The *a priori* calculation of NMR nuclear spin–spin coupling constants

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**Overview**

• the mechanisms responsible for nuclear spin–spin couplings
• the calculation of indirect nuclear spin–spin couplings
• comparison of theoretical methods
  – what $N$-electron models and basis sets are needed?
  – are the results in qualitative or quantitative agreement with experiment?
  – how does DFT perform relative to wave-function theory?
• applications to small and large molecules
Nuclear spin–spin coupling

• With each nuclear spin $I_P$ in a molecule, there is an associated magnetic moment:

$$M_P = \gamma_P \hbar I_P \approx 10^{-4} \text{ a.u.}$$

• These moments interact directly with one another, by a classical dipole mechanism:

$$M_P^T K_{PQ}^{\text{direct}} M_Q = \alpha^2 \frac{R_{PQ}^2 (M_P \cdot M_Q) - 3(M_P \cdot R_{PQ})(R_{PQ} \cdot M_Q)}{R_{PQ}^5} \approx 10^{-12} \text{ a.u.}$$

  – the direct coupling is anisotropic and vanishes in isotropic media (gases and liquids)

• However, there is also an indirect contribution to the coupling, arising from hyperfine interactions with the intervening electrons:

  – the indirect coupling is exceedingly small:

    $$\approx 10^{-16} \text{ a.u.} \approx 1 \text{ Hz}$$

  – it does not vanish in isotropic media

  – fine structure of high-resolution NMR spectra

• Analogy with molecular electrostatic interactions may be helpful:

  – the bare nuclei repel one another by a classical Coulomb mechanism

  – this interaction is modified by the intervening electrons, which couple to the nuclei

  – the combined interactions may provide stable molecular structures
Indirect nuclear spin–spin coupling tensors

- To second order in the nuclear moments, the change in the electronic energy is described in terms of the (reduced) indirect spin–spin coupling tensors $K_{PQ}$:

$$E(M_P) = E(0) + \sum_{P>Q} M_P^T K_{PQ} M_Q + \mathcal{O}(M^3)$$

  - for closed-shell molecules, there are no first-order contributions
  - the $K_{PQ}$ are simply the second derivatives of $E(M_P)$ at $M_P = 0$
  - they may be calculated by standard techniques for second-order molecular properties

- In what manner is the electronic energy affected by the magnetic moments?
- The nuclear moments set up a magnetic vector potential and a field ($\approx 10^{-8}$ a.u.):

$$A(r) = \alpha^2 \sum_P \frac{M_P \times r_P}{r_P^3}, \quad B(r) = \nabla \times A(r)$$

- In the presence of $A$ and $B$, the kinetic-energy operator is modified and becomes:

$$H_{\text{kin}} = \frac{1}{2} p^2 + \underbrace{A(r) \cdot p}_{\text{orbital hyperfine}} + \frac{1}{2} A(r)^2 + \underbrace{B(r) \cdot s}_{\text{spin hyperfine}}$$

- In nonrelativistic theory, therefore, there are two distinct contributions to the coupling:
  - hyperfine coupling to the orbital motion of the electrons
  - hyperfine coupling to the spin of the electrons
Orbital-hyperfine interactions

- The orbital hyperfine or spin–orbit (SO) coupling represents the interaction of charged particles (electrons) moving in the vector potential \( \mathbf{A}(\mathbf{r}) \) generated by the nuclei.

- There are two types of orbital hyperfine operators:

  \[
  \frac{1}{2} A^2 = \sum_{PQ} M_P^T h_{PQ}^{DSO} M_Q, \quad h_{PQ}^{DSO} = \alpha^4 \frac{r_P^T r_Q I_3 - r_P r_Q^T}{r_P^3 r_Q^3} \quad \leftrightarrow \text{diamagnetic SO (DSO)}
  \]

  \[
  \mathbf{A} \cdot \mathbf{p} = \sum_P M_P^T h_P^{PSO}, \quad h_P^{PSO} = \alpha^2 \frac{r_P \times \mathbf{p}}{r_P^3} \quad \leftrightarrow \text{paramagnetic SO (PSO)}
  \]

- Whereas the second-order real DSO operator contributes to the expectation value, the first-order imaginary PSO operator contributes to second order in perturbation theory:

  \[
  K_{PQ}^{SO} = \langle 0 | h_{PQ}^{DSO} | 0 \rangle + 2 \sum_{n_S \neq 0} \frac{\langle 0 | h_P^{PSO} | n_S \rangle \langle n_S | (h_Q^{PSO})^T | 0 \rangle}{E_{n_S} - E_0}
  \]

  - The DSO contribution is calculated by numerical quadrature.
  - The PSO contribution is calculated using linear response theory, in much the same manner as we calculate for example static polarizabilities.

- The SO contributions (especially DSO) are usually but not invariably small.

- For large internuclear separations, the DSO and PSO contributions cancel.
Spin-hyperfine interactions

- To treat the spin-hyperfine interactions \( \mathbf{B} \cdot \mathbf{s} \), we need the nuclear magnetic field:

\[
\mathbf{B}(\mathbf{r}) = \nabla \times \mathbf{A}(\mathbf{r}) = \frac{8\pi\alpha^2}{3} \sum_P \delta(\mathbf{r}_P) \mathbf{M}_P + \alpha^2 \sum_P \frac{3\mathbf{r}_P(\mathbf{r}_P \cdot \mathbf{M}_P) - r_P^2 \mathbf{M}_P}{r_P^5}
\]

- This magnetic field \( \mathbf{B}(\mathbf{r}) \) then gives rise to two distinct first-order triplet operators:

\[
\mathbf{B} \cdot \mathbf{s} = \sum_P \mathbf{M}_P^T (\mathbf{h}_P^{\text{FC}} + \mathbf{h}_P^{\text{SD}}), \quad \left\{ \begin{array}{l}
\mathbf{h}_P^{\text{FC}} = \frac{8\pi\alpha^2}{3} \delta(\mathbf{r}_P) \mathbf{s} & \text{Fermi contact (FC)} \\
\mathbf{h}_P^{\text{SD}} = \alpha^2 \frac{3\mathbf{r}_P \mathbf{r}_P^T - r_P^2 \mathbf{I}_3}{r_P^5} \mathbf{s} & \text{spin–dipole (SD)}
\end{array} \right.
\]

where FC represents interaction at the nucleus and SD interaction at a distance.

- The FC and SD operators both contribute to second order in perturbation theory:

\[
\mathbf{K}_{PQ}^{\text{FC+SD}} = 2 \sum_{n_T} \frac{\langle 0 \mid \mathbf{h}_P^{\text{FC}} + \mathbf{h}_P^{\text{SD}} \mid n_T \rangle \langle n_T \mid (\mathbf{h}_Q^{\text{FC}})^T + (\mathbf{h}_Q^{\text{SD}})^T \mid 0 \rangle}{E_{n_T} - E_0}
\]

- The \( \mathbf{K}_{PQ}^{\text{FC+SD}} \) are evaluated by linear response theory, just like the \( \mathbf{K}_{PQ}^{\text{PSO}} \).

- Relative importance of the terms:
  - the isotropic FC/FC term often dominates short-range coupling constants
  - the FC/SD and SD/FC terms often dominate the anisotropic part of \( \mathbf{K}_{PQ} \)
The expression for the indirect spin–spin coupling tensors $K_{PQ}$ was first derived by Ramsey in 1953:

\[
K_{PQ} = \left< 0 \left| h_{PQ}^{\text{DSO}} \right| 0 \right> \quad \text{← diamagnetic orbital (singlet)}
\]

\[
+ 2 \sum_{n_S \neq 0} \frac{\left< 0 \left| h_{P}^{\text{PSO}} \right| n_S \right> \left< n_S \left| (h_{Q}^{\text{PSO}})^T \right| 0 \right>}{E_{n_S} - E_0} \quad \text{← paramag. orbital (singlet)}
\]

\[
+ 2 \sum_{n_T} \frac{\left< 0 \left| h_{P}^{\text{FC}} + h_{P}^{\text{SD}} \right| n_T \right> \left< n_T \left| (h_{Q}^{\text{FC}})^T + (h_{Q}^{\text{SD}})^T \right| 0 \right>}{E_{n_T} - E_0} \quad \text{← spin (triplet)}
\]

In 1950, Ramsey had already derived an expression for nuclear shieldings $\sigma_P$, describing the interaction of the nuclei with an external magnetic field in the presence of electrons.

Together, $\sigma_P$ and $K_{PQ}$ determine the spin Hamiltonian of high-resolution NMR:

\[
H_{\text{NMR}} = -B^T \sum_P (I_3 - \sigma_P) M_P + \sum_{P > Q} M_P^T K_{PQ} M_Q
\]

– experimentalists determine $\sigma_P$ and $K_{PQ}$ from observed spectra

– our task is to determine these from the molecular electronic structure
Spin–spin coupling constants by linear response theory

- In linear response theory, we may express the $\alpha\beta$ Cartesian component of the spin–spin coupling tensor $K_{PQ}$ in this manner:

$$K_{P\alpha,Q\beta} = \langle h_{P\alpha,Q\beta}^{\text{DSO}} \rangle - [F_{P\alpha}^{\text{PSO}}]^T [G_{ii}^{\text{ss}}]^{-1} F_{Q\beta}^{\text{PSO}} - \sum_{\gamma} [F_{P\alpha\gamma}^{\text{FC+SD}}]^T [G_{rr}^{\text{tt}}]^{-1} F_{Q\gamma\beta}^{\text{FC+SD}}$$

- Right-hand side elements:

$$[F_{P}^{\text{PSO}}]_{ai} = 2\alpha^2 \left\langle a \left| \frac{1}{r_P^3} i \right\rangle \right), \quad [F_{P}^{\text{FC+SD}}]_{ai} = \alpha^2 \left\langle a \left| \frac{8\pi}{3} \delta(r_P) I + \frac{3 r_P r_P^T - r_P^3 I}{r_P^5} \right| i \right\rangle$$

- Leading Hessian terms are diagonal orbital-energy differences:

$$[G_{ii}^{\text{ss}}]_{ai,bj} = \delta_{ij} \delta_{ab} (\varepsilon_a - \varepsilon_i) + \gamma (g_{ajib} - g_{abij}) \quad \leftarrow \text{diagonal in pure DFT}$$

$$[G_{rr}^{\text{tt}}]_{ai,bj} = \delta_{ij} \delta_{ab} (\varepsilon_a - \varepsilon_i) - \gamma (g_{ajib} + g_{abij}) + \int \frac{\partial^2 f}{\partial \rho_i^2} \phi_a \phi_i \phi_b \phi_j dr + \cdots$$

- In practice, Hessian inversion is avoided by the solution of linear equations:

$$G_{rr}^{\text{tt}} \gamma_{Q\gamma\beta}^{\text{FC+SD}} = -F_{Q\gamma\beta}^{\text{FC+SD}}$$

- There are a total of 9 (10) such equations to be solved for each nucleus.
Calculations of indirect spin–spin calculations

- The calculation of spin–spin coupling constants is a challenging task:
  - triplet as well as singlet perturbations are involved
  - electron correlation important—the Hartree–Fock model fails abysmally
  - the dominant FC contribution requires an accurate description of the electron density at the nuclei (large decontracted s sets)

- We must solve a large number of response equations:
  - 3 singlet equations and 7 triplet equations for each nucleus
  - for shieldings, only 3 equations are required, for molecules of all sizes

- Spin–spin couplings are very sensitive to the molecular geometry:
  - equilibrium structures must be chosen carefully
  - large vibrational corrections (often 5%–10%)

- However, unlike in shielding calculations, there is no need for London orbitals since no external magnetic field is involved.

- For heavy elements, a relativistic treatment may be necessary:
  - four-component theory, ZORA (Pyykkö, Saue, Ziegler)
• The isotropic indirect spin–spin coupling constants can be uniquely decomposed as:

\[ K_{PQ} = K_{PQ}^{DSO} + K_{PQ}^{PSO} + K_{PQ}^{FC} + K_{PQ}^{SD} \]

• The spin–spin coupling constants are often dominated by the FC term.
• Since the FC term is relatively easy to calculate, it is tempting to ignore the other terms.
• However, none of the contributions can be \textit{a priori} neglected (N₂ and CO)!

Relative importance of the contributions to spin–spin coupling constants
RHF and the triplet instability problem

• RHF does not in general work for spin–spin calculations:
  – the RHF wave function often becomes triplet unstable
  – at or close to such instabilities, the RHF description of spin interactions becomes unphysical
  – the spin–spin coupling constants of C₂H₄:

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<th>( ^1J_{CH} )</th>
<th>( ^2J_{CH} )</th>
<th>( ^2J_{HH} )</th>
<th>( ^3J_{cis} )</th>
<th>( ^3J_{trans} )</th>
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• Indeed, any method based on the RHF reference state may have problems:
  – \( ^1J_{CN} \) in HCN [Auer and Gauss, JCP 115 (2001) 1619]

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  – in CC theory, orbital relaxation should be treated through singles amplitudes
  – noniterative CCSD(T) cannot be used; iterative CC3 must be used instead
  – all electrons must be correlated in unrelaxed CC calculations
Correlated methods for spin–spin calculations

- For the reliable calculation of spin–spin coupling constants, there is clearly a need for **correlated** methods.

- Traditional **wave-function methods** used for spin-spin calculations:
  - **CISD** (Kowalewski, Roos, Siegbahn and Vestin, 1974)
  - **SOPPA** (Geertsen and Oddershede, 1984)
  - **MCSCF** (Vahtras, Ågren, Jørgensen, Jensen, Padkjær and Helgaker, 1992)
    * static correlation with CAS
    * dynamical correlation with RAS
  - **EOM-CCSD** (Perera, Sekino and Bartlett, 1994)
  - **CCSD(T), CC3, CCSDT** (Auer and Gauss, 2001)

- Most widely used: SOPPA, MCSCF, EOM-CCSD

- Typical **errors** are a few Hz in small systems, but often 10%–20% for small couplings

- However, all of these methods are (at least for now) restricted to **small systems**.
<table>
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*at $R_e$
DFT calculations of spin–spin coupling constants

- DFT offers an alternative approach to spin–spin calculations:
  - Malkin, Malkina, Salahub (1994):
    LDA and GGA with neglect of SD contribution
    FPT & SOS; GTOs
  - Dickson and Ziegler (1996):
    LDA with neglect of SD contribution
    FPT & SOS; STOs
  - Sychrovský, Gräfenstein and Cremer; Helgaker, Watson and Handy (2000)
    LDA, GGA and hybrid DFT,
    response theory; GTOs
  - Autschbach and Ziegler (2000);
    LDA and GGA
    response theory; STOs; ZORA

- All of these apply standard exchange–correlation functionals
  - current density functionals should be tried!
### Reduced spin–spin coupling constants \((10^{19} \text{kg m}^{-2} \text{s}^{-2} \text{Å}^{-2})\)

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Comparison of density-functional and wave-function theory

- normal distributions of errors for these molecules and some other systems for which vibrational corrections have been made:

  - HF has a very broad distribution and overestimates strongly
  - LDA underestimates only slightly, but has a large standard deviation
  - BLYP reduces the LDA errors by a factor of two
  - B3LYP improves upon GGA (but not as dramatically as for other properties)
  - B3LYP errors are similar to those of CASSCF and about twice those of the dynamically correlated methods RASSCF, SOPPA, and CCSD
  - the most accurate method appears to be CCSD
  - the situation is much less satisfactory than for geometries and atomization energies
DFT failures and successes

- DFT failures: couplings to electronegative and lone-pair atoms
  - fluorine couplings, in particular, are strongly underestimated:
    
    \[
    \begin{array}{l|rrrrrr|c}
    & \text{RHF} & \text{LDA} & \text{BLYP} & \text{B3LYP} & \text{CCSD} & \text{exp} \\
    \text{HF} & 669 & 396 & 390 & 417 & 522 & 538 \\
    \text{FHF}^- & 657 & -175 & -113 & 25 & 439 & \approx 274
    \end{array}
    \]
  - this is obviously a failure of the functionals rather than of DFT as such
  - the KT1 functional of Keal and Tozer gives the following one-bond couplings:
    
    \[
    \begin{array}{l|rrrrrrrr}
    & \text{HF} & \text{CO} & \text{NN} & \text{OH} & \text{NH} & \text{CC} & \text{CH} & \text{CC} \\
    \text{KT1} & 507 & 19 & 1 & -81 & 44 & 51 & 147 & 13 \\
    \text{exp.} & 538 & 16 & 2 & -86 & 44 & 67 & 151 & 35 \\
    \text{B3LYP} & 417 & 18 & 3 & -76 & 46 & 75 & 165 & 33
    \end{array}
    \]

- Successes of DFT:
  - trends are well reproduced
  - hydrocarbons are well reproduced (Malkin, Malkina, and Salahub)
    mean abs. err. 4 Hz and std. dev. 6 Hz (vs. 5 and 15 Hz in general)
    even better with small basis sets :)

\[\text{16}\]
• comparison of calculated (red) and B3LYP (blue) spin–spin coupling constants
  – plotted in order of decreasing experimental value

• trends are quite well reproduced by B3LYP, in particular for large couplings
## Spin–spin coupling constants of hydrocarbons

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<thead>
<tr>
<th></th>
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<th>emp</th>
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**Pyroorle**

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**Furan**

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**Cyclopropane**

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Basis-set requirements

• Accurate spin–spin calculations require large basis sets, augmented with steep $s$ functions
  – Huz-III-$su_0$: [11s6p2d/6s2p]
  – Huz-III-$su_3$: [14s6p2d/9s2p]

• B3LYP calculations on benzene with and without added $s$ functions:

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<td>0.7</td>
<td>0.6</td>
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</table>

• Cancellation of errors gives excellent agreement without added steep functions :)
The Karplus curve

- Vicinal couplings depend critically on the dihedral angle:
  - $^3J_{HH}$ in ethane as a function of the dihedral angle:
  - The agreement with the empirical Karplus curve is good.

For the spin–spin coupling constants in C$_{60}$, we find (at the B3LYP level):
- $^1J$ couplings within one pentagon and between two pentagons are 62 and 77 Hz.
- $^2J$ couplings within one pentagon and between two pentagons are 7 and 1 Hz.
- $^3J$ couplings are 4 Hz.
- $^4J$ couplings and all other couplings are smaller than 1 Hz.
DFT can be applied to large molecular systems such as valinomycin (168 atoms)

- There are a total of 7587 spin–spin couplings to carbon atoms in valinomycin.
- Most of the indirect couplings are small and cannot be detected.

We have calculated the FC contributions at the LDA/6-31G level of theory.

- The FC contributions fall off exponentially with increasing separation.
Valinomycin spin–spin couplings $|J| > 0.1$ Hz
The FC contribution dominates at short separations but decays exponentially.

To compare the long-distance behavior of the contributions to the spin–spin couplings, we have carried out calculations for $C_{60}H_{120}$ at the LDA/4-31G level.

Below we have plotted, on logarithmic scale, the contributions to the spin–spin couplings of the central and a terminal carbon atom.

- The FC contribution (red) decays exponentially.
- The DSO and PSO contributions (blue) decay as $R^{-2}$ but tend to cancel for large separations.
- The SD contribution (green) decays in a less predictable manner.
Conclusions

- The calculation of spin–spin coupling constants is a challenging task, requiring the solution of 9 or 10 linear equations for each magnetic nucleus.

- The calculation of indirect nuclear spin-spin couplings constants can be carried out at a variety of levels of theory:
  - wave-function theory: RHF, CASSCF, RASSCF, SOPPA, CCSD
  - density-functional theory: LDA, GGA, hybrid DFT

- The most accurate results are provided by the wave-function methods, although these are mostly restricted to rather small systems.

- Because of triplet-instability problems, the RHF model is unsuitable for spin–spin calculations.

- Whereas LDA provide results of low accuracy, BLYP and in particular B3LYP provide results of almost the same quality as RASSCF, SOPPA, and CCSD.
  - current functionals have difficulties with highly electronegative elements
  - on the other hand, they work very well for hydrocarbons

- DFT can be applied to large systems, using linear-scaling techniques, opening up the possibility of studying couplings in molecules of biological interest.