

Molecular Magnetic Properties

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Magnetic perturbations

- In atomic units, the molecular Hamiltonian is given by

$$H = H_0 + \underbrace{\sum_i \mathbf{A}_i(\mathbf{r}_i) \cdot \mathbf{p}_i}_{\text{orbital paramagnetic}} + \underbrace{\sum_i \mathbf{B}_i(\mathbf{r}_i) \cdot \mathbf{s}_i}_{\text{spin paramagnetic}} - \sum_i \phi_i(\mathbf{r}_i) + \underbrace{\frac{1}{2} \sum_i A_i^2(\mathbf{r}_i)}_{\text{diamagnetic}}$$

- In the study of magnetic properties, we are interested in the following two types of perturbations:

- uniform external magnetic field \mathbf{B} , with vector potential

$$\mathbf{A}_{\text{ext}}(\mathbf{r}) = \frac{1}{2} \mathbf{B} \times \mathbf{r} \quad \text{leads to Zeeman interactions}$$

- nuclear magnetic moments \mathbf{M}_K , with vector potential

$$\mathbf{A}_{\text{nuc}}(\mathbf{r}) = \alpha^2 \sum_K \frac{\mathbf{M}_K \times \mathbf{r}_K}{r_K^3} \quad \text{leads to hyperfine interactions}$$

where $\alpha \approx 1/137$ is the fine-structure constant

- in both cases, we may set $\phi = 0$

- In the following, we shall consider each of these perturbations in turn.

Zeeman interactions

- The scalar and vector potentials of the uniform (static) fields \mathbf{E} and \mathbf{B} are given by:

$$\left. \begin{aligned} \mathbf{E} &= -\nabla\phi - \frac{\partial\mathbf{A}}{\partial t} = \text{const} \\ \mathbf{B} &= \nabla \times \mathbf{A} = \text{const} \end{aligned} \right\} \Rightarrow \begin{cases} \phi(\mathbf{r}) = -\mathbf{E} \cdot \mathbf{r} \\ \mathbf{A}(\mathbf{r}) = \frac{1}{2}\mathbf{B} \times \mathbf{r} \end{cases}$$

- Interaction with the electrostatic field:

$$-\sum_i \phi(\mathbf{r}_i) = \mathbf{E} \cdot \sum_i \mathbf{r}_i = -\mathbf{E} \cdot \mathbf{d}_e, \quad \mathbf{d}_e = -\sum_i \mathbf{r}_i \quad \leftarrow \text{electric dipole operator}$$

- Orbital paramagnetic interaction with the magnetostatic field:

$$\sum_i \mathbf{A} \cdot \mathbf{p}_i = \frac{1}{2} \sum_i \mathbf{B} \times \mathbf{r}_i \cdot \mathbf{p}_i = \frac{1}{2} \mathbf{B} \cdot \mathbf{L}, \quad \mathbf{L} = \sum_i \mathbf{r}_i \times \mathbf{p}_i \quad \leftarrow \text{orbital ang. mom. op.}$$

- Spin paramagnetic interaction with the magnetostatic field:

$$\sum_i \mathbf{B} \cdot \mathbf{s}_i = \mathbf{B} \cdot \mathbf{S}, \quad \mathbf{S} = \sum_i \mathbf{s}_i \quad \leftarrow \text{spin ang. mom. op.}$$

- Total paramagnetic interaction with a uniform magnetic field:

$$H_Z = -\mathbf{B} \cdot \mathbf{d}_m, \quad \mathbf{d}_m = -\frac{1}{2}(\mathbf{L} + 2\mathbf{S}) \quad \leftarrow \text{Zeeman interaction}$$

Hyperfine interactions

- The nuclear moments set up a magnetic vector potential ($\approx 10^{-8}$ a.u.):

$$\mathbf{A}(\mathbf{r}) = \alpha^2 \sum_K \frac{\mathbf{M}_K \times \mathbf{r}_K}{r_K^3}, \quad \alpha^2 = c^{-2} \approx 10^{-4} \text{ a.u.}, \quad \mathbf{M}_K = \gamma_K \hbar \mathbf{I}_K \approx 10^{-4} \text{ a.u.}$$

- This vector potential gives rise to the following paramagnetic hyperfine interaction

$$\mathbf{A} \cdot \mathbf{p} = \sum_K \mathbf{M}_K^T \mathbf{h}_K^{\text{PSO}}, \quad \mathbf{h}_K^{\text{PSO}} = \alpha^2 \frac{\mathbf{r}_K \times \mathbf{p}}{r_K^3} = \alpha^2 \frac{\mathbf{L}_K}{r_K^3} \quad \leftarrow \text{paramagnetic SO (PSO)}$$

– magnetic moment interacts with the electron's **orbital motion about the nucleus**

- Taking the curl of this vector potential, we obtain:

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

– 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 $\mathbf{B}(\mathbf{r})$ then gives rise to two distinct **first-order triplet operators**:

$$\mathbf{B} \cdot \mathbf{s} = \sum_K \mathbf{M}_K^T (\mathbf{h}_K^{\text{FC}} + \mathbf{h}_K^{\text{SD}}), \quad \left\{ \begin{array}{ll} \mathbf{h}_K^{\text{FC}} = \frac{8\pi\alpha^2}{3} \delta(\mathbf{r}_K) \mathbf{s} & \text{Fermi contact (FC)} \\ \mathbf{h}_K^{\text{SD}} = \alpha^2 \frac{3\mathbf{r}_K \mathbf{r}_K^T - r_K^2 \mathbf{I}_3}{r_K^5} \mathbf{s} & \text{spin-dipole (SD)} \end{array} \right.$$

Review

- The nonrelativistic electronic Hamiltonian:

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

- Rayleigh–Schrödinger perturbation theory to second order:

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

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

- Vector potentials of the **uniform external field** and the **nuclear magnetic moments**:

$$\mathbf{A}(\mathbf{r}) = \frac{1}{2} \mathbf{B} \times \mathbf{r}_O, \quad \mathbf{A}_K(\mathbf{r}) = \alpha^2 \frac{\mathbf{M}_K \times \mathbf{r}_K}{r_K^3}, \quad \nabla \times \mathbf{A}(\mathbf{r}) = \mathbf{B}(\mathbf{r}), \quad \nabla \cdot \mathbf{A}(\mathbf{r}) = 0$$

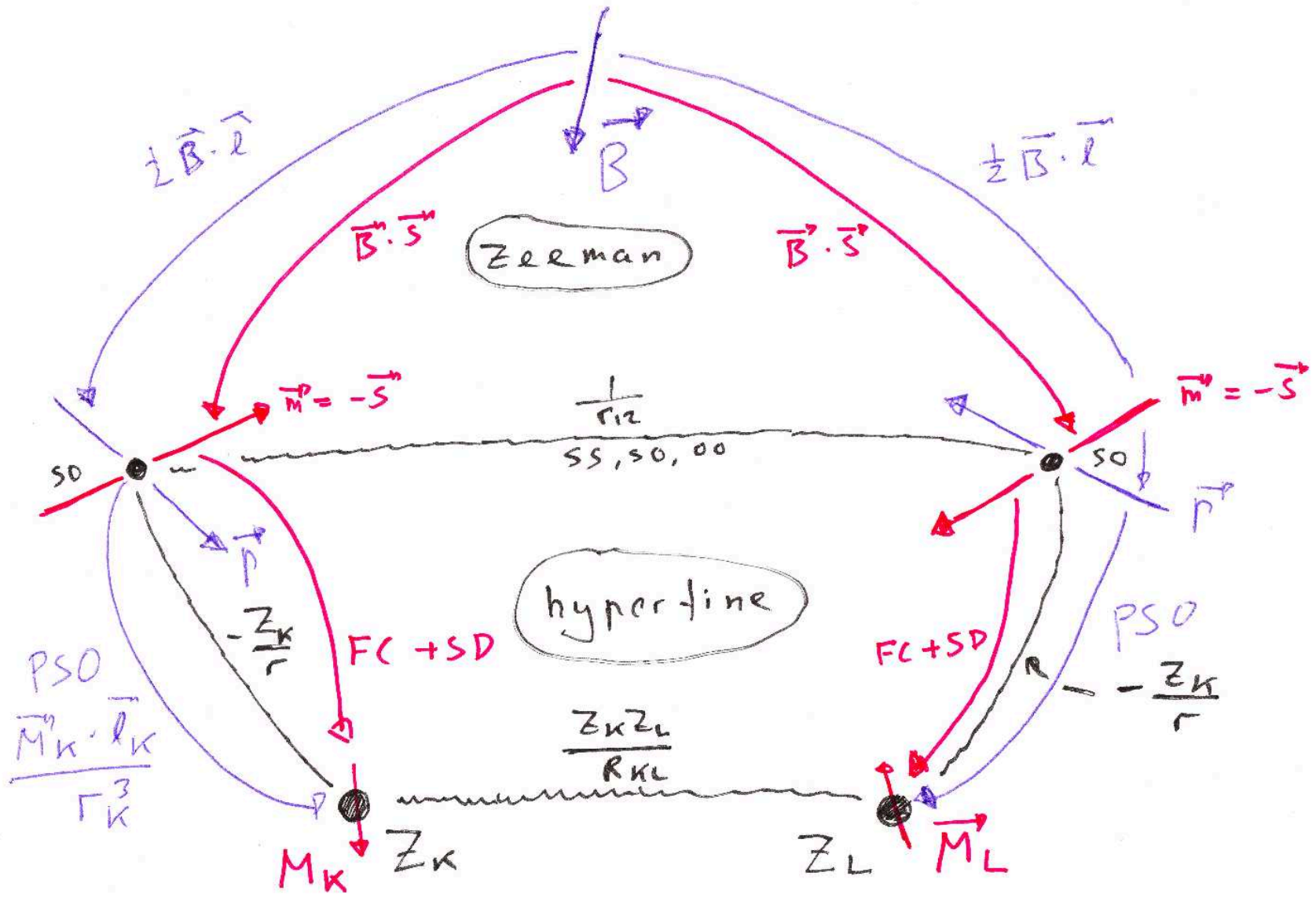
- Orbital and spin **Zeeman interactions** with the external magnetic field:

$$H_{\text{Zeeman}}^{(1)} = \frac{1}{2} \mathbf{B} \cdot \mathbf{L}_O + \mathbf{B} \cdot \mathbf{s}$$

- Orbital and spin **hyperfine interactions** with the nuclear magnetic moments:

$$H_{\text{hyperfine}}^{(1)} = \underbrace{\alpha^2 \frac{\mathbf{M}_K \cdot \mathbf{L}_K}{r_K^3}}_{\text{PSO}} + \underbrace{\frac{8\pi\alpha^2}{3} \delta(\mathbf{r}_K) \mathbf{M}_K \cdot \mathbf{s}}_{\text{FC}} + \underbrace{\alpha^2 \frac{3(\mathbf{s} \cdot \mathbf{r}_K)(\mathbf{r}_K \cdot \mathbf{M}_K) - (\mathbf{M}_K \cdot \mathbf{s})r_K^2}{r_K^5}}_{\text{SD}}$$

The many interactions: Coulomb, Zeeman and hyperfine



Gauge transformation of the Schrödinger equation

- Consider a general gauge transformation for the electron (atomic units):

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

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

$$\left(H' - i\frac{\partial}{\partial t} \right) = \exp(-if) \left(H - i\frac{\partial}{\partial t} \right) \exp(if)$$

- 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 be related to the old one by a compensating unitary transformation:

$$\Psi' = \exp(-if) \Psi$$

- No observable properties such as the electron density are then affected:

$$\rho' = (\Psi')^* \Psi' = [\Psi \exp(-if)]^* [\exp(-if) \Psi] = \Psi^* \Psi = \rho$$

Gauge-origin transformations

- Different choices of **gauge origin** in the external vector potential

$$\mathbf{A}_{\mathbf{O}}(\mathbf{r}) = \frac{1}{2}\mathbf{B} \times (\mathbf{r} - \mathbf{O})$$

are related by a gauge transformation:

$$\mathbf{A}_{\mathbf{K}}(\mathbf{r}) = \mathbf{A}_{\mathbf{O}}(\mathbf{r}) - \mathbf{A}_{\mathbf{O}}(\mathbf{K}) = \mathbf{A}_{\mathbf{O}}(\mathbf{r}) + \nabla f, \quad f(\mathbf{r}) = -\mathbf{A}_{\mathbf{O}}(\mathbf{K}) \cdot \mathbf{r}$$

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

$$\Psi_{\mathbf{K}}^{\text{exact}} = \exp[i\mathbf{A}_{\mathbf{O}}(\mathbf{K}) \cdot \mathbf{r}] \Psi_{\mathbf{O}}^{\text{exact}}$$

- approximate wave functions are in general not able to carry out this transformation:

$$\Psi_{\mathbf{K}}^{\text{approx}} \neq \exp[i\mathbf{A}_{\mathbf{O}}(\mathbf{K}) \cdot \mathbf{r}] \Psi_{\mathbf{O}}^{\text{approx}}$$

- different gauge origins may therefore give different results!

- We might contemplate attaching an explicit phase factor to the wave function:

$$\Psi_{\mathbf{K}}^{\text{approx}} \stackrel{\text{def}}{=} \exp[i\mathbf{A}_{\mathbf{O}}(\mathbf{K}) \cdot \mathbf{r}] \Psi_{\mathbf{O}}^{\text{approx}}$$

- for any \mathbf{K} , this approach produces the same result as with the gauge origin at \mathbf{O}
- however, no natural, best gauge origin can usually be identified (except for atoms)
- in any case, we might as well carry out the calculation with the origin at \mathbf{O} !
- applied to **individual AOs**, however, this approach makes much more sense!

Natural gauge origin for AOs

- Assume AOs positioned at \mathbf{K} with the following properties:

$$H_0 \chi_{lm} = E_0 \chi_{lm}, \quad L_z^{\mathbf{K}} \chi_{lm} = m_l \chi_{lm}, \quad \mathbf{L}^{\mathbf{K}} = -i(\mathbf{r} - \mathbf{K}) \times \nabla$$

- We first choose the gauge origin to be at \mathbf{K} :

$$\mathbf{A}_{\mathbf{K}}(\mathbf{r}) = \frac{1}{2} \mathbf{B} \times (\mathbf{r} - \mathbf{K})$$

- the AOs χ_{lm} are then correct to first order in \mathbf{B} :

$$H_{\mathbf{K}}(\mathbf{B}) \chi_{lm} = \left[H_0 + \frac{1}{2} B L_z^{\mathbf{K}} + \mathcal{O}(B^2) \right] \chi_{lm} = \left[E_0 + \frac{1}{2} m_l B + \mathcal{O}(B^2) \right] \chi_{lm}$$

- Next, we put the gauge origin at $\mathbf{O} \neq \mathbf{K}$:

$$\mathbf{A}_{\mathbf{O}}(\mathbf{r}) = \frac{1}{2} \mathbf{B} \times (\mathbf{r} - \mathbf{O})$$

- the AOs χ_{lm} are now correct only to zero order in \mathbf{B} :

$$H_{\mathbf{O}}(\mathbf{B}) \chi_{lm} = \left[H_0 + \frac{1}{2} B L_z^{\mathbf{O}} + \mathcal{O}(B^2) \right] \chi_{lm} \neq \left[E_0 + \frac{1}{2} m_l B + \mathcal{O}(B^2) \right] \chi_{lm}$$

- Standard AOs are biased towards \mathbf{K} !

London orbitals

- A traditional AO gives best description with the gauge origin at its position \mathbf{K} .
- Attach to each AO a phase factor that represents the gauge-origin transformation to its position \mathbf{K} from the global origin \mathbf{O} :

$$\omega_{lm} = \exp [i\mathbf{A}_{\mathbf{K}}(\mathbf{O}) \cdot \mathbf{r}] \chi_{lm} = \exp [i\frac{1}{2}\mathbf{B} \times (\mathbf{O} - \mathbf{K}) \cdot \mathbf{r}] \chi_{lm}$$

- Each AO now behaves as if the global gauge origin were at its position!
- In particular, all AOs are now correct to first order in \mathbf{B} , for any global origin \mathbf{O} .
- The calculations become gauge-origin independent
 - uniform (good) quality follows
- These are the London orbitals (1937), also known as GIAOs (gauge-origin independent AOs or gauge-origin including AOs).

Review

- The nonrelativistic electronic Hamiltonian:

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

- Rayleigh–Schrödinger perturbation theory to second order:

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

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

- Vector potentials of the **uniform external field** and the **nuclear magnetic moments**:

$$\mathbf{A}(\mathbf{r}) = \frac{1}{2} \mathbf{B} \times \mathbf{r}_O, \quad \mathbf{A}_K(\mathbf{r}) = \alpha^2 \frac{\mathbf{M}_K \times \mathbf{r}_K}{r_K^3}, \quad \nabla \times \mathbf{A}(\mathbf{r}) = \mathbf{B}(\mathbf{r}), \quad \nabla \cdot \mathbf{A}(\mathbf{r}) = 0$$

- Orbital and spin **Zeeman interactions** with the external magnetic field:

$$H_{\text{Zeeman}}^{(1)} = \frac{1}{2} \mathbf{B} \cdot \mathbf{L}_O + \mathbf{B} \cdot \mathbf{s}$$

- Orbital and spin **hyperfine interactions** with the nuclear magnetic moments:

$$H_{\text{hyperfine}}^{(1)} = \underbrace{\alpha^2 \frac{\mathbf{M}_K \cdot \mathbf{L}_K}{r_K^3}}_{\text{PSO}} + \underbrace{\frac{8\pi\alpha^2}{3} \delta(\mathbf{r}_K) \mathbf{M}_K \cdot \mathbf{s}}_{\text{FC}} + \underbrace{\alpha^2 \frac{3(\mathbf{s} \cdot \mathbf{r}_K)(\mathbf{r}_K \cdot \mathbf{M}_K) - (\mathbf{M}_K \cdot \mathbf{s})r_K^2}{r_K^5}}_{\text{SD}}$$

Taylor expansion of the 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:

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

- The first-order terms vanish for closed-shell systems because of symmetry:

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

- Higher-order terms are negligible since the perturbations are tiny:
 - 1) the magnetic induction \mathbf{B} is weak ($\approx 10^{-5}$ a.u.)
 - 2) the nuclear magnetic moments \mathbf{M}_K couple weakly ($\mu_0 \mu_N \approx 10^{-8}$ a.u.)
- We shall therefore consider only the second-order terms:
the magnetizability, the shieldings, and the spin-spin couplings

The magnetizability

- Assume zero nuclear magnetic moments and expand the molecular electronic energy in the external magnetic induction \mathbf{B} :

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

- The molecular magnetic moment at \mathbf{B} is now given by

$$\mathbf{M}_{\text{mol}}(\mathbf{B}) \stackrel{\text{def}}{=} -\frac{dE(\mathbf{B})}{d\mathbf{B}} = -\mathbf{E}^{(10)} - \mathbf{E}^{(20)} \mathbf{B} + \dots = \mathbf{M}_{\text{perm}} + \boldsymbol{\xi} \mathbf{B} + \dots,$$

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

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

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

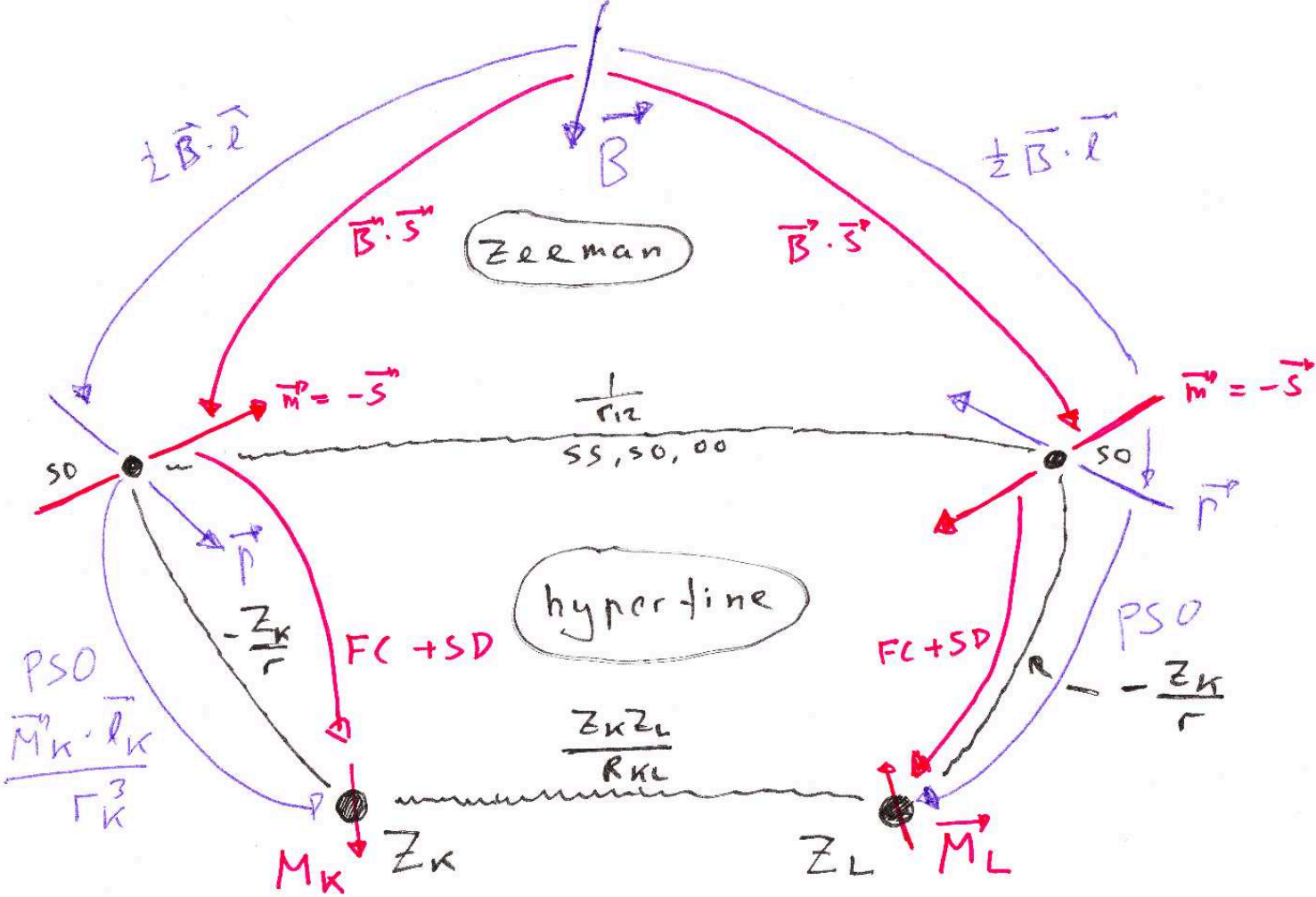
$$\boldsymbol{\xi} = -\mathbf{E}^{(20)} = -\left. \frac{d^2 E}{d\mathbf{B}^2} \right|_{\mathbf{B}=0} \quad \leftarrow \text{molecular magnetizability}$$

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

- The magnetizability is responsible for molecular diamagnetism, important for molecules without a permanent magnetic moment.

Paramagnetic interactions for the magnetizability

- For magnetizability we need the Zeeman interactions $\frac{1}{2}\mathbf{B} \cdot \mathbf{L}$ and $\mathbf{B} \cdot \mathbf{S}$
 - the triplet operator $\mathbf{B} \cdot \mathbf{S}$ does not contribute for closed shells



The calculation of magnetizabilities

- The molecular magnetizability of a closed-shell system:

$$\begin{aligned}\xi &= -\frac{d^2 E}{d\mathbf{B}^2} = -\left\langle 0 \left| \frac{\partial^2 H}{\partial \mathbf{B}^2} \right| 0 \right\rangle + 2 \sum_n \frac{\langle 0 | \frac{\partial H}{\partial \mathbf{B}} | n \rangle \langle n | \frac{\partial H}{\partial \mathbf{B}} | 0 \rangle}{E_n - E_0} \\ &= \underbrace{\frac{1}{4} \left\langle 0 \left| \mathbf{r}_O \mathbf{r}_O^T - (\mathbf{r}_O^T \mathbf{r}_O) \mathbf{I}_3 \right| 0 \right\rangle}_{\text{diamagnetic term}} + \underbrace{\frac{1}{2} \sum_n \frac{\langle 0 | \mathbf{L}_O | n \rangle \langle n | \mathbf{L}_O^T | 0 \rangle}{E_n - E_0}}_{\text{paramagnetic term}}\end{aligned}$$

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

$$\frac{1}{2} A^2(\mathbf{B}) = \frac{1}{8} (\mathbf{B} \times \mathbf{r}_O) \cdot (\mathbf{B} \times \mathbf{r}_O) = \frac{1}{8} [B^2 r_O^2 - (\mathbf{B} \cdot \mathbf{r}_O)(\mathbf{B} \cdot \mathbf{r}_O)]$$

- the isotropic part of the diamagnetic contribution is given by:

$$\xi_{\text{dia}} = \frac{1}{3} \text{Tr} \boldsymbol{\xi}_{\text{dia}} = -\frac{1}{6} \langle 0 | x_O^2 + y_O^2 + z_O^2 | 0 \rangle = -\frac{1}{6} \langle 0 | r_O^2 | 0 \rangle \quad \leftarrow \text{system surface}$$

- 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:

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

Hartree–Fock magnetizabilities

- Basis-set requirements for magnetizabilities are modest if London orbitals are used:

basis	cc-pVDZ	cc-pVTZ	cc-pVQZ
HF basis-set error	2.8%	1.0%	0.4%

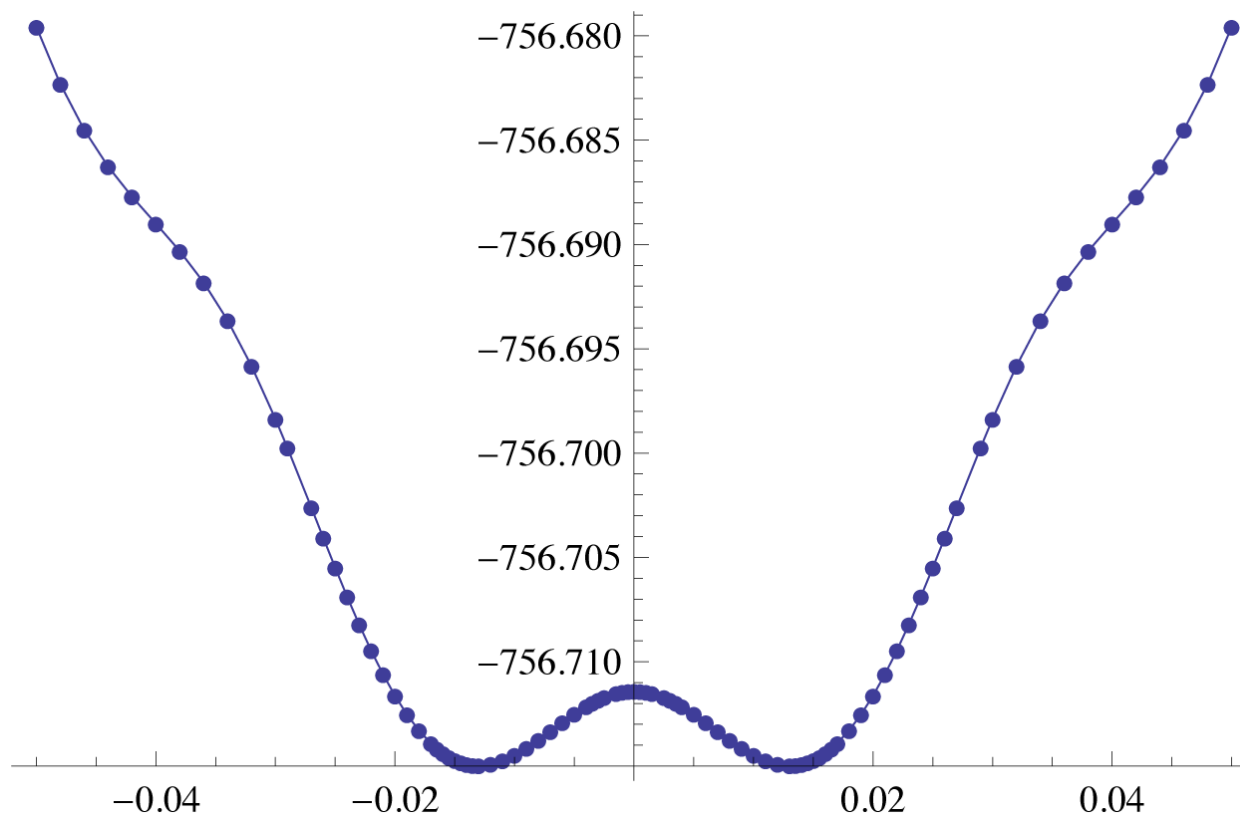
- The HF model overestimates the magnitude of magnetizabilities by 5%–10%:

10^{-30} JT^{-2}	HF	exp.	diff.
H ₂ O	−232	−218	−6.4%
NH ₃	−289	−271	−6.6%
CH ₄	−315	−289	−9.0%
CO ₂	−374	−349	−7.2%
PH ₃	−441	−435	−1.4%
H ₂ S	−446	−423	−5.4%
C ₃ H ₄	−482	−420	−14.8%
CSO	−595	−538	−10.6%
CS ₂	−752	−701	−7.3%

– compare with polarizabilities, which require large basis sets and are underestimated

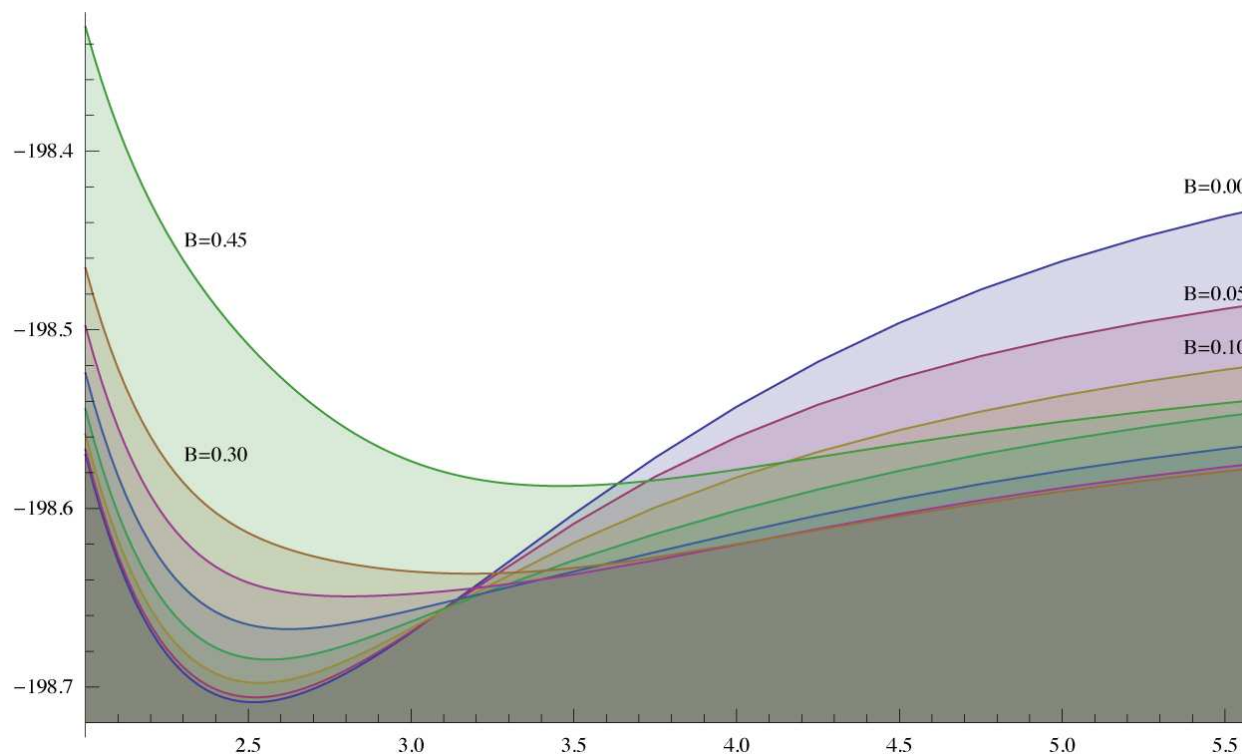
Nonperturbative calculations of molecules in magnetic fields

- It is possible to carry out nonperturbative studies of molecules in magnetic fields
- Below we have plotted the energy of C_{20} as a function of the magnetic field strength
 - C_{20} is paramagnetic in weak fields but diamagnetic in strong fields
 - this behaviour cannot be reproduced by expansions, which diverge for strong fields



Nonperturbative calculations of molecules in magnetic fields

- Strong magnetic fields affect molecules in many ways
- Below we have plotted the potential energy curve of F_2 in different perpendicular fields
 - at short internuclear separations, the electronic system is always diamagnetic
 - at large separations, it is paramagnetic for weak and diamagnetic for strong fields
 - the molecule is stretched by the applied field



High-resolution NMR spin Hamiltonian

- Consider a molecule in the presence of an external 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**:

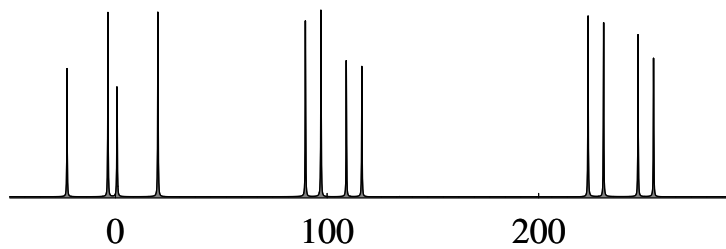
$$H_{\text{NMR}} = \underbrace{- \sum_K \gamma_K \hbar (1 - \sigma_K) B I_{Kz}}_{\text{nuclear Zeeman interaction}} + \underbrace{\sum_{K>L} \gamma_K \gamma_L \hbar^2 K_{KL} \mathbf{I}_K \cdot \mathbf{I}_L}_{\text{nuclear spin-spin interaction}}$$

where we have introduced

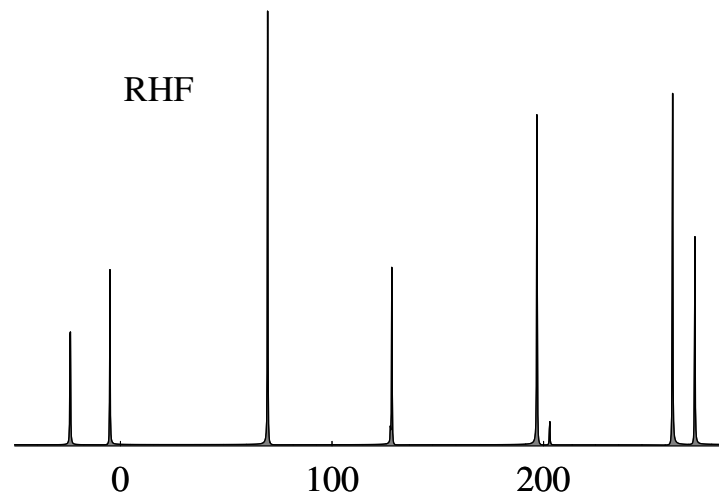
- the **nuclear shielding constants** σ_K
- the **(reduced) indirect nuclear spin-spin coupling constants** K_{KL}
- This is an **effective** nuclear spin Hamiltonian:
 - it reproduces NMR spectra without considering the electrons explicitly
 - the spin parameters σ_K and K_{KL} are adjusted to fit the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

Simulated 200 MHz NMR spectra of vinyl lithium

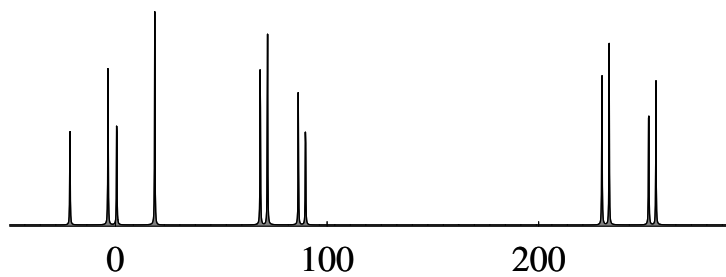
experiment



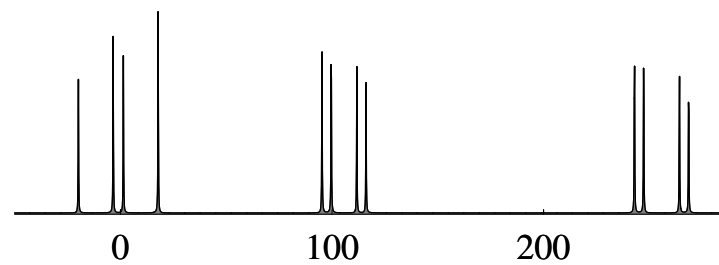
RHF



MCSCF



B3LYP



Nuclear shielding constants

- Recall the energy expansion for a closed-shell molecule in the presence of an external field \mathbf{B} and nuclear magnetic moments \mathbf{M}_K :

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

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

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

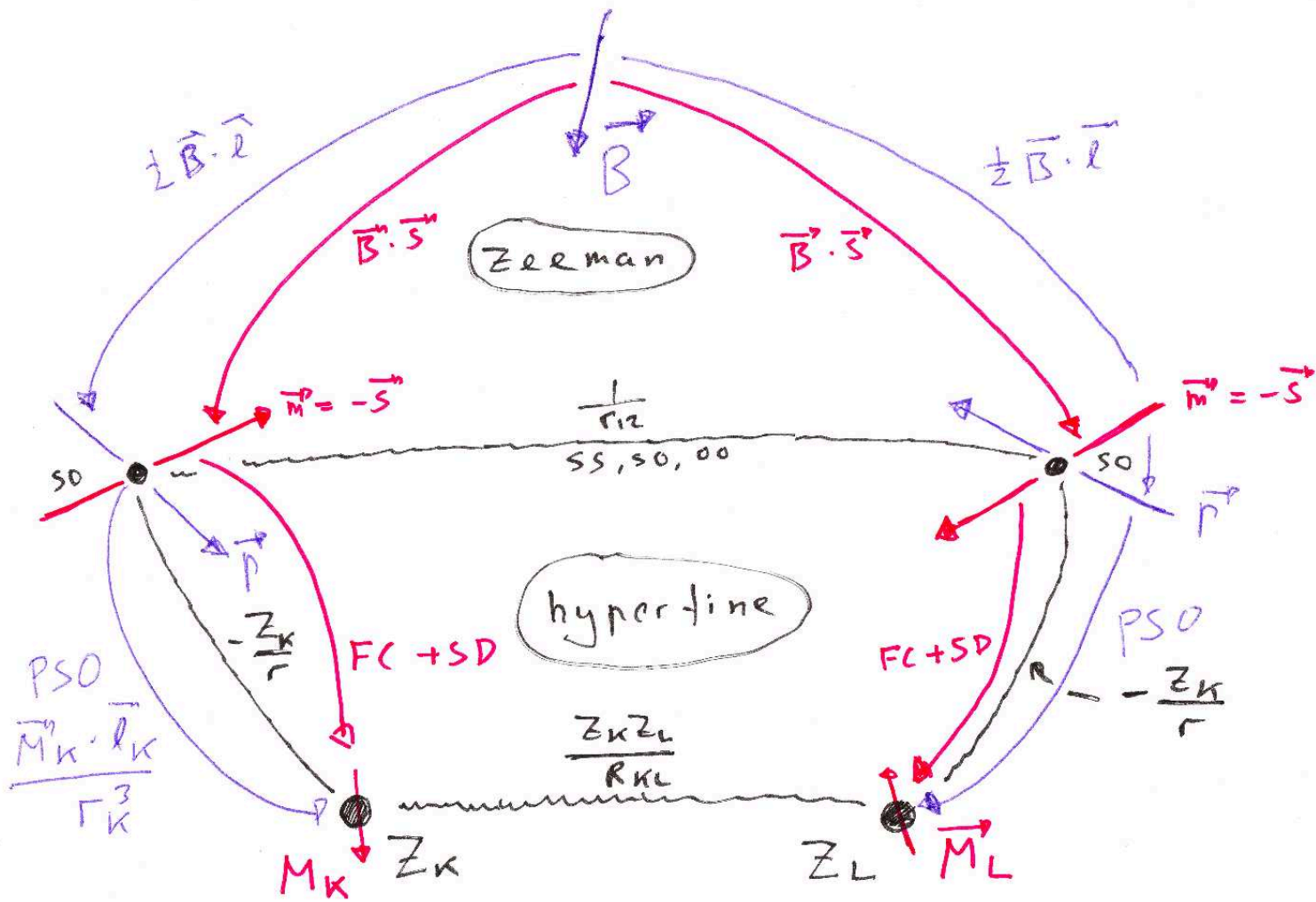
- in the presence of electrons (i.e., in a molecule), the coupling is modified slightly:

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

- Since the nuclear shielding constants arise from a hyperfine interaction between the electrons and the nuclei, it is proportional to $\alpha^2 \approx 5 \cdot 10^{-5}$ and is measured in ppm.
- The nuclear Zeeman interaction, which does not enter the electronic problem, has here been introduced in a purely ad hoc fashion. Its status is otherwise similar to that of the Coulomb nuclear–nuclear repulsion operator.

Paramagnetic interactions for shielding constants

- For shieldings, we must combine Zeeman and hyperfine interactions
 - for closed shells, only the singlet operators $\frac{1}{2}\mathbf{B} \cdot \mathbf{L}$ and $\mathbf{M}_K \cdot r_K^{-3}\mathbf{L}_K$ contribute



The calculation of nuclear shielding tensors

- Nuclear shielding tensors of a closed-shell system:

$$\begin{aligned} \sigma_K &= \frac{d^2 E_{\text{el}}}{d\mathbf{B}d\mathbf{M}_K} = \left\langle 0 \left| \frac{\partial^2 H}{\partial \mathbf{B} \partial \mathbf{M}_K} \right| 0 \right\rangle - 2 \sum_n \frac{\langle 0 | \frac{\partial H}{\partial \mathbf{B}} | n \rangle \langle n | \frac{\partial H}{\partial \mathbf{M}_K} | 0 \rangle}{E_n - E_0} \\ &= \underbrace{\frac{\alpha^2}{2} \left\langle 0 \left| \frac{\mathbf{r}_O^T \mathbf{r}_K \mathbf{I}_3 - \mathbf{r}_O \mathbf{r}_K^T}{r_K^3} \right| 0 \right\rangle}_{\text{diamagnetic term}} - \underbrace{\alpha^2 \sum_n \frac{\langle 0 | \mathbf{L}_O | n \rangle \langle n | r_K^{-3} \mathbf{L}_K^T | 0 \rangle}{E_n - E_0}}_{\text{paramagnetic term}} \end{aligned}$$

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

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

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

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

- For 1S systems (closed-shell atoms), the paramagnetic term vanishes completely and the 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

	$\sigma(^{11}\text{B})$	$\Delta\sigma(^{11}\text{B})$	$\sigma(^1\text{H})$	$\Delta\sigma(^1\text{H})$
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

Calculated and experimental shielding constants

		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 ₂ O	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 experimental CO and H₂O, see Wasylishen and Bryce, JCP 117 (2002) 10061

DFT shielding constants

		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 ₂ O	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)

Coupled-cluster convergence of shielding constants in CO

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

Nuclear spin–spin couplings

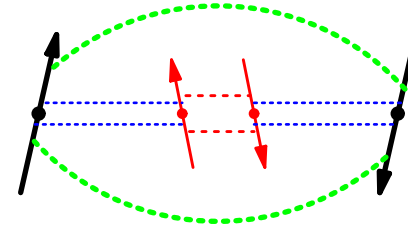
- The last term in the expansion of the molecular electronic energy in \mathbf{B} and \mathbf{M}_K

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

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:

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

– 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: $\mathbf{K}_{KL} \approx 10^{-16} \text{ a.u.} \approx 1 \text{ Hz}$

– it does not vanish in isotropic media

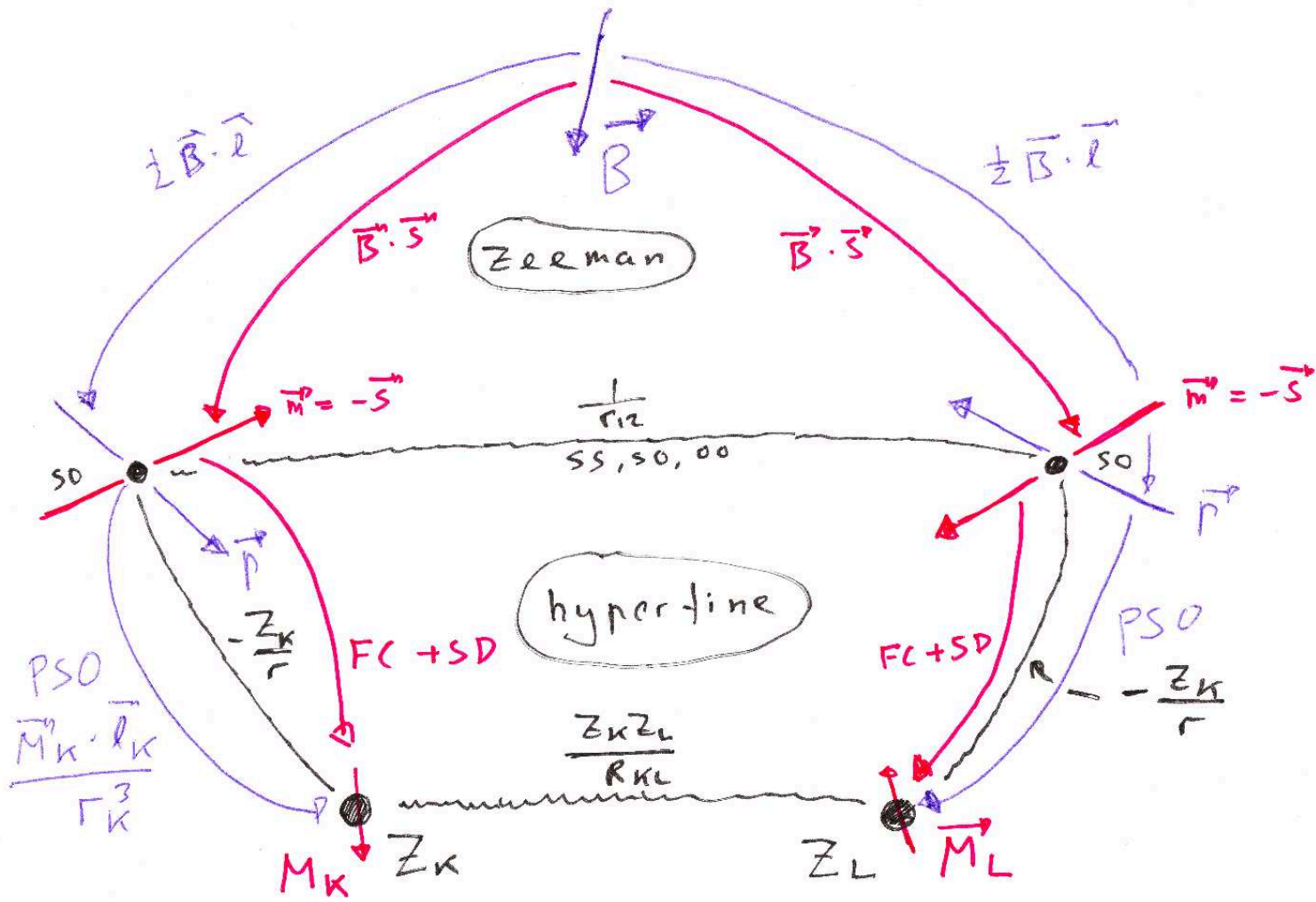
– it gives the fine structure of high-resolution NMR spectra

- Experimentalists usually work in terms of the (nonreduced) spin–spin couplings

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

Paramagnetic interactions for spin-spin coupling constants

- For spin-spin coupling constants, only hyperfine interactions contribute
 - both singlet (PSO) and triplet (FC and SD) operators are now needed



The calculation of indirect nuclear spin–spin coupling tensors

- The indirect nuclear spin–spin coupling tensor of a closed-shell system is given by:

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

- Carrying out the differentiation, we obtain:

$$\begin{aligned} \mathbf{K}_{KL} = & \underbrace{\alpha^4 \left\langle 0 \left| \frac{\mathbf{r}_K^T \mathbf{r}_L \mathbf{I}_3 - \mathbf{r}_K \mathbf{r}_L^T}{r_K^3 r_L^3} \right| 0 \right\rangle}_{\text{diamagnetic spin-orbit (DSO)}} - 2\alpha^4 \underbrace{\sum_n \frac{\left\langle 0 \left| r_K^{-3} \mathbf{L}_K \right| n \right\rangle \left\langle n \left| r_L^{-3} \mathbf{L}_L^T \right| 0 \right\rangle}{E_n - E_0}}_{\text{paramagnetic spin-orbit (PSO)}} \\ & - 2\alpha^4 \underbrace{\sum_n \frac{\left\langle 0 \left| \frac{8\pi}{3} \delta(\mathbf{r}_K) \mathbf{s} + \frac{3\mathbf{r}_K \mathbf{r}_K^T - r_K^2 \mathbf{I}_3}{r_K^5} \mathbf{s} \right| n \right\rangle \left\langle n \left| \frac{8\pi}{3} \delta(\mathbf{r}_L) \mathbf{s}^T + \frac{3\mathbf{r}_L \mathbf{r}_L^T - r_L^2 \mathbf{I}_3}{r_L^5} \mathbf{s}^T \right| 0 \right\rangle}{E_n - E_0}}_{\text{Fermi contact (FC) and spin-dipole (SD)}} \end{aligned}$$

- 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

Calculations of indirect nuclear spin–spin coupling constants

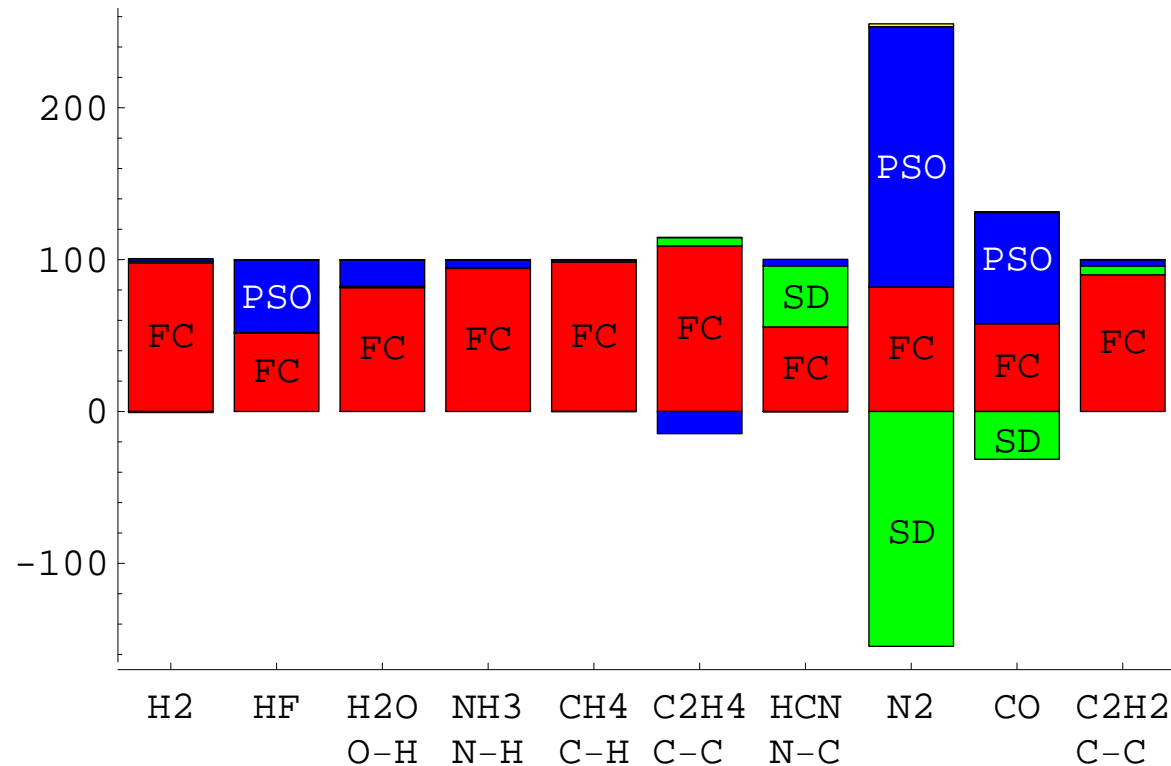
- The calculation of spin–spin coupling constants is a **challenging task**:
 - triplet as well as singlet perturbations are involved
 - electron correlation important—the Hartree–Fock model fails abysmally
 - the dominant FC contribution requires an accurate description of the electron density at the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

Relative importance of the contributions to spin–spin coupling constants

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

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

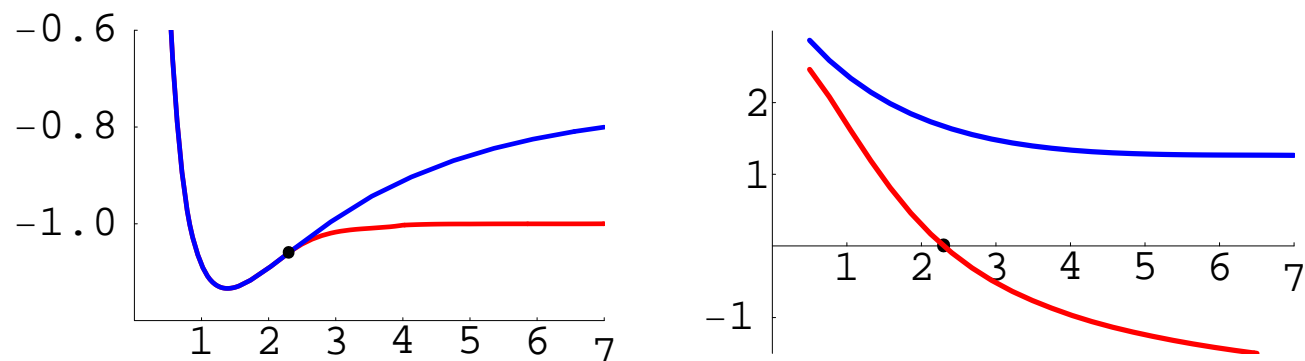
- The spin–spin coupling constants are often dominated by the FC term.
- Since the FC term is relatively easy to calculate, it is tempting to ignore the other terms.
- However, none of the contributions can be *a priori* neglected (N₂ and CO)!



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 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 ($10^{19} \text{kg m}^{-2} \text{s}^{-2} \text{\AA}^{-2}$)

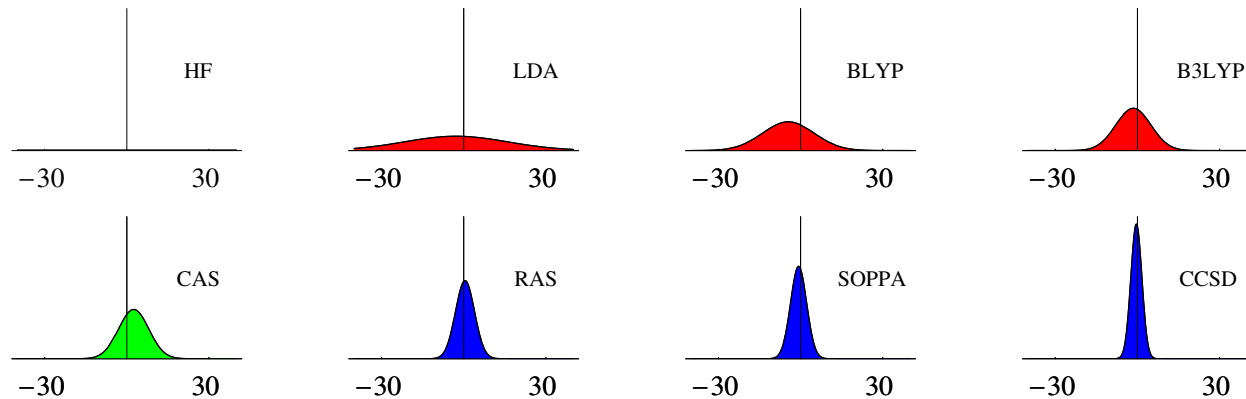
		RHF	CAS	RAS	SOPPA	CCSD	CC3	exp*	vib
HF	$^1J_{\text{HF}}$	59.2	48.0	48.1	46.8	46.1	46.1	47.6	−3.4
CO	$^1J_{\text{CO}}$	13.4	−28.1	−39.3	−45.4	−38.3	−37.3	−38.3	−1.7
N ₂	$^1J_{\text{NN}}$	175.0	−5.7	−9.1	−23.9	−20.4	−20.4	−19.3	−1.1
H ₂ O	$^1J_{\text{OH}}$	63.7	51.5	47.1	49.5	48.4	48.2	52.8	−3.3
	$^2J_{\text{HH}}$	−1.9	−0.8	−0.6	−0.7	−0.6	−0.6	−0.7	0.1
NH ₃	$^1J_{\text{NH}}$	61.4	48.7	50.2	51.0	48.1		50.8	−0.3
	$^2J_{\text{HH}}$	−1.9	−0.8	−0.9	−0.9	−1.0		−0.9	0.1
C ₂ H ₄	$^1J_{\text{CC}}$	1672.0	99.6	90.5	92.5	92.3		87.8	1.2
	$^1J_{\text{CH}}$	249.7	51.5	50.2	52.0	50.7		50.0	1.7
	$^2J_{\text{CH}}$	−189.3	−1.9	−0.5	−1.0	−1.0		−0.4	−0.4
	$^2J_{\text{HH}}$	−28.7	−0.2	0.1	0.1	0.0		0.2	0.0
	$^3J_{\text{cis}}$	30.0	1.0	1.0	1.0	1.0		0.9	0.1
	$^3J_{\text{tns}}$	33.3	1.5	1.5	1.5	1.5		1.4	0.2
$ \bar{\Delta} $	abs.	180.3	3.3	1.6	1.8	1.2	1.6	*at R_e	
	%	5709	60	14	24	23	6		

Reduced spin–spin coupling constants ($10^{19} \text{kg m}^{-2} \text{s}^{-2} \text{\AA}^{-2}$)

		LDA	BLYP	B3LYP	PBE	B97-3	RAS	exp*	vib
HF	$^1 J_{\text{HF}}$	35.0	34.5	38.9	32.6	40.5	48.1	47.6	−3.4
CO	$^1 J_{\text{CO}}$	−65.4	−55.7	−47.4	−62.0	−43.4	−39.3	−38.3	−1.7
N ₂	$^1 J_{\text{NN}}$	32.9	−46.6	−20.4	−43.2	−12.5	−9.1	−19.3	−1.1
H ₂ O	$^1 J_{\text{OH}}$	40.3	44.6	47.2	41.2	46.3	47.1	52.8	−3.3
	$^2 J_{\text{HH}}$	−0.3	−0.9	−0.7	−0.5	−0.6	−0.6	−0.7	0.1
NH ₃	$^1 J_{\text{NH}}$	41.0	49.6	52.3	47.0	50.1	50.2	50.8	−0.3
	$^2 J_{\text{HH}}$	−0.4	−0.7	−0.9	−0.7	−0.8	−0.9	−0.9	0.1
C ₂ H ₄	$^1 J_{\text{CC}}$	66.6	90.3	96.2	83.4	92.9	90.5	87.8	1.2
	$^1 J_{\text{CH}}$	42.5	55.3	55.0	50.0	51.4	50.2	50.0	1.7
	$^2 J_{\text{CH}}$	0.4	0.0	−0.5	−0.2	−0.3	−0.5	−0.4	−0.4
	$^2 J_{\text{HH}}$	0.4	0.4	0.3	0.3	0.3	0.1	0.2	0.0
	$^3 J_{\text{cis}}$	0.8	1.1	1.1	1.0	1.0	1.0	0.9	0.1
	$^3 J_{\text{tns}}$	1.2	1.7	1.7	1.6	1.5	1.5	1.4	0.2
$ \bar{\Delta} $	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

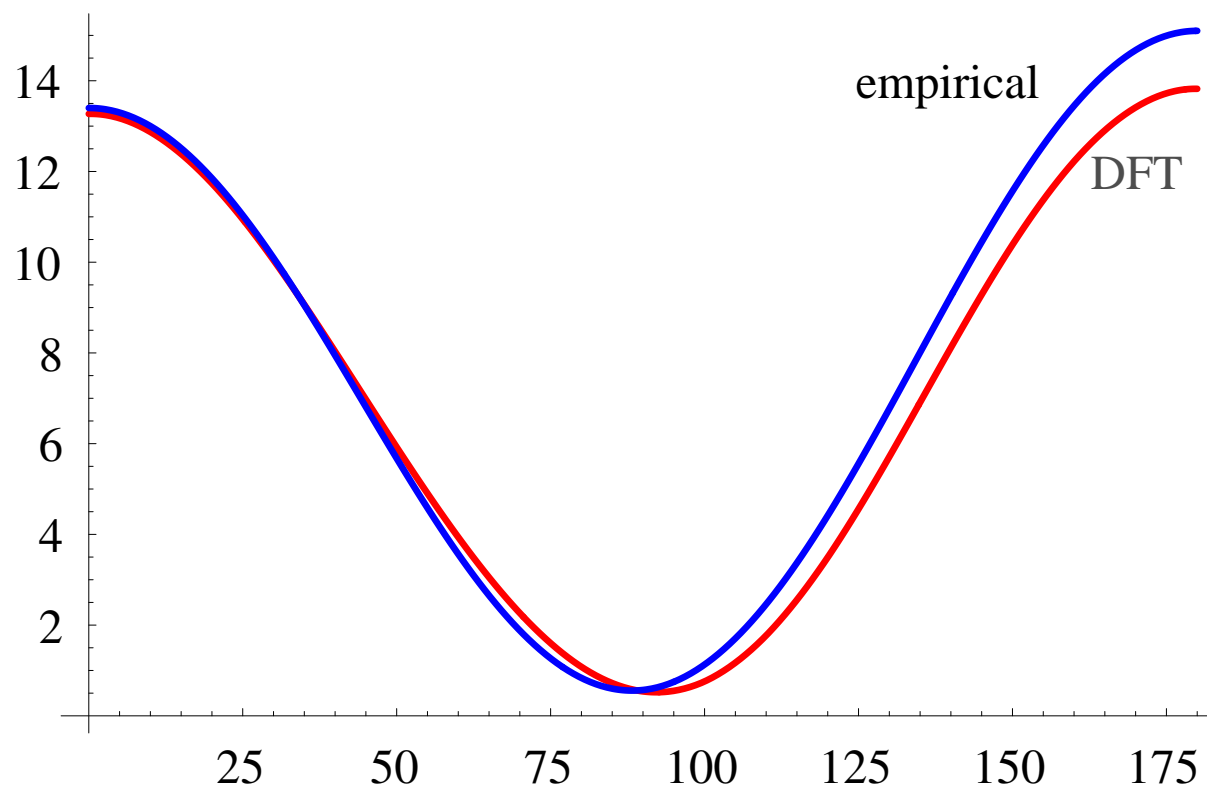
- normal distributions of errors for these molecules and some other systems for which vibrational corrections have been made:



- some observations:
 - 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

The Karplus curve

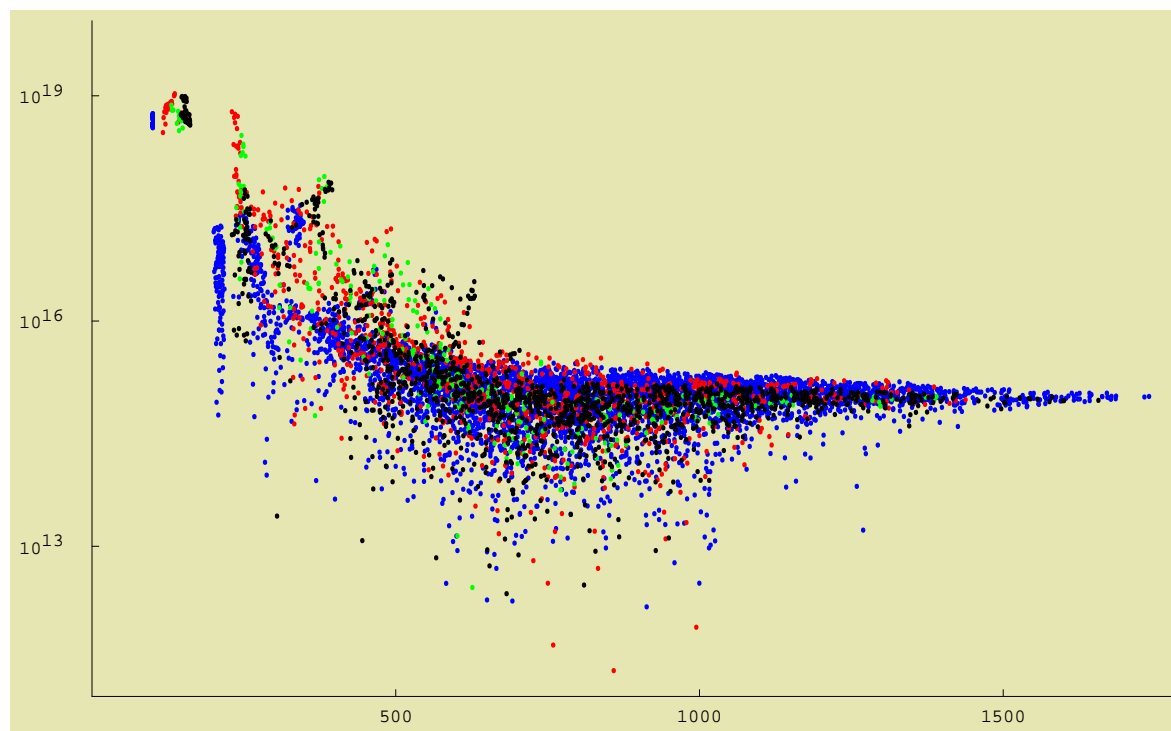
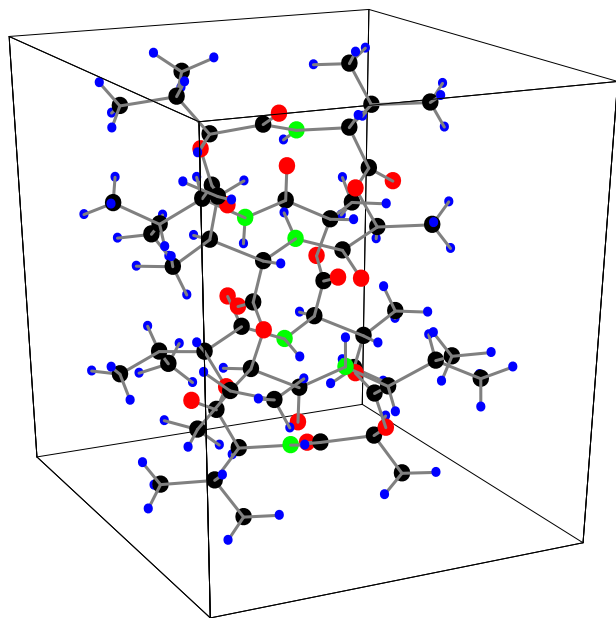
- Vicinal couplings depend critically on the dihedral angle:
- ${}^3J_{\text{HH}}$ in ethane as a function of the dihedral angle:



- The agreement with the empirical Karplus curve is good.

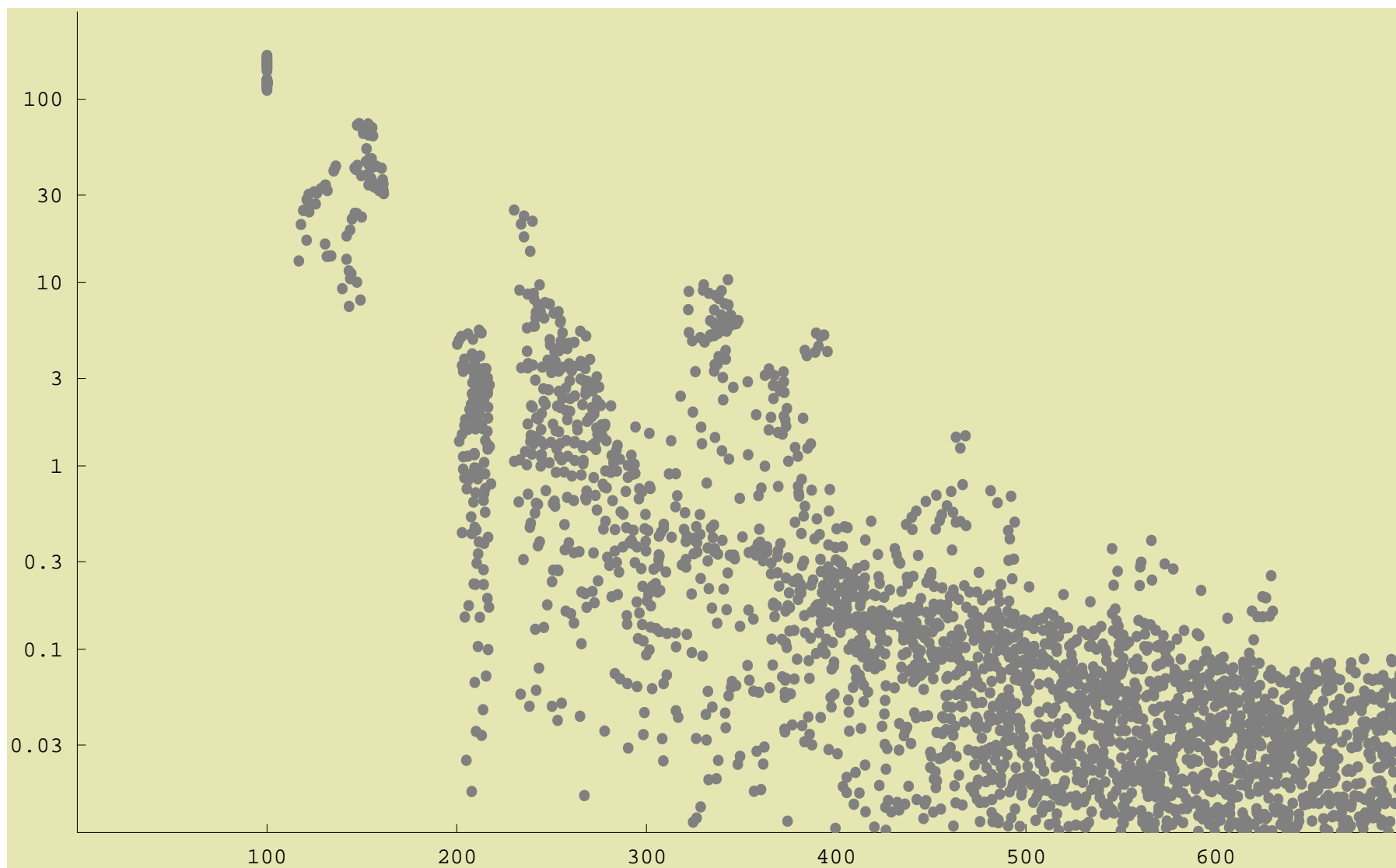
Valinomycin $C_{54}H_{90}N_8O_{18}$

- 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:

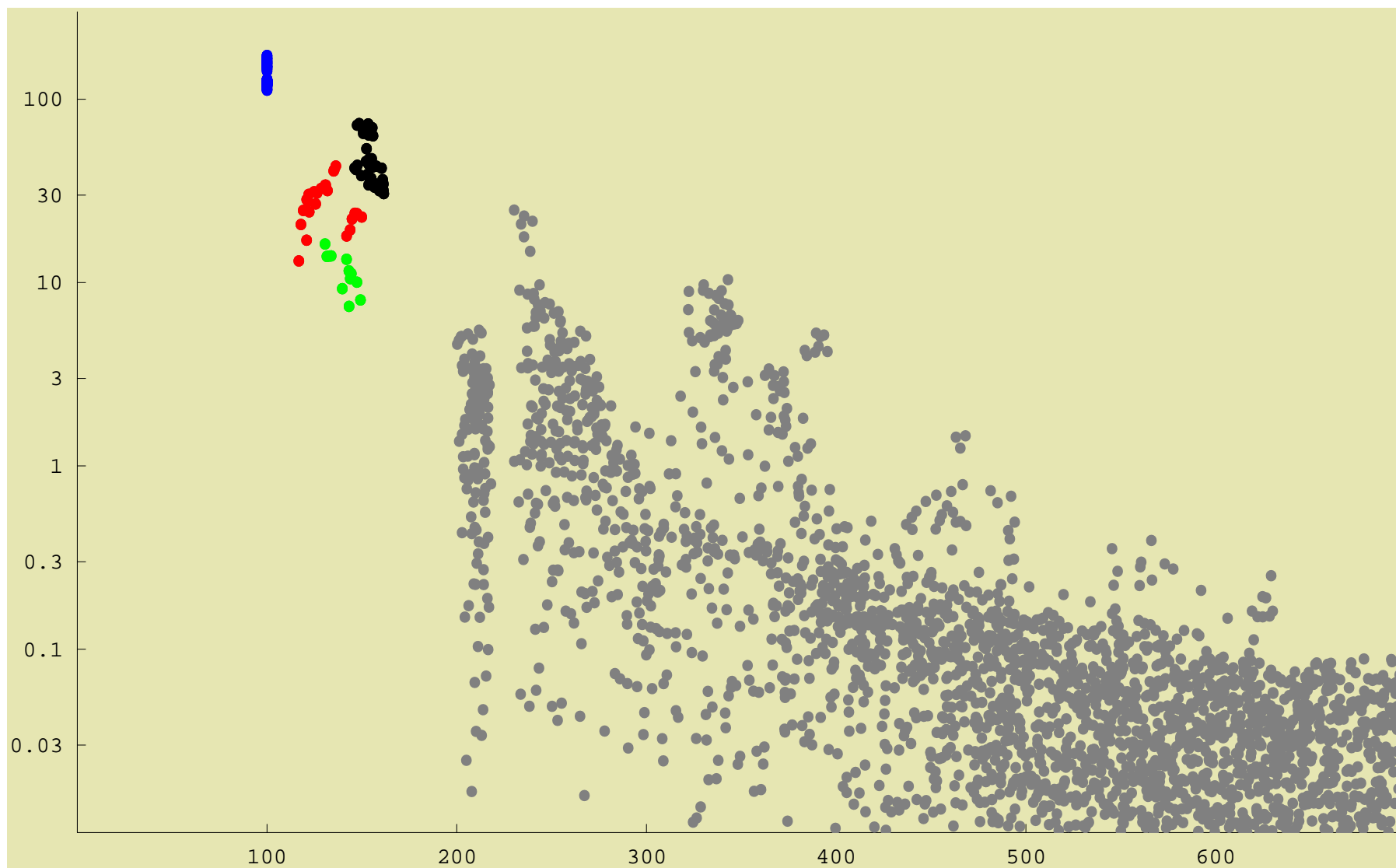


- the coupling constants decay in characteristic fashion, which we shall examine
- most of the indirect couplings beyond 500 pm are small and cannot be detected

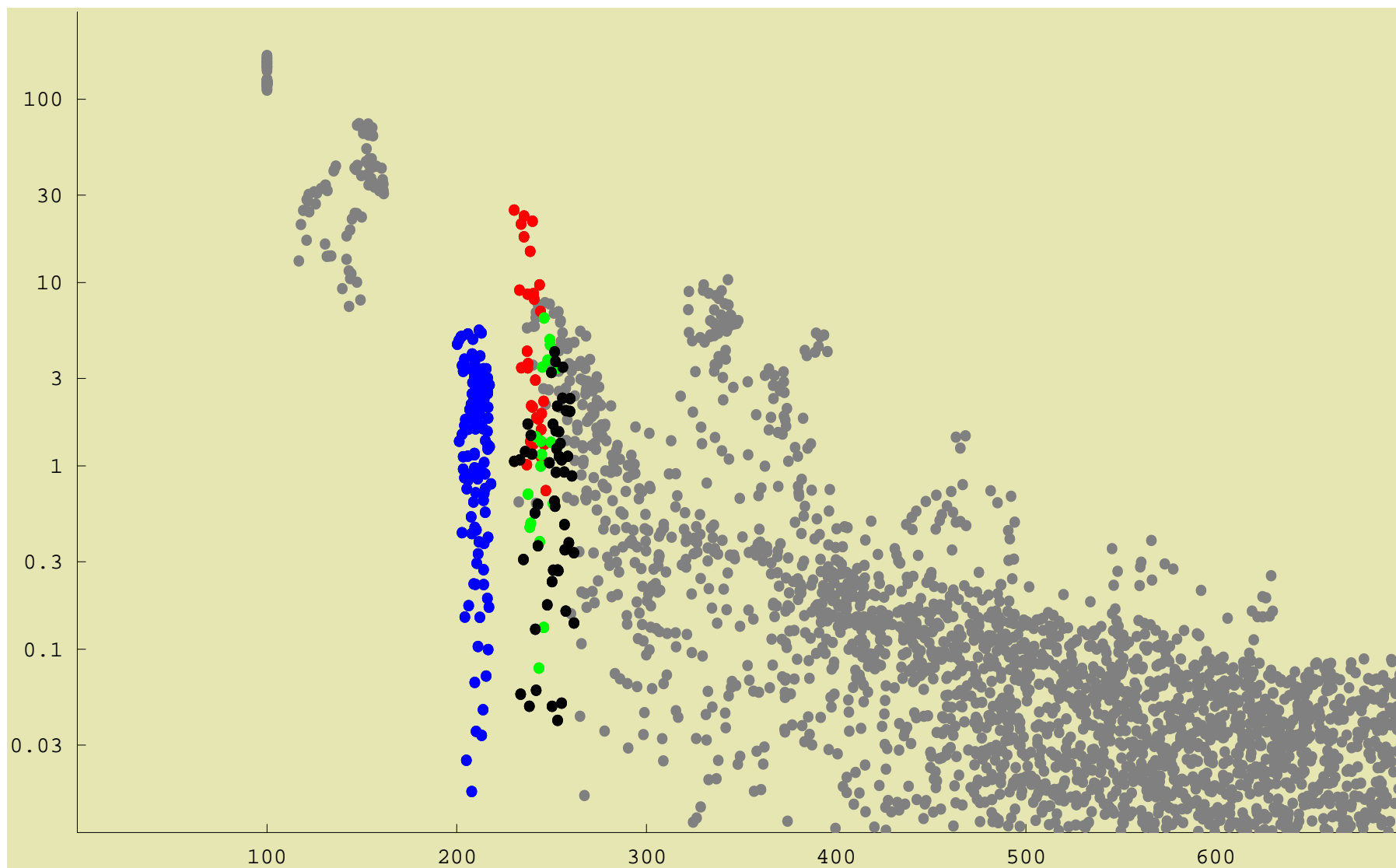
Valinomycin LDA/6-31G spin-spin couplings to CH, CO, CN, CC greater than 0.01 Hz



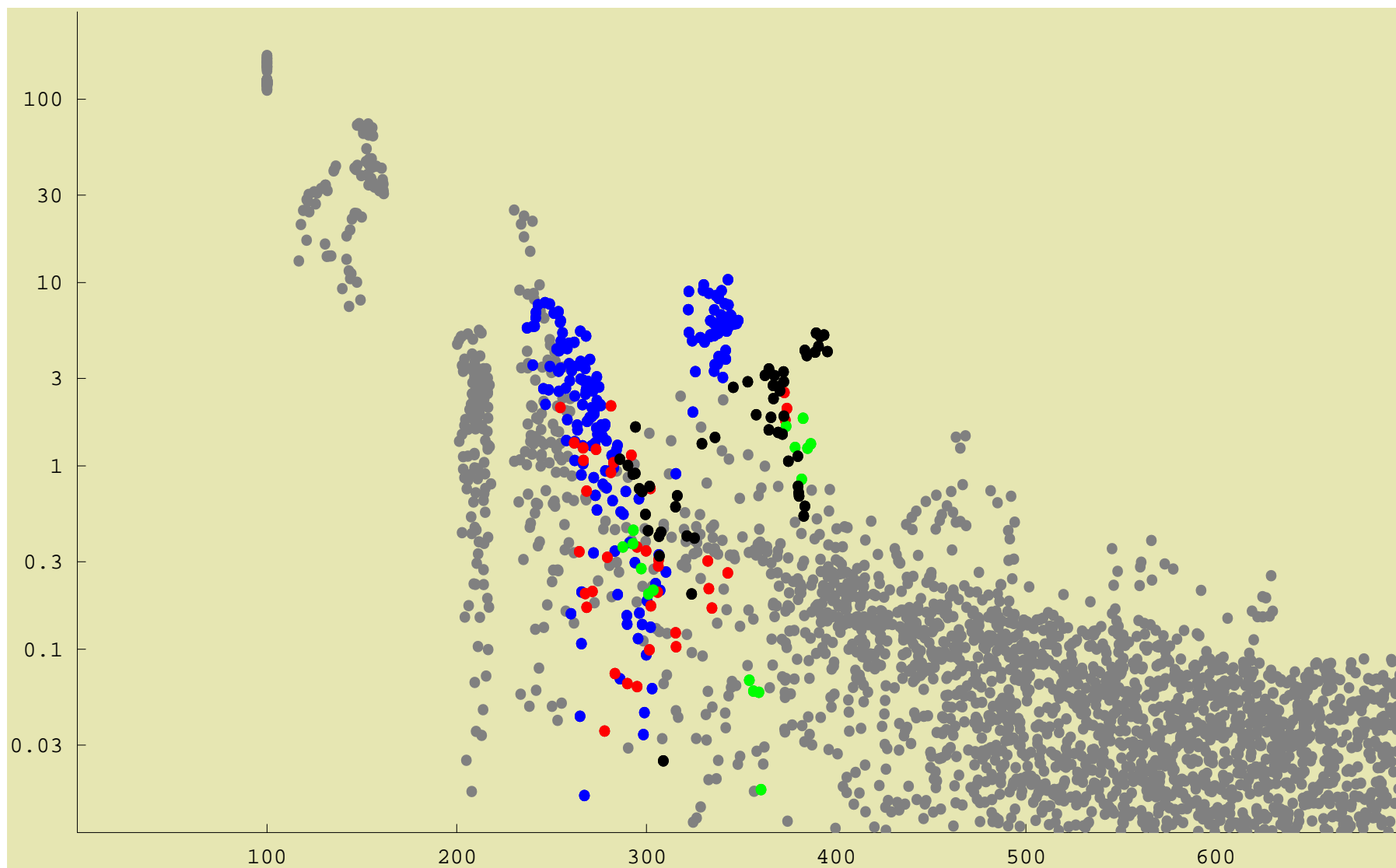
Valinomycin LDA/6-31G spin-spin couplings to CH, CO, CN, CC greater than 0.01 Hz



Valinomycin LDA/6-31G spin-spin couplings to CH, CO, CN, CC greater than 0.01 Hz



Valinomycin LDA/6-31G spin-spin couplings to CH, CO, CN, CC greater than 0.01 Hz



Valinomycin LDA/6-31G spin-spin couplings to CH, CO, CN, CC greater than 0.01 Hz

