mathrm{p}}(\mathbf{R}') + \sigma_{\Delta\mathrm{d}}(\mathbf{R}')$$

Validation: molecules

- Quantum chemical approaches have long been able to calculate the NMR chemical shifts of small molecules
- GAUSSIAN94 is one such widely used (nearly standard) quantum chemical code
- Gregor *et al* used this code to demonstrate that the core contribution is rigid
- We compare our GIPAW calculated NMR isotropic chemical shifts with his IGAIM results
- The GIPAW results agree very closely in all cases
- The paramagnetic correction term is seen to be strongly chemically dependent
- The validity of adding an all-electron atomic core contribution is confirmed





Validation: solids

- We perform an all-electron plane-wave calculation of the valence contribution to the chemical shift of carbon in diamond
- A very hard (r_c=0.4 Bohr) all-electron local pseudopotential is used
- The results agree very closely to the pseudopotential results
- The remaining difference if likely due to the slight pseudisation error due to the all-electron potential

Table 1: The valence contribution to the isotropic chemical shift of crystalline diamond (ppm).

Method	Valence contribution to σ
GIPAW	-65.85
All-electron at 800 Ry	-64.89
All-electron at 1400 Ry	-64.46

Conclusions

- In combination with MPL's solution to the problem of magnetic response in periodic systems, we have a full pseudopotential theory of NMR in the solid state
- The formalism will be useful in the calculation of other properties that depend on magnetic linear response
- Combination of the method with modern efficient parallel plane-wave pseudopotential algorithms and supercomputers will allow calculations in systems of a size undreamt of by the quantum chemical community
- For applications to porphyrin chemistry see Jonathan Yates' poster "Whaterver"

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