

# Molecular Magnetic Properties

ESQC 09

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## Overview

- the electronic Hamiltonian in an electromagnetic field
  - external and nuclear magnetic fields
  - gauge transformations and London orbitals
  - first- and second-order magnetic properties
    - magnetizabilities
    - nuclear shielding constants
  - indirect nuclear spin–spin coupling constants

## Hamiltonian mechanics

- In classical Hamiltonian mechanics, a system of particles is described in terms their positions  $q_i$  and conjugate momenta  $p_i$ .
- For each such system, there exists a scalar Hamiltonian function  $H(q_i, p_i)$  such that the classical equations of motion are given by:

$$\dot{q}_i = \frac{\partial H}{\partial p_i}, \quad \dot{p}_i = -\frac{\partial H}{\partial q_i} \quad (\text{Hamilton's equations of motion})$$

- Example: a single particle of mass  $m$  in a conservative force field  $F(q)$ 
  - the Hamiltonian function is constructed from the corresponding scalar potential:

$$H(q, p) = \frac{p^2}{2m} + V(q), \quad F(q) = -\frac{\partial V(q)}{\partial q}$$

- Hamilton's equations are equivalent to Newton's equations:

$$\left. \begin{aligned} \dot{q} &= \frac{\partial H(q, p)}{\partial p} = \frac{p}{m} \\ \dot{p} &= -\frac{\partial H(q, p)}{\partial q} = -\frac{\partial V(q)}{\partial q} \end{aligned} \right\} \Rightarrow m\ddot{q} = F(q) \quad (\text{Newton's equations of motion})$$

- Whereas Newton's equations of motion are second-order differential equations, Hamilton's equations are first-order.
- Note: the Hamiltonian function is not unique!

## Quantization of a particle in conservative force field

- The Hamiltonian formulation is more general than the Newtonian formulation:
  - it is invariant to coordinate transformations
  - it provides a uniform description of matter and field
  - it constitutes the springboard to quantum mechanics
- The Hamiltonian function (the total energy) of a particle in a conservative force field:

$$H(q, p) = \frac{p^2}{2m} + V(q)$$

- Standard rule for quantization (in Cartesian coordinates):
  - carry out the substitutions

$$\mathbf{p} \rightarrow -i\hbar\nabla, \quad H \rightarrow i\hbar\frac{\partial}{\partial t}$$

- multiply the resulting expression by the wave function  $\Psi(q)$  from the right:

$$i\hbar\frac{\partial\Psi(q)}{\partial t} = \left[ -\frac{\hbar^2}{2m}\nabla^2 + V(q) \right] \Psi(q)$$

- This approach is sufficient for a treatment of electrons in an electrostatic field.
- It is insufficient for nonconservative systems—that is, for systems in a general electromagnetic field.

## The Lorentz force and Maxwell's equations

- In the presence of an electric field  $\mathbf{E}$  and a magnetic field (magnetic induction)  $\mathbf{B}$ , a classical particle of charge  $z$  experiences the Lorentz force:

$$\mathbf{F} = z(\mathbf{E} + \mathbf{v} \times \mathbf{B})$$

– since this force depends on the velocity  $\mathbf{v}$  of the particle, it is not conservative

- The electric and magnetic fields  $\mathbf{E}$  and  $\mathbf{B}$  satisfy Maxwell's equations (1861–1868):

$$\nabla \cdot \mathbf{E} = \rho/\epsilon_0 \quad \leftarrow \text{Coulomb's law}$$

$$\nabla \times \mathbf{B} - \epsilon_0\mu_0 \partial\mathbf{E}/\partial t = \mu_0\mathbf{J} \quad \leftarrow \text{Ampère's law with Maxwell's correction}$$

$$\nabla \cdot \mathbf{B} = 0$$

$$\nabla \times \mathbf{E} + \partial\mathbf{B}/\partial t = \mathbf{0} \quad \leftarrow \text{Faraday's law of induction}$$

– when the charge and current densities  $\rho(\mathbf{r}, t)$  and  $\mathbf{J}(\mathbf{r}, t)$  are known, Maxwell's equations can be solved for  $\mathbf{E}(\mathbf{r}, t)$  and  $\mathbf{B}(\mathbf{r}, t)$

– on the other hand, since the charges (particles) are driven by the Lorentz force,  $\rho(\mathbf{r}, t)$  and  $\mathbf{J}(\mathbf{r}, t)$  are functions of  $\mathbf{E}(\mathbf{r}, t)$  and  $\mathbf{B}(\mathbf{r}, t)$

- In the following, we shall consider the motion of particles in a given (fixed) electromagnetic field.

## Scalar and vector potentials

- The second, homogeneous pair of Maxwell's equations involves only  $\mathbf{E}$  and  $\mathbf{B}$ :

$$\nabla \cdot \mathbf{B} = 0 \quad (1)$$

$$\nabla \times \mathbf{E} + \frac{\partial \mathbf{B}}{\partial t} = \mathbf{0} \quad (2)$$

1. Equation (1) is satisfied by introducing the vector potential  $\mathbf{A}$ :

$$\nabla \cdot \mathbf{B} = 0 \Rightarrow \mathbf{B} = \nabla \times \mathbf{A} \quad \leftarrow \text{vector potential} \quad (3)$$

2. Inserting Eq. (3) in Eq. (2) and introducing a scalar potential  $\phi$ , we obtain

$$\nabla \times \left( \mathbf{E} + \frac{\partial \mathbf{A}}{\partial t} \right) = \mathbf{0} \Rightarrow \mathbf{E} + \frac{\partial \mathbf{A}}{\partial t} = -\nabla \phi \quad \leftarrow \text{scalar potential}$$

- The second pair of Maxwell's equations is thus automatically satisfied by writing

$$\mathbf{E} = -\nabla \phi - \frac{\partial \mathbf{A}}{\partial t}$$

$$\mathbf{B} = \nabla \times \mathbf{A}$$

- The potentials  $(\phi, \mathbf{A})$  contain four rather than six components as in  $(\mathbf{E}, \mathbf{B})$ .
- They are obtained by solving the first, inhomogeneous pair of Maxwell's equations, which contains  $\rho$  and  $\mathbf{J}$ .

## Gauge transformations

- The scalar and vector potentials  $\phi$  and  $\mathbf{A}$  are not unique.
- Consider the following transformation of the potentials:

$$\left. \begin{aligned} \phi' &= \phi - \frac{\partial f}{\partial t} \\ \mathbf{A}' &= \mathbf{A} + \nabla f \end{aligned} \right\} f = f(q, t) \quad \leftarrow \text{gauge function of position and time}$$

- This **gauge transformation** of the potentials does not affect the physical fields:

$$\begin{aligned} \mathbf{E}' &= -\nabla\phi' - \frac{\partial\mathbf{A}'}{\partial t} = -\nabla\phi + \nabla\frac{\partial f}{\partial t} - \frac{\partial\mathbf{A}}{\partial t} - \frac{\partial\nabla f}{\partial t} = \mathbf{E} \\ \mathbf{B}' &= \nabla \times (\mathbf{A} + \nabla f) = \mathbf{B} + \nabla \times \nabla f = \mathbf{B} \end{aligned}$$

- We are free to choose  $f(q, t)$  so as to make  $\phi$  and  $\mathbf{A}$  satisfy additional conditions.
- In the **Coulomb gauge**, the gauge function is chosen such that the vector potential becomes divergenceless:

$$\nabla \cdot \mathbf{A} = 0 \quad \leftarrow \text{Coulomb gauge}$$

- Note: the Hamiltonian changes in the following manner upon a gauge transformation:

$$H' = H - z \frac{\partial f}{\partial t}$$

- However, the equations of motion are unaffected!

## The Hamiltonian in an electromagnetic field

- We must construct a Hamiltonian function such that Hamilton's equations are equivalent to Newton's equation with the Lorentz force:

$$\dot{q}_i = \frac{\partial H}{\partial p_i} \quad \& \quad \dot{p}_i = -\frac{\partial H}{\partial q_i} \quad \Leftrightarrow \quad m\mathbf{a} = z(\mathbf{E} + \mathbf{v} \times \mathbf{B})$$

- To this end, we introduce scalar and vector potentials  $\phi$  and  $\mathbf{A}$  such that

$$\mathbf{E} = -\nabla\phi - \frac{\partial\mathbf{A}}{\partial t}, \quad \mathbf{B} = \nabla \times \mathbf{A}$$

- In terms of these potentials, the classical Hamiltonian function becomes

$$H = \frac{\pi^2}{2m} + z\phi, \quad \boldsymbol{\pi} = \mathbf{p} - z\mathbf{A} \quad \leftarrow \text{kinetic momentum}$$

- Quantization is then accomplished in the usual manner, by the substitutions

$$\mathbf{p} \rightarrow -i\hbar\nabla, \quad H \rightarrow i\hbar\frac{\partial}{\partial t}$$

- This results in the following time-dependent Schrödinger equation for a particle in an electromagnetic field:

$$i\hbar\frac{\partial\Psi}{\partial t} = \frac{1}{2m} (-i\hbar\nabla - z\mathbf{A}) \cdot (-i\hbar\nabla - z\mathbf{A}) \Psi + z\phi\Psi$$

## Electron spin

- According to our previous discussion, the nonrelativistic Hamiltonian for an electron in an electromagnetic field is given by:

$$H = \frac{\pi^2}{2m} - e\phi, \quad \boldsymbol{\pi} = -i\hbar\nabla + e\mathbf{A}$$

- However, this description ignores a fundamental property of the electron: spin.
- Spin was introduced by Pauli in 1927, to fit experimental observations:

$$H = \frac{(\boldsymbol{\sigma} \cdot \boldsymbol{\pi})^2}{2m} - e\phi = \frac{\pi^2}{2m} + \frac{e\hbar}{2m} \mathbf{B} \cdot \boldsymbol{\sigma} - e\phi$$

where  $\boldsymbol{\sigma}$  contains three operators, represented by the two-by-two Pauli spin matrices

$$\sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad \sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \quad \sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

- The Schrödinger equation now becomes a two-component equation

$$\begin{pmatrix} \frac{\pi^2}{2m} - e\phi + \frac{e\hbar}{2m} B_z & \frac{e\hbar}{2m} (B_x - iB_y) \\ \frac{e\hbar}{2m} (B_x + iB_y) & \frac{\pi^2}{2m} - e\phi - \frac{e\hbar}{2m} B_z \end{pmatrix} \begin{pmatrix} \Psi_\alpha \\ \Psi_\beta \end{pmatrix} = E \begin{pmatrix} \Psi_\alpha \\ \Psi_\beta \end{pmatrix}$$

– the two components are only coupled in the presence of an external magnetic field



## Spin and relativity

- The introduction of spin by Pauli in 1927 may appear somewhat ad hoc.
- By contrast, spin arises naturally from Dirac's relativistic treatment in 1928.
  - is spin a relativistic effect?
- However, reduction of Dirac's equation to nonrelativistic form yields the Hamiltonian

$$H = \frac{(\boldsymbol{\sigma} \cdot \boldsymbol{\pi})^2}{2m} - e\phi = \frac{\pi^2}{2m} + \frac{e\hbar}{2m} \mathbf{B} \cdot \boldsymbol{\sigma} - e\phi \neq \frac{\pi^2}{2m} - e\phi$$

- spin is therefore not a relativistic property of the electron
- Indeed, it is possible to take the factorized form

$$H = \frac{(\boldsymbol{\sigma} \cdot \boldsymbol{\pi})^2}{2m} - e\phi$$

as the starting point for a nonrelativistic treatment, with unspecified operators  $\boldsymbol{\sigma}$ .

- All algebraic properties of  $\boldsymbol{\sigma}$  then follow from the requirement  $(\boldsymbol{\sigma} \cdot \mathbf{p})^2 = p^2$ :

$$[\sigma_i, \sigma_j]_+ = 2\delta_{ij}, \quad [\sigma_i, \sigma_j]_- = 2\sum_k i\epsilon_{ijk}\sigma_k$$

- these operators are represented by the two-by-two Pauli spin matrices
- We interpret  $\boldsymbol{\sigma}$  by associating an intrinsic angular momentum (spin) with the electron:

$$\mathbf{s} = \hbar\boldsymbol{\sigma}/2$$

## Molecular Hamiltonian

- The nonrelativistic Hamiltonian for an electron in an electromagnetic field is therefore

$$H = \frac{\pi^2}{2m} + \frac{e}{m} \mathbf{B} \cdot \mathbf{s} - e\phi, \quad \boldsymbol{\pi} = \mathbf{p} + e\mathbf{A}, \quad \mathbf{p} = -i\hbar \nabla$$

- expanding  $\pi^2$  and assuming the Coulomb gauge  $\nabla \cdot \mathbf{A} = 0$ , we obtain

$$\begin{aligned} \pi^2 \Psi &= (\mathbf{p} + e\mathbf{A}) \cdot (\mathbf{p} + e\mathbf{A}) \Psi = p^2 \Psi + e\mathbf{p} \cdot \mathbf{A} \Psi + e\mathbf{A} \cdot \mathbf{p} \Psi + e^2 A^2 \Psi \\ &= p^2 \Psi + e(\mathbf{p} \cdot \mathbf{A}) \Psi + 2e\mathbf{A} \cdot \mathbf{p} \Psi + e^2 A^2 \Psi = (p^2 + 2e\mathbf{A} \cdot \mathbf{p} + e^2 A^2) \Psi \end{aligned}$$

- in a molecule, the dominant electromagnetic contribution is from the nuclear charges:

$$\phi = \frac{1}{4\pi\epsilon_0} \sum_K \frac{Z_K e}{r_K} + \phi_{\text{ext}}$$

- Summing over all electrons and adding pairwise Coulomb interactions, we obtain

$$\begin{aligned} H &= \sum_i \frac{1}{2m} p_i^2 - \frac{e^2}{4\pi\epsilon_0} \sum_{K_i} \frac{Z_K}{r_{iK}} + \frac{e^2}{4\pi\epsilon_0} \sum_{i>j} r_{ij}^{-1} && \leftarrow \text{zero-order Hamiltonian} \\ &+ \frac{e}{m} \sum_i \mathbf{A}_i \cdot \mathbf{p}_i + \frac{e}{m} \sum_i \mathbf{B}_i \cdot \mathbf{s}_i - e \sum_i \phi_i && \leftarrow \text{first-order Hamiltonian} \\ &+ \frac{e^2}{2m} \sum_i A_i^2 && \leftarrow \text{second-order Hamiltonian} \end{aligned}$$

## 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 second 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:

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

## 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  $\chi_{lm}$  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  $\chi_{lm}$  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**:

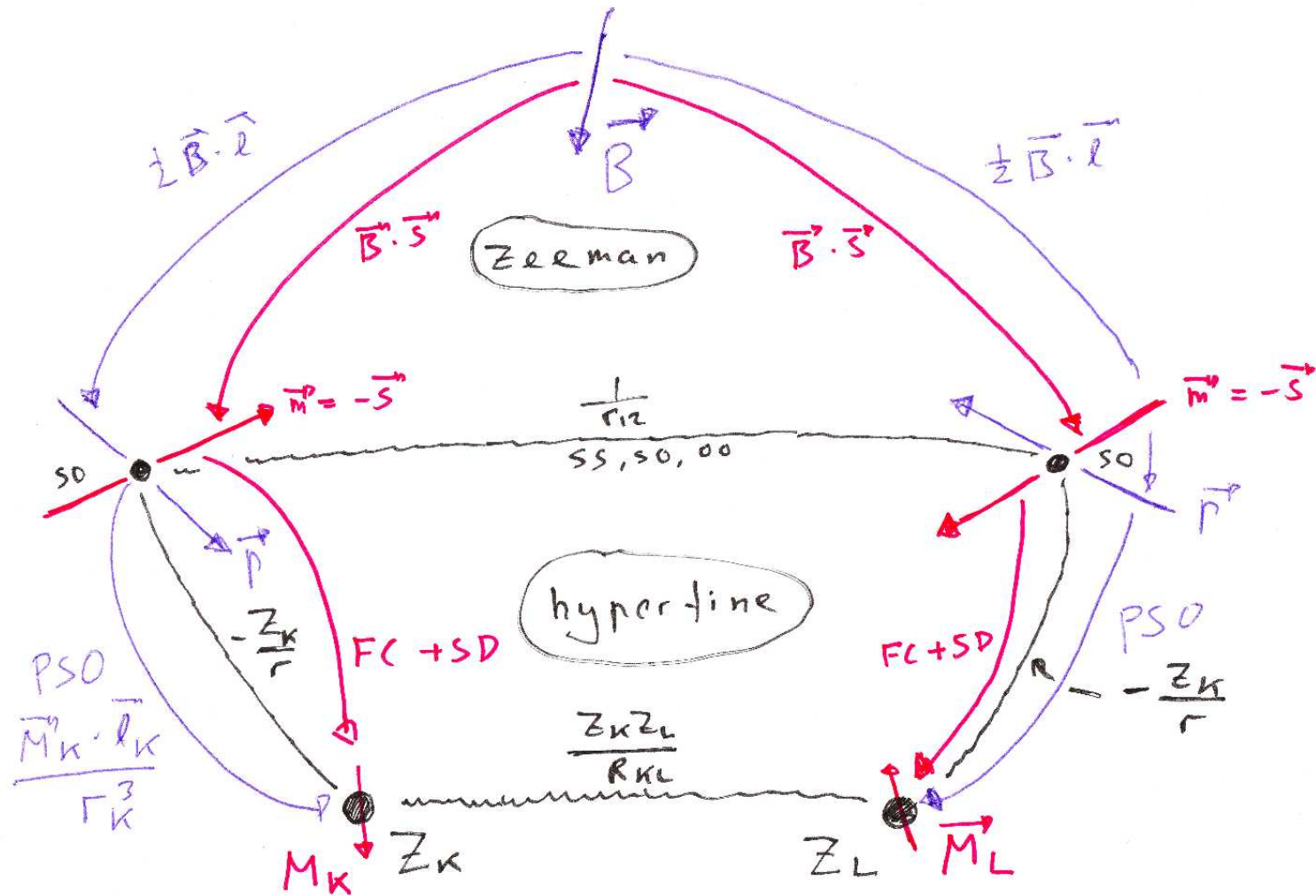
$$\mathbf{A}(\mathbf{r}) = \frac{1}{2} \mathbf{B} \times \mathbf{r}_O, \quad \mathbf{A}_K(\mathbf{r}) = \alpha^2 \frac{\mathbf{M}_K \times \mathbf{r}_K}{r_K^3}, \quad \nabla \times \mathbf{A}(\mathbf{r}) = \mathbf{B}(\mathbf{r}), \quad \nabla \cdot \mathbf{A}(\mathbf{r}) = 0$$

- 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.

## The calculation of magnetizabilities

- The molecular magnetizability of a closed-shell system:

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

- 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:

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

- 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%:

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

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



## 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  $\gamma_K$  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**:

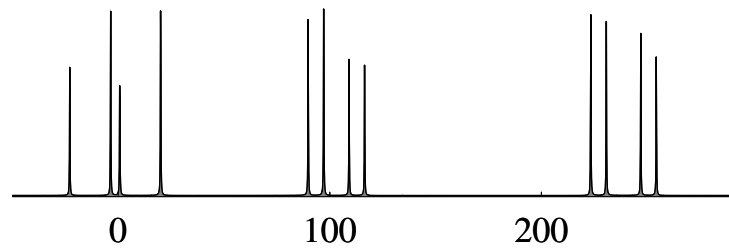
$$H_{\text{NMR}} = \underbrace{- \sum_K \gamma_K \hbar (1 - \sigma_K) B I_{Kz}}_{\text{nuclear Zeeman interaction}} + \underbrace{\sum_{K>L} \gamma_K \gamma_L \hbar^2 K_{KL} \mathbf{I}_K \cdot \mathbf{I}_L}_{\text{nuclear spin-spin interaction}}$$

where we have introduced

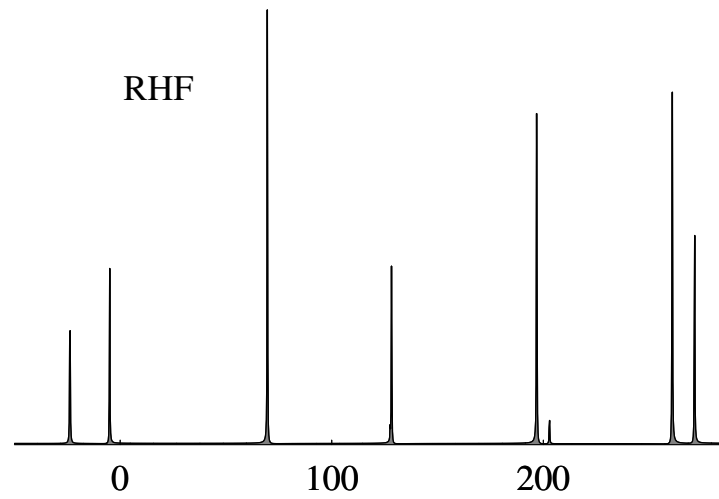
- the **nuclear shielding constants**  $\sigma_K$
- the **(reduced) indirect nuclear spin-spin coupling constants**  $K_{KL}$
- This is an **effective** nuclear spin Hamiltonian:
  - it reproduces NMR spectra without considering the electrons explicitly
  - the spin parameters  $\sigma_K$  and  $K_{KL}$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

Simulated 200 MHz NMR spectra of vinyl lithium

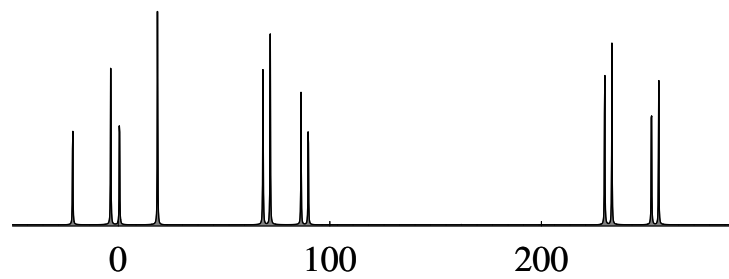
experiment



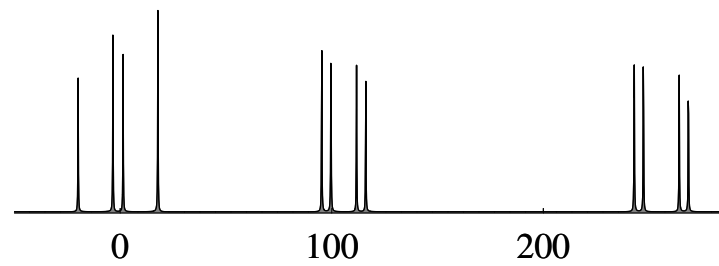
RHF



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.

## 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 <sub>2</sub> 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 <sub>3</sub>	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 <sub>4</sub>	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 <sub>2</sub>	F	-167.9	-136.6	-170.0	-171.1	-186.5	-192.8
N <sub>2</sub>	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 H<sub>2</sub>O, 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 <sub>2</sub> O	O	328.1	334.8	318.2	325.0	329.5	337.9	323.6 ± 6
NH <sub>3</sub>	N	262.3	266.3	254.6	259.2	264.6	270.7	264.5
CH <sub>4</sub>	C	194.8	193.1	184.2	188.1	195.1	198.9	198.7
F <sub>2</sub>	F	-167.9	-284.2	-336.7	-208.3	-211.0	-186.5	-192.8
N <sub>2</sub>	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

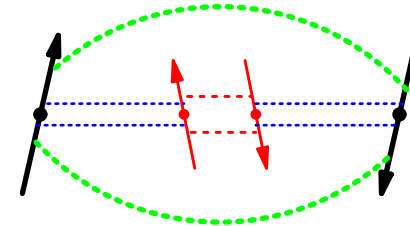
- The last term in the expansion of the molecular electronic energy in  $\mathbf{B}$  and  $\mathbf{M}_K$

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

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

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

## The calculation of indirect nuclear spin–spin coupling tensors

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

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

- 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

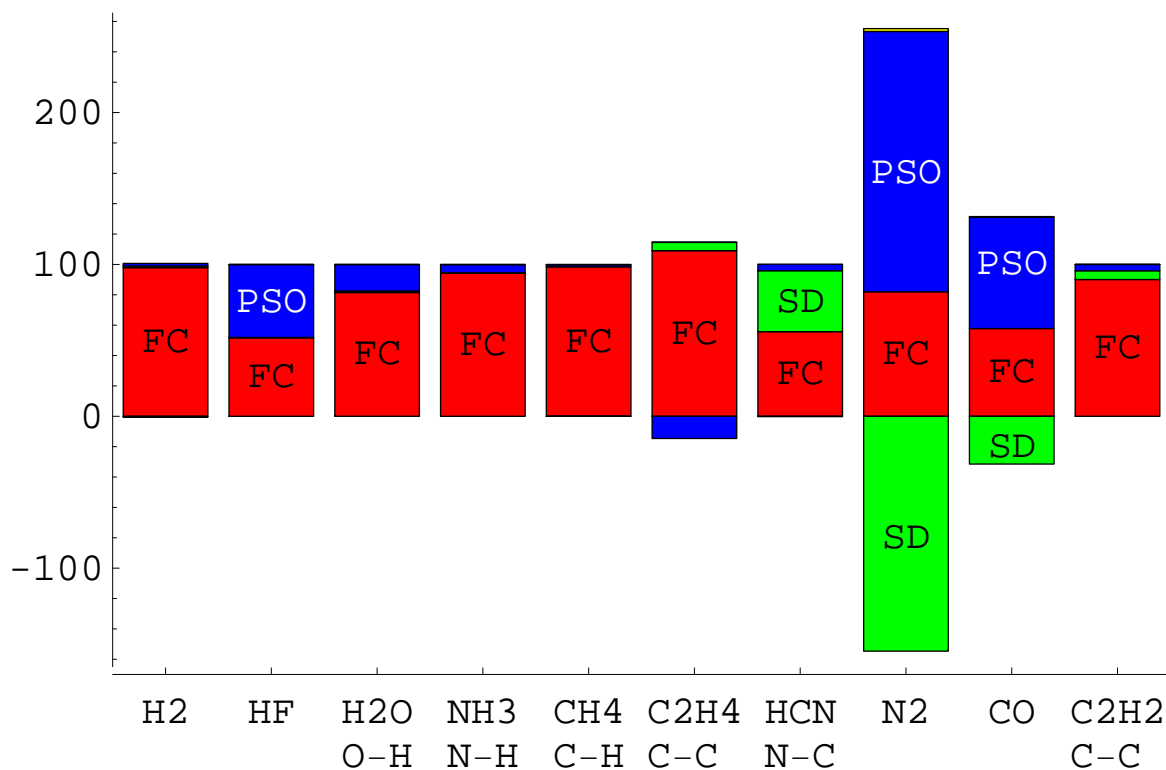
- The calculation of spin–spin coupling constants is a **challenging task**:
  - triplet as well as singlet perturbations are involved
  - electron correlation important—the Hartree–Fock model fails abysmally
  - the dominant FC contribution requires an accurate description of the electron density at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

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

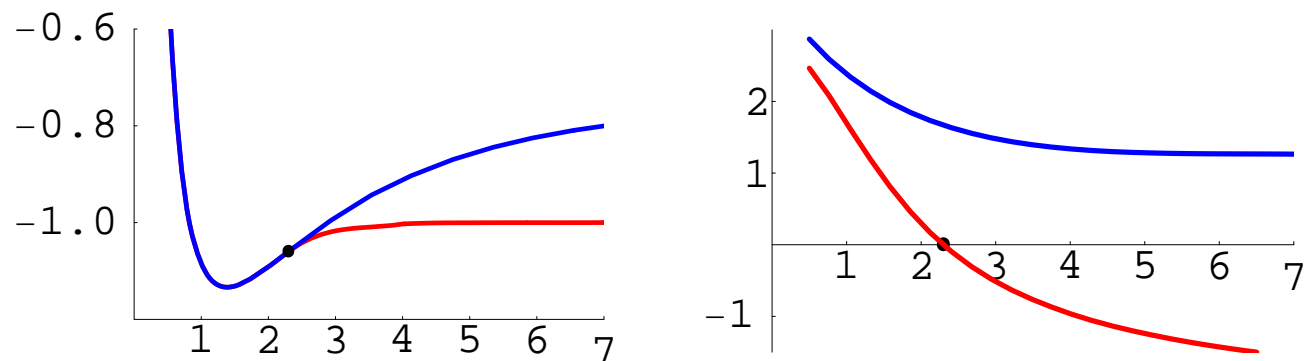
- The spin–spin coupling constants are often dominated by the FC term.
- Since the FC term is relatively easy to calculate, it is tempting to ignore the other terms.
- However, none of the contributions can be *a priori* neglected (N<sub>2</sub> and CO)!



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

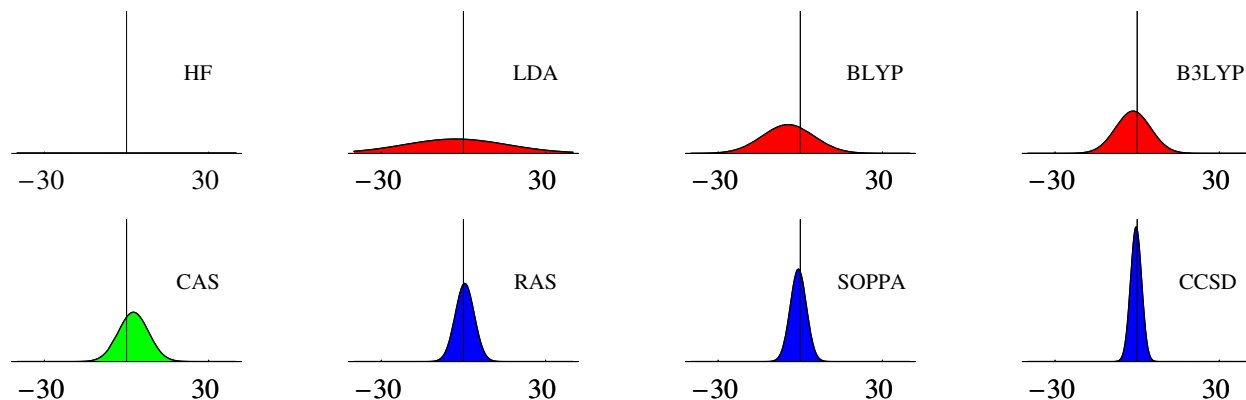
		RHF	CAS	RAS	SOPPA	CCSD	CC3	exp*	vib
HF	$^1J_{\text{HF}}$	59.2	48.0	48.1	46.8	46.1	46.1	47.6	-3.4
CO	$^1J_{\text{CO}}$	13.4	-28.1	-39.3	-45.4	-38.3	-37.3	-38.3	-1.7
N <sub>2</sub>	$^1J_{\text{NN}}$	175.0	-5.7	-9.1	-23.9	-20.4	-20.4	-19.3	-1.1
H <sub>2</sub> O	$^1J_{\text{OH}}$	63.7	51.5	47.1	49.5	48.4	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 <sub>3</sub>	$^1J_{\text{NH}}$	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 <sub>2</sub> H <sub>4</sub>	$^1J_{\text{CC}}$	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 <sub>2</sub>	$^1 J_{\text{NN}}$	32.9	−46.6	−20.4	−43.2	−12.5	−9.1	−19.3	−1.1
H <sub>2</sub> 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 <sub>3</sub>	$^1 J_{\text{NH}}$	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 <sub>2</sub> H <sub>4</sub>	$^1 J_{\text{CC}}$	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:

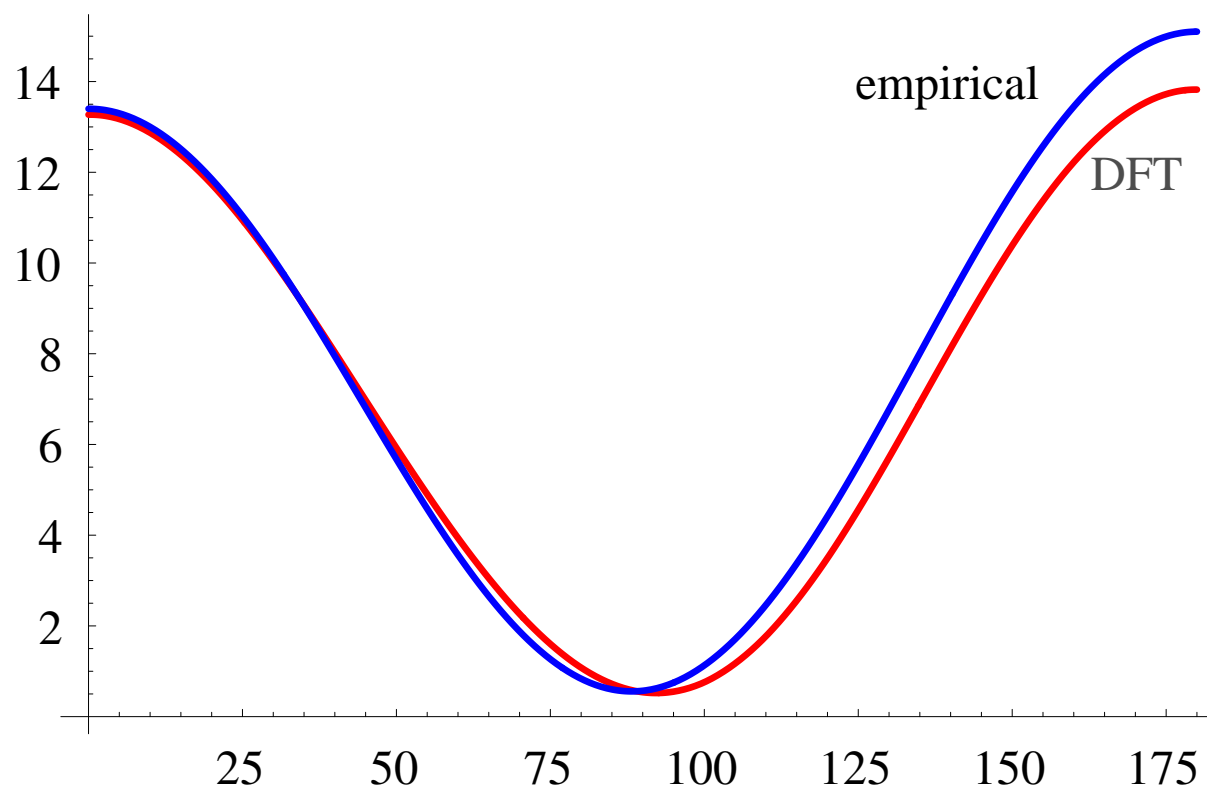


- some observations:
  - HF has a very broad distribution and overestimates strongly
  - LDA underestimates only slightly, but has a large standard deviation
  - BLYP reduces the LDA errors by a factor of two
  - B3LYP improves upon GGA (but not as dramatically as for other properties)
  - B3LYP errors 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

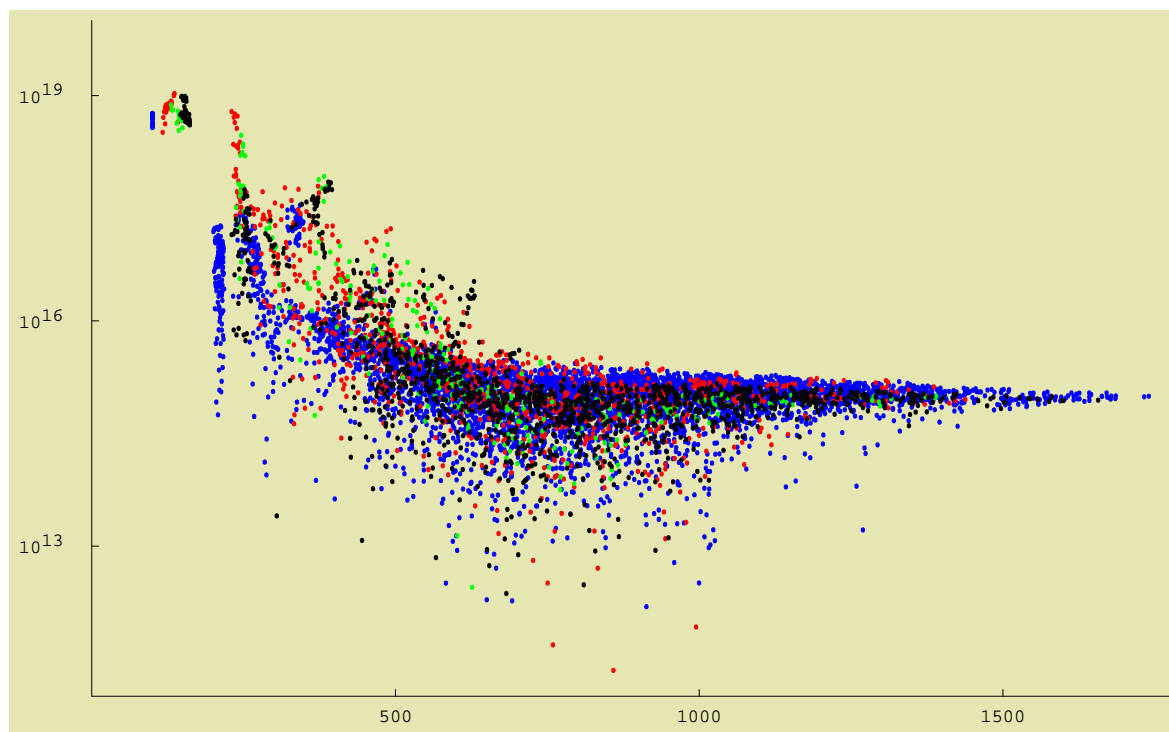
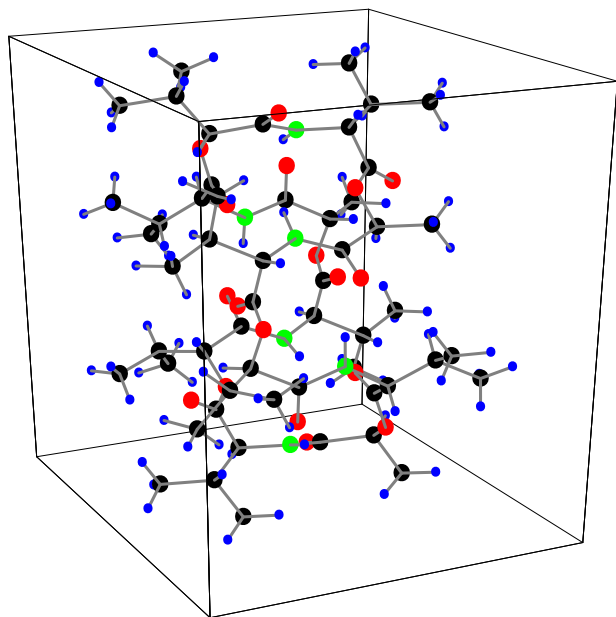
- Vicinal couplings depend critically on the dihedral angle:
- ${}^3J_{\text{HH}}$  in ethane as a function of the dihedral angle:



- The agreement with the empirical Karplus curve is good.

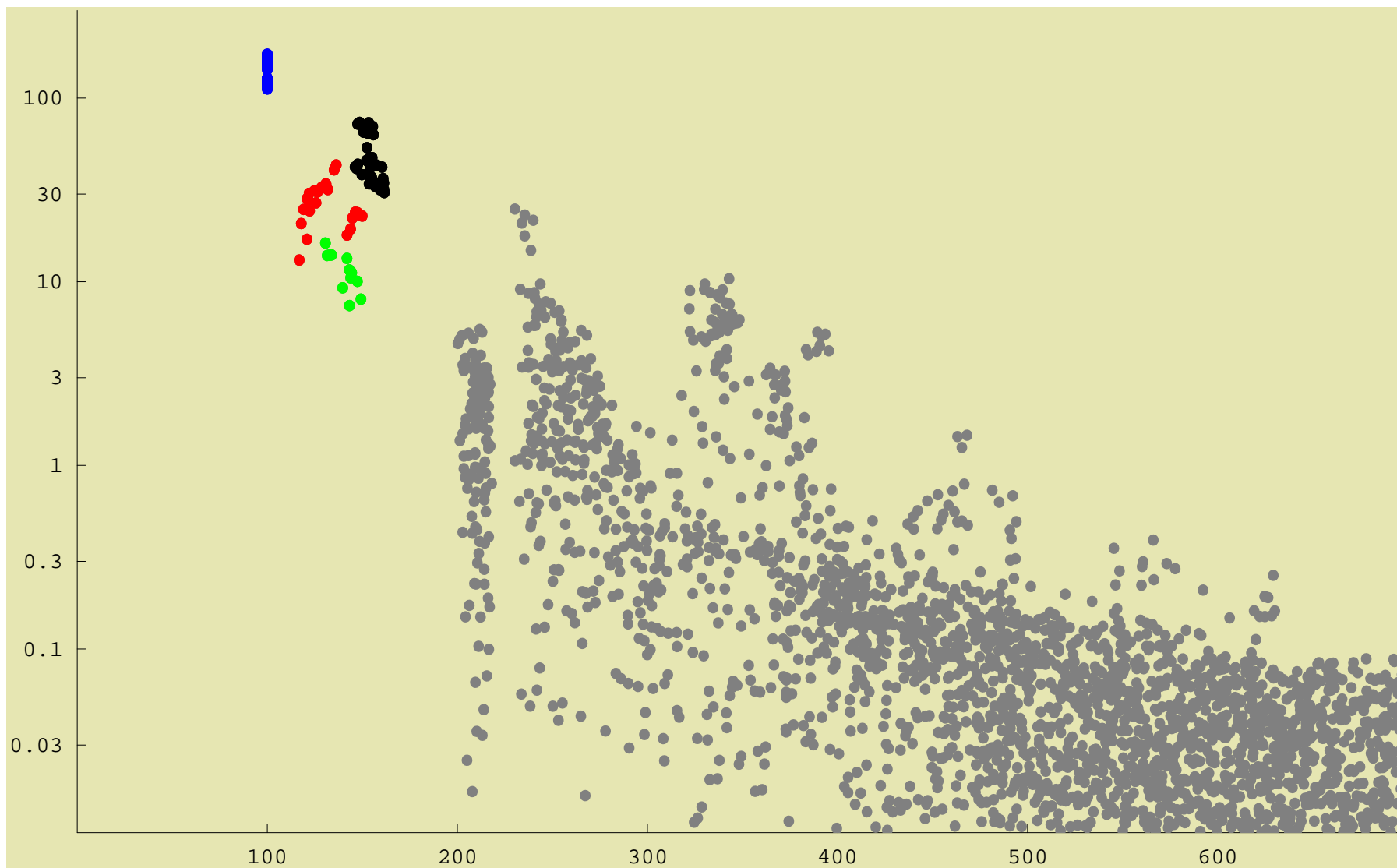
## Valinomycin $C_{54}H_{90}N_8O_{18}$

- 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:

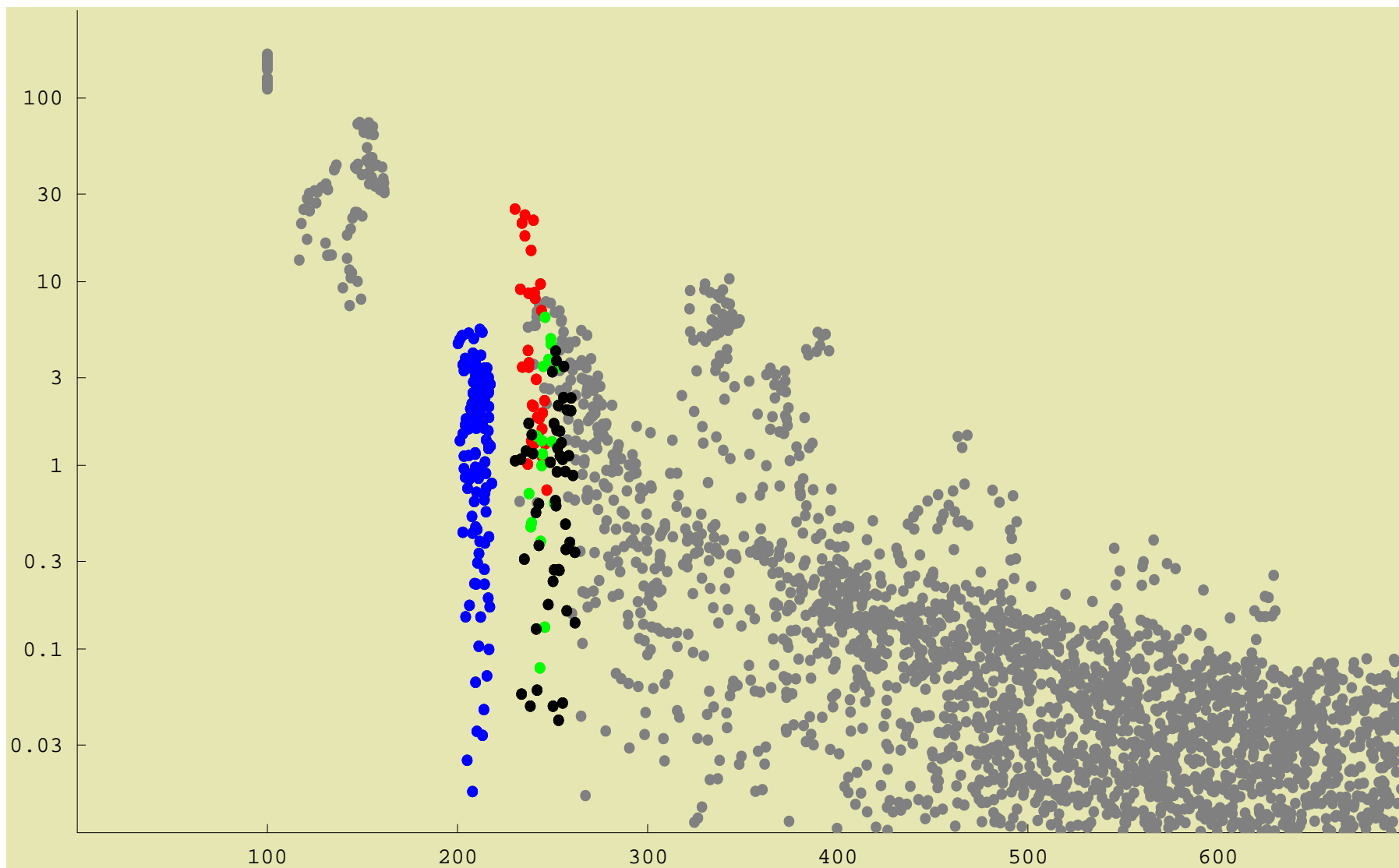


- the coupling constants decay in characteristic fashion, which we shall examine
- most of the indirect couplings beyond 500 pm are small and cannot be detected

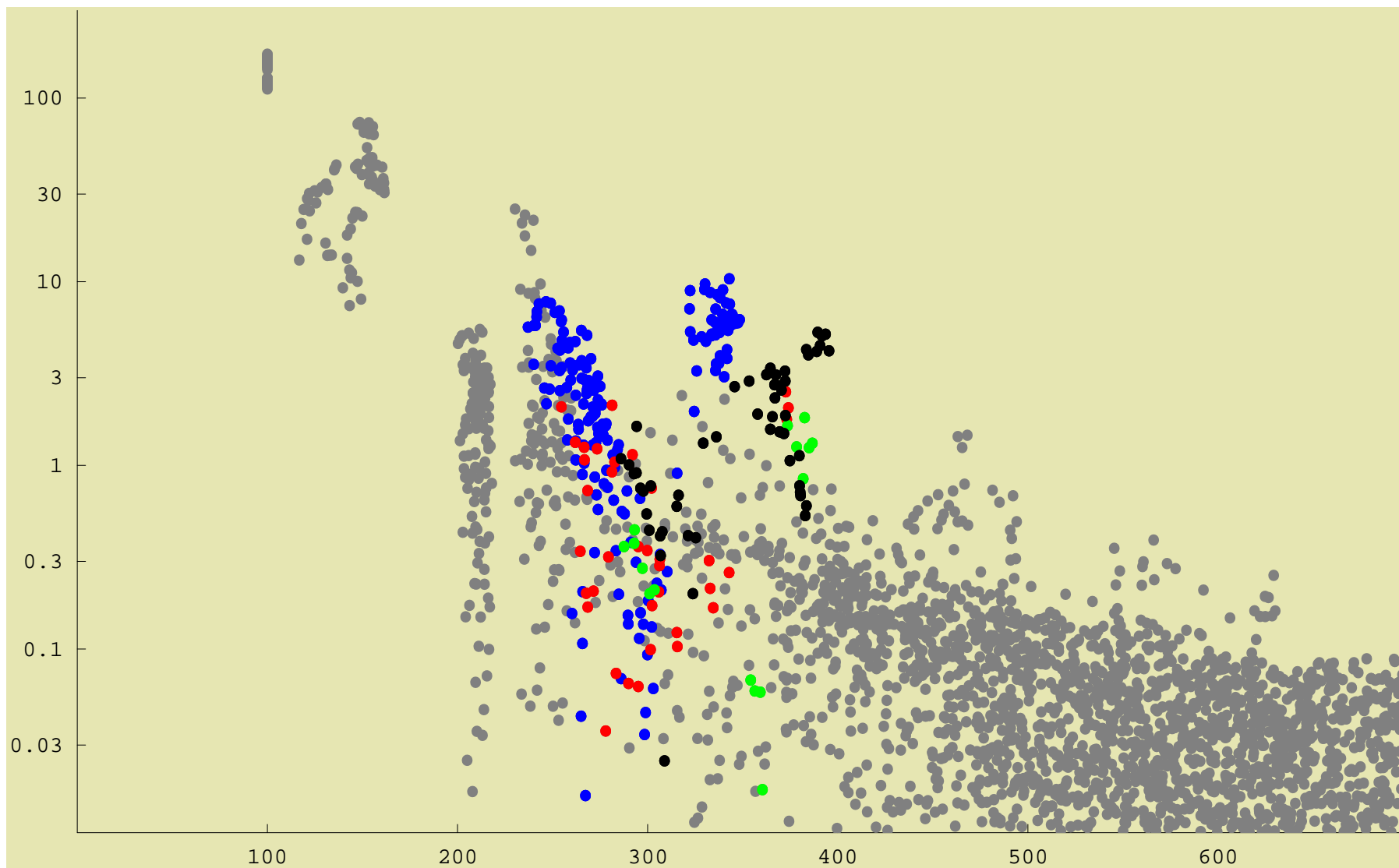
Valinomycin one-bond spin-spin couplings to CH, CO, CN, CC greater than 0.01 Hz



Valinomycin two-bond spin-spin couplings to CH, CO, CN, CC greater than 0.01 Hz



Valinomycin three-bond spin-spin couplings to CH, CO, CN, CC greater than 0.01 Hz



Valinomycin four-bond spin-spin couplings to CH, CO, CN, CC greater than 0.01 Hz

