Molecular Magnetic Properties

Trygve Helgaker

Centre for Theoretical and Computational Chemistry
Department of Chemistry, University of Oslo, Norway

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Magnetic perturbations

In atomic units, the molecular Hamiltonian is given by

\[ H = H_0 + \sum_i A_i(r_i) \cdot p_i + \sum_i B_i(r_i) \cdot s_i - \sum_i \phi_i(r_i) + \frac{1}{2} \sum_i A_i^2(r_i) \]

- orbital paramagnetic
- spin paramagnetic
- diamagnetic

There are two kinds of magnetic perturbation operators:
- the paramagnetic operator is linear and may lower or raise the energy
- the diamagnetic operator is quadratic and always raises the energy

There are two kinds of paramagnetic operators:
- the orbital paramagnetic operator couples the field to the electron’s orbital motion
- the spin paramagnetic operator couples the field to the electron’s spin

In the study of magnetic properties, we are interested in two types of perturbations:
- uniform external magnetic field \( B \), with vector potential

\[ A_{\text{ext}}(r) = \frac{1}{2} B \times r \quad \text{leads to Zeeman interactions} \]

- nuclear magnetic moments \( M_K \), with vector potential

\[ A_{\text{nuc}}(r) = \alpha^2 \sum_K \frac{M_K \times r_K}{r_K^3} \quad \text{leads to hyperfine interactions} \]

where \( \alpha \approx 1/137 \) is the fine-structure constant
Part 1: Molecules in an external magnetic field
- Hamiltonian in an external magnetic field
- gauge transformations and London orbitals
- diamagnetism and paramagnetism
- induced currents

Part 2: Magnetic resonance parameters
- Zeeman and hyperfine operators
- magnetizabilities
- nuclear shielding constants
- indirect nuclear spin–spin coupling constants
The nonrelativistic electronic Hamiltonian (implied summation over electrons):

\[ H = H_0 + A(r) \cdot p + B(r) \cdot s + \frac{1}{2} A(r)^2 \]

The vector potential of the uniform (static) fields \( B \) is given by:

\[ B = \nabla \times A = \text{const} \Rightarrow A_0(r) = \frac{1}{2} B \times (r - O) = \frac{1}{2} B \times r_0 \]

note: the gauge origin \( O \) is arbitrary!

The orbital paramagnetic interaction:

\[ A_0(r) \cdot p = \frac{1}{2} B \times (r - O) \cdot p = \frac{1}{2} B \cdot (r - O) \times p = \frac{1}{2} B \cdot L_0 \]

where we have introduced the angular momentum relative to the gauge origin:

\[ L_0 = r_0 \times p \]

The diamagnetic interaction:

\[ \frac{1}{2} A^2(B) = \frac{1}{8} (B \times r_0) \cdot (B \times r_0) = \frac{1}{8} \left[ B^2 r_0^2 - (B \cdot r_0)^2 \right] \]

The electronic Hamiltonian in a uniform magnetic field depends on the gauge origin:

\[ H = H_0 + \frac{1}{2} B \cdot L_0 + B \cdot s + \frac{1}{8} \left[ B^2 r_0^2 - (B \cdot r_0)^2 \right] \]

a change of the origin is a gauge transformation
Gauge transformation of the Schrödinger equation

- What is the effect of a gauge transformation on the wave function?
- Consider a general **gauge transformation** for the electron (atomic units):

\[ A' = A + \nabla f, \quad \phi' = \phi - \frac{\partial f}{\partial t} \]

- It can be shown this represents a **unitary transformation** of \( H - i \partial / \partial t \):

\[
\left( H' - i \frac{\partial}{\partial t} \right) = \exp \left( -i f \right) \left( H - i \frac{\partial}{\partial t} \right) \exp \left( i f \right)
\]

- In order that the Schrödinger equation is still satisfied

\[
\left( H' - i \frac{\partial}{\partial t} \right) \Psi' \Leftrightarrow \left( H - i \frac{\partial}{\partial t} \right) \Psi,
\]

the new wave function must undergo a **compensating unitary transformation**:

\[ \Psi' = \exp \left( -i f \right) \Psi \]

- All **observable properties** such as the electron density are then **unaffected**:

\[
\rho' = (\Psi')^* \Psi' = [\Psi \exp(-i f)]^* [\exp(-i f) \Psi] = \Psi^* \Psi = \rho
\]
Gauge-origin transformations

- Different choices of **gauge origin** in the external vector potential
  \[ A_0 (r) = \frac{1}{2} B \times (r - O) \]

are related by **gauge transformations**:

\[ A_G (r) = A_0 (r) - A_0 (G) = A_0 (r) + \nabla f, \quad f (r) = -A_0 (G) \cdot r \]

- The exact wave function transforms accordingly and gives gauge-invariant results:

  \[
  \psi_G^{\text{exact}} = \exp [-i f (r)] \psi_0^{\text{exact}} = \exp [i A_0 (G) \cdot r] \psi_0^{\text{exact}} \quad \text{rapid oscillations}
  \]

- **Illustration**: \( H_2 \) on the \( z \) axis in a magnetic field \( B = 0.2 \text{ a.u.} \) in the \( y \) direction
  - **wave function** with gauge origin at \( O = (0, 0, 0) \) (left) and \( G = (100, 0, 0) \) (right)

![](image)
The exact wave function transforms in the following manner:

\[ \psi_G^{\text{exact}} = \exp\left[i\frac{1}{2}B \times (G - O) \cdot r\right] \psi_0^{\text{exact}} \]

- this behaviour cannot easily be modelled by standard atomic orbitals

Let us build this behaviour directly into the atomic orbitals:

\[ \omega_{lm}(r_K, B, G) = \exp\left[i\frac{1}{2}B \times (G - K) \cdot r\right] \chi_{lm}(r_K) \]

- \( \chi_{lm}(r_K) \) is a normal atomic orbital centered at \( K \) and quantum numbers \( lm \)
- \( \omega_{lm}(r_K, B, G) \) is a field-dependent orbital at \( K \) with field \( B \) and gauge origin \( G \)

Each AO now responds in a physically sound manner to an applied magnetic field

- indeed, all AOs are now correct to first order in \( B \), for any gauge origin \( G \)
- the calculations become rigorously gauge-origin independent
- uniform (good) quality follows, independent of molecule size

These are the London orbitals after Fritz London (1937)

- also known as GIAOs (gauge-origin independent AOs or gauge-origin including AOs)

Questions:

- are London orbitals needed in atoms?
- why not attach the phase factor to the total wave function instead?
Let us consider the FCI dissociation of $\text{H}_2$ in a magnetic field.

- **Full lines**: London atomic orbitals
- **Dashed lines**: AOs with gauge origin between atoms
- **Dotted lines**: AOs with gauge origin on one of the atoms

Without London orbitals, the FCI method is not size extensive in magnetic fields.
Diamagnetism and paramagnetism

- The Hamiltonian has **paramagnetic** and **diamagnetic** parts:
  \[ H = H_0 + \frac{1}{2} BL_z + Bs_z + \frac{1}{8} B^2(x^2 + y^2) \]
  \( \leftarrow \) linear and quadratic \( B \) terms

- Most closed-shell molecules are **diamagnetic**
  - their energy **increases** in an applied magnetic field
  - induced currents oppose the field according to Lenz's law

- Some closed-shell systems are **paramagnetic**
  - their energy **decreases** in a magnetic field
  - relaxation of the wave function lowers the energy

- RHF calculations of the field-dependence for two closed-shell systems:

  - left: benzene: **diamagnetic dependence** on an out-of-plane field, \( \xi < 0 \)
  - right: BH: **paramagnetic dependence** on a perpendicular field, \( \xi > 0 \)
Transition from para- to diamagnetism

- However, all closed-shell systems become diamagnetic in sufficiently strong fields:

- One atomic unit field strength is $2.2 \times 10^5$ T
  - highest fields created in laboratories is $10^{-3}$ a.u.
- The transition occurs at a characteristic stabilizing critical field strength $B_c$
  - $B_c \approx 0.1$ for $C_{20}$ (ring conformation) above
  - $B_c$ is inversely proportional to the area of the molecule normal to the field
  - $B_c$ should be observable for $C_{72}H_{72}$
Closed-shell paramagnetic molecules

- Ground and (singlet) excited states of BH along the $z$ axis

$$|zz\rangle = |s_B^2\sigma_{BH}^2p_z^2\rangle, \quad |zx\rangle = |s_B^2\sigma_{BH}^2p_zp_x\rangle, \quad |zy\rangle = |s_B^2\sigma_{BH}^2p_zp_y\rangle$$

- All expectation values increase quadratically in a perpendicular field in the $y$ direction:

$$\langle n|H_0 + \frac{1}{2}BL_y + \frac{1}{8}B^2(x^2 + z^2)|n\rangle = E_n + \frac{1}{8}\langle n|x^2 + z^2|n\rangle B^2 = E_n - \frac{1}{2}\chi_n B^2$$

- The $|zz\rangle$ ground state is coupled to the low-lying $|zx\rangle$ excited state by this field:

$$\langle zz|H_0 + \frac{1}{2}BL_y + \frac{1}{8}B^2(x^2 + z^2)|xz\rangle = \frac{1}{2}\langle zz|L_y|xz\rangle B \neq 0$$

- A paramagnetic ground-state with a double minimum is generated by strong coupling
Induced electron rotation

- The magnetic field induces a rotation of the electrons about the field direction:
  - the amount of rotation is the expectation value of the kinetic angular-momentum operator
  \[ \langle 0 | \Lambda | 0 \rangle = 2E'(B), \quad \Lambda = r \times \pi, \quad \pi = p + A \]

- Paramagnetic closed-shell molecules (here BH):

  ![Energy vs. Angular momentum graph]

  - there is no rotation at the field-free energy maximum: \( B = 0 \)
  - the onset of paramagnetic rotation (against the field) reduces the energy for \( B > 0 \)
  - the strongest paramagnetic rotation occurs at the energy inflexion point
  - the rotation comes to a halt at the stabilizing field strength: \( B = B_c \)
  - the onset of diamagnetic rotation (with the field) increases the energy for \( B > B_c \)

- Diamagnetic closed-shell molecules:
  - diamagnetic rotation always increases the energy according to Lenz’s law
Expansion of the molecular energy in a magnetic field

Expand the molecular electronic energy in the external magnetic induction $B$:

$$E(B) = E_0 + B^T E^{(10)} + \frac{1}{2} B^T E^{(20)} B + \cdots$$

The molecular magnetic moment at $B$ is now given by

$$M_{\text{mol}}(B) \overset{\text{def}}{=} -\frac{dE(B)}{dB} = -E^{(10)} - E^{(20)} B + \cdots = M_{\text{perm}} + \xi B + \cdots,$$

where we have introduced the permanent magnetic moment and the magnetizability:

$$M_{\text{perm}} = -E^{(10)} = -\left.\frac{dE}{dB}\right|_{B=0} \quad \leftarrow \text{permanent magnetic moment}$$

describes the first-order change in the energy but vanishes for closed-shell systems

$$\xi = -E^{(20)} = -\left.\frac{d^2E}{dB^2}\right|_{B=0} \quad \leftarrow \text{molecular magnetizability}$$

describes the second-order energy and the first-order induced magnetic moment

First-order energies for imaginary and triplet perturbations vanish for closed-shell systems:

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

Such molecules therefore do not have a permanent magnetic moment.
The magnetizability

- The electronic Hamiltonian in a uniform magnetic field:

\[ H = H_0 + \frac{1}{2} \mathbf{B} \cdot \mathbf{L}_0 + \mathbf{B} \cdot \mathbf{s} + \frac{1}{8} [B^2 r_0^2 - (\mathbf{B} \cdot \mathbf{r}_0)^2] \]

- The molecular magnetizability of a closed-shell system:

\[ \xi = -\frac{\text{d}^2 E}{\text{d}B^2} = \frac{1}{4} \left\langle 0 | \mathbf{r}_0 \mathbf{r}_0^T - \left( \mathbf{r}_0^T \mathbf{r}_0 \right) I_3 | 0 \right\rangle + \frac{1}{2} \sum_n \frac{\langle 0 | \mathbf{L}_0 | n \rangle \langle n | \mathbf{L}_0^T | 0 \rangle}{E_n - E_0} \]

- The isotropic part of the diamagnetic term is given by:

\[ \xi_{\text{dia}} = \frac{1}{3} \text{Tr} \xi_{\text{dia}} = -\frac{1}{6} \left\langle 0 | x_0^2 + y_0^2 + z_0^2 | 0 \right\rangle = -\frac{1}{6} \langle 0 | r_0^2 | 0 \rangle \]

- Only the orbital Zeeman interaction contributions to the paramagnetic term:

\[ \mathbf{S} | 0 \rangle \equiv 0 \quad \leftarrow \text{singlet state} \]

- for \( ^1S \) systems (closed-shell atoms), the paramagnetic term vanishes altogether:

\[ \frac{1}{2} \mathbf{L}_0 | ^1S \rangle \equiv 0 \quad \leftarrow \text{gauge origin at nucleus} \]

- In most (but not all) systems the diamagnetic term dominates:

<table>
<thead>
<tr>
<th>( 10^{-30} \text{ JT}^{-2} )</th>
<th>RHF</th>
<th>exp.</th>
<th>diff.</th>
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</thead>
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<td>( \text{H}_2\text{O} )</td>
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<td>-6.4%</td>
</tr>
<tr>
<td>( \text{NH}_3 )</td>
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<tr>
<td>( \text{PH}_3 )</td>
<td>-441</td>
<td>-435</td>
<td>-1.4%</td>
</tr>
</tbody>
</table>
The $\text{H}_2$ molecule

- Earth magnetism is $10^{-10}$ a.u., whereas NMR uses $10^{-3}$ a.u.
- In stellar atmospheres, much stronger fields exist
- Polar plots of the singlet (left) and triplet (right) energy $E(R, \Theta)$ at $B = 1$ a.u.

- Bond distance $R_e$ (pm), orientation $\Theta_e$ (°), diss. energy $D_e$, and rot. barrier $\Delta E_0$ (kJ/mol)

<table>
<thead>
<tr>
<th></th>
<th>singlet</th>
<th></th>
<th>triplet</th>
<th></th>
</tr>
</thead>
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<td>$\theta_e$</td>
<td>$D_e$</td>
<td>$\Delta E_0$</td>
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<td>0</td>
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</table>
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  - magnetizabilities
  - nuclear shielding constants
  - indirect nuclear spin–spin coupling constants
Magnetic perturbations

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- uniform external magnetic field \( B \), with vector potential
  \[ A_{\text{ext}}(r) = \frac{1}{2} B \times r \quad \text{leads to Zeeman interactions} \]

- nuclear magnetic moments \( M_K \), with vector potential
  \[ A_{\text{nuc}}(r) = \alpha^2 \sum_K \frac{M_K \times r_K}{r_K^3} \quad \text{leads to hyperfine interactions} \]

where \( \alpha \approx 1/137 \) is the fine-structure constant
Perturbation theory

- **The nonrelativistic electronic Hamiltonian:**
  \[ H = H_0 + H^{(1)} + H^{(2)} = H_0 + A(r) \cdot p + B(r) \cdot s + \frac{1}{2} A(r)^2, \quad \mathbf{B}(r) = \nabla \times A(r) \]

- **Second-order Rayleigh–Schrödinger perturbation theory:**
  \[
  E^{(1)} = \langle 0 | A \cdot p + B \cdot s | 0 \rangle \\
  E^{(2)} = \frac{1}{2} \langle 0 | A^2 | 0 \rangle - \sum_n \frac{\langle 0 | A \cdot p + B \cdot s | n \rangle \langle n | A \cdot p + B \cdot s | 0 \rangle}{E_n - E_0}
  \]

- **Zeeman interactions** with uniform external field:
  \[ A(r) = \frac{1}{2} \mathbf{B} \times \mathbf{r}_0 \quad \Rightarrow \quad H^{(1)}_Z = \frac{1}{2} \mathbf{B} \cdot \mathbf{L}_0 + \mathbf{B} \cdot \mathbf{s} \]

- **Hyperfine interactions** with nuclear magnetic moments \(10^{-8}\) a.u.
  \[ A_K(r) = \alpha^2 \frac{\mathbf{M}_K \times \mathbf{r}_K}{r_K^3} \quad \Rightarrow \quad H^{(1)}_{\text{hf}} = \alpha^2 \frac{\mathbf{M}_K \cdot \mathbf{L}_K}{r_K^3} \]

  - **paramagnetic spin–orbit (PSO)**
  - **Fermi contact (FC)**
  - **spin–dipole (SD)**
Zeeman and hyperfine interactions
Taylor expansion of the energy

- Expand the energy in the presence of an external magnetic field \( B \) and nuclear magnetic moments \( M_K \) around zero field and zero moments:

\[
E (B, M) = E_0 + B^T E^{(10)} + \sum_K M_K^T E^{(01)}_K \\
+ \frac{1}{2} B^T E^{(20)} B + \frac{1}{2} \sum_K B^T E^{(11)}_K M_K + \frac{1}{2} \sum_{KL} M_K^T E^{(02)}_{KL} M_L + \cdots
\]

- **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 \( B \) is weak \((\approx 10^{-4} \text{ a.u.})\)
  2) the nuclear magnetic moments \( M_K \) couple weakly \((\mu_0\mu_N \approx 10^{-8} \text{ a.u.})\)
First-order molecular properties

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

- Permanent magnetic moment

$$
M = \langle 0 \left| H^{(1)}_Z \right| 0 \rangle = \langle 0 \left| \frac{1}{2} L_0 + s \right| 0 \rangle
$$

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

- Hyperfine coupling constants

$$
A_K = \langle 0 \left| H^{(1)}_{hf} \right| 0 \rangle = \frac{8\pi\alpha^2}{3} \langle 0 \left| \delta(\mathbf{r}_K)s \right| 0 \rangle \cdot \mathbf{M}_K + 
$$

- measure spin density at the nucleus
- important in electron paramagnetic resonance (EPR)
- recall: there are three hyperfine mechanisms: FC, SD and PSO

$$
H^{(1)}_{hf} = \frac{8\pi\alpha^2}{3} \delta(\mathbf{r}_K) \mathbf{M}_K \cdot \mathbf{s} + \alpha^2 \frac{3(\mathbf{s} \cdot \mathbf{r}_K)(\mathbf{r}_K \cdot \mathbf{M}_K) - (\mathbf{M}_K \cdot \mathbf{s})r_K^2}{r_K^5} + \alpha^2 \frac{\mathbf{M}_K \cdot \mathbf{L}_K}{r_K^3}
$$

- Note: there are no first-order Zeeman or hyperfine couplings for closed-shell molecules

$$
\langle \text{c.c.} \left| \hat{\Omega}_{\text{imaginary}} \right| \text{c.c.} \rangle \equiv \langle \text{c.c.} \left| \hat{\Omega}_{\text{triplet}} \right| \text{c.c.} \rangle \equiv 0
$$
Consider a molecule in an external magnetic field $B$ along the $z$ axis and with nuclear spins $I_K$ related to the nuclear magnetic moments $M_K$ as:

$$M_K = \gamma_K \hbar I_K \approx 10^{-4} \text{ a.u.}$$

where $\gamma_K$ 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:

$$H_{\text{NMR}} = -\sum_K \gamma_K \hbar (1 - \sigma_K) B I_K z + \sum_{K>L} \gamma_K \gamma_L \hbar^2 K_{KL} I_K \cdot I_L$$

where we have introduced

- the nuclear shielding constants $\sigma_K$
- 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 $\sigma_K$ 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 $^{12}\text{C}_2\text{H}_3^6\text{Li}$

- Experiment
- RHF
- MCSCF
- B3LYP
Expansion of closed-shell energy in an external field $\mathbf{B}$ and nuclear magnetic moments $\mathbf{M}_K$:

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

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 $-I_3$:

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

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

$$ E_K^{(11)} = -I_3 + \sigma_K \quad \leftarrow \text{the nuclear shielding tensor} $$

Shielding constants arise from a hyperfine interaction between the electrons and the nuclei

- 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

Diagram:

- Zeeman
- Hyperfine

Equations and symbols:

- $B \cdot \hat{s}$
- $\frac{1}{r^2}$
- $\frac{Z_K Z_L}{R_{KL}}$
- $M_K$
- $Z_K$
- $Z_L$
- $M_L$
- $\vec{m} = -\hat{s}$
- $\vec{m} = -\hat{s}$
- $PSO$
- $\frac{M_K \cdot \vec{b}_K}{\Gamma_K}$

Notations:

- SO
- FC + SD

Context:

- 12th Sostrup Summer School (2012)
- Trygve Helgaker (CTCC, University of Oslo)
- Molecular Magnetic Properties
Ramsey’s expression for the nuclear shielding tensors

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

\[
\sigma_K = \frac{d^2E_{el}}{dB dM_K} = \left\langle 0 \left| \frac{\partial^2 H}{\partial B \partial M_K} \right| 0 \right\rangle - 2 \sum_n \frac{\left\langle 0 \left| \frac{\partial H}{\partial B} \right| n \right\rangle \left\langle n \left| \frac{\partial H}{\partial M_K} \right| 0 \right\rangle}{E_n - E_0}
\]

\[
= \frac{\alpha^2}{2} \left\langle 0 \left| r_0^T r_K l_3 - r_0 r_K^T \right| 0 \right\rangle - \alpha^2 \sum_n \frac{\left\langle 0 \left| L_0 \right| n \right\rangle \left\langle n \left| r_K^{-3} L_K^T \right| 0 \right\rangle}{E_n - E_0}
\]

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

\[
A(B) \cdot A(M_K) = \frac{1}{2} \alpha^2 r_K^{-3} (B \times r_0) \cdot (M_K \times r_K)
\]

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

\[
S |0\rangle \equiv 0 \quad \leftarrow \text{singlet state}
\]

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

\[
\sigma_{\text{Lamb}} = \frac{1}{3} \alpha^2 \left\langle 1S \left| r_K^{-1} \right| 1S \right\rangle \quad \leftarrow \text{Lamb formula}
\]
## Benchmark calculations of BH shieldings (ppm)

<table>
<thead>
<tr>
<th>Method</th>
<th>$\sigma^{(11\text{B})}$</th>
<th>$\Delta\sigma^{(11\text{B})}$</th>
<th>$\sigma^{(1\text{H})}$</th>
<th>$\Delta\sigma^{(1\text{H})}$</th>
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<tr>
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<tr>
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- TZP+ basis, $R_{\text{BH}} = 123.24$ pm, all electrons correlated
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For references and details, see *Chem. Rev.* **99** (1999) 293.

- for exp. CO and H₂O values, see Wasylishen and Bryce, *JCP* **117** (2002) 10061
Kohn–Sham shielding constants (ppm)

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Direct and indirect nuclear spin–spin couplings

The last term in the expansion of the molecular electronic energy in $B$ and $M_K$

$$E (B, M) = E_0 + \frac{1}{2} B^T E^{(20)} B + \frac{1}{2} \sum_K B^T E^{(11)}_K M_K + \frac{1}{2} \sum_{KL} M_K^T E^{(02)}_{KL} M_L + \cdots$$

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

$$E^{(02)}_{KL} = D_{KL} + K_{KL}$$

The direct coupling occurs by a classical dipole mechanism:

$$D_{KL} = \alpha^2 R_{KL}^5 \left( R_{KL}^2 I_3 - 3 R_{KL} R_{KL}^T \right) \approx 10^{-12} \text{ a.u.}$$

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

$$J_{KL} = h \frac{\gamma_K}{2\pi} \frac{\gamma_L}{2\pi} K_{KL}$$ ← isotope dependent
Zeeman and hyperfine interactions

\[ \mathbf{B} \cdot \mathbf{s} \]

\[ \mathbf{m} = -\mathbf{s} \]

\[ \frac{1}{\mu_2} \]

\[ SS, SO, OO \]

\[ \mathbf{FC} + \mathbf{SD} \]

\[ \frac{Z_k Z_L}{R_{KL}} \]

\[ \mathbf{M}_k, \mathbf{M}_L \]

\[ \mathbf{P}_k, \mathbf{P}_L \]

\[ \mathbf{s}_0 \]
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:

\[ K_{KL} = \frac{d^2 E_{el}}{dM_K dM_L} = \left\langle 0 \left| \frac{\partial^2 H}{\partial M_K \partial M_L} \right| 0 \right\rangle - 2 \sum_n \frac{\left\langle 0 \left| \frac{\partial H}{\partial M_K} \right| n \right\rangle \left\langle n \left| \frac{\partial H}{\partial M_L} \right| 0 \right\rangle}{E_n - E_0} \]

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

\[ K_{KL} = \alpha^4 \left[ \left\langle 0 \left| \frac{\partial^4 H}{\partial M_K \partial M_L \partial M_L} \right| 0 \right\rangle - 2 \sum_n \frac{\left\langle 0 \left| \frac{\partial^3 H}{\partial M_K \partial M_L^2} \right| n \right\rangle \left\langle n \left| \frac{\partial H}{\partial M_L} \right| 0 \right\rangle}{E_n - E_0} \right] \]

- **Diamagnetic spin–orbit (DSO)**

\[ \left\langle 0 \left| \frac{\partial^4 H}{\partial M_K \partial M_L \partial M_L} \right| 0 \right\rangle \]

- **Paramagnetic spin–orbit (PSO)**

\[ \left\langle 0 \left| \frac{\partial^3 H}{\partial M_K \partial M_L^2} \right| n \right\rangle \]

\[ \sum_n \frac{\left\langle n \left| \frac{\partial H}{\partial M_L} \right| 0 \right\rangle}{E_n - E_0} \]

\[ \sum_n \frac{\left\langle n \left| \frac{\partial H}{\partial M_L} \right| 0 \right\rangle}{E_n - E_0} \]

- **Fermi contact (FC) and spin–dipole (SD)**

\[ \left\langle 0 \left| \frac{\partial^4 H}{\partial M_K \partial M_L \partial M_L} \right| 0 \right\rangle \]

\[ \sum_n \frac{\left\langle n \left| \frac{\partial H}{\partial M_L} \right| 0 \right\rangle}{E_n - E_0} \]

» the isotropic FC/FC term often dominates short-range coupling constants

» the FC/SD and SD/FC terms often dominate the anisotropic part of \( K_{KL} \)

» the orbital contributions (especially DSO) are usually but not invariably small

» for large internuclear separations, the DSO and PSO contributions cancel
Relative importance of the contributions to spin–spin coupling constants

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

\[ J_{KL} = J_{DSO}^{KL} + J_{PSO}^{KL} + J_{FC}^{KL} + J_{SD}^{KL} \]

- 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 \emph{a priori} neglected (N\textsubscript{2} and CO)!

![Diagram showing the contribution of different terms to the spin–spin coupling constants for various molecules.](image-url)
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.
  - more generally, the lowest RHF triplet excitations are underestimated.

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

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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.
Reduced spin–spin coupling constants by wave-function theory

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* at $R_e$

**SOPPA:** second-order polarization-propagator approximation
### Reduced spin–spin coupling constants by density-functional theory

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<td>C$_2$H$_4$</td>
<td>$1K_{CC}$</td>
<td>66.6</td>
<td>90.3</td>
<td>96.2</td>
<td>83.4</td>
<td>92.9</td>
<td>90.5</td>
<td>87.8</td>
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<tr>
<td></td>
<td>$1K_{CH}$</td>
<td>42.5</td>
<td>55.3</td>
<td>55.0</td>
<td>50.0</td>
<td>51.4</td>
<td>50.2</td>
<td>50.0</td>
</tr>
<tr>
<td></td>
<td>$2K_{CH}$</td>
<td>0.4</td>
<td>0.0</td>
<td>−0.5</td>
<td>−0.2</td>
<td>−0.3</td>
<td>−0.5</td>
<td>−0.4</td>
</tr>
<tr>
<td></td>
<td>$2K_{HH}$</td>
<td>0.4</td>
<td>0.4</td>
<td>0.3</td>
<td>0.3</td>
<td>0.3</td>
<td>0.1</td>
<td>0.2</td>
</tr>
<tr>
<td></td>
<td>$3K_{cis}$</td>
<td>0.8</td>
<td>1.1</td>
<td>1.1</td>
<td>1.0</td>
<td>1.0</td>
<td>1.0</td>
<td>0.9</td>
</tr>
<tr>
<td></td>
<td>$3K_{tans}$</td>
<td>1.2</td>
<td>1.7</td>
<td>1.7</td>
<td>1.6</td>
<td>1.5</td>
<td>1.5</td>
<td>1.4</td>
</tr>
</tbody>
</table>

| $|\Delta|$ | abs. | 11.2 | 5.9  | 3.1  | 6.4  | 2.6  | 1.6  | * at Re |
|------|------|------|------|------|------|------|------|--------|
| %    | 72   | 48   | 14   | 33   | 14   | 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:
- $^{3}J_{HH}$ in ethane as a function of the dihedral angle:

![Graph showing the comparison between DFT and empirical values of $^{3}J_{HH}$ in ethane, with good agreement with the Karplus curve.]

- Good agreement with the (empirically constructed) Karplus curve
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, which we shall examine
- most of the indirect couplings beyond 500 pm are small and cannot be detected
Valinomycin $\text{C}_{54}\text{H}_{90}\text{N}_8\text{O}_{18}$

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

Trygve Helgaker (CTCC, University of Oslo)
Molecular Magnetic Properties
12th Sostrup Summer School (2012) 41 / 44
Valinomycin $\text{C}_{54}\text{H}_{90}\text{N}_{8}\text{O}_{18}$

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

Trygve Helgaker (CTCC, University of Oslo)
Valinomycin $\text{C}_{54}\text{H}_{90}\text{N}_{8}\text{O}_{18}$

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