Molecular Magnetic Properties

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Sections

Section 1

Introduction

Taylor Expansion of Energy

- Expand the energy in the presence of an external magnetic field $\mathbf{B}$ and nuclear magnetic moments $\mathbf{M}_K$ around zero field and zero moments:

$$E(\mathbf{B},\mathbf{M}) = E_0 + \overbrace{\mathbf{B}^{\mathrm{T}}\mathbf{E}^{(10)}}^{\text{perm. magnetic moments}} + \overbrace{\sum_K \mathbf{M}_K^{\mathrm{T}}\mathbf{E}_K^{(01)}}^{\text{hyperfine coupling}}$$
$$+ \underbrace{\frac{1}{2}\mathbf{B}^{\mathrm{T}}\mathbf{E}^{(20)}\mathbf{B}}_{-\text{ magnetizability}} + \underbrace{\frac{1}{2}\sum_K \mathbf{B}^{\mathrm{T}}\mathbf{E}_K^{(11)}\mathbf{M}_K}_{\text{shieldings} + 1} + \underbrace{\frac{1}{2}\sum_{KL} \mathbf{M}_K^{\mathrm{T}}\mathbf{E}_{KL}^{(02)}\mathbf{M}_L}_{\text{spin–spin couplings}} + \cdots$$

- First-order terms vanish for closed-shell systems because of symmetry
  - they shall be considered only briefly here
- Second-order terms are important for many molecular properties
  - magnetizabilities
  - nuclear shieldings constants of NMR
  - nuclear spin–spin coupling constants of NMR
  - electronic g tensors of EPR (not dealt with here)
- Higher-order terms are negligible since the perturbations are tiny:
  1) the magnetic induction $\mathbf{B}$ is weak ($\approx 10^{-4}$ a.u.)
  2) the nuclear magnetic moments $\mathbf{M}_K$ couple weakly ($\mu_0\mu_{\mathrm{N}} \approx 10^{-8}$ a.u.)

Derivatives and Perturbation Theory I

- Consider a normalized CI wave function:

$$|\mathbf{c}\rangle = \sum\nolimits_{n=0}^{\infty} c_n |n\rangle, \quad \mathbf{c}^{\mathrm{T}}\mathbf{c} = 1, \quad \langle m|n\rangle = \delta_{mn}$$

- The basis functions $|n\rangle$ are the normalized CI eigenstates of the unperturbed problem:

$$\langle m|H|n\rangle = \delta_{mn} E_n, \quad E_0 \leq E_1 \leq E_2 \cdots$$

- We here assume that the ground-state energy function depends on two external parameters:

$$\langle \mathbf{c}|H(x,y)|\mathbf{c}\rangle = \sum\nolimits_{mn} c_m \langle m|H(x,y)|n\rangle c_n, \quad \sum_n c_n^2 = 1$$

- We construct a variational CI Lagrangian:

$$L(x,y,\mathbf{c},\mu) = \sum_{mn} c_m \langle m|H(x,y)|n\rangle c_n - \mu\Big(\sum_n c_n^2 - 1\Big)$$

- The stationary conditions are given by

$$\begin{aligned}
\frac{\partial L(x,y,\mathbf{c},\mu)}{\partial c_n} = 0 \quad &\Longrightarrow \quad 2\langle n|H(x,y)|\mathbf{c}\rangle - 2\mu c_n = 0 \quad &&\Longrightarrow \quad \mathbf{H}(x,y)\mathbf{c} = E_0(x,y)\mathbf{c} \\
\frac{\partial L(x,y,\mathbf{c},\mu)}{\partial \mu} = 0 \quad &\Longrightarrow \quad \sum_n c_n^2 - 1 = 0 \quad &&\Longrightarrow \quad \mathbf{c}^{\mathrm{T}}\mathbf{c} = 1
\end{aligned}$$

  - the first condition is the CI eigenvalue problem with ground-state energy $E_0(x,y) = \mu$
  - the second condition is the CI normalization condition

Derivatives and Perturbation Theory II

- Using the CI Lagrangian, we calculate CI energy derivative in the usual way:

$$\frac{\mathrm{d}E}{\mathrm{d}x} = \frac{\partial L}{\partial x}, \quad \frac{\mathrm{d}^2 E}{\mathrm{d}x\mathrm{d}y} = \frac{\partial^2 L}{\partial x \partial y} + \sum_n \frac{\partial^2 L}{\partial x \partial c_n}\frac{\partial c_n}{\partial x}, \quad \sum_n \frac{\partial^2 L}{\partial c_m \partial c_n}\frac{\partial c_n}{\partial x} = -\frac{\partial^2 L}{\partial x \partial c_m}$$

- By inverting the electronic Hessian, we obtain the more compact expression:

$$\frac{\mathrm{d}^2 E}{\mathrm{d}x\mathrm{d}y} = \frac{\partial^2 L}{\partial x \partial y} - \sum_{mn} \frac{\partial^2 L}{\partial x \partial c_m}\left[\frac{\partial^2 L}{\partial c_m \partial c_n}\right]^{-1}\frac{\partial^2 L}{\partial c_n \partial y}$$

- We next evaluate the various partial derivatives at $x = y = 0$ where $|\mathbf{c}\rangle = |0\rangle$:

$$\frac{\partial L}{\partial x} = \left\langle 0 \left| \tfrac{\partial H}{\partial x} \right| 0 \right\rangle, \quad \frac{\partial^2 L}{\partial x \partial y} = \left\langle 0 \left| \tfrac{\partial^2 H}{\partial x \partial y} \right| 0 \right\rangle, \quad \frac{\partial^2 L}{\partial x \partial c_n} = 2\left\langle n \left| \tfrac{\partial H}{\partial x} \right| 0 \right\rangle$$

$$\frac{\partial^2 L}{\partial c_m \partial c_n} = 2\left\langle m \left| H - E_0 \right| n \right\rangle = 2(E_n - E_0)\delta_{mn}$$

- Inserted above, we recover Rayleigh–Schrödinger perturbation theory to second order:

$$\frac{\mathrm{d}E}{\mathrm{d}x} = \left\langle 0 \left| \tfrac{\partial H}{\partial x} \right| 0 \right\rangle, \quad \frac{\mathrm{d}^2 E}{\mathrm{d}x\mathrm{d}y} = \left\langle 0 \left| \tfrac{\partial^2 H}{\partial x \partial y} \right| 0 \right\rangle - 2\sum_n \frac{\left\langle 0 \left| \tfrac{\partial H}{\partial x} \right| n \right\rangle \left\langle n \left| \tfrac{\partial H}{\partial y} \right| 0 \right\rangle}{E_n - E_0}$$

Section 2

The Hamiltonian — Zeeman and Hyperfine Interactions

Hamiltonian in Magnetic Field

- In atomic units, the molecular Hamiltonian is given by

$$H = H_0 + \underbrace{\mathbf{A}(\mathbf{r}) \cdot \mathbf{p}}_{\text{orbital paramagnetic}} + \underbrace{\mathbf{B}(\mathbf{r}) \cdot \mathbf{s}}_{\text{spin paramagnetic}} + \underbrace{\tfrac{1}{2} A^2(\mathbf{r})}_{\text{diamagnetic}}$$

- There are two kinds of magnetic perturbation operators:
  - paramagnetic (may lower or raise energy) and diamagnetic (always raises energy)
- There are two kinds of paramagnetic operators:
  - the orbital paramagnetic and spin paramagnetic
- First- and second-order Rayleigh–Schrödinger perturbation theory gives:

$$E^{(1)} = \langle 0 \left| \mathbf{A} \cdot \mathbf{p} + \mathbf{B} \cdot \mathbf{s} \right| 0 \rangle$$

$$E^{(2)} = \frac{1}{2} \langle 0 \left| A^2 \right| 0 \rangle - \sum_n \frac{\langle 0 \left| \mathbf{A} \cdot \mathbf{p} + \mathbf{B} \cdot \mathbf{s} \right| n \rangle \langle n \left| \mathbf{A} \cdot \mathbf{p} + \mathbf{B} \cdot \mathbf{s} \right| 0 \rangle}{E_n - E_0}$$

- In the study of magnetic properties, we are interested in two types of perturbations:
  - externally applied uniform magnetic fields **B**
  - fields generated internally by nuclear magnetic moments $\mathbf{M}_K$
- Both fields are weak—well described by perturbation (response) theory

Orbital Paramagnetic Interactions: $\mathbf{A} \cdot \mathbf{p}$

- Vector potentials corresponding to uniform fields and nuclear magnetic moments:

$$\mathbf{A}_\mathbf{O} = \frac{1}{2}\mathbf{B} \times \mathbf{r}_\mathbf{O}, \quad \mathbf{A}_K = \alpha^2 \frac{\mathbf{M}_K \times \mathbf{r}_K}{r_K^3}, \quad \alpha \approx 1/137$$

  - the external field is typically about 10^{-4} a.u. (NMR experiments)
  - the nuclear vector potential is exceedingly small (about 10^{-8} a.u.) since:

$$\alpha^2 = c^{-2} \approx 10^{-4}\ \text{a.u.}, \quad \mathbf{M}_K = \gamma_K \hbar \mathbf{I}_K \approx 10^{-4}\ \text{a.u.}$$

- We obtain the following orbital paramagnetic operators:

$$\begin{aligned} \mathbf{A}_\mathbf{O} \cdot \mathbf{p} &= \frac{1}{2}\mathbf{B} \times \mathbf{r}_\mathbf{O} \cdot \mathbf{p} = \frac{1}{2}\mathbf{B} \cdot \mathbf{r}_\mathbf{O} \times \mathbf{p} = \frac{1}{2}\mathbf{B} \cdot \mathbf{L}_\mathbf{O} && \leftarrow \text{orbital Zeeman} \\ \mathbf{A}_K \cdot \mathbf{p} &= \alpha^2 \frac{\mathbf{M}_K \times \mathbf{r}_K \cdot \mathbf{p}}{r_K^3} = \alpha^2 \frac{\mathbf{M}_K \cdot \mathbf{r}_K \times \mathbf{p}}{r_K^3} = \alpha^2 \mathbf{M}_K \cdot \frac{\mathbf{L}_\mathbf{K}}{r_K^3} && \leftarrow \text{orbital hyperfine} \end{aligned}$$

  - interactions depend on angular momenta $\mathbf{L}_\mathbf{O}$ and $\mathbf{L}_K$ relative to $\mathbf{O}$ and $\mathbf{R}_K$, respectively
  - orbital hyperfine interaction expressed in terms of the paramagnetic spin–orbit operator:

$$\mathbf{A}_K \cdot \mathbf{p} = \mathbf{M}_K \cdot \mathbf{h}_K^{\text{PSO}}, \quad \mathbf{h}_K^{\text{PSO}} = \alpha^2 \frac{\mathbf{L}_K}{r_K^3}$$

- These are imaginary singlet operators
  - they have zero expectation values of closed-shell states
  - they generate complex wave functions

Spin Paramagnetic Interactions: $\mathbf{B} \cdot \mathbf{s}$

- The spin interaction with the external uniform field $\mathbf{B}$ is trivial:

$$\mathbf{B} \cdot \mathbf{s} \quad \leftarrow \text{spin Zeeman interaction}$$

  - should be compared with the orbital Zeeman interaction $\frac{1}{2}\mathbf{B} \cdot \mathbf{L}_O$ (different prefactor!)
- Taking the curl of $\mathbf{A}_K$, we obtain the nuclear magnetic field:

$$\mathbf{B}_K = \boldsymbol{\nabla} \times \mathbf{A}_K = \frac{8\pi\alpha^2}{3}\delta(\mathbf{r}_K)\mathbf{M}_K + \alpha^2 \frac{3\mathbf{r}_K(\mathbf{r}_K \cdot \mathbf{M}_K) - r_K^2\mathbf{M}_K}{r_K^5}$$

  - the first term is a contact interaction and contributes only at the nucleus
  - the second term is a classical dipole field and contributes at a distance
- This magnetic field $\mathbf{B}_K$ thus gives rise to two spin hyperfine interactions:

$$\mathbf{B}_K \cdot \mathbf{s} = \mathbf{M}_K \cdot (\mathbf{h}_K^{\mathrm{FC}} + \mathbf{h}_K^{\mathrm{SD}}), \qquad \begin{cases} \mathbf{h}_K^{\mathrm{FC}} = \frac{8\pi\alpha^2}{3}\delta(\mathbf{r}_K)\,\mathbf{s} & \text{Fermi contact (FC)} \\ \mathbf{h}_K^{\mathrm{SD}} = \alpha^2 \frac{3\mathbf{r}_K\mathbf{r}_K^{\mathrm{T}} - r_K^2\mathbf{I}_3}{r_K^5}\mathbf{s} & \text{spin–dipole (SD)} \end{cases}$$

  - the FC operator contributes when the electron passes through the nucleus
  - the SD operator is a classical dipolar interaction, decaying as r_K^{-3}
- These are real triplet operators, which change the spin of the wave function
  - they have zero expectation values of closed-shell states
  - they couple closed-shell states to triplet states

Perturbation Theory with Zeeman and Hyperfine Operators

- Hamiltonian with a uniform external field and with nuclear magnetic moments:

$$H = H_0 + H^{(1)} + H^{(2)} = H_0 + H_{\mathrm{z}}^{(1)} + H_{\mathrm{hf}}^{(1)} + \tfrac{1}{2} A^2$$

  - Zeeman interactions with the external magnetic field $\mathbf{B}$:

$$H_{\mathrm{z}}^{(1)} = \frac{1}{2}\mathbf{B}\cdot\mathbf{L}_{\mathbf{O}} + \mathbf{B}\cdot\mathbf{s} \sim 10^{-4}$$

  - hyperfine interactions with the nuclear magnetic moments $\mathbf{M}_K$:

$$H_{\mathrm{hf}}^{(1)} = \sum_K \mathbf{M}_K \cdot \mathbf{h}_K^{\mathrm{PSO}} + \sum_K \mathbf{M}_K \cdot \left(\mathbf{h}_K^{\mathrm{FC}} + \mathbf{h}_K^{\mathrm{SD}}\right) \sim 10^{-8}$$

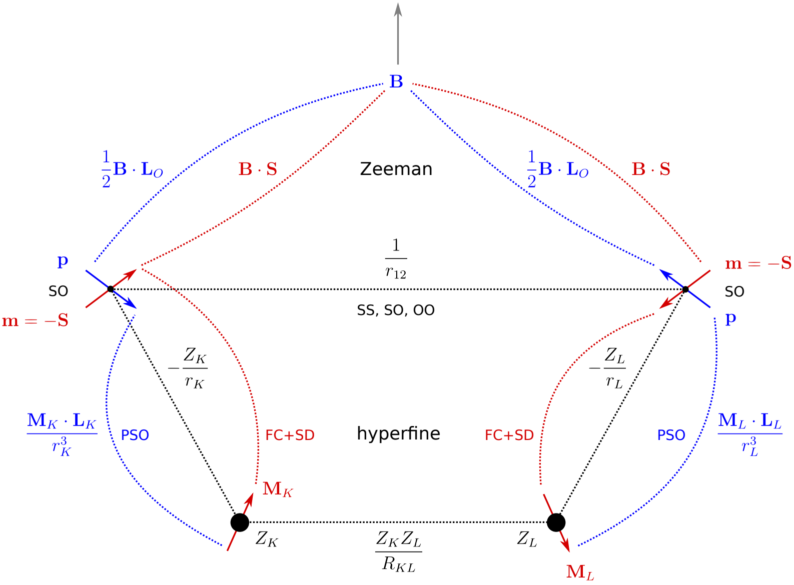
$$\mathbf{h}_K^{\mathrm{PSO}} = \alpha^2 \frac{\mathbf{L}_K}{r_K^3}, \quad \mathbf{h}_K^{\mathrm{FC}} = \frac{8\pi\alpha^2}{3}\delta(\mathbf{r}_K)\,\mathbf{s}, \quad \mathbf{h}_K^{\mathrm{SD}} = \alpha^2 \frac{3\mathbf{r}_K\mathbf{r}_K^{\mathrm{T}} - r_K^2\mathbf{I}_3}{r_K^5}\mathbf{s}$$

- Second-order Rayleigh–Schrödinger perturbation theory:

$$E^{(1)} = \left\langle 0 \middle| H_{\mathrm{z}}^{(1)} + H_{\mathrm{hf}}^{(1)} \middle| 0 \right\rangle$$

$$E^{(2)} = \frac{1}{2}\left\langle 0 \left| A^2 \right| 0 \right\rangle - \sum_n \frac{\left\langle 0 \middle| H_{\mathrm{z}}^{(1)} + H_{\mathrm{hf}}^{(1)} \middle| n \right\rangle \left\langle n \middle| H_{\mathrm{z}}^{(1)} + H_{\mathrm{hf}}^{(1)} \middle| 0 \right\rangle}{E_n - E_0}$$

Zeeman and Hyperfine Interactions



$\mathbf{B}$

$\frac{1}{2}\mathbf{B}\cdot\mathbf{L}_O$ $\mathbf{B}\cdot\mathbf{S}$ Zeeman $\frac{1}{2}\mathbf{B}\cdot\mathbf{L}_O$ $\mathbf{B}\cdot\mathbf{S}$

$\mathbf{p}$ $\frac{1}{r_{12}}$ $\mathbf{m}=-\mathbf{S}$

SO SO

$\mathbf{m}=-\mathbf{S}$ SS, SO, OO $\mathbf{p}$

$-\frac{Z_K}{r_K}$ $-\frac{Z_L}{r_L}$

$\frac{\mathbf{M}_K\cdot\mathbf{L}_K}{r_K^3}$ PSO FC+SD hyperfine FC+SD PSO $\frac{\mathbf{M}_L\cdot\mathbf{L}_L}{r_L^3}$

$\mathbf{M}_K$

Z_K $\frac{Z_K Z_L}{R_{KL}}$ Z_L

$\mathbf{M}_L$

Diamagnetic Operators: $\frac{1}{2}A^2$

- From $\mathbf{A}_\mathrm{O}$ and $\mathbf{A}_K$, we obtain three diamagnetic operators:

$$\mathbf{A} = \mathbf{A}_\mathrm{O} + \mathbf{A}_K \Longrightarrow A^2 = \mathbf{A}_\mathrm{O} \cdot \mathbf{A}_\mathrm{O} + 2\mathbf{A}_\mathrm{O} \cdot \mathbf{A}_K + \mathbf{A}_K \cdot \mathbf{A}_K$$

- Their explicit forms and typical magnitudes (atomic units) are given by

$$\begin{aligned}
\mathbf{A}_\mathrm{O} \cdot \mathbf{A}_\mathrm{O} &= \frac{1}{4}(\mathbf{B} \times \mathbf{r}_\mathrm{O}) \cdot (\mathbf{B} \times \mathbf{r}_\mathrm{O}) && \sim 10^{-8} \\
\mathbf{A}_\mathrm{O} \cdot \mathbf{A}_K &= \frac{\alpha^2}{2} \frac{(\mathbf{B} \times \mathbf{r}_\mathrm{O}) \cdot (\mathbf{M}_K \times \mathbf{r}_K)}{r_K^3} && \sim 10^{-12} \\
\mathbf{A}_K \cdot \mathbf{A}_L &= \alpha^4 \frac{(\mathbf{M}_K \times \mathbf{r}_K) \cdot (\mathbf{M}_L \times \mathbf{r}_L)}{r_K^3 r_L^3} && \sim 10^{-16}
\end{aligned}$$

- These are all real singlet operators
  - their expectation values contribute to second-order magnetic properties
  - they are all exceedingly small but nonetheless all observable

Section 3

First-Order Magnetic Properties

Taylor Expansion of Energy

- Expand the energy in the presence of an external magnetic field $\mathbf{B}$ and nuclear magnetic moments $\mathbf{M}_K$ around zero field and zero moments:

$$E(\mathbf{B},\mathbf{M}) = E_0 + \overbrace{\mathbf{B}^{\mathrm{T}}\mathbf{E}^{(10)}}^{\text{perm. magnetic moments}} + \overbrace{\sum_K \mathbf{M}_K^{\mathrm{T}}\mathbf{E}_K^{(01)}}^{\text{hyperfine coupling}}$$
$$+ \underbrace{\frac{1}{2}\mathbf{B}^{\mathrm{T}}\mathbf{E}^{(20)}\mathbf{B}}_{-\text{ magnetizability}} + \underbrace{\frac{1}{2}\sum_K \mathbf{B}^{\mathrm{T}}\mathbf{E}_K^{(11)}\mathbf{M}_K}_{\text{shieldings} + 1} + \underbrace{\frac{1}{2}\sum_{KL} \mathbf{M}_K^{\mathrm{T}}\mathbf{E}_{KL}^{(02)}\mathbf{M}_L}_{\text{spin–spin couplings}} + \cdots$$

- First-order terms vanish for closed-shell systems because of symmetry
  - they shall be considered only briefly here
- Second-order terms are important for many molecular properties
  - magnetizabilities
  - nuclear shieldings constants of NMR
  - nuclear spin–spin coupling constants of NMR
  - electronic g tensors of EPR (not dealt with here)
- Higher-order terms are negligible since the perturbations are tiny:
  1) the magnetic induction $\mathbf{B}$ is weak ($\approx 10^{-4}$ a.u.)
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First-Order Molecular Properties

- The first-order properties are expectation values of $H^{(1)}$
- Permanent magnetic moment

$$\mathbf{M} = \langle 0 | H_z^{(1)} | 0 \rangle = \langle 0 | \tfrac{1}{2}\mathbf{L_O} + \mathbf{s} | 0 \rangle$$

  - permanent magnetic moment dominates the magnetism of molecules
  - the molecule reorients itself and enters the field
  - such molecules are therefore paramagnetic
- Hyperfine coupling constants

$$\mathbf{A}_K = \langle 0 | H_{\text{hf}}^{(1)} | 0 \rangle = \tfrac{8\pi\alpha^2}{3} \langle 0 | \delta\left(\mathbf{r}_K\right) \mathbf{s} | 0 \rangle \cdot \mathbf{M}_K + \cdots$$

  - measure spin density at the nucleus
  - important in electron paramagnetic resonance (EPR)
  - recall: there are three hyperfine mechanisms: FC, SD and PSO
- Note: there are no first-order Zeeman or hyperfine couplings for closed-shell molecules
  - all expectation values vanish for imaginary operators and triplet operators:

$$\left\langle \text{c.c.} \middle| \hat{\Omega}_{\text{imaginary}} \middle| \text{c.c.} \right\rangle \equiv \left\langle \text{c.c.} \middle| \hat{\Omega}_{\text{triplet}} \middle| \text{c.c.} \right\rangle \equiv 0$$

Section 4

Molecular Magnetizabilities

Molecular Magnetizabilities

- Expand the molecular electronic energy in the external magnetic field:

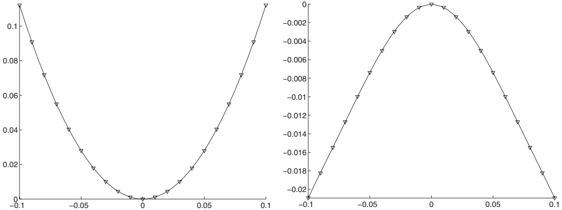
$$E(\mathbf{B}) = E_0 - \mathbf{B}^{\mathrm{T}}\mathbf{M} - \frac{1}{2}\mathbf{B}^{\mathrm{T}}\boldsymbol{\xi}\mathbf{B} + \cdots$$

- The magnetizability describes the second-order energy:

$$\boldsymbol{\xi} = -\frac{\mathrm{d}^2 E}{\mathrm{d}\mathbf{B}^2} = -\left\langle 0 \left| \frac{\partial^2 H}{\partial \mathbf{B}^2} \right| 0 \right\rangle + 2\sum_n \frac{\left\langle 0 \left| \frac{\partial H}{\partial \mathbf{B}} \right| n \right\rangle \left\langle n \left| \frac{\partial H}{\partial \mathbf{B}} \right| 0 \right\rangle}{E_n - E_0}$$

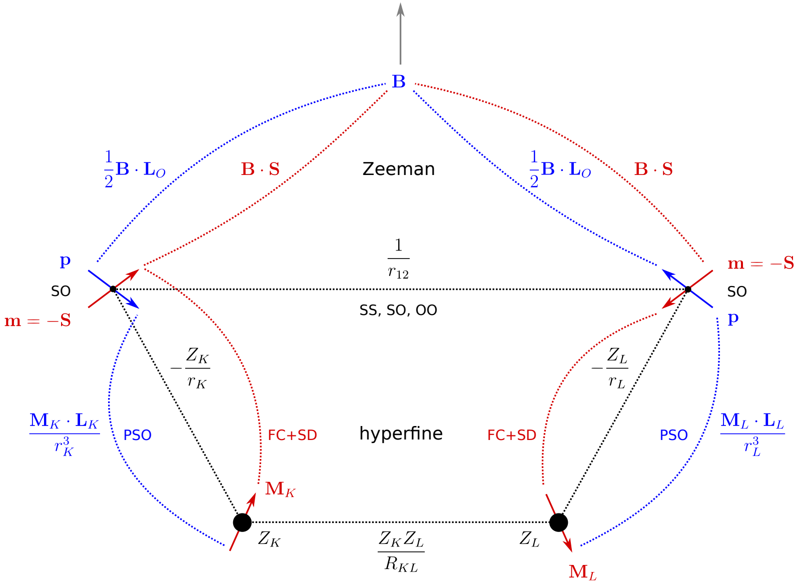
$$= \underbrace{-\frac{1}{4}\left\langle 0 \left| \mathbf{r}_{\mathbf{O}}^{\mathrm{T}}\mathbf{r}_{\mathbf{O}}\mathbf{I}_3 - \mathbf{r}_{\mathbf{O}}\mathbf{r}_{\mathbf{O}}^{\mathrm{T}} \right| 0 \right\rangle}_{\text{diamagnetic term}} \underbrace{+\frac{1}{2}\sum_n \frac{\left\langle 0 \left| \mathbf{L}_{\mathbf{O}} \right| n \right\rangle \left\langle n \left| \mathbf{L}_{\mathbf{O}}^{\mathrm{T}} \right| 0 \right\rangle}{E_n - E_0}}_{\text{paramagnetic term}}$$

- The magnetizability describes the curvature at zero magnetic field:



  - left: diamagnetic dependence on the field ($\xi < 0$); right: paramagnetic dependence on the field ($\xi > 0$)

Zeeman and Hyperfine Interactions

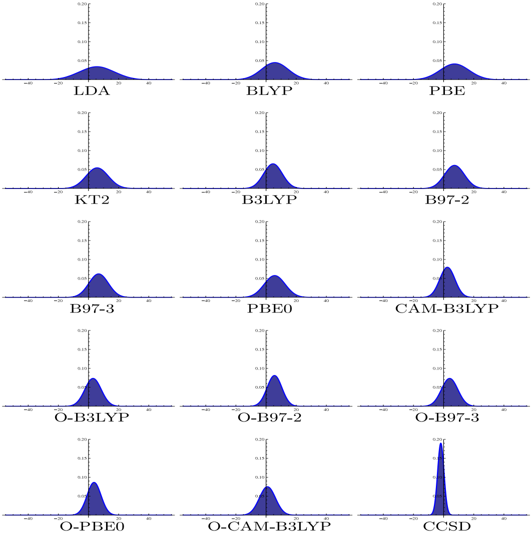


Basis-Set Convergence of Hartree–Fock Magnetizabilities

- London orbitals are correct to first-order in the external magnetic field
- For this reason, basis-set convergence is usually improved
- RHF magnetizabilities of benzene:

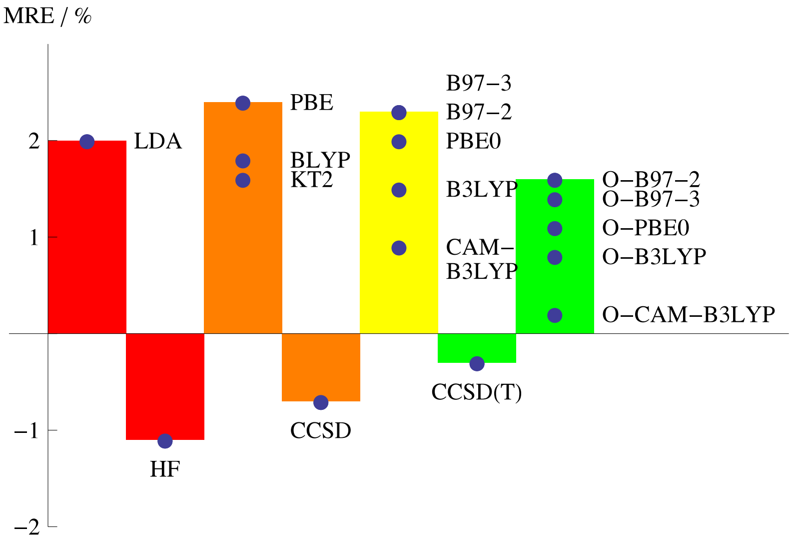
	basis set	χ_{xx}	χ_{yy}	χ_{zz}
London	STO-3G	-8.1	-8.1	-23.0
	6-31G	-8.2	-8.2	-23.1
	cc-pVDZ	-8.1	-8.1	-22.3
	aug-cc-pVDZ	-8.0	-8.0	-22.4
origin CM	STO-3G	-35.8	-35.8	-48.1
	6-31G	-31.6	-31.6	-39.4
	cc-pVDZ	-15.4	-15.4	-26.9
	aug-cc-pVDZ	-9.9	-9.9	-25.2
origin H	STO-3G	-35.8	-176.3	-116.7
	6-31G	-31.6	-144.8	-88.0
	cc-pVDZ	-15.4	-48.0	-41.6
	aug-cc-pVDZ	-9.9	-20.9	-33.9

Normal Distributions of Errors for Magnetizabilities



- Normal distributions of magnetizability errors for 27 molecules in the aug-cc-pCVQZ basis relative to CCSD(T)/aug-cc-pCV[TQ]Z values (Lutnæs *et al.*, JCP **131**, 144104 (2009))

Mean Absolute Errors for Magnetizabilities



- Mean relative errors (MREs, %) in magnetizabilities of 27 molecules relative to the CCSD(T)/aug-cc-pCV[TQ]Z values. The DFT results are grouped by functional type. The heights of the bars correspond to the largest MRE in each category. (Lutnæs *et al.*, JCP **131**, 144104 (2009))

Section 5

High-Resolution NMR Spectra

High-Resolution NMR Spin Hamiltonian

- Consider a molecule in an external magnetic field B along the z axis and with nuclear spins $\mathbf{I}_K$ related to the nuclear magnetic moments $\mathbf{M}_K$ as:

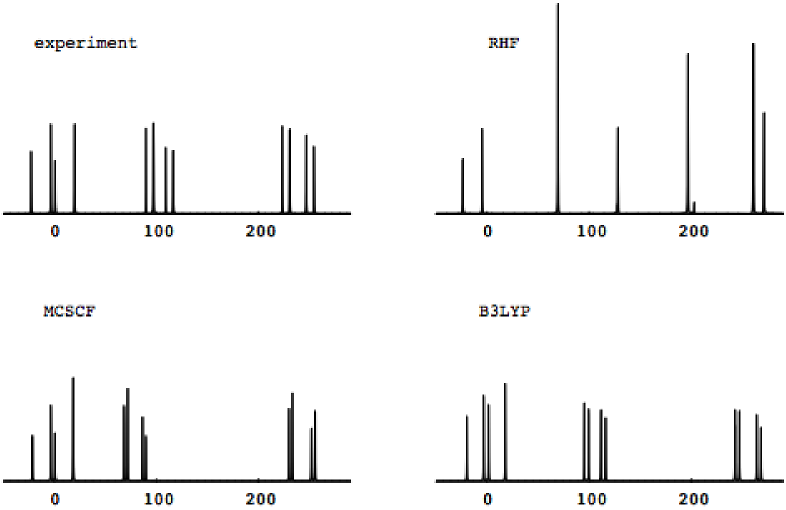
  $$\mathbf{M}_K = \gamma_K \hbar \mathbf{I}_K \approx 10^{-4}\ \text{a.u.}$$

  where γ_K is the magnetogyric ratio of the nucleus.
- Assuming free molecular rotation, the nuclear magnetic energy levels can be reproduced by the following high-resolution NMR spin Hamiltonian:

  $$H_{\text{NMR}} = \underbrace{-\sum_K \gamma_K \hbar (1 - \sigma_K) B I_{K_z}}_{\text{nuclear Zeeman interaction}} + \underbrace{\sum_{K>L} \gamma_K \gamma_L \hbar^2 K_{KL} \mathbf{I}_K \cdot \mathbf{I}_L}_{\text{nuclear spin–spin interaction}}$$

  where we have introduced
  - the nuclear shielding constants σ_K
  - the (reduced) indirect nuclear spin–spin coupling constants K_{KL}
- This is an effective nuclear spin Hamiltonian:
  - it reproduces NMR spectra without considering the electrons explicitly
  - the spin parameters σ_K and K_{KL} are adjusted to fit the observed spectra
  - we shall consider their evaluation from molecular electronic-structure theory

Simulated 200 MHz NMR spectra of Vinyllithium $^{12}C_2H_3{}^6Li$



Section 6

NMR Shielding Constants

Nuclear Shielding Constants

- Expansion of closed-shell energy in an external field $\mathbf{B}$ and nuclear magnetic moments $\mathbf{M}_K$:

$$E\left(\mathbf{B},\mathbf{M}\right) = E_0 + \frac{1}{2}\mathbf{B}^{\mathrm{T}}\mathbf{E}^{(20)}\mathbf{B} + \frac{1}{2}\sum_K \mathbf{B}^{\mathrm{T}}\mathbf{E}_K^{(11)}\mathbf{M}_K + \frac{1}{2}\sum_{KL}\mathbf{M}_K^{\mathrm{T}}\mathbf{E}_{KL}^{(02)}\mathbf{M}_L + \cdots$$

- Here $\mathbf{E}_K^{(11)}$ describes the coupling between the applied field and the nuclear moments:
  - in the absence of electrons (i.e., in vacuum), this coupling is identical to $-\mathbf{I}_3$:

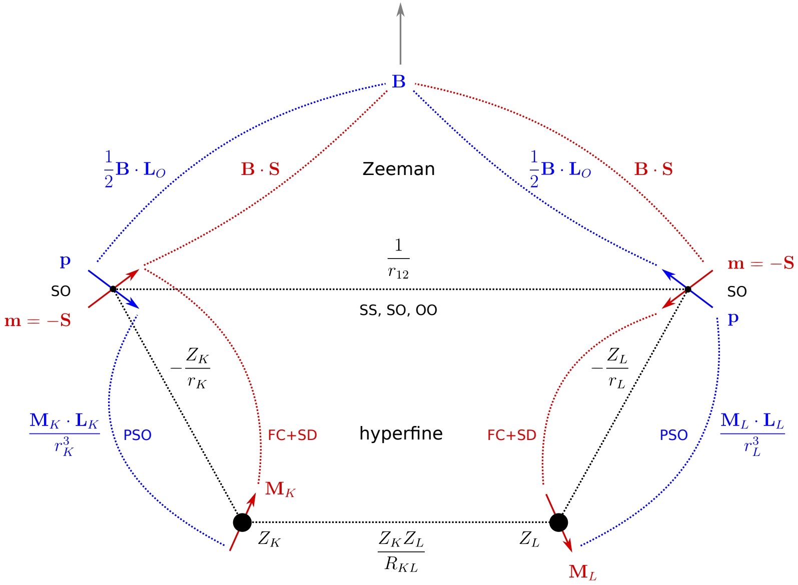
$$H_{\mathrm{z}}^{\mathrm{nuc}} = -\mathbf{B}\cdot\sum_K \mathbf{M}_K \quad \leftarrow \text{the purely nuclear Zeeman interaction}$$

  - in the presence of electrons (i.e., in a molecule), the coupling is modified slightly:

$$\mathbf{E}_K^{(11)} = -\mathbf{I}_3 + \boldsymbol{\sigma}_K \quad \leftarrow \text{the nuclear shielding tensor}$$

- Shielding constants arise from a hyperfine interaction between the electrons and the nuclei and Zeeman interaction between the electrons and the field
  - they are of the order of $\alpha^2 \approx 5\cdot 10^{-5}$ and are measured in ppm
- The nuclear Zeeman interaction does not enter the electronic problem
  - compare with the nuclear–nuclear Coulomb repulsion

Zeeman and Hyperfine Interactions



Ramsey's Expression for Nuclear Shielding Tensors

- Ramsey's expression for nuclear shielding tensors of a closed-shell system:

$$\boldsymbol{\sigma}_K = \frac{\mathrm{d}^2 E_{\mathrm{el}}}{\mathrm{d}\mathbf{B}\mathrm{d}\mathbf{M}_K} = \left\langle 0 \left| \frac{\partial^2 H}{\partial \mathbf{B} \partial \mathbf{M}_K} \right| 0 \right\rangle - 2 \sum_n \frac{\left\langle 0 \left| \frac{\partial H}{\partial \mathbf{B}} \right| n \right\rangle \left\langle n \left| \frac{\partial H}{\partial \mathbf{M}_K} \right| 0 \right\rangle}{E_n - E_0}$$

$$= \underbrace{\frac{\alpha^2}{2} \left\langle 0 \left| \frac{\mathbf{r}_O^{\mathrm{T}} \mathbf{r}_K \mathbf{I}_3 - \mathbf{r}_O \mathbf{r}_K^{\mathrm{T}}}{r_K^3} \right| 0 \right\rangle}_{\text{diamagnetic term}} \underbrace{- \alpha^2 \sum_n \frac{\left\langle 0 \left| \mathbf{L}_O \right| n \right\rangle \left\langle n \left| r_K^{-3} \mathbf{L}_K^{\mathrm{T}} \right| 0 \right\rangle}{E_n - E_0}}_{\text{paramagnetic term}}$$

- The (usually) dominant diamagnetic term arises from differentiation of the operator:

$$\mathbf{A}_O \cdot \mathbf{A}_K = \frac{1}{2} \alpha^2 r_K^{-3} (\mathbf{B} \times \mathbf{r}_O) \cdot (\mathbf{M}_K \times \mathbf{r}_K)$$

- As for the magnetizability, there is no spin contribution for singlet states:

$$\mathbf{S} \left| 0 \right\rangle \equiv 0 \quad \leftarrow \text{singlet state}$$

- For ^{1}S systems (closed-shell atoms), the paramagnetic term vanishes completely and the shielding is given by (assuming gauge origin at the nucleus):

$$\sigma_{\mathrm{Lamb}} = \frac{1}{3} \alpha^2 \left\langle {}^1\mathrm{S} \left| r_K^{-1} \right| {}^1\mathrm{S} \right\rangle \quad \leftarrow \text{Lamb formula}$$

Benchmark Calculations of BH Shieldings (ppm)

	$\sigma(^{11}\text{B})$	$\Delta\sigma(^{11}\text{B})$	$\sigma(^{1}\text{H})$	$\Delta\sigma(^{1}\text{H})$
HF	−261.3	690.1	24.21	14.15
MP2	−220.7	629.9	24.12	14.24
CCSD	−166.6	549.4	24.74	13.53
CCSD(T)	−171.5	555.2	24.62	13.69
CCSDT	−171.8	557.3	24.59	13.72
CCSDTQ	−170.1	554.7	24.60	13.70
CISD	−182.4	572.9	24.49	13.87
CISDT	−191.7	587.0	24.35	14.06
CISDTQ	−170.2	554.9	24.60	13.70
FCI	−170.1	554.7	24.60	13.70

- TZP+ basis, $R_{\text{BH}} = 123.24$ pm, all electrons correlated

- J. Gauss and K. Ruud, *Int. J. Quantum Chem.* **S29** (1995) 437
  - M. Kállay and J. Gauss, *J. Chem. Phys.* **120** (2004) 6841

Coupled-Cluster Convergence of Shielding Constants in CO (ppm)

	CCSD	CCSD(T)	CCSDT	CCSDTQ	CCSDTQ5	FCI
$\sigma(^{13}\mathrm{C})$	32.23	35.91	35.66	36.10	36.14	36.15
$\Delta\sigma(^{13}\mathrm{C})$	361.30	356.10	356.47	355.85	355.80	355.79
$\sigma(^{17}\mathrm{O})$	-13.93	-13.03	-13.16	-12.81	-12.91	-12.91
$\Delta\sigma(^{17}\mathrm{O})$	636.01	634.55	634.75	634.22	634.52	634.35

- All calculations in the cc-pVDZ basis and with a frozen core.
- Kállay and Gauss, *J. Chem. Phys.* **120** (2004) 6841.

Calculated and Experimental Shielding Constants (ppm)

		HF	CAS	MP2	CCSD	CCSD(T)	exp.
HF	F	413.6	419.6	424.2	418.1	418.6	410 ± 6 (300K)
	H	28.4	28.5	28.9	29.1	29.2	28.5 ± 0.2 (300K)
H_2O	O	328.1	335.3	346.1	336.9	337.9	323.6 ± 6 (300K)
	H	30.7	30.2	30.7	30.9	30.9	30.05 ± 0.02
NH_3	N	262.3	269.6	276.5	269.7	270.7	264.5
	H	31.7	31.0	31.4	31.6	31.6	31.2 ± 1.0
CH_4	C	194.8	200.4	201.0	198.7	198.9	198.7
	H	31.7	31.2	31.4	31.5	31.6	30.61
F_2	F	-167.9	-136.6	-170.0	-171.1	-186.5	-192.8
N_2	N	-112.4	-53.0	-41.6	-63.9	-58.1	-61.6 ± 0.2 (300K)
CO	C	-25.5	8.2	10.6	0.8	5.6	3.0 ± 0.9 (eq)
	O	-87.7	-38.9	-46.5	-56.0	-52.9	-56.8 ± 6 (eq)

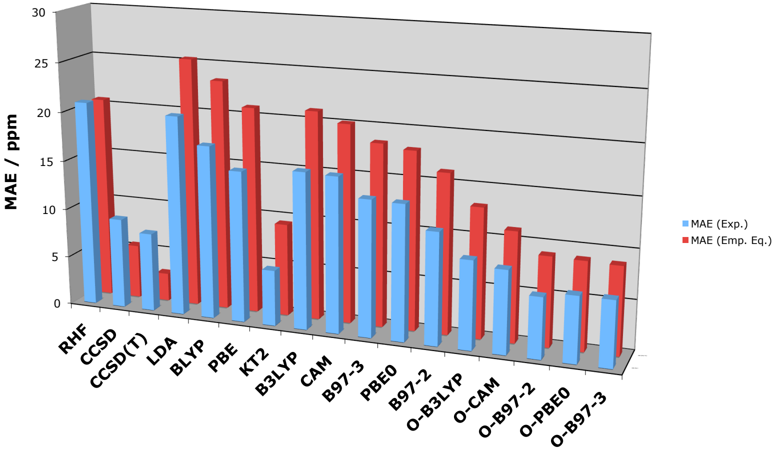
- For references and details, see *Chem. Rev.* **99** (1999) 293.
  - for exp. CO and H_2O values, see Wasylishen and Bryce, JCP 117 (2002) 10061

Kohn–Sham shielding constants (ppm)

		HF	LDA	BLYP	B3LYP	KT2	CCSD(T)	exp.
HF	F	413.6	416.2	401.0	408.1	411.4	418.6	410 ± 6
H_2O	O	328.1	334.8	318.2	325.0	329.5	337.9	323.6 ± 6
NH_3	N	262.3	266.3	254.6	259.2	264.6	270.7	264.5
CH_4	C	194.8	193.1	184.2	188.1	195.1	198.9	198.7
F_2	F	−167.9	−284.2	−336.7	−208.3	−211.0	−186.5	−192.8
N_2	N	−112.4	−91.4	−89.8	−86.4	−59.7	−58.1	−61.6 ± 0.2
CO	C	−25.5	−20.3	−19.3	−17.5	7.4	5.6	3.0 ± 0.9 (eq)
	O	−87.7	−87.5	−85.4	−78.1	−57.1	−52.9	−56.8 ± 6 (eq)

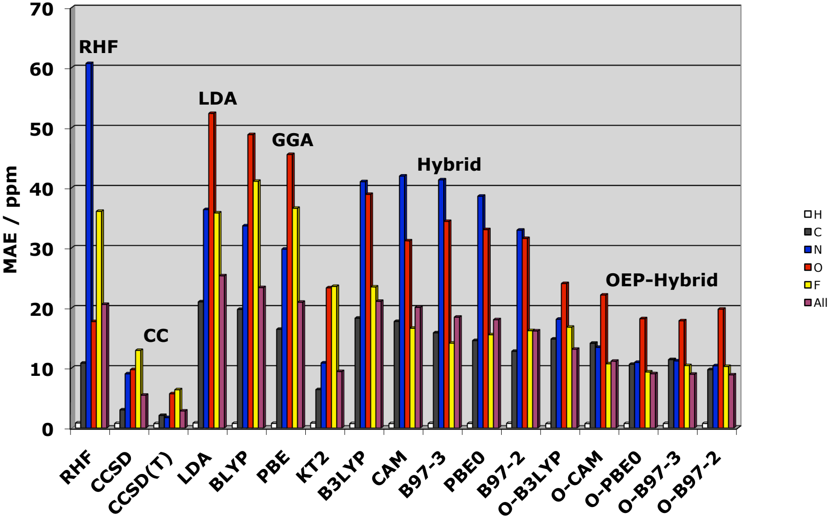
NMR: Mean Absolute Errors Relative to Experiment

- Mean absolute errors relative to experimental (blue) and empirical equilibrium values (red)



- Kohn–Sham calculations give shielding constants of uneven quality
  - errors increase when vibrational corrections are applied
  - Teale *et al.* JCP **138**, 024111 (2013)

Mean absolute NMR shielding errors relative to empirical equilibrium values



- Mean absolute errors (in ppm) for NMR shielding constants relative to empirical equilibrium values for H (white), C (grey), N (blue), O (red), and F (yellow). The total mean absolute errors over all nuclear types are shown by the purple bars. The DFT methodologies are arranged in the categories LDA, GGA, hybrid and OEP-hybrid. (Teal *et al.*, JCP)

Section 7

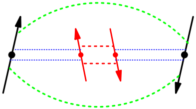
NMR Spin–Spin Coupling Constants

Direct and Indirect Nuclear Spin–Spin Couplings

- The last term in the expansion of the molecular electronic energy in $\mathbf{B}$ and $\mathbf{M}_K$

$$E(\mathbf{B}, \mathbf{M}) = E_0 + \tfrac{1}{2}\mathbf{B}^{\mathrm{T}}\mathbf{E}^{(20)}\mathbf{B} + \tfrac{1}{2}\sum\nolimits_K \mathbf{B}^{\mathrm{T}}\mathbf{E}_K^{(11)}\mathbf{M}_K + \tfrac{1}{2}\sum\nolimits_{KL} \mathbf{M}_K^{\mathrm{T}}\mathbf{E}_{KL}^{(02)}\mathbf{M}_L + \cdots$$

  describes the coupling of the nuclear magnetic moments in the presence of electrons
- There are two distinct contributions to the coupling: the direct and indirect contributions



$$\mathbf{E}_{KL}^{(02)} = \mathbf{D}_{KL} + \mathbf{K}_{KL}$$

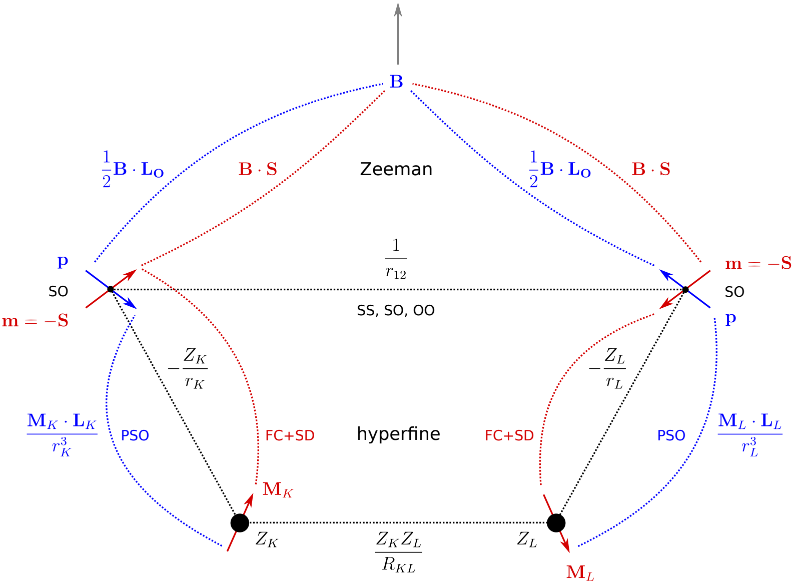
- The direct coupling occurs by a classical dipole mechanism:

$$\mathbf{D}_{KL} = \alpha^2 R_{KL}^{-5}\left(R_{KL}^2\mathbf{I}_3 - 3\mathbf{R}_{KL}\mathbf{R}_{KL}^{\mathrm{T}}\right) \sim 10^{-12}\ \text{a.u.}$$

  - it is anisotropic and vanishes in isotropic media such as gases and liquids
- The indirect coupling arises from hyperfine interactions with the surrounding electrons:
  - it is exceedingly small: $\mathbf{K}_{KL} \sim 10^{-16}$ a.u. $\sim$ 1 Hz
  - it does not vanish in isotropic media
  - it gives the fine structure of high-resolution NMR spectra
- Experimentalists usually work in terms of the (nonreduced) spin–spin couplings

$$\mathbf{J}_{KL} = h\frac{\gamma_K}{2\pi}\frac{\gamma_L}{2\pi}\mathbf{K}_{KL} \quad \leftarrow \text{isotope dependent}$$

Zeeman and Hyperfine Interactions



Ramsey's Expression for Indirect Nuclear Spin–Spin Coupling Tensors

- The indirect nuclear spin–spin coupling tensors of a closed-shell system are given by:

$$\mathbf{K}_{KL} = \frac{\mathrm{d}^2 E_{\mathrm{el}}}{\mathrm{d}\mathbf{M}_K \mathrm{d}\mathbf{M}_L} = \left\langle 0 \middle| \frac{\partial^2 H}{\partial \mathbf{M}_K \partial \mathbf{M}_L} \middle| 0 \right\rangle - 2 \sum_n \frac{\left\langle 0 \middle| \frac{\partial H}{\partial \mathbf{M}_K} \middle| n \right\rangle \left\langle n \middle| \frac{\partial H}{\partial \mathbf{M}_L} \middle| 0 \right\rangle}{E_n - E_0}$$

- Carrying out the differentiation of the Hamiltonian, we obtain Ramsey's expression:

$$\mathbf{K}_{KL} = \underbrace{\alpha^4 \left\langle 0 \middle| \frac{\mathbf{r}_K^{\mathrm{T}} \mathbf{r}_L \mathbf{I}_3 - \mathbf{r}_K \mathbf{r}_L^{\mathrm{T}}}{r_K^3 r_L^3} \middle| 0 \right\rangle}_{\text{diamagnetic spin–orbit (DSO)}} - \underbrace{2\alpha^4 \sum_n \frac{\left\langle 0 \middle| r_K^{-3} \mathbf{L}_K \middle| n \right\rangle \left\langle n \middle| r_L^{-3} \mathbf{L}_L^{\mathrm{T}} \middle| 0 \right\rangle}{E_n - E_0}}_{\text{paramagnetic spin–orbit (PSO)}}$$

$$\underbrace{- 2\alpha^4 \sum_n \frac{\left\langle 0 \middle| \frac{8\pi}{3} \delta(\mathbf{r}_K) \mathbf{s} + \frac{3\mathbf{r}_K \mathbf{r}_K^{\mathrm{T}} - r_K^2 \mathbf{I}_3}{r_K^5} \mathbf{s} \middle| n \right\rangle \left\langle n \middle| \frac{8\pi}{3} \delta(\mathbf{r}_L) \mathbf{s}^{\mathrm{T}} + \frac{3\mathbf{r}_L \mathbf{r}_L^{\mathrm{T}} - r_L^2 \mathbf{I}_3}{r_L^5} \mathbf{s}^{\mathrm{T}} \middle| 0 \right\rangle}{E_n - E_0}}_{\text{Fermi contact (FC) and spin–dipole (SD)}}$$

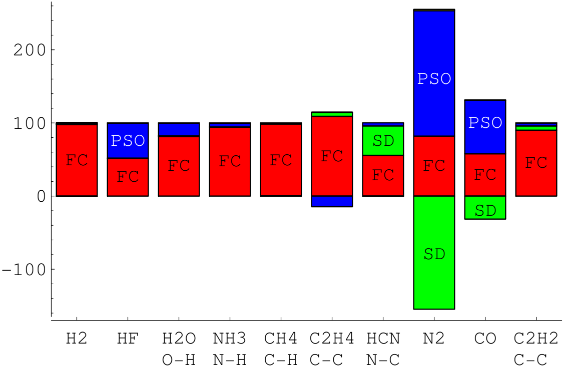
  - the isotropic FC/FC term often dominates short-range coupling constants
  - the FC/SD and SD/FC terms often dominate the anisotropic part of $\mathbf{K}_{KL}$
  - the orbital contributions (especially DSO) are usually but not invariably small
  - for large internuclear separations, the DSO and PSO contributions cancel

Relative Importance of Contributions to Spin–Spin Coupling Constants

- The isotropic indirect spin–spin coupling constants can be uniquely decomposed as:

$$\mathbf{J}_{KL} = \mathbf{J}_{KL}^{\mathrm{DSO}} + \mathbf{J}_{KL}^{\mathrm{PSO}} + \mathbf{J}_{KL}^{\mathrm{FC}} + \mathbf{J}_{KL}^{\mathrm{SD}}$$

- 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 *a priori* neglected (N_2 and CO)!

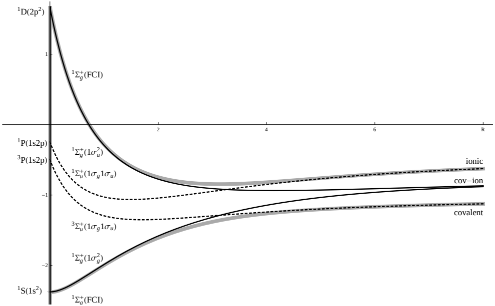


Calculation of Indirect Nuclear Spin–Spin Coupling Constants

- The calculation of spin–spin coupling constants is a challenging task
- Spin–spin coupling constants depend on many coupling mechanisms:
  - 3 singlet response equations and 7 triplet equations for each nucleus
  - for shieldings, only 3 equations are required, for molecules of all sizes
- Spin–spin coupling constants require a proper description of static correlation
  - the Hartree–Fock model fails abysmally
  - MCSCF theory treats static correlation properly but is expensive
- Spin–spin couplings are sensitive to the basis set
  - the FC contribution requires an accurate electron density at the nuclei
  - steep s functions must be included in the basis
- Spin–spin couplings are sensitive to the molecular geometry
  - equilibrium structures must be chosen carefully
  - large vibrational corrections (often 5%–10%)
- For heavy elements, a relativistic treatment may be necessary.
- However, there is no need for London orbitals since no external magnetic field is involved.

Restricted Hartree–Fock Theory and Triplet Instabilities

- The correct description of triplet excitations is important for spin–spin coupling constants
- In restricted Hartree–Fock (RHF) theory, triplet excitations are often poorly described
  - upon H_2 dissociation, RHF does not describe the singlet ground state correctly
  - but the lowest triplet state dissociates correctly, leading to triplet instabilities



- Near such instabilities, the RHF description of spin interactions becomes unphysical

C_2H_4/Hz	$^1J_{CC}$	$^1J_{CH}$	$^2J_{CH}$	$^2J_{HH}$	$^3J_{cis}$	$^3J_{trans}$
exp.	68	156	−2	2	12	19
RHF	1270	755	−572	−344	360	400
CAS	76	156	−6	−2	12	18
B3LYP	75	165	−1	3	14	21

Reduced Spin–Spin Coupling Constants by Wave-Function Theory

		RHF	CAS	RAS	SOPPA	CCSD	CC3	exp*	vib
HF	$^1K_{HF}$	59.2	48.0	48.1	46.8	46.1	46.1	47.6	−3.4
CO	$^1K_{CO}$	13.4	−28.1	−39.3	−45.4	−38.3	−37.3	−38.3	−1.7
N_2	$^1K_{NN}$	175.0	−5.7	−9.1	−23.9	−20.4	−20.4	−19.3	−1.1
H_2O	$^1K_{OH}$	63.7	51.5	47.1	49.5	48.4	48.2	52.8	−3.3
	$^2K_{HH}$	−1.9	−0.8	−0.6	−0.7	−0.6	−0.6	−0.7	0.1
NH_3	$^1K_{NH}$	61.4	48.7	50.2	51.0	48.1		50.8	−0.3
	$^2K_{HH}$	−1.9	−0.8	−0.9	−0.9	−1.0		−0.9	0.1
C_2H_4	$^1K_{CC}$	1672.0	99.6	90.5	92.5	92.3		87.8	1.2
	$^1K_{CH}$	249.7	51.5	50.2	52.0	50.7		50.0	1.7
	$^2K_{CH}$	−189.3	−1.9	−0.5	−1.0	−1.0		−0.4	−0.4
	$^2K_{HH}$	−28.7	−0.2	0.1	0.1	0.0		0.2	0.0
	$^3K_{cis}$	30.0	1.0	1.0	1.0	1.0		0.9	0.1
	$^3K_{tns}$	33.3	1.5	1.5	1.5	1.5		1.4	0.2
$\lvert\bar{\Delta}\rvert$	abs.	180.3	3.3	1.6	1.8	1.2	1.6	*at R_e	
	%	5709	60	14	24	23	6		

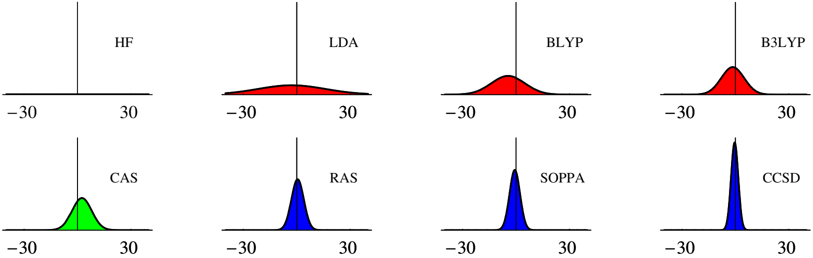
- SOPPA: second-order polarization-propagator approximation

Reduced spin–spin coupling constants by density-functional theory

		LDA	BLYP	B3LYP	PBE	B97-3	RAS	exp*	vib
HF	${}^1K_{\mathrm{HF}}$	35.0	34.5	38.9	32.6	40.5	48.1	47.6	−3.4
CO	${}^1K_{\mathrm{CO}}$	−65.4	−55.7	−47.4	−62.0	−43.4	−39.3	−38.3	−1.7
N_2	${}^1K_{\mathrm{NN}}$	32.9	−46.6	−20.4	−43.2	−12.5	−9.1	−19.3	−1.1
H_2O	${}^1K_{\mathrm{OH}}$	40.3	44.6	47.2	41.2	46.3	47.1	52.8	−3.3
	${}^2K_{\mathrm{HH}}$	−0.3	−0.9	−0.7	−0.5	−0.6	−0.6	−0.7	0.1
NH_3	${}^1K_{\mathrm{NH}}$	41.0	49.6	52.3	47.0	50.1	50.2	50.8	−0.3
	${}^2K_{\mathrm{HH}}$	−0.4	−0.7	−0.9	−0.7	−0.8	−0.9	−0.9	0.1
C_2H_4	${}^1K_{\mathrm{CC}}$	66.6	90.3	96.2	83.4	92.9	90.5	87.8	1.2
	${}^1K_{\mathrm{CH}}$	42.5	55.3	55.0	50.0	51.4	50.2	50.0	1.7
	${}^2K_{\mathrm{CH}}$	0.4	0.0	−0.5	−0.2	−0.3	−0.5	−0.4	−0.4
	${}^2K_{\mathrm{HH}}$	0.4	0.4	0.3	0.3	0.3	0.1	0.2	0.0
	${}^3K_{\mathrm{cis}}$	0.8	1.1	1.1	1.0	1.0	1.0	0.9	0.1
	${}^3K_{\mathrm{tns}}$	1.2	1.7	1.7	1.6	1.5	1.5	1.4	0.2
$\lvert\bar{\Delta}\rvert$	abs.	11.2	5.9	3.1	6.4	2.6	1.6	*at R_e	
	%	72	48	14	33	14	14		

Comparison of Density-Functional and Wave-Function Theory

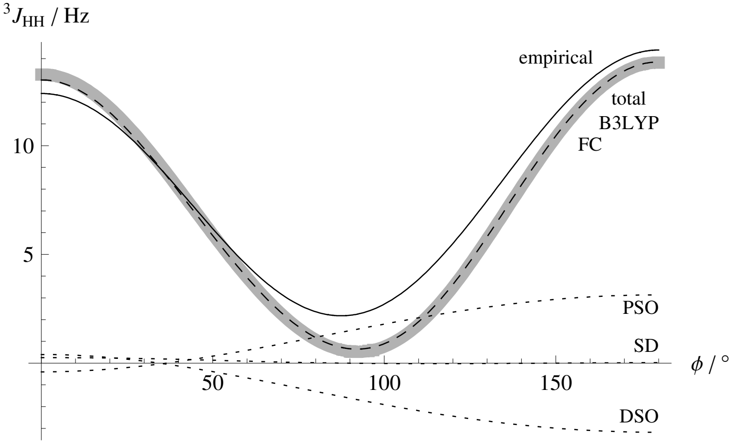
- Normal distributions of errors for indirect nuclear spin–spin coupling constants
  - for the same molecules as on the previous slides



- Some observations:
  - LDA underestimates only slightly, but has a large standard deviation
  - BLYP reduces the LDA errors by a factor of two
  - B3LYP errors are similar to those of CASSCF
  - The CCSD method is slightly better than the SOPPA method

The Karplus curve

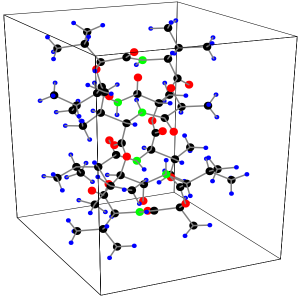
- Vicinal (three-bond) spin–spin coupling constants depend critically on the dihedral angle:
- ${}^3J_{\mathrm{HH}}$ in ethane as a function of the dihedral angle:

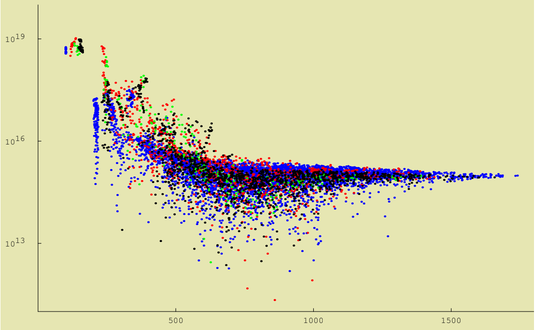


- Good agreement with the (empirically constructed) Karplus curve

Valinomycin $C_{54}H_{90}N_8O_{18}$

- DFT can be applied to large molecular systems such as valinomycin (168 atoms)
  - there are a total of 7587 spin–spin couplings to the carbon atoms in valinomycin
  - below, we have plotted the magnitude of the reduced LDA/6-31G coupling constants on a logarithmic scale, as a function of the internuclear distance:

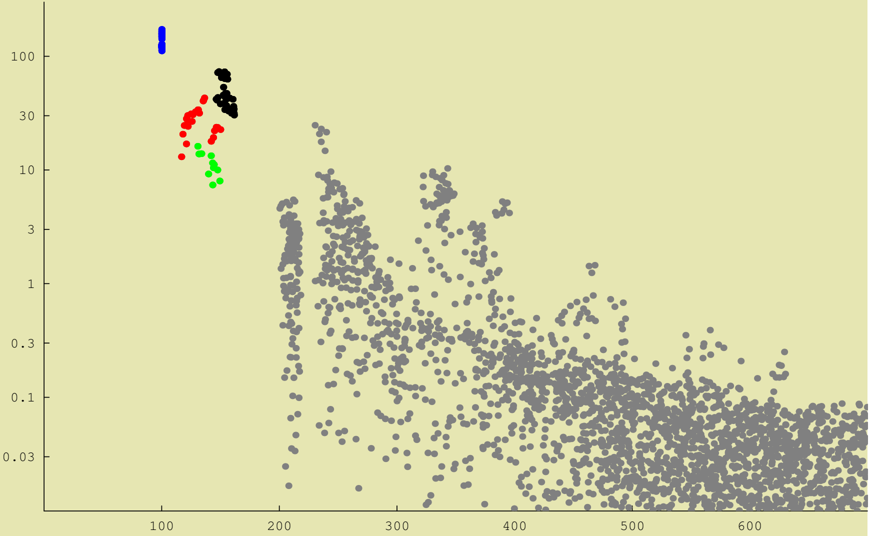




  - the coupling constants decay in characteristic fashion
  - most of the indirect couplings beyond 500 pm are small and cannot be detected

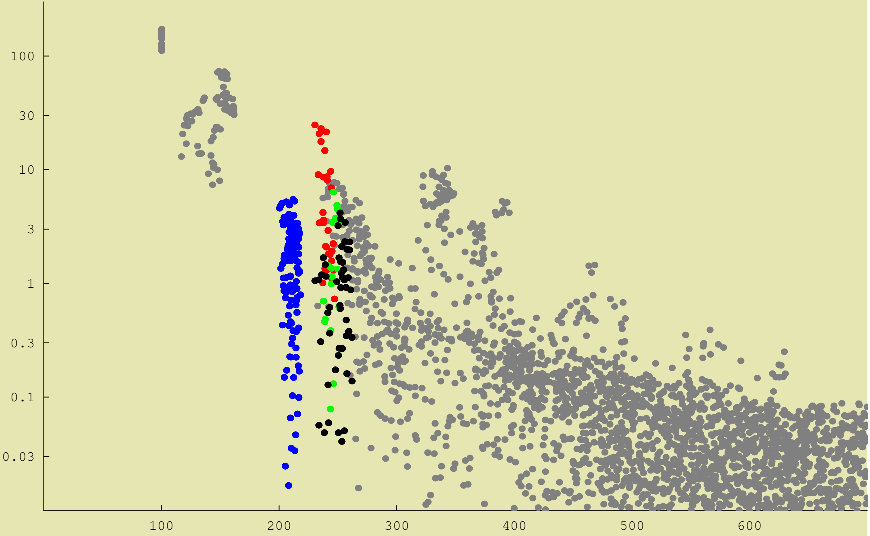
Valinomycin $C_{54}H_{90}N_8O_{18}$

One-bond spin–spin couplings to CH, CO, CN, CC greater than 0.01 Hz



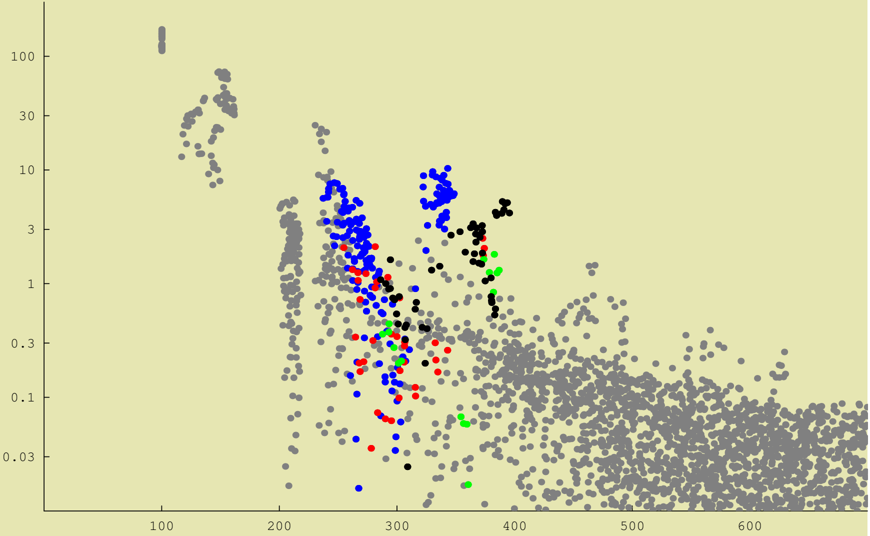
Valinomycin $C_{54}H_{90}N_8O_{18}$

Two-bond spin–spin couplings to CH, CO, CN, CC greater than 0.01 Hz



Valinomycin $C_{54}H_{90}N_8O_{18}$

Three-bond spin–spin couplings to CH, CO, CN, CC greater than 0.01 Hz



Valinomycin $C_{54}H_{90}N_8O_{18}$

Four-bond spin–spin couplings to CH, CO, CN, CC greater than 0.01 Hz