

## Introduction

We propose an alternative method for the ab-initio calculation of indirect spin-spin, or J-coupling, constants. Our method first employs a method very similar to the converse method for NMR,<sup>1</sup> then uses a finite-differences scheme to calculate the energy derivatives which define the J-coupling tensor.

The J-coupling constant is used in high-resolution nuclear magnetic resonance (NMR) experiments to extract additional structural information from the spectra. Like previous methods<sup>2-4</sup> based on linear response and perturbation theory, our method is designed to calculate all four terms from the non relativistic Ramsey theory<sup>5</sup> from first-principles, with no a prior knowledge of the NMR spectra needed.

Our method is being implemented as part of a pseudopotential-based plane wave code using density functional theory (DFT).

## Theory – spin-spin coupling

The indirect spin-spin coupling is defined as the relationship between the magnetic field induced at site  $k$  by the nuclear magnetic moment at site  $l$ :

$$\mathbf{B}_l(\mathbf{r}) = \frac{2\pi}{\hbar\gamma_l\gamma_k} \mathbf{J}_{lk} \cdot \boldsymbol{\mu}_k \quad (1)$$

Using equation (1) and the fact

$$-\mathbf{B} \cdot \boldsymbol{\mu} = E$$

the J-coupling tensor can be rewritten in terms of the total electron energy of the system as:

$$\mathbf{J}_{kl} = \hbar \frac{\gamma_k\gamma_l}{2\pi} \frac{d^2 E}{d\boldsymbol{\mu}_k d\boldsymbol{\mu}_l} \quad (2)$$

Now all that remains is to calculate the total energy and take a numerical derivative with respect to the nuclear dipole strength. For the former, we use PWscf, a plane wave DFT code that is part of the Quantum Espresso package.<sup>6</sup>

## Theory – Hamiltonian

To calculate the total energy, we insert the magnetic field of a dipole

$$\begin{aligned} \mathbf{B}(\mathbf{r}) &= \frac{\mu_0}{4\pi} \left[ \frac{3\hat{r}(\hat{r} \cdot \boldsymbol{\mu}) - \boldsymbol{\mu}}{|\mathbf{r}|^3} + \frac{8\pi}{3} \boldsymbol{\mu} \delta(\mathbf{r}) \right] \\ &= \nabla \times \mathbf{A} + \frac{2\mu_0}{3} \boldsymbol{\mu} \delta(\mathbf{r}) \end{aligned} \quad (3)$$

and the corresponding vector potential

$$\mathbf{A}(\mathbf{r}) = \frac{\mu_0}{4\pi} \frac{\boldsymbol{\mu} \times \mathbf{r}}{|\mathbf{r}|^3} \quad (4)$$

into the Hamiltonian which is defined as:

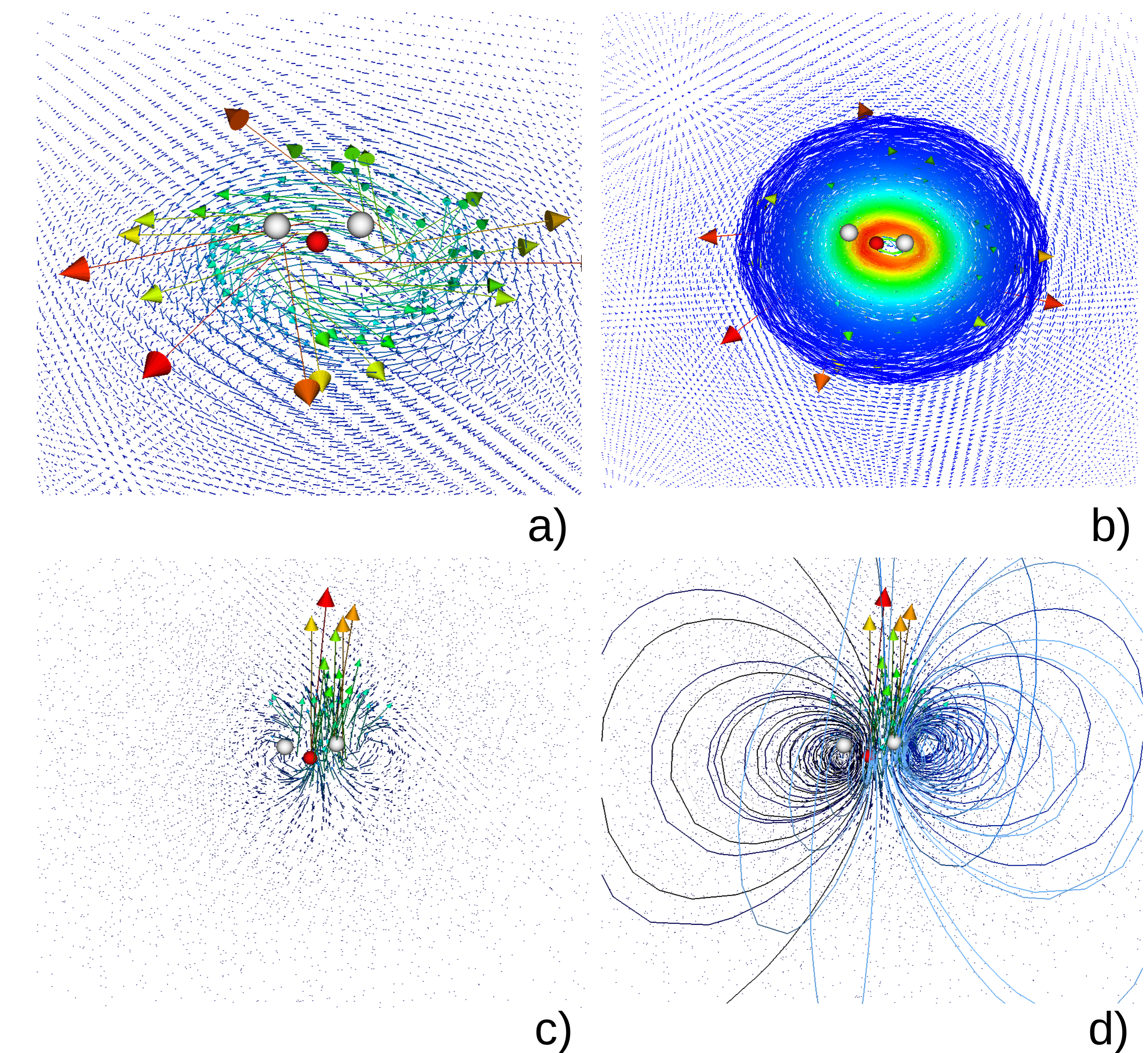
$$H = \frac{1}{2m_e} (\mathbf{p} + e\mathbf{A})^2 + \mathbf{B} \cdot \boldsymbol{\mu}_e \quad (5)$$

When we insert the definitions from (3) and (4) into equation (5), we then get the four components first identified by Ramsey. These are shown in equation group (6) as the paramagnetic, diamagnetic, spin-dipolar, and Fermi contact terms of the Hamiltonian, in that order.

$$\begin{aligned} H_p &= \frac{e}{m_e} \mathbf{p} \cdot \mathbf{A} \\ H_d &= \frac{e^2}{2m_e} \mathbf{A}^2 \\ H_s &= (\nabla \times \mathbf{A}) \cdot \boldsymbol{\mu}_e \\ H_f &= \frac{2\mu_0}{3} \boldsymbol{\mu} \delta(\mathbf{r}) \cdot \boldsymbol{\mu}_e \end{aligned} \quad (6)$$

## Implementation details

Having modified PWscf to include the additional terms of the Hamiltonian shown in (6), a dipole is placed at the center of each nucleus of interest. As an example, to calculate the indirect H-O coupling in water, we place the molecule in a box of suitable size, and add a non-zero point dipole at the center of both the oxygen and one of the hydrogen atoms.



**Figure 1:** A water molecule in a box with two dipoles inserted at the oxygen (red) and one hydrogen (white) atoms. Also shown are the magnetic vector potential vectors (a), and streamlines (b), the magnetic field vectors (c) and contours (d).

### References

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- <sup>3</sup>V. G. Malkin, et al. Chem. Phys. Lett. **221**, 91 (1994).
- <sup>4</sup>R. M. Dickson and T. Ziegler, JCP, **100**, 5286 (1996).
- <sup>5</sup>N. F. Ramsey, Phys. Rev. **91**, 303 (1953).
- <sup>6</sup>P. Giannozzi, et al. J. Phys. Cond. Mat. **21**, 395502 (2009).