# Molecular Magnetic Properties

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# Sections

# Section 1

## Electronic Hamiltonian

# Outline

# 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:

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

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

# Quantization of a Particle in a 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

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

  - 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
  - it is therefore inappropriate for systems in a general electromagnetic field

# 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:

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

  - 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):

$$\nabla \cdot \mathbf{E} = \rho/\varepsilon_0 \qquad \leftarrow \text{Coulomb's law}$$
$$\nabla \times \mathbf{B} - \varepsilon_0\mu_0\,\partial\mathbf{E}/\partial t = \mu_0\mathbf{J} \qquad \leftarrow \text{Ampère's law with Maxwell's correction}$$
$$\nabla \cdot \mathbf{B} = 0$$
$$\nabla \times \mathbf{E} + \partial\mathbf{B}/\partial t = \mathbf{0} \qquad \leftarrow \text{Faraday's law of induction}$$

- Note:
  - 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 $\mathbf{B}(\mathbf{r}, t)$

- We here 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 **E** and **B**:

$$\boldsymbol{\nabla} \cdot \mathbf{B} = 0 \tag{1}$$

$$\boldsymbol{\nabla} \times \mathbf{E} + \frac{\partial \mathbf{B}}{\partial t} = \mathbf{0} \tag{2}$$

① Eq. (1) is satisfied by introducing the vector potential **A**:

$$\boldsymbol{\nabla} \cdot \mathbf{B} = 0 \quad \Longrightarrow \quad \mathbf{B} = \boldsymbol{\nabla} \times \mathbf{A} \qquad \leftarrow \text{vector potential} \tag{3}$$

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

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

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

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

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

▶ 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 **J**.

# Gauge Transformations

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

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

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

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

$$\mathbf{B}' = \boldsymbol{\nabla} \times \mathbf{A}' = \boldsymbol{\nabla} \times (\mathbf{A} + \boldsymbol{\nabla} f) = \mathbf{B} + \boldsymbol{\nabla} \times \boldsymbol{\nabla} f = \mathbf{B}$$

- We are free to choose $f(q, t)$ to make the potentials satisfy additional conditions
- Typically, we require the vector potential to be divergenceless:

$$\boldsymbol{\nabla} \cdot \mathbf{A}' = 0 \implies \boldsymbol{\nabla} \cdot (\mathbf{A} + \boldsymbol{\nabla} f) = 0 \implies \nabla^2 f = -\nabla \cdot \mathbf{A} \quad \leftarrow \text{Coulomb gauge}$$

- We shall always assume that the vector potential satisfies the Coulomb gauge:

$$\boldsymbol{\nabla} \times \mathbf{A} = \mathbf{B}, \quad \boldsymbol{\nabla} \cdot \mathbf{A} = 0 \quad \leftarrow \text{Coulomb gauge}$$

- Note: **A** is still not uniquely determined, the following transformation being allowed:

$$\mathbf{A}' = \mathbf{A} + \boldsymbol{\nabla} f, \quad \nabla^2 f = 0$$

# 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:

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

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

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

▶ 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

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

▶ The time-dependent Schrödinger equation for a particle in an electromagnetic field:

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

# Electron Spin

▶ The nonrelativistic Hamiltonian for an electron in an electromagnetic field is then given by:

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

▶ 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:

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

▶ Note: 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

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

    - in this sense, spin is not a relativistic property of the electron
    - but we note that, in the nonrelativistic limit, all magnetic fields disappear. . .

- We interpret $\boldsymbol{\sigma}$ by associating an intrinsic angular momentum (spin) with the electron:

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

# Molecular Electronic Hamiltonian

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

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

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

$$\pi^2\Psi = (\mathbf{p} + e\mathbf{A}) \cdot (\mathbf{p} + e\mathbf{A})\,\Psi = p^2\Psi + e\mathbf{p} \cdot \mathbf{A}\Psi + e\mathbf{A} \cdot \mathbf{p}\Psi + e^2A^2\Psi$$

$$= p^2\Psi + e(\mathbf{p} \cdot \mathbf{A})\Psi + 2e\mathbf{A} \cdot \mathbf{p}\Psi + e^2A^2\Psi = \left(p^2 + 2e\mathbf{A} \cdot \mathbf{p} + e^2A^2\right)\Psi$$

▶ in molecules, 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

$$H = \sum_i \frac{1}{2m}p_i^2 - \frac{e^2}{4\pi\epsilon_0} \sum_{Ki} \frac{Z_K}{r_{iK}} + \frac{e^2}{4\pi\epsilon_0} \sum_{i>j} r_{ij}^{-1} \quad \leftarrow \text{zero-order Hamiltonian}$$

$$+ \frac{e}{m} \sum_i \mathbf{A}_i \cdot \mathbf{p}_i + \frac{e}{m} \sum_i \mathbf{B}_i \cdot \mathbf{s}_i - e \sum_i \phi_i \quad \leftarrow \text{first-order Hamiltonian}$$

$$+ \frac{e^2}{2m} \sum_i A_i^2 \quad \leftarrow \text{second-order Hamiltonian}$$

# Magnetic Perturbations

▶ In atomic units, the molecular Hamiltonian is given by

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

▶ 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 $\mathbf{B}$, 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

Section 2

London Orbitals

# Outline

# Hamiltonian in a Uniform Magnetic Field

▶ The nonrelativistic electronic Hamiltonian (implied summation over electrons):

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

▶ The vector potential of the uniform field **B** is given by:

$$\mathbf{B} = \boldsymbol{\nabla} \times \mathbf{A} = \text{const} \quad \Longrightarrow \quad \mathbf{A_O}(\mathbf{r}) = \tfrac{1}{2}\mathbf{B} \times (\mathbf{r} - \mathbf{O}) = \tfrac{1}{2}\mathbf{B} \times \mathbf{r_O}$$

  ▶ note: the gauge origin **O** is arbitrary!

▶ The orbital paramagnetic interaction:

$$\mathbf{A_O}(\mathbf{r}) \cdot \mathbf{p} = \tfrac{1}{2}\mathbf{B} \times (\mathbf{r} - \mathbf{O}) \cdot \mathbf{p} = \tfrac{1}{2}\mathbf{B} \cdot (\mathbf{r} - \mathbf{O}) \times \mathbf{p} = \tfrac{1}{2}\mathbf{B} \cdot \mathbf{L_O}$$

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

$$\mathbf{L_O} = \mathbf{r_O} \times \mathbf{p}$$

▶ The diamagnetic interaction:

$$\tfrac{1}{2} A_\mathbf{O}^2(\mathbf{r}) = \tfrac{1}{8}(\mathbf{B} \times \mathbf{r_O}) \cdot (\mathbf{B} \times \mathbf{r_O}) = \tfrac{1}{8}\left[B^2 r_\mathbf{O}^2 - (\mathbf{B} \cdot \mathbf{r_O})^2\right]$$

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

$$H = H_0 + \frac{1}{2}\mathbf{B} \cdot \mathbf{L_O} + \mathbf{B} \cdot \mathbf{s} + \frac{1}{8}\left[B^2 r_\mathbf{O}^2 - (\mathbf{B} \cdot \mathbf{r_O})^2\right]$$

  ▶ a change of the origin is a gauge transformation

# Gauge Transformation of Schrödinger Equation

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

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

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

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

- In order that the Schrödinger equation is still satisfied

$$\left(H' - i\frac{\partial}{\partial t}\right)\Psi' \quad \Longleftrightarrow \quad \left(H - i\frac{\partial}{\partial t}\right)\Psi,$$

  the new wave function must undergo a compensating unitary transformation:

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

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

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

# Gauge-Origin Transformations

- Different choices of gauge origin in the external vector potential

$$\mathbf{A_O}\left(\mathbf{r}\right) = \tfrac{1}{2}\mathbf{B} \times \left(\mathbf{r} - \mathbf{O}\right)$$

  are related by gauge transformations:

$$\mathbf{A_G}\left(\mathbf{r}\right) = \mathbf{A_O}\left(\mathbf{r}\right) - \mathbf{A_O}\left(\mathbf{G}\right) = \mathbf{A_O}\left(\mathbf{r}\right) + \boldsymbol{\nabla}f, \quad f\left(\mathbf{r}\right) = -\mathbf{A_O}\left(\mathbf{G}\right) \cdot \mathbf{r}$$

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

$$\Psi_{\mathbf{G}}^{\text{exact}} = \exp\left[-\mathrm{i}f(\mathbf{r})\right]\Psi_{\mathbf{O}}^{\text{exact}} = \exp\left[\mathrm{i}\mathbf{A_O}\left(\mathbf{G}\right) \cdot \mathbf{r}\right]\Psi_{\mathbf{O}}^{\text{exact}} \quad \text{(rapid) oscillations}$$

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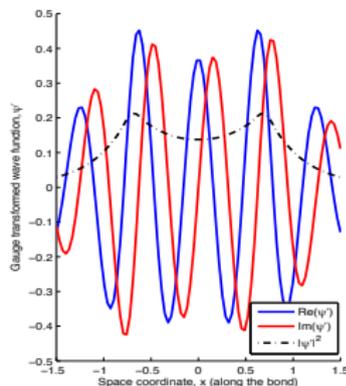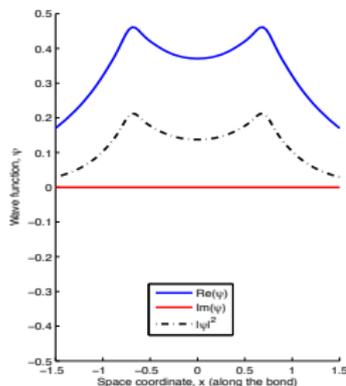
# London Orbitals

- The exact wave function transforms in the following manner:

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

  - this behaviour cannot easily be modelled by standard atomic orbitals

- Let us build this behaviour directly into the atomic orbitals:

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

  - $\chi_{lm}(\mathbf{r}_K)$ is a normal atomic orbital centred at $\mathbf{K}$ and quantum numbers $lm$
  - $\omega_{lm}(\mathbf{r}_K, \mathbf{B}, \mathbf{G})$ is a field-dependent orbital at $\mathbf{K}$ with field $\mathbf{B}$ and gauge origin $\mathbf{G}$

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

  - indeed, all AOs are now correct to first order in $\mathbf{B}$, for any gauge origin $\mathbf{G}$
  - 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?

# Dissociation With and Without London Orbitals

- Let us consider the FCI dissociation of $H_2$ in a magnetic field
    - full lines: with London atomic orbitals
    - dashed lines: without London atomic orbitals
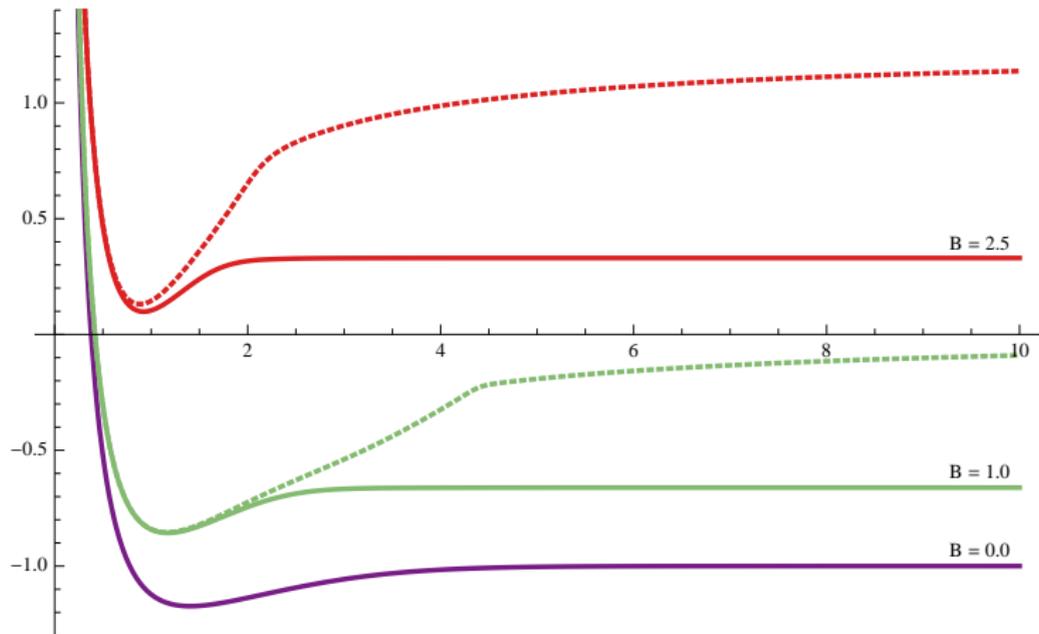


- Without London orbitals, the FCI method is not size extensive in magnetic fields

Section 3

## Zeeman and Hyperfine Interactions

# Outline

# Hamiltonian in Magnetic Field

- In atomic units, the molecular Hamiltonian is given by

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

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

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

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

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

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

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

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

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

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

▶ We obtain the following orbital paramagnetic operators:

$$\mathbf{A_O} \cdot \mathbf{p} = \quad \frac{1}{2}\mathbf{B} \times \mathbf{r_O} \cdot \mathbf{p} = \quad \frac{1}{2}\mathbf{B} \cdot \mathbf{r_O} \times \mathbf{p} = \quad \frac{1}{2}\mathbf{B} \cdot \mathbf{L_O} \quad \leftarrow \text{orbital Zeeman}$$

$$\mathbf{A}_K \cdot \mathbf{p} = \alpha^2 \frac{\mathbf{M}_K \times \mathbf{r}_K \cdot \mathbf{p}}{r_K^3} = \alpha^2 \frac{\mathbf{M}_K \cdot \mathbf{r}_K \times \mathbf{p}}{r_K^3} = \alpha^2 \mathbf{M}_K \cdot \frac{\mathbf{L}_K}{r_K^3} \quad \leftarrow \text{orbital hyperfine}$$

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

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

▶ These are imaginary singlet operators

- ▶ they have zero expectation values of closed-shell states
- ▶ they generate complex wave functions

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

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

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

  - should be compared with the orbital Zeeman interaction $\frac{1}{2}\mathbf{B} \cdot \mathbf{L_O}$ (different prefactor!)

- Taking the curl of $\mathbf{A}_K$, we obtain the nuclear magnetic field:

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

  - the first term is a contact interaction and contributes only at the nucleus
  - the second term is a classical dipole field and contributes at a distance

- This magnetic field $\mathbf{B}_K$ thus gives rise to two spin hyperfine interactions:

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

  - the FC operator contributes when the electron passes through the nucleus
  - the SD operator is a classical dipolar interaction, decaying as $r_K^{-3}$

- These are real triplet operators, which change the spin of the wave function

  - they have zero expectation values of closed-shell states
  - they couple closed-shell states to triplet states

# Perturbation Theory with Zeeman and Hyperfine Operators

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

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

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

  $$H_z^{(1)} = \frac{1}{2}\mathbf{B} \cdot \mathbf{L_O} + \mathbf{B} \cdot \mathbf{s} \sim 10^{-4}$$

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

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

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

- Second-order Rayleigh–Schrödinger perturbation theory:

$$E^{(1)} = \langle 0|H_z^{(1)} + H_{hf}^{(1)}|0\rangle$$

$$E^{(2)} = \frac{1}{2}\langle 0\,|A^2|\,0\rangle - \sum_n \frac{\langle 0|H_z^{(1)} + H_{hf}^{(1)}|n\rangle\langle n|H_z^{(1)} + H_{hf}^{(1)}|0\rangle}{E_n - E_0}$$

# Zeeman and Hyperfine Interactions



$\mathbf{B}$

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

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

SO  SO

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

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

$\mathbf{M}_K$

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

$\mathbf{M}_L$
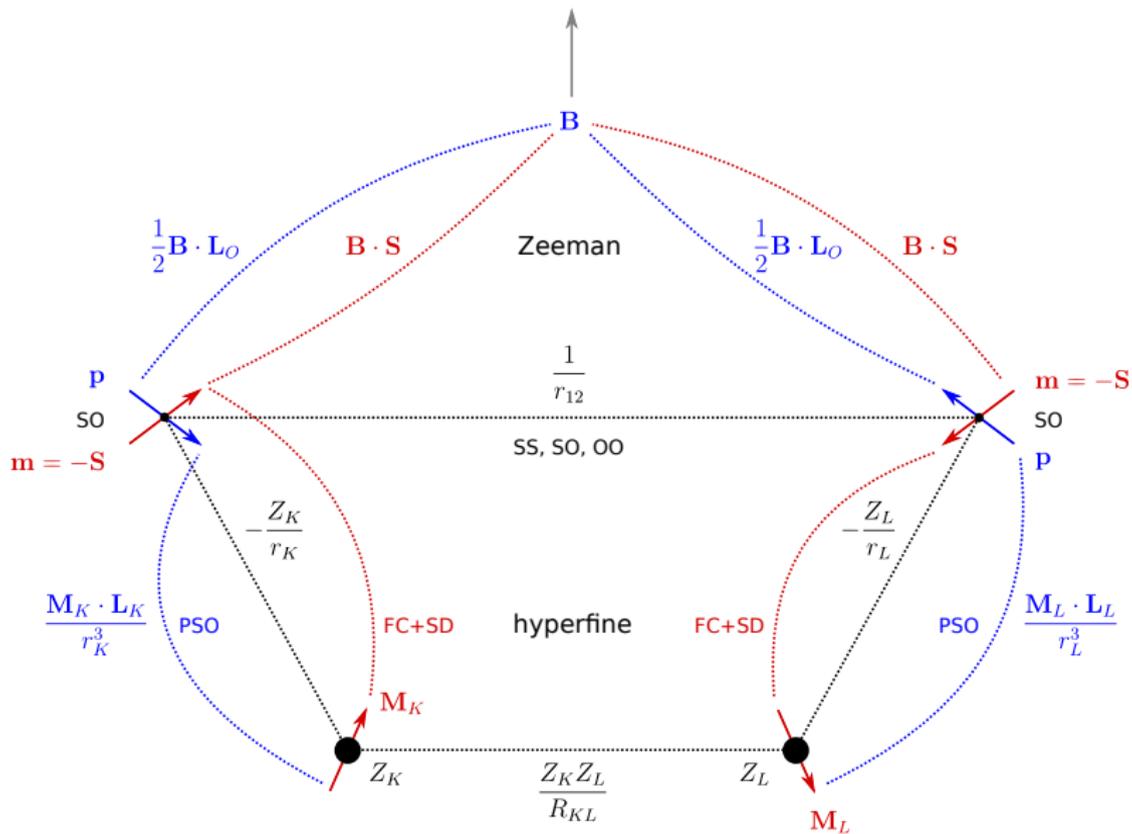
# Diamagnetic Operators: $\frac{1}{2}A^2$

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

$$\mathbf{A} = \mathbf{A}_O + \mathbf{A}_K \implies A^2 = \mathbf{A_O} \cdot \mathbf{A_O} + 2\mathbf{A_O} \cdot \mathbf{A}_K + \mathbf{A}_K \cdot \mathbf{A}_K$$

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

$$\mathbf{A_O} \cdot \mathbf{A_O} = \frac{1}{4}(\mathbf{B} \times \mathbf{r_O}) \cdot (\mathbf{B} \times \mathbf{r_O}) \qquad \sim 10^{-8}$$

$$\mathbf{A_O} \cdot \mathbf{A}_K = \frac{\alpha^2}{2} \frac{(\mathbf{B} \times \mathbf{r_O}) \cdot (\mathbf{M}_K \times \mathbf{r}_K)}{r_K^3} \sim 10^{-12}$$

$$\mathbf{A}_K \cdot \mathbf{A}_L = \alpha^4 \frac{(\mathbf{M}_K \times \mathbf{r}_K) \cdot (\mathbf{M}_L \times \mathbf{r}_L)}{r_K^3 r_L^3} \sim 10^{-16}$$

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

# Section 4

## Molecular Magnetic Properties

# Outline

# Taylor Expansion of Energy

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

$$E\left(\mathbf{B}, \mathbf{M}\right) = E_0 + \overbrace{\mathbf{B}^{\mathrm{T}}\mathbf{E}^{(10)}}^{\text{perm. magnetic moments}} + \overbrace{\sum_K \mathbf{M}_K^{\mathrm{T}}\mathbf{E}_K^{(01)}}^{\text{hyperfine coupling}}$$

$$+ \underbrace{\frac{1}{2}\mathbf{B}^{\mathrm{T}}\mathbf{E}^{(20)}\mathbf{B}}_{-\text{ magnetizability}} + \underbrace{\frac{1}{2}\sum_K \mathbf{B}^{\mathrm{T}}\mathbf{E}_K^{(11)}\mathbf{M}_K}_{\text{shieldings} + 1} + \underbrace{\frac{1}{2}\sum_{KL} \mathbf{M}_K^{\mathrm{T}}\mathbf{E}_{KL}^{(02)}\mathbf{M}_L}_{\text{spin–spin couplings}} + \cdots$$

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

# First-Order Molecular Properties

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

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

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

- Hyperfine coupling constants

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

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

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

  - all expectation values vanish for imaginary operators and triplet operators:

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

# Molecular Magnetizabilities

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

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

▶ The magnetizability describes the second-order energy:

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

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

▶ The magnetizability describes the curvature at zero magnetic field:
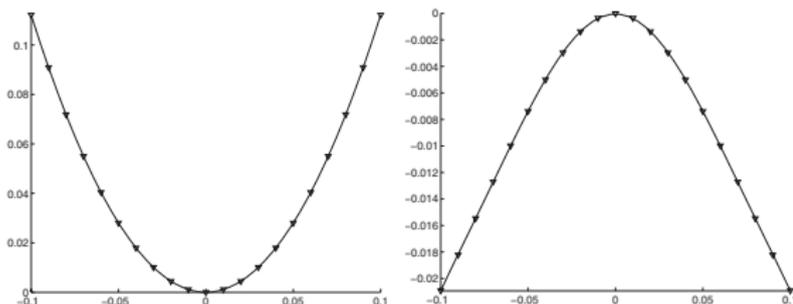


▶ left: diamagnetic dependence on the field ($\xi < 0$); right: paramagnetic dependence on the field ($\xi > 0$)

# Basis-Set Convergence of Hartree–Fock Magnetizabilities

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

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

# Mean Absolute Errors for Magnetizabilities
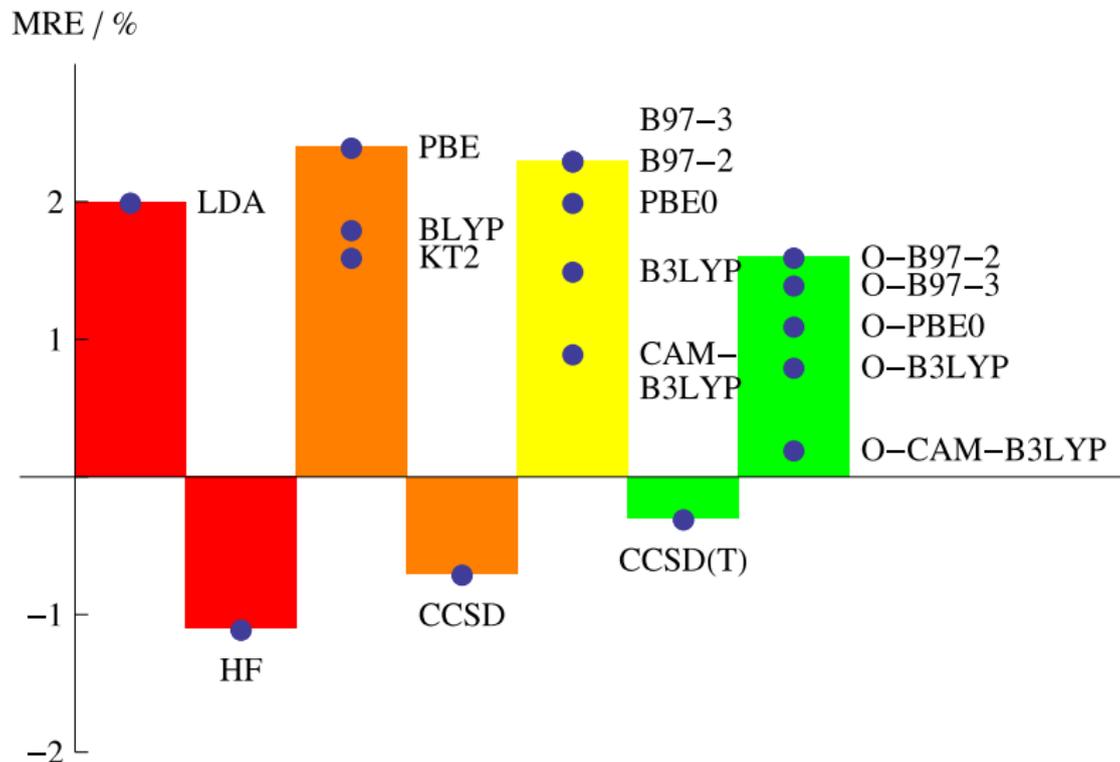


Mean relative errors (MREs, %) in magnetizabilities of 27 molecules relative to the CCSD(T)/aug-cc-pCV[TQ]Z values. The DFT results are grouped by functional type. The heights of the bars correspond to the largest MRE in each category. (Lutnæs *et al.*, JCP **131**, 144104 (2009))

# C$_{20}$ in a Perpendicular Magnetic Field

▶ All systems become diamagnetic in sufficiently strong fields:
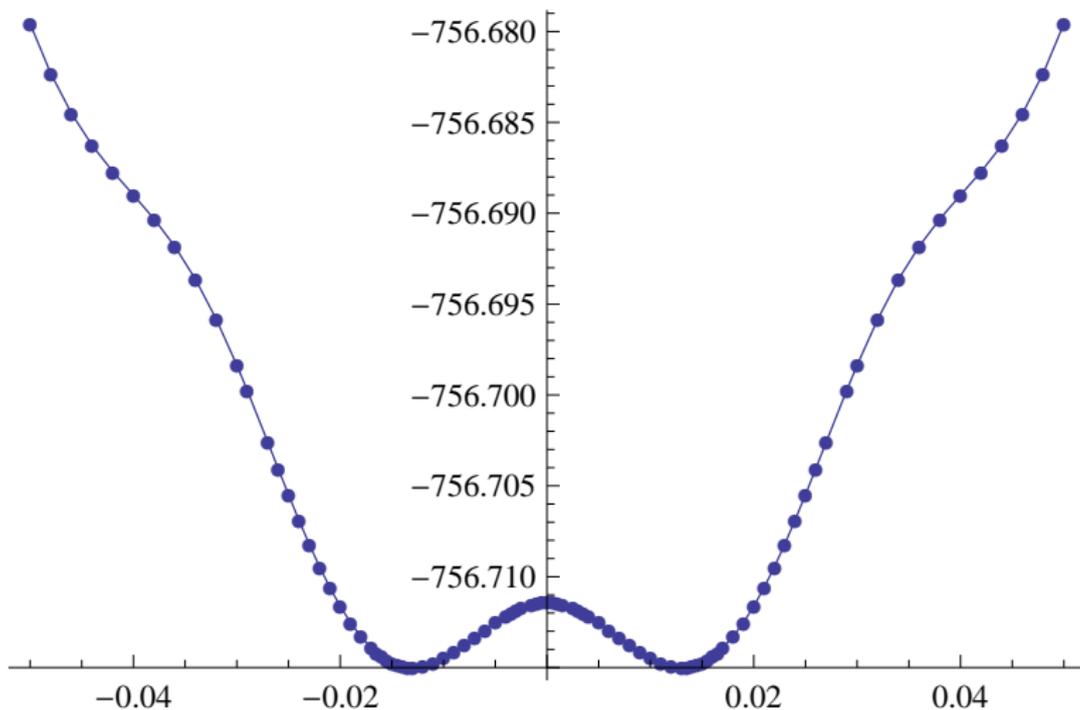
# High-Resolution NMR Spin Hamiltonian

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

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

where $\gamma_K$ 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:

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

where we have introduced

  ▶ the nuclear shielding constants $\sigma_K$
  ▶ 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 $^{12}C_2H_3{}^6Li$
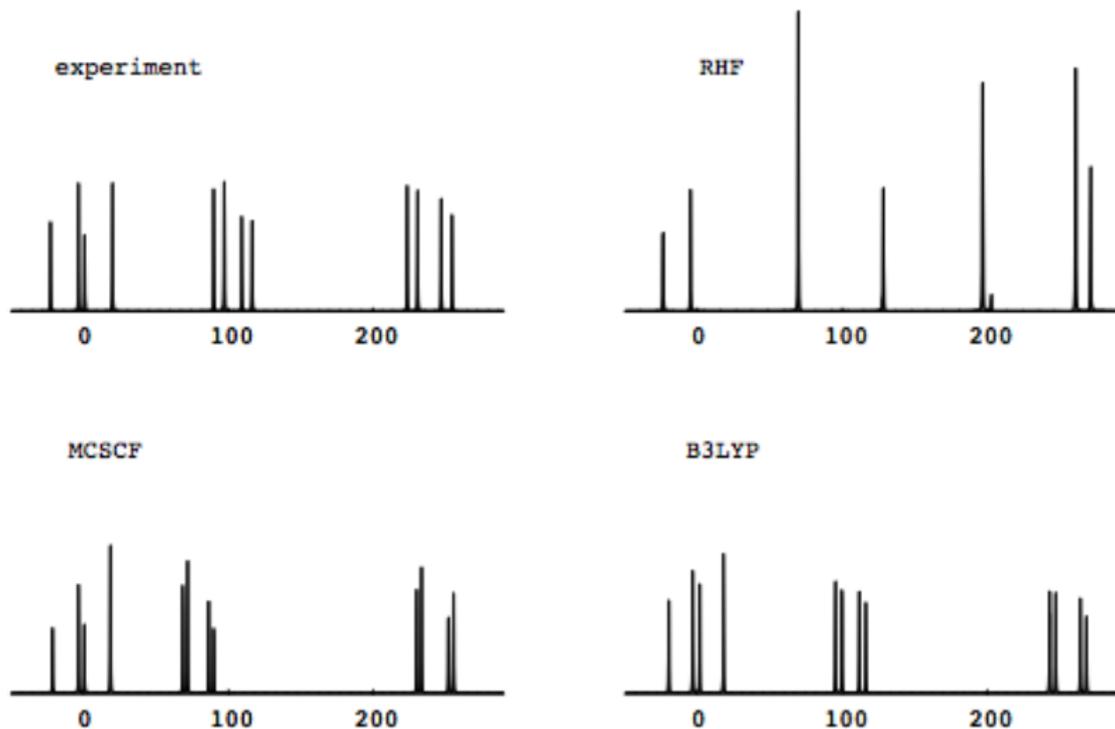
# Nuclear Shielding Constants

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

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

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

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

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

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

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



$$\mathbf{B}$$

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

$$\mathbf{p} \qquad \text{SO} \qquad \mathbf{m} = -\mathbf{S}$$

$$\frac{1}{r_{12}}$$

$$\text{SS, SO, OO}$$

$$\mathbf{m} = -\mathbf{S} \qquad \text{SO} \qquad \mathbf{p}$$

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

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

$$\mathbf{M}_K$$

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

$$\mathbf{M}_L$$
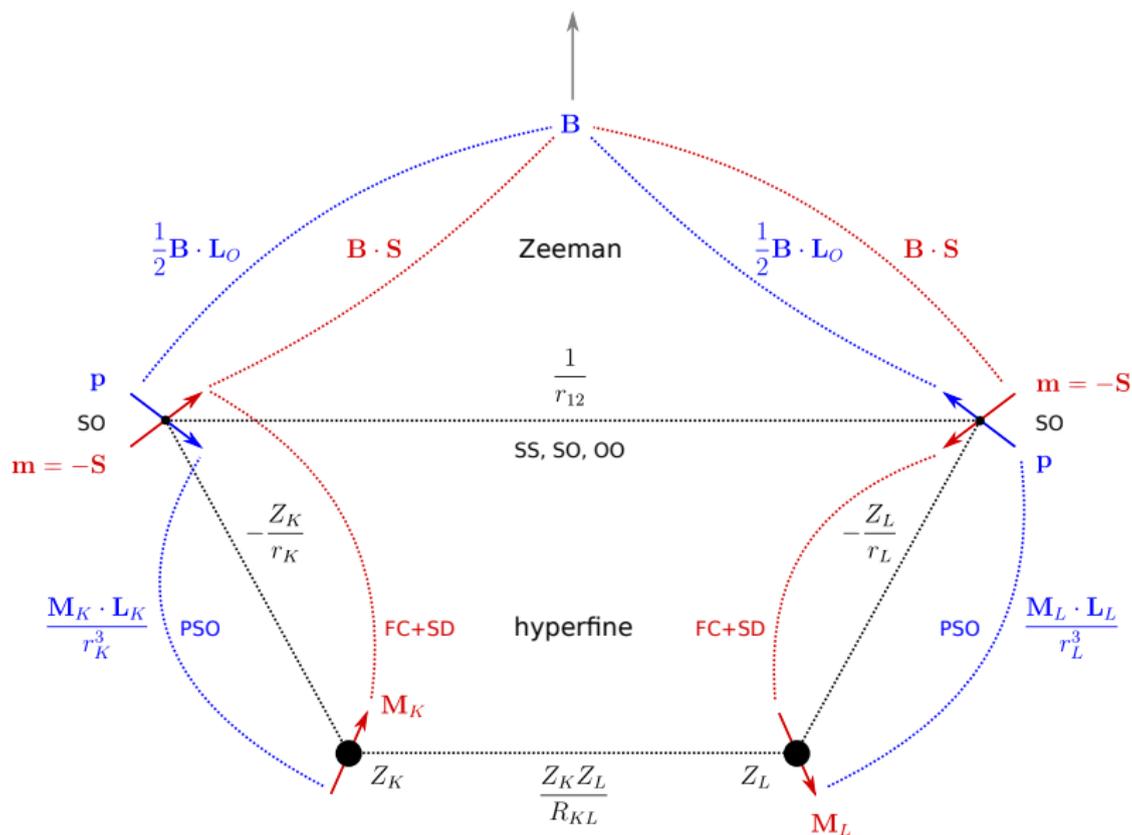
# Ramsey's Expression for Nuclear Shielding Tensors

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

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

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

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

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

▶ 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 shielding is given by (assuming gauge origin at the nucleus):

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

# Benchmark Calculations of BH Shieldings (ppm)

| | $\sigma(^{11}B)$ | $\Delta\sigma(^{11}B)$ | $\sigma(^{1}H)$ | $\Delta\sigma(^{1}H)$ |
|---|---|---|---|---|
| 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, $R_{BH} = 123.24$ pm, all electrons correlated
- ▸ J. Gauss and K. Ruud, *Int. J. Quantum Chem.* **S29** (1995) 437
  - ▸ M. Kállay and J. Gauss, *J. Chem. Phys.* **120** (2004) 6841

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

| | CCSD | CCSD(T) | CCSDT | CCSDTQ | CCSDTQ5 | FCI |
|---|---|---|---|---|---|---|
| $\sigma(^{13}\text{C})$ | 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.

# Calculated and Experimental Shielding Constants (ppm)

|        |   | HF     | CAS    | MP2    | CCSD   | CCSD(T) | exp.               |
|--------|---|--------|--------|--------|--------|---------|--------------------|
| HF     | F | 413.6  | 419.6  | 424.2  | 418.1  | 418.6   | $410 \pm 6$ (300K) |
|        | H | 28.4   | 28.5   | 28.9   | 29.1   | 29.2    | $28.5 \pm 0.2$ (300K) |
| $H_2O$ | O | 328.1  | 335.3  | 346.1  | 336.9  | 337.9   | $323.6 \pm 6$ (300K) |
|        | H | 30.7   | 30.2   | 30.7   | 30.9   | 30.9    | $30.05 \pm 0.02$   |
| $NH_3$ | N | 262.3  | 269.6  | 276.5  | 269.7  | 270.7   | 264.5              |
|        | H | 31.7   | 31.0   | 31.4   | 31.6   | 31.6    | $31.2 \pm 1.0$     |
| $CH_4$ | 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 | $-112.4$ | $-53.0$  | $-41.6$  | $-63.9$  | $-58.1$  | $-61.6 \pm 0.2$ (300K) |
| CO     | C | $-25.5$  | 8.2    | 10.6   | 0.8    | 5.6     | $3.0 \pm 0.9$ (eq) |
|        | O | $-87.7$  | $-38.9$  | $-46.5$  | $-56.0$  | $-52.9$  | $-56.8 \pm 6$ (eq) |

▶ For references and details, see *Chem. Rev.* **99** (1999) 293.

  ▶ for exp. CO and $H_2O$ values, see Wasylishen and Bryce, JCP 117 (2002) 10061

# NMR: Mean Absolute Errors Relative to Experiment

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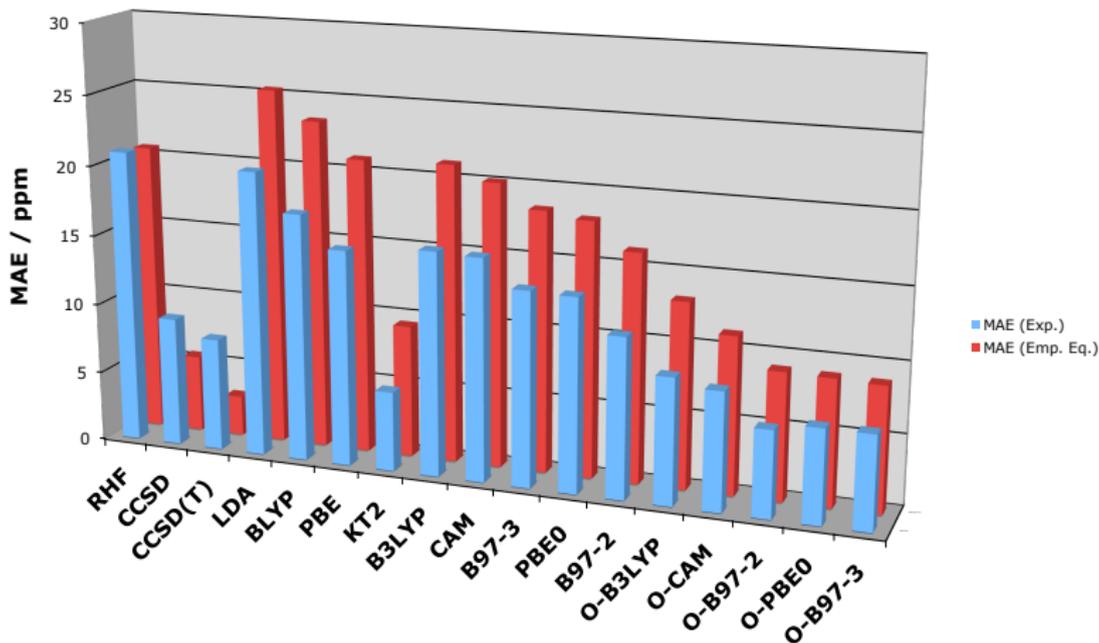


▶ Kohn–Sham calculations give shielding constants of uneven quality
  ▶ errors increase when vibrational corrections are applied
  ▶ Teale *et al.* JCP **138**, 024111 (2013)

# Direct and Indirect Nuclear Spin–Spin Couplings

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

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

describes the coupling of the nuclear magnetic moments in the presence of electrons

▶ There are two distinct contributions to the coupling:
the direct and indirect contributions

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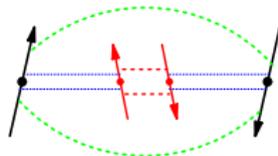


▶ The direct coupling occurs by a classical dipole mechanism:

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

  ▶ it is anisotropic and vanishes in isotropic media such as gases and liquids

▶ The indirect coupling arises from hyperfine interactions with the surrounding electrons:
  – it is exceedingly small: $\mathbf{K}_{KL} \sim 10^{-16}$ a.u. $\sim$ 1 Hz
  – it does not vanish in isotropic media
  – it gives the fine structure of high-resolution NMR spectra

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

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

# Zeeman and Hyperfine Interactions
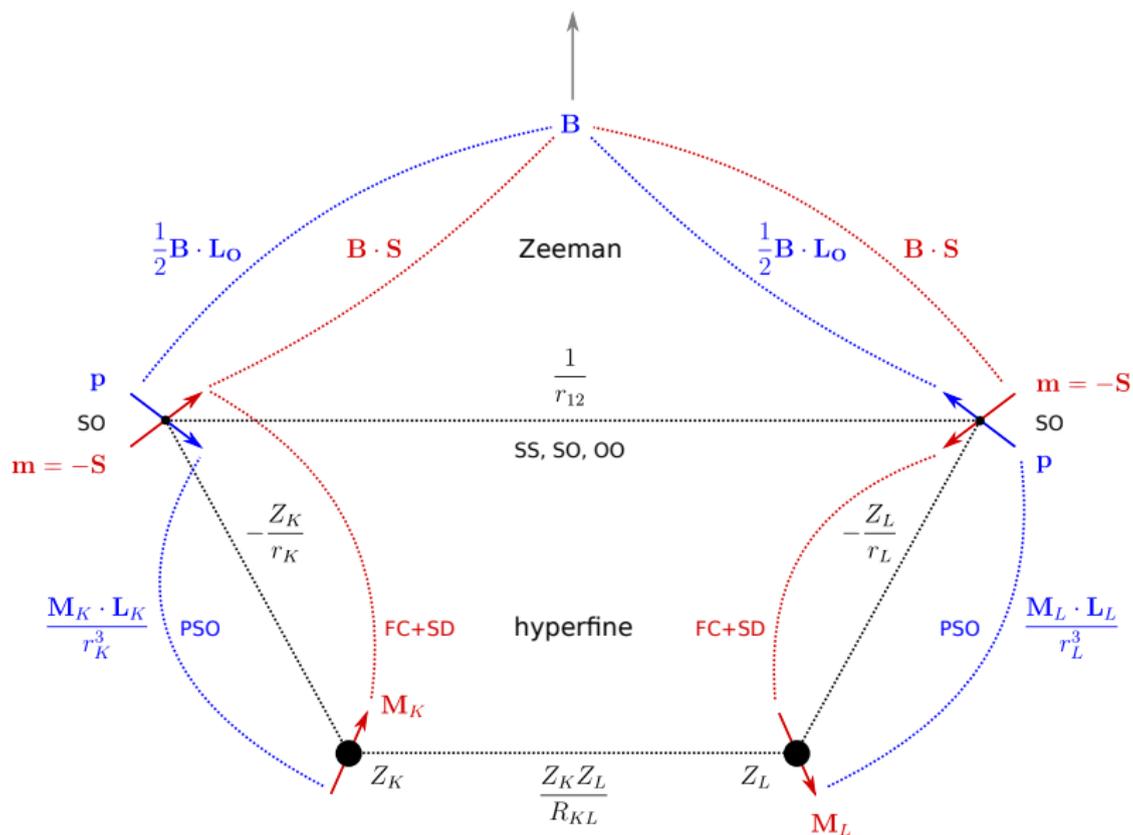
# Ramsey's Expression for Indirect Nuclear Spin–Spin Coupling Tensors

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

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

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

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

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

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

# Relative Importance of Contributions to Spin–Spin Coupling Constants

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

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

- 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 ($N_2$ and CO)!
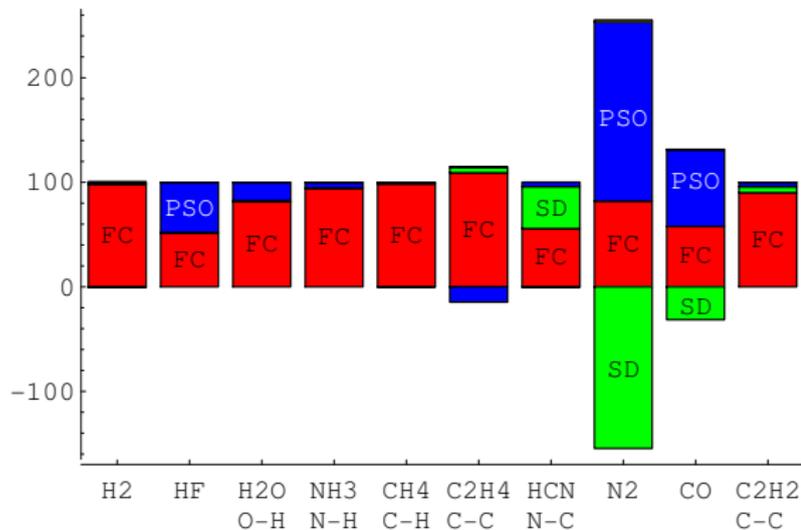
# Calculation of Indirect Nuclear Spin–Spin Coupling Constants

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

# Restricted Hartree–Fock Theory and Triplet Instabilities

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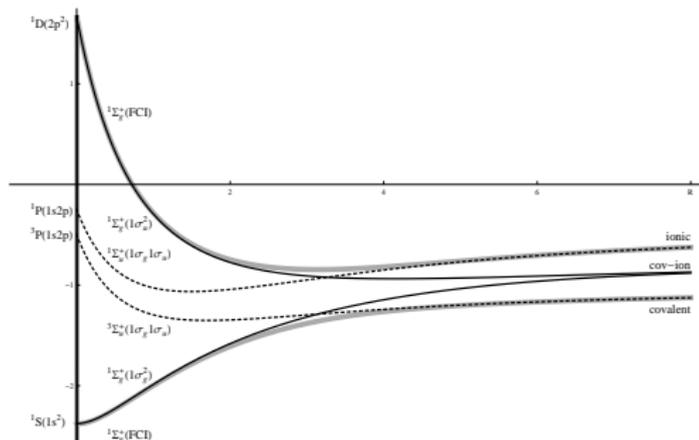


- Near such instabilities, the RHF description of spin interactions becomes unphysical

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

# Reduced Spin–Spin Coupling Constants by Wave-Function Theory

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

▶ SOPPA: second-order polarization-propagator approximation

# 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
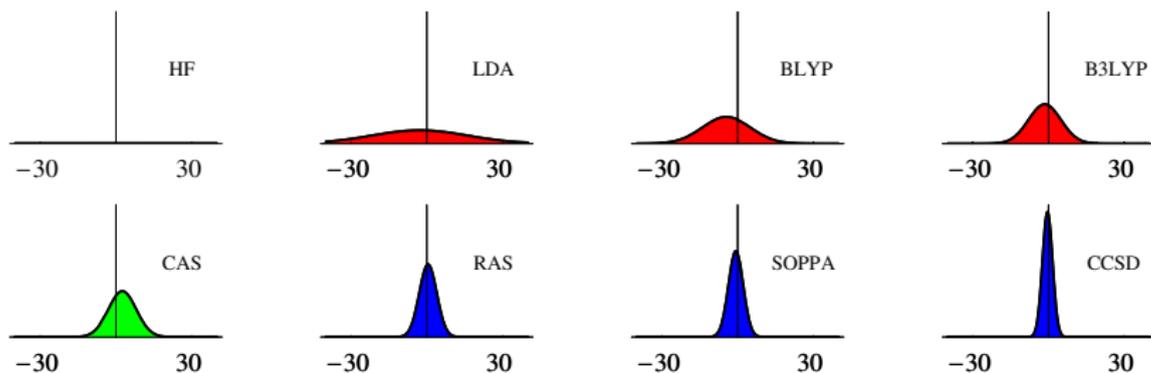


▶ Some observations:
  ▶ LDA underestimates only slightly, but has a large standard deviation
  ▶ BLYP reduces the LDA errors by a factor of two
  ▶ B3LYP errors are similar to those of CASSCF
  ▶ The CCSD method is slightly better than the SOPPA method