Molecular Magnetic Properties

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Trygve Helgaker

Department of Chemistry, University of Oslo, Norway

Overview

- The electronic Hamiltonian in an electromagnetic field
- The calculation of molecular magnetic properties

Classical mechanics

- Matter is described by Newton's equations:

$$\mathbf{F}(\mathbf{r}, \mathbf{v}, t) = m\mathbf{a}$$

  - the force defines the system and is obtained from experiment
  - conservative forces (e.g., gravitational forces) are obtained from potentials:

$$\mathbf{F}(\mathbf{r}) = -\boldsymbol{\nabla} V(\mathbf{r})$$

- Radiation is described by Maxwell's equations:

$$\begin{aligned}
\boldsymbol{\nabla} \cdot \mathbf{E} &= \rho/\varepsilon_0 && \leftarrow \text{Coulomb's law} \\
\boldsymbol{\nabla} \times \mathbf{B} - \varepsilon_0\mu_0\, \partial\mathbf{E}/\partial t &= \mu_0\mathbf{J} && \leftarrow \text{Ampère's law} \\
\boldsymbol{\nabla} \cdot \mathbf{B} &= 0 && \\
\boldsymbol{\nabla} \times \mathbf{E} + \partial\mathbf{B}/\partial t &= \mathbf{0} && \leftarrow \text{Faraday's law of induction}
\end{aligned}$$

- The interaction between matter and radiation is described by the Lorentz force:

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

Lagrangian mechanics

- A more general formulation than the Newtonian one:
  - unified description of matter and fields (Newton's and Maxwell's equations)
  - springboard for quantum mechanics
  - invariant to coordinate transformations
  - handles constraints naturally

Overview

- the Lagrangian and Lagrange's equations
- the Hamiltonian and Hamilton's equations
- electromagnetic fields and potentials
- gauge transformations
- the Lagrangian and the Hamiltonian of a particle in an electromagnetic field
- the Dirac equation and electron spin
- the nonrelativistic electronic Hamiltonian in an electromagnetic field

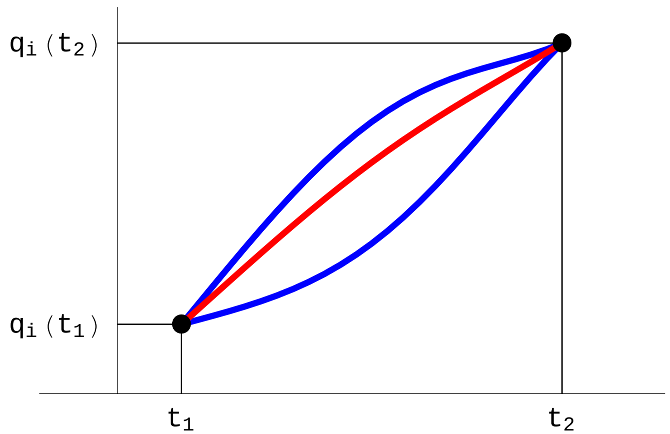
Principle of least action

- For a system of n degrees of freedom, there are
  - n generalized coordinates q_i in configuration space
  - n generalized velocities $\dot{q}_i$
- The principle of least action (Hamilton's principle):

  For each system, there exists a Lagrangian $L(q_i, \dot{q}_i, t)$ such that the action integral

$$S = \int_{t_1}^{t_2} L(q_i, \dot{q}_i, t)\, \mathrm{d}t$$

  assumes an extremum along the trajectory in configuration space taken by the system.



Lagrange's equations

- From the principle of least action, we obtain

$$\begin{aligned} \delta S &= \delta \int_{t_1}^{t_2} L(q_i, \dot{q}_i, t)\, \mathrm{d}t = \int_{t_1}^{t_2} \left(\frac{\partial L}{\partial q_i} \delta q_i + \frac{\partial L}{\partial \dot{q}_i} \delta \dot{q}_i \right) \mathrm{d}t \\ &= \int_{t_1}^{t_2} \left[\frac{\partial L}{\partial q_i} \delta q_i - \left(\frac{\mathrm{d}}{\mathrm{d}t} \frac{\partial L}{\partial \dot{q}_i} \right) \delta q_i \right] \mathrm{d}t = 0 \end{aligned}$$

- We conclude that the Lagrangian satisfies the following second-order differential equations (one for each degree of freedom):

$$\boxed{\frac{\mathrm{d}}{\mathrm{d}t} \frac{\partial L}{\partial \dot{q}_i} = \frac{\partial L}{\partial q_i}}$$

← Lagrange's equations of motion

- The Lagrangian defines the system and is determined so that it reproduces the equations of motion consistent with experiment.
- Unlike Newton's equations of motion, Lagrange's equations preserve their form in any coordinate system.
- The Lagrangian is just a scalar.

Arbitrariness of the Lagrangian and gauge transformations

- The scalar Lagrangian is not uniquely defined.
- Assume that the Lagrangian $L(q, \dot{q}, t)$ satisfies the equations:

$$\frac{\mathrm{d}}{\mathrm{d}t}\frac{\partial L}{\partial \dot{q}} = \frac{\partial L}{\partial q}.$$

- Consider now the following transformed Lagrangian where a is a constant and where the arbitrary gauge function $f\,(q, t)$ is independent of the velocity $\dot{q}$:

$$L'\,(q, \dot{q}, t) = aL\,(q, \dot{q}, t) + \frac{\mathrm{d}}{\mathrm{d}t} f\,(q, t).$$

- The new Lagrangian satisfies the same equations of motion as the old one:

$$\begin{aligned}
\frac{\mathrm{d}}{\mathrm{d}t}\frac{\partial L'}{\partial \dot{q}} &= a\frac{\mathrm{d}}{\mathrm{d}t}\frac{\partial L}{\partial \dot{q}} + \frac{\mathrm{d}}{\mathrm{d}t}\frac{\partial}{\partial \dot{q}}\left(\frac{\partial f}{\partial q}\dot{q} + \frac{\partial f}{\partial t}\right) \\
&= a\frac{\partial L}{\partial q} + \frac{\mathrm{d}}{\mathrm{d}t}\frac{\partial f}{\partial q} \\
&= \frac{\partial}{\partial q}\left(aL + \frac{\mathrm{d}}{\mathrm{d}t} f\right) = \frac{\partial L'}{\partial q}.
\end{aligned}$$

- This is an example of a gauge transformation.

Conservative systems

- The Lagrangian of a particle in a conservative field may be written as

$$L = \underbrace{T(q, \dot{q})}_{\text{kinetic energy}} - \underbrace{V(q)}_{\text{potential energy}}$$

- The Lagrangian is thus easily set up for any conservative system, in any convenient coordinate system.

- Example: Assuming a Cartesian coordinate system

$$L = \frac{1}{2}mv^2 - V(\mathbf{r}),$$

we find that Lagrange's equations immediately reduce to Newton's equations:

$$\frac{\mathrm{d}}{\mathrm{d}t}\frac{\partial L}{\partial \mathbf{v}} = \frac{\partial L}{\partial \mathbf{r}} \quad \Rightarrow \quad \frac{\mathrm{d}}{\mathrm{d}t}m\mathbf{v} = -\boldsymbol{\nabla}V(\mathbf{r}) \quad \Rightarrow \quad m\mathbf{a} = \mathbf{F}.$$

- For particles in a (nonconservative) electromagnetic field, the Lagrangian can be cast in similar but slightly different form as discussed later.

The energy function

- In Lagrangian mechanics, the energy function is defined as:

$$h(q, \dot{q}, t) = \frac{\partial L}{\partial \dot{q}} \dot{q} - L(q, \dot{q}, t) \,.$$

- Assume a conservative Cartesian system with Lagrangian $L = \frac{1}{2} m v^2 - V(\mathbf{r})$:

$$h = \frac{\partial L}{\partial \mathbf{v}} \mathbf{v} - L = \frac{\partial T}{\partial \mathbf{v}} \mathbf{v} - (T - V) = 2T - T + V = T + V = \text{total energy}$$

  – More generally, h is equal to the total energy if $T(\dot{q})$ is quadratic in $\dot{q}$ and $V(q)$ is independent of $\dot{q}$.

- The energy function h is conserved if L does not depend explicitly on time:

$$\frac{\mathrm{d}h}{\mathrm{d}t} = -\frac{\partial L}{\partial t}$$

  – Proof:

$$\begin{aligned} \frac{\mathrm{d}h}{\mathrm{d}t} &= \frac{\mathrm{d}}{\mathrm{d}t} \left(\frac{\partial L}{\partial \dot{q}} \dot{q} \right) - \frac{\mathrm{d}L}{\mathrm{d}t} \\ &= \left[\left(\frac{\mathrm{d}}{\mathrm{d}t} \frac{\partial L}{\partial \dot{q}} \right) \dot{q} + \frac{\partial L}{\partial \dot{q}} \ddot{q} \right] - \left[\frac{\partial L}{\partial q} \dot{q} + \frac{\partial L}{\partial \dot{q}} \ddot{q} + \frac{\partial L}{\partial t} \right] = -\frac{\partial L}{\partial t} \end{aligned}$$

Generalized momentum

- The generalized momentum p_i conjugate to the generalized coordinate q_i is defined as

$$\boxed{p_i = \frac{\partial L}{\partial \dot{q}_i}} \quad \leftarrow \text{generalized momentum}$$

- For a conservative system in Cartesian coordinates $L = \frac{1}{2}mv^2 - V(\mathbf{r})$, the conjugate momentum corresponds to the linear momentum:

$$\mathbf{p} = \frac{\partial L}{\partial \mathbf{v}} = \frac{\partial T}{\partial \mathbf{v}} = \frac{1}{2}m\frac{\partial v^2}{\partial \mathbf{v}} = m\mathbf{v} \quad \leftarrow \text{linear momentum}$$

- The momentum conjugate to a coordinate that does not occur in the Lagrangian is conserved:

$$\frac{\mathrm{d}p_i}{\mathrm{d}t} = \frac{\mathrm{d}}{\mathrm{d}t}\frac{\partial L}{\partial \dot{q}_i} = \frac{\partial L}{\partial q_i} = 0 \quad \leftarrow \text{if } L \text{ is independent of } q_i$$

  – such coordinates are said to be cyclic

- Compare: h is conserved if L does not depend explicitly on t,
  p_i is conserved if L does not depend explicitly on q_i

Hamiltonian mechanics

- For a system of n degrees of freedom, there are n second-order differential equations (Lagrange's equations):

$$\frac{\mathrm{d}}{\mathrm{d}t}\frac{\partial L}{\partial \dot{q}_i} = \frac{\partial L}{\partial q_i}$$

- The motion is completely specified by the initial values of the n coordinates and the n velocities.
- In this sense, we may view q_i and $\dot{q}_i$ as $2n$ independent variables.
- Alternatively, let us treat q_i and p_i as $2n$ independent variables:

$$\{q_i, \dot{q}_i\} \quad \rightarrow \quad \{q_i, p_i\}$$

- Possible advantages of such a scheme:
  - first-order equations
  - better suited to cyclic coordinates

The Hamiltonian

- The differential of the Lagrangian $L\,(q,\dot{q},t)$ is given by

$$\mathrm{d}L\,(q,\dot{q},t) = \frac{\partial L}{\partial q}\,\mathrm{d}q + \frac{\partial L}{\partial \dot{q}}\,\mathrm{d}\dot{q} + \frac{\partial L}{\partial t}\,\mathrm{d}t = \dot{p}\,\mathrm{d}q + p\,\mathrm{d}\dot{q} + \frac{\partial L}{\partial t}\,\mathrm{d}t$$

- We now introduce the Hamiltonian, whose differential should be given by:

$$\mathrm{d}H\,(q,p,t) = \frac{\partial H}{\partial q}\,\mathrm{d}q + \frac{\partial H}{\partial p}\,\mathrm{d}p + \frac{\partial H}{\partial t}\,\mathrm{d}t. \tag{1}$$

- The Legendre transformation

$$\boxed{H = p\dot{q} - L} \quad \leftarrow \text{the Hamiltonian function}$$

gives the required differential:

$$\mathrm{d}H = (p\,\mathrm{d}\dot{q} + \dot{q}\,\mathrm{d}p) - (\dot{p}\,\mathrm{d}q + p\,\mathrm{d}\dot{q} + \frac{\partial L}{\partial t}\,\mathrm{d}t) = -\dot{p}\,\mathrm{d}q + \dot{q}\,\mathrm{d}p - \frac{\partial L}{\partial t}\,\mathrm{d}t. \tag{2}$$

- A comparison of (1) and (2) yields

$$\boxed{\frac{\partial H}{\partial q} = -\dot{p}, \qquad \frac{\partial H}{\partial p} = \dot{q}} \quad \leftarrow \text{Hamilton's equations}$$

Prescription for setting up the Hamiltonian

1. Choose n generalized coordinates q_i.
2. Set up the Lagrangian $L\left(q_i, \dot{q}_i, t\right)$ such that
$$\frac{\mathrm{d}}{\mathrm{d}t}\frac{\partial L}{\partial \dot{q}_i} = \frac{\partial L}{\partial q_i} \tag{1}$$
reproduces the equations of motion.
3. Introduce the conjugate momenta
$$p_i = \frac{\partial L}{\partial \dot{q}_i}. \tag{2}$$
4. Construct the Hamiltonian
$$H = \sum_i p_i \dot{q}_i - L\left(q_i, \dot{q}_i, t\right) \tag{3}$$
and invert (2) to express the Hamiltonian $H\left(q_i, p_i\right)$ in terms of q_i and p_i.
5. Write down Hamilton's equations of motion:
$$\dot{q}_i = \frac{\partial H}{\partial p_i}, \quad \dot{p}_i = -\frac{\partial H}{\partial q_i}. \tag{4}$$

Comparison of Lagrangian and Hamiltonian mechanics

Lagrangian mechanics	Hamiltonian mechanics
n second-order equations: $\frac{\mathrm{d}}{\mathrm{d}t}\frac{\partial L}{\partial \dot{q}_i} = \frac{\partial L}{\partial q_i}$	$2n$ first-order equations: $\dot{q}_i = \frac{\partial H}{\partial p_i}, \quad \dot{p}_i = -\frac{\partial H}{\partial q_i}$
q_i are the primary variables in configuration space, $\dot{q}_i$ secondary variables	q_i and p_i are independent variables in phase space, connected only by the equations of motion
the state of the system is determined when the variables $(q_i, \dot{q}_i)$ are known at a given time t	the state of the system is defined by a point (q_i, p_i) in phase space, moving on a trajectory that satisfies Hamilton's equations of motion

Poisson brackets

- The Poisson bracket of two dynamical variables $A\,(q,p,t)$ and $B\,(q,p,t)$ is defined as

$$[A,B]=\sum_i\left(\frac{\partial A}{\partial q_i}\frac{\partial B}{\partial p_i}-\frac{\partial B}{\partial q_i}\frac{\partial A}{\partial p_i}\right)$$

  – the fundamental Poisson brackets among conjugate coordinates and momenta:

$$[q_i,q_j]=0,\quad [p_i,p_j]=0,\quad [q_i,p_j]=\delta_{ij}$$

- The total time derivatives are given by

$$\frac{\mathrm{d}A}{\mathrm{d}t}=\frac{\partial A}{\partial q}\dot{q}+\frac{\partial A}{\partial p}\dot{p}+\frac{\partial A}{\partial t}=\frac{\partial A}{\partial q}\frac{\partial H}{\partial p}-\frac{\partial A}{\partial p}\frac{\partial H}{\partial q}+\frac{\partial A}{\partial t},$$

  and may therefore be expressed compactly as

$$\frac{\mathrm{d}A}{\mathrm{d}t}=[A,H]+\frac{\partial A}{\partial t}.$$

  – important special cases:

$$\dot{q}=[q,H]\,,\quad \dot{p}=[p,H]\,,\quad \frac{\mathrm{d}H}{\mathrm{d}t}=\frac{\partial H}{\partial t}$$

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 radiation
  - 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

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

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

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

- 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.

Review: 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 a 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:

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

- Whereas Newton's equations of motion are second-order differential equations, Hamilton's equations are first-order.
- We must now generalize this approach to particles in an 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):

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

  - 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 involve only **E** and **B**:

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

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

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

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

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

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

- The second pair of Maxwell's equations are 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 ρ and **J**.

Particle in an electromagnetic field

- For a particle in an electromagnetic field, we must set up a Lagrangian such that

$$\frac{\mathrm{d}}{\mathrm{d}t}\frac{\partial L}{\partial \dot{q}_i} = \frac{\partial L}{\partial q_i}$$

reduces to Newton's equations with the Lorentz force

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

- This is not a conservative system, for which

$$L = T - V, \quad F_i = -\frac{\partial V}{\partial q_i}$$

- Rather, it belongs to a broader class of systems, for which

$$L = T - U, \quad F_i = -\frac{\partial U}{\partial q_i} + \frac{\mathrm{d}}{\mathrm{d}t}\left(\frac{\partial U}{\partial \dot{q}_i}\right)$$

- For a particle subject to the Lorentz force, the generalized potential is given by

$$U = z\,(\phi - \mathbf{v} \cdot \mathbf{A}) \quad \leftarrow \text{velocity-dependent potential}$$

and the Lagrangian becomes

$$\boxed{L = T - z\,(\phi - \mathbf{v} \cdot \mathbf{A})} \quad \leftarrow \text{particle in an electromagnetic field}$$

Conjugate momentum in an electromagnetic field

- We recall that, for a conservative system described by Lagrangian of the form

$$L(q,\dot{q}) = T(\dot{q}) - V(q)\,,$$

the conjugate momentum in Cartesian coordinates

$$\mathbf{p} = \frac{\partial L}{\partial \mathbf{v}} = \frac{\partial T}{\partial \mathbf{v}} = m\mathbf{v} \equiv \boldsymbol{\pi}$$

is equal to the linear (kinetic) momentum $\boldsymbol{\pi}$:

$$\boxed{\mathbf{p} = \boldsymbol{\pi}} \quad \leftarrow \text{particle in a conservative field}$$

- By contrast, for a nonconservative system described by Lagrangian

$$L(q,\dot{q}) = T(\dot{q}) - U(q,\dot{q})\,,$$

the conjugate and kinetic momenta are no longer the same.

- In particular, for a particle in an eletromagnetic field

$$L = T - z(\phi - \mathbf{v}\cdot\mathbf{A})$$

we obtain

$$\mathbf{p} = \frac{\partial L}{\partial \mathbf{v}} = \frac{\partial T}{\partial \mathbf{v}} + z\mathbf{A} \quad \Rightarrow \quad \boxed{\mathbf{p} = \boldsymbol{\pi} + z\mathbf{A}} \quad \leftarrow \text{particle in an electromagnetic field}$$

The Hamiltonian in an electromagnetic field

- We recall that, for a conservative system with Lagrangian

$$L = T(\dot{q}) - V(q),$$

where $T(\dot{q})$ is quadratic in $\dot{q}$, the Hamiltonian is given by

$$H = T(\dot{q}) + V(q).$$

- Let us now consider the nonconservative system consisting of a particle in a field

$$L = T(\dot{q}) - U(q, \dot{q}) = \frac{1}{2}mv^2 - z(\phi - \mathbf{v} \cdot \mathbf{A}).$$

- From the conjugate momentum

$$\mathbf{p} = m\mathbf{v} + z\mathbf{A},$$

we obtain the Hamiltonian

$$H = \mathbf{p} \cdot \mathbf{v} - L = \left(mv^2 + z\mathbf{v} \cdot \mathbf{A}\right) - \left(\frac{1}{2}mv^2 - z\phi + z\mathbf{v} \cdot \mathbf{A}\right) = \frac{1}{2}mv^2 + z\phi = T + z\phi.$$

- Expressed in canonical coordinates, the Hamiltonian now becomes:

$$\boxed{H = T + z\phi = \frac{(\mathbf{p} - z\mathbf{A}) \cdot (\mathbf{p} - z\mathbf{A})}{2m} + z\phi}$$

  – note: $H = T + U + z\mathbf{v} \cdot \mathbf{A} \neq T + U$

Gauge transformations

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

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

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

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

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

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

- Note: Gauge transformations induce the following transformations:

$$L' = L + z\frac{\mathrm{d}f}{\mathrm{d}t}, \quad \mathbf{p}' = \mathbf{p} + z\boldsymbol{\nabla} f, \quad H' = H - z\frac{\partial f}{\partial t}, \quad T' = T$$

  - However, the equations of motion are unaffected!

Quantization of a particle in an electromagnetic field

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

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

- To this end, we introduced scalar and vector potentials ϕ 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 takes the form

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

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

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

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

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

Electron spin

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

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

- However, this description ignores a fundamental property of the electron: spin.
- Spin may be incorporated in our description by introducing a Pauli two-component wave function and the Pauli spin matrices:

$$\Psi = \begin{pmatrix} \Psi_\alpha \\ \Psi_\beta \end{pmatrix}, \quad \sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad \sigma_y = \begin{pmatrix} 0 & -\mathrm{i} \\ \mathrm{i} & 0 \end{pmatrix}, \quad \sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

- The nonrelativistic Hamiltonian may now be written in the form

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

- Spin was first explained by the relativistic theory of Dirac.
- One justification for our nonrelativistic operator is to be found in the Lévy–Leblond equation—that is, the nonrelativistic limit of the four-component Dirac equation.

Classical relativistic Hamiltonian

- Hamiltonian for an electron in an electromagnetic field

$$H = \sqrt{m^2c^4 + c^2(\mathbf{p} + e\mathbf{A})^2} - e\phi$$

- Hamilton's equations give us

$$\dot{\mathbf{r}} = \frac{\partial H}{\partial \mathbf{p}} \quad \Rightarrow \quad \mathbf{p} = \boldsymbol{\pi} - e\mathbf{A} \quad \leftarrow \text{conjugate momentum}$$

$$\dot{\mathbf{p}} = -\frac{\partial H}{\partial \mathbf{r}} \quad \Rightarrow \quad \dot{\boldsymbol{\pi}} = -e(\mathbf{E} + \mathbf{v} \times \mathbf{B}) \quad \leftarrow \text{Lorentz force}$$

where the relativistic kinetic momentum is given by

$$\boldsymbol{\pi} = \frac{m\mathbf{v}}{\sqrt{1 - v^2/c^2}} \quad \leftarrow \text{Lorentz factor} \times \text{nonrelativistic momentum}$$

- Relationship to nonrelativistic mechanics

$$\sqrt{m^2c^4 + c^2\pi^2} = mc^2 + \frac{\pi^2}{2m} + \mathcal{O}\left[(v/c)^2\right]$$

$$\boldsymbol{\pi} = m\mathbf{v} + \mathcal{O}\left[(v/c)^2\right]$$

  – the nonrelativistic limit is obtained as $(v/c)^2 \rightarrow 0$

Linearization of Hamiltonian

- The Hamiltonian is given by

$$H = c\sqrt{\pi^2 + m^2c^2} - e\phi$$

but we would like time and space coordinates to appear symmetrically in the equation

$$\mathrm{i}\hbar\frac{\partial\Psi}{\partial t} = H\Psi$$

- Following Dirac, we write

$$\pi^2 + m^2c^2 = (\alpha_x\pi_x + \alpha_y\pi_y + \alpha_z\pi_z + \alpha_0 mc)^2$$

- To determine the α_i, we note that

$$(\alpha_x\pi_x + \alpha_y\pi_y + \cdots)^2 = \alpha_x^2\pi_x^2 + \alpha_y^2\pi_y^2 + (\alpha_x\alpha_y + \alpha_y\alpha_x)\,\pi_x\pi_y + \cdots = \pi_x^2 + \pi_y^2 \cdots$$

if the α_i operators anticommute

$$\left.\begin{aligned} \alpha_x^2 &= \alpha_y^2 = 1 \\ \alpha_x\alpha_y + \alpha_y\alpha_x &= 0 \end{aligned}\right\} \Rightarrow [\alpha_i, \alpha_j]_+ = 2\delta_{ij}$$

- The Hamiltonian may now be written as

$$H_{\mathrm{D}} = c\boldsymbol{\alpha}\cdot\boldsymbol{\pi} + \beta mc^2 - e\phi, \quad \boldsymbol{\alpha} = [\alpha_x, \alpha_y, \alpha_z], \quad \beta = \alpha_0$$

The Dirac equation

- In matrix representation, the anticommuting operators α_i are represented by four 4×4 matrices

$$\alpha_i = \begin{pmatrix} \mathbf{0} & \sigma_i \\ \sigma_i & \mathbf{0} \end{pmatrix}, \quad \beta = \begin{pmatrix} \mathbf{I} & \mathbf{0} \\ \mathbf{0} & -\mathbf{I} \end{pmatrix},$$

where $\mathbf{I}$ is the 2×2 unit matrix and the σ_i are the usual Pauli spin matrices:

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

- In this representation, the Dirac equation

$$\mathrm{i}\hbar \frac{\partial \Psi}{\partial t} = \left(c\boldsymbol{\alpha} \cdot \boldsymbol{\pi} + \beta mc^2 - e\phi \right) \Psi$$

therefore has a four-component solution:

$$\mathrm{i}\hbar \begin{pmatrix} \frac{\partial \Psi_1}{\partial t} \\ \frac{\partial \Psi_2}{\partial t} \\ \frac{\partial \Psi_3}{\partial t} \\ \frac{\partial \Psi_4}{\partial t} \end{pmatrix} = \begin{pmatrix} mc^2 - e\phi & 0 & c\pi_z & c(\pi_x - \mathrm{i}\pi_y) \\ 0 & mc^2 - e\phi & c(\pi_x + \mathrm{i}\pi_y) & -c\pi_z \\ c\pi_z & c(\pi_x - \mathrm{i}\pi_y) & -mc^2 - e\phi & 0 \\ c(\pi_x + \mathrm{i}\pi_y) & -c\pi_z & 0 & -mc^2 - e\phi \end{pmatrix} \begin{pmatrix} \Psi_1 \\ \Psi_2 \\ \Psi_3 \\ \Psi_4 \end{pmatrix}$$

- Positive solutions are associated with electrons (α and β spin), negative with positrons.

Electron spin

- The Dirac Hamiltonian does not commute with the orbital angular momentum operator but rather with the operator

$$\mathbf{l} + \frac{1}{2}\boldsymbol{\sigma}$$

- We therefore assign to the electron an intrinsic spin angular momentum

$$\mathbf{s} = \frac{1}{2}\boldsymbol{\sigma}$$

- Likewise, we shall later interpret the Zeeman term by assigning to the electron a magnetic moment

$$\mu_{\mathbf{B}}\boldsymbol{\sigma}\cdot\mathbf{B} = -\mathbf{m}\cdot\mathbf{B}, \quad \mu_{\mathrm{B}} = \frac{e\hbar}{2m}$$

where we have introduced is the anomalous spin magnetic moment:

$$\mathbf{m} = -2\mu_{\mathrm{B}}\mathbf{s}$$

- From quantum electrodynamics, one finds that the true spin magnetic moment differs slightly from that given by Dirac's theory:

$$\mathbf{m} = -g\mu_{\mathrm{B}}\mathbf{s}, \quad g \approx 2.002$$

The Lévy-Leblond equation

- The time-independent Dirac equation may be written in the form:

$$\begin{pmatrix} -e\phi & c\boldsymbol{\sigma}\cdot\boldsymbol{\pi} \\ c\boldsymbol{\sigma}\cdot\boldsymbol{\pi} & -2mc^2 - e\phi \end{pmatrix} \begin{pmatrix} \varphi \\ \chi \end{pmatrix} = (E - mc^2) \begin{pmatrix} \varphi \\ \chi \end{pmatrix}.$$

- Introducing the scaled energy and scaled small component

$$E' = E - mc^2, \quad \chi' = c\chi,$$

  and rearranging, we obtain an equation where c occurs only as c^{-2}:

$$\begin{pmatrix} -e\phi & \boldsymbol{\sigma}\cdot\boldsymbol{\pi} \\ \boldsymbol{\sigma}\cdot\boldsymbol{\pi} & -2m - c^{-2}e\phi \end{pmatrix} \begin{pmatrix} \varphi \\ \chi' \end{pmatrix} = E' \begin{pmatrix} \varphi \\ c^{-2}\chi' \end{pmatrix}.$$

- Letting $c \to \infty$, we obtain the Lévy-Leblond equation:

$$\begin{pmatrix} -e\phi & \boldsymbol{\sigma}\cdot\boldsymbol{\pi} \\ \boldsymbol{\sigma}\cdot\boldsymbol{\pi} & -2m \end{pmatrix} \begin{pmatrix} \varphi \\ \chi' \end{pmatrix} = E' \begin{pmatrix} \varphi \\ 0 \end{pmatrix}.$$

- This is the nonrelativistic limit of the Dirac equation—a useful zero-order equation for relativistic perturbation theory.

The Schrödinger equation

- The Lévy-Leblond equation is given by (dropping primes):

$$\begin{pmatrix} -e\phi & \boldsymbol{\sigma}\cdot\boldsymbol{\pi} \\ \boldsymbol{\sigma}\cdot\boldsymbol{\pi} & -2m \end{pmatrix}\begin{pmatrix} \varphi \\ \chi \end{pmatrix} = E\begin{pmatrix} \varphi \\ 0 \end{pmatrix}.$$

- Solving the second equation for the small component χ

$$\chi = \frac{1}{2m}\boldsymbol{\sigma}\cdot\boldsymbol{\pi}\varphi$$

and substituting the result into the first equation, we obtain

$$\left[\frac{1}{2m}\left(\boldsymbol{\sigma}\cdot\boldsymbol{\pi}\right)\left(\boldsymbol{\sigma}\cdot\boldsymbol{\pi}\right) - e\phi\right]\varphi = E\varphi$$

- Finally, invoking the identity

$$\left(\boldsymbol{\sigma}\cdot\mathbf{u}\right)\left(\boldsymbol{\sigma}\cdot\mathbf{v}\right) = \mathbf{u}\cdot\mathbf{v} + \mathrm{i}\boldsymbol{\sigma}\cdot\mathbf{u}\times\mathbf{v}$$

we arrive at the two-component Schrödinger equation:

$$\left[\frac{1}{2m}\pi^2 + \frac{1}{2m}\mathrm{i}\boldsymbol{\sigma}\cdot\boldsymbol{\pi}\times\boldsymbol{\pi} - e\phi\right]\varphi = E\varphi$$

- In the absence of a vector potential, the second term vanishes:

$$\mathbf{A} = \mathbf{0} \quad \Rightarrow \quad \boldsymbol{\pi}\times\boldsymbol{\pi} = \mathbf{p}\times\mathbf{p} = \mathbf{0}$$

Expansion of the kinetic momentum

- Assuming the Coulomb gauge $\boldsymbol{\nabla} \cdot \mathbf{A} = \mathbf{0}$, we obtain

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

- Recalling the relation $\boldsymbol{\nabla} \times \mathbf{A} = \mathbf{B}$, we obtain

$$\begin{aligned}
(\boldsymbol{\pi} \times \boldsymbol{\pi})\, \Psi &= (\mathbf{p} + e\mathbf{A}) \times (\mathbf{p} + e\mathbf{A})\, \Psi \\
&= e\mathbf{p} \times \mathbf{A}\Psi + e\mathbf{A} \times \mathbf{p}\Psi \\
&= e\,(\mathbf{p} \times \mathbf{A})\,\Psi + e\,(\mathbf{p}\Psi) \times \mathbf{A} + e\mathbf{A} \times \mathbf{p}\Psi \\
&= -\mathrm{i}\hbar e\,(\boldsymbol{\nabla} \times \mathbf{A})\,\Psi = -\mathrm{i}\hbar e\mathbf{B}\Psi
\end{aligned}$$

- In the Coulomb gauge, the kinetic energy operator is therefore given by:

$$T = \frac{1}{2m}\pi^2 + \frac{1}{2m}\mathrm{i}\boldsymbol{\sigma} \cdot \boldsymbol{\pi} \times \boldsymbol{\pi} = \frac{1}{2m}p^2 + \frac{e}{m}\mathbf{A} \cdot \mathbf{p} + \frac{e}{m}\mathbf{B} \cdot \mathbf{s} + \frac{e^2}{2m}A^2$$

where we have used $\hbar\boldsymbol{\sigma} = 2\mathbf{s}$.

The nonrelativistic electronic Hamiltonian

- The general form of the nonrelativistic electronic Hamiltonian is

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

- Assuming the Coulomb gauge $\boldsymbol{\nabla}\cdot\mathbf{A} = 0$, we may expand squared kinetic momentum:

$$H = \frac{p^2}{2m} + \frac{e}{m}(\mathbf{A}\cdot\mathbf{p} + \mathbf{B}\cdot\mathbf{s}) + \frac{e^2}{2m}A^2 - e\phi, \quad \mathbf{s} = \frac{\hbar}{2}\boldsymbol{\sigma} \quad \leftarrow \text{spin operator}$$

- For a many-electron system, we add the instantaneous Coulomb interactions and obtain:

$$H_{\text{mol}} = H_0 - \sum_i \phi_i + \sum_i \mathbf{A}_i\cdot\mathbf{p}_i + \sum_i \mathbf{B}_i\cdot\mathbf{s}_i + \frac{1}{2}\sum_i A_i^2$$

  where (in atomic units) H_0 is the spin- and field-free molecular electronic Hamiltonian and where the perturbation operators are given by:

  1. $-\phi_i$ real singlet
  2. $\mathbf{A}_i\cdot\mathbf{p}_i$ paramagnetic imaginary singlet
  3. $\mathbf{B}_i\cdot\mathbf{s}_i$ paramagnetic real triplet
  4. $\frac{1}{2}A_i^2$ diamagnetic real singlet

- We shall in the following consider nuclear magnetic fields and uniform external magnetic fields.

Uniform static electric and magnetic fields

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

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

- Interaction with the electrostatic field:

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

- Orbital paramagnetic interaction with the magnetostatic field:

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

- 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:

$$H_{\mathrm{z}} = -\mathbf{B}\cdot\mathbf{d}_{\mathrm{m}}, \quad \mathbf{d}_{\mathrm{m}} = -\frac{1}{2}(\mathbf{L}+2\mathbf{S}) \quad \leftarrow \text{Zeeman interaction}$$

Nuclear magnetic fields and 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

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

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

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

  - the first term contributes only when the electron is at the position of the nuclei
  - 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:

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

Gauge transformation of the Schrödinger equation

- Consider a general gauge transformation:

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

- It can be shown that the Hamiltonian then transforms in the following manner

$$H' = H + \frac{\partial f}{\partial t},$$

which constitutes a unitary transformation:

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

- In order that the Schrödinger equation is still satisfied

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

the new wave function must be related to the old one by a compensating unitary transformation:

$$\Psi' = \exp\left(-\mathrm{i}f\right) \Psi$$

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

$$\rho' = (\Psi')^* \Psi' = [\Psi \exp(-\mathrm{i}f)]^* [\exp(-\mathrm{i}f)\Psi] = \Psi^* \Psi = \rho$$

Gauge-origin transformations

- Different choices of gauge origin in the external vector potential

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

  are related by a divergenceless gauge transformation:

$$\mathbf{A_K}(\mathbf{r}) = \mathbf{A_O}(\mathbf{r}) - \mathbf{A_O}(\mathbf{K}) = \mathbf{A_O}(\mathbf{r}) + \boldsymbol{\nabla} f, \quad f(\mathbf{r}) = -\mathbf{A_O}(\mathbf{K}) \cdot \mathbf{r}$$

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

$$\Psi_{\mathbf{K}}^{\text{exact}} = \exp\left[\mathrm{i}\mathbf{A_O}(\mathbf{K}) \cdot \mathbf{r}\right] \Psi_{\mathbf{O}}^{\text{exact}}$$

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

$$\Psi_{\mathbf{K}}^{\text{approx}} \neq \exp\left[\mathrm{i}\mathbf{A_O}(\mathbf{K}) \cdot \mathbf{r}\right] \Psi_{\mathbf{O}}^{\text{approx}}$$

  – different gauge origins therefore give different results

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

$$\Psi_{\mathbf{K}}^{\text{approx}} \stackrel{\text{def}}{=} \exp\left[\mathrm{i}\mathbf{A_O}(\mathbf{K}) \cdot \mathbf{r}\right] \Psi_{\mathbf{O}}^{\text{approx}}$$

  – for any **K**, this approach produces the same result as with the gauge origin at **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 **O**!
  – applied to individual AOs, however, this approach makes much more sense!

Natural gauge origin for AOs

- Assume AOs positioned at **K** with the following properties:

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

- We first choose the gauge origin to be at **K**:

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

  – The AOs χ_{lm} are then correct to first order in **B**:

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

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

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

  – The AOs χ_{lm} are now correct only to zero order in **B**:

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

- Standard AOs are biased towards **K**!

London orbitals

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

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

- 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 **B**, for any global origin **O**.
- The calculations become gauge-origin independent and uniform (good) quality is guaranteed.
- These are the London orbitals (1937), also known as GIAOs (gauge-origin independent 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:

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

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

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

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

$$H^{(1)}_{\text{Zeeman}} = \frac{1}{2} \mathbf{B} \cdot \mathbf{L_O} + \mathbf{B} \cdot \mathbf{s}$$

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

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

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:

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

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

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

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

- 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 $\mathbf{M}_K$ are small ($\mu_0\mu_{\mathrm{N}} \approx 10^{-8}$ 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 $\mathbf{B}$:

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

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

$$\mathbf{M}_{\mathrm{mol}}(\mathbf{B}) \overset{\mathrm{def}}{=} -\frac{\mathrm{d}E(\mathbf{B})}{\mathrm{d}\mathbf{B}} = -\mathbf{E}^{(10)} - \mathbf{E}^{(20)}\mathbf{B} + \cdots = \mathbf{M}_{\mathrm{perm}} + \boldsymbol{\xi}\mathbf{B} + \cdots,$$

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

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

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

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

  - 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:

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

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

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

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

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

$$\xi_{\mathrm{dia}} = \frac{1}{3} \mathrm{Tr}\, \boldsymbol{\xi}_{\mathrm{dia}} = -\frac{1}{6} \langle 0 | x_{\mathbf{O}}^2 + y_{\mathbf{O}}^2 + z_{\mathbf{O}}^2 | 0 \rangle = -\frac{1}{6} \langle 0 | r_{\mathbf{O}}^2 | 0 \rangle \quad \leftarrow \text{system surface}$$

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

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

  – for ${}^1S$ systems (closed-shell atoms), the paramagnetic term vanishes altogether:

$$\tfrac{1}{2} \mathbf{L_O} \left| {}^1 S \right\rangle \equiv 0 \quad \leftarrow \text{gauge origin at nucleus}$$

Hartree–Fock magnetizabilities

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

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

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

10^{-30} JT^{-2}	HF	exp.	diff.
H_2O	−232	−218	−6.4%
NH_3	−289	−271	−6.6%
CH_4	−315	−289	−9.0%
CO_2	−374	−349	−7.2%
PH_3	−441	−435	−1.4%
H_2S	−446	−423	−5.4%
C_3H_4	−482	−420	−14.8%
CSO	−595	−538	−10.6%
CS_2	−752	−701	−7.3%

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

High-resolution NMR spin Hamiltonian

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

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

  where γ_K is the magnetogyric ratio of the nucleus.

- Assuming free molecular rotation, the nuclear magnetic energy levels can be reproduced by the following high-resolution NMR spin Hamiltonian:

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

  where we have introduced
  - the nuclear shielding constants σ_K
  - the (reduced) indirect nuclear spin–spin coupling constants K_{KL}

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

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 $\mathbf{M}_K$:

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

- 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 $-\mathbf{I}_3$:

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

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

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

- Since the nuclear shielding constants arises 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:

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

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

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

- 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):

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

Benchmark calculations of BH shieldings

	HF	MP2	CCSD	CCSD(T)	FCI
$\sigma(^{11}\mathrm{B})$	-261.3	-220.7	-166.6	-170.5	-170.1
$\sigma(^{1}\mathrm{H})$	24.21	24.12	24.74	24.62	24.60
$\Delta\sigma(^{11}\mathrm{B})$	690.1	629.9	549.4	555.2	554.7
$\Delta\sigma(^{1}\mathrm{H})$	14.15	14.24	13.52	13.69	13.70

- TZP+ basis, $R_{\mathrm{BH}} = 123.24$ pm
- J. Gauss and K. Ruud, *Int. J. Quantum Chem.* **S29** (1995) 437
- J. Gauss and J. F. Stanton, *J. Chem. Phys.* **104** (1996) 2574

Calculated and experimental equilibrium shielding constants

		HF	CAS	MP2	CCSD	CCSD(T)	exp.
HF	F	413.6	419.6	424.2	418.1	418.6	410 ± 6
	H	28.4	28.5	28.9	29.1	29.2	28.5 ± 0.2
H_2O	O	328.1	335.3	346.1	336.9	337.9	344 ± 17
	H	30.7	30.2	30.7	30.9	30.9	30.05 ± 0.02
NH_3	N	262.3	269.6	276.5	269.7	270.7	264.5
	H	31.7	31.0	31.4	31.6	31.6	31.2 ± 1.0
CH_4	N	194.8	200.4	201.0	198.7	198.9	198.7
	H	31.7	31.2	31.4	31.5	31.6	30.61
F_2	F	−167.9	−136.6	−170.0	−171.1	−186.5	−192.8
N_2	N	−112.4	−53.0	−41.6	−63.9	−58.1	-61.6 ± 0.2
CO	C	−25.5	8.2	10.6	0.8	5.6	3.0 ± 0.9
	O	−87.7	−38.9	−46.5	−56.0	−52.9	-42.3 ± 17

- For references and details, see Helgaker, Jaszuński, and Ruud, *Chem. Rev.* **99** (1999) 293.

Nuclear spin–spin couplings

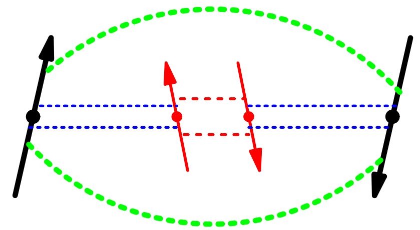
- The last term in the expansion of the molecular electronic energy in $\mathbf{B}$ and $\mathbf{M}_K$

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

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:

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

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

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

The calculation of indirect nuclear spin–spin coupling tensors

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

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

- Carrying out the differentiation, we obtain:

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

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

  - 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

Calculations of indirect spin–spin calculations

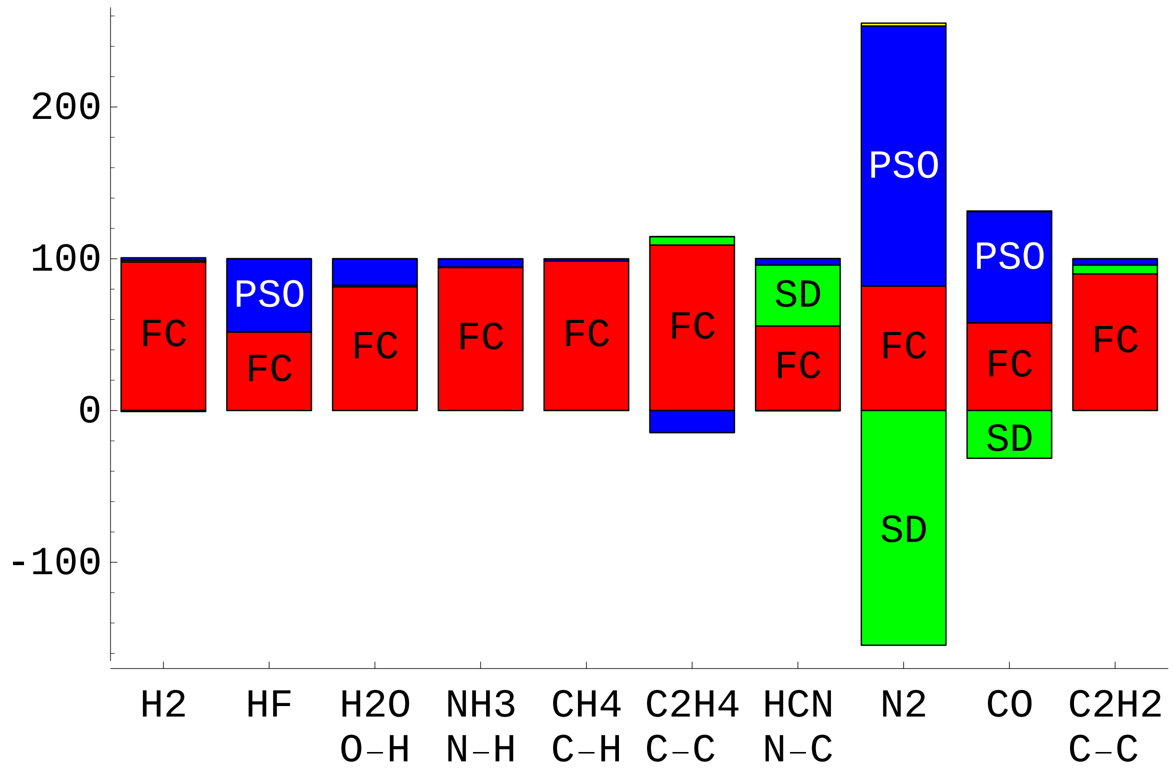
- The calculation of spin–spin coupling constants is a challenging task:
  - triplet as well as singlet perturbations are involved
  - electron correlation important—the Hartree–Fock model fails abysmally
  - the dominant FC contribution requires an accurate description of the electron density at the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

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

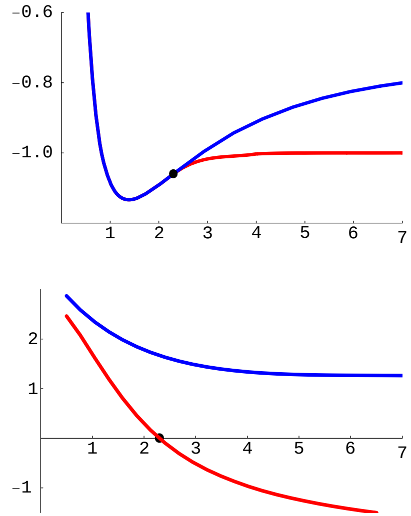
- The spin–spin coupling constants are often dominated by the FC term.
- Since the FC term is relatively easy to calculate, it is tempting to ignore the other terms.
- However, none of the contributions can be *a priori* neglected (N_2 and CO)!



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	−1	3	14	21



- Indeed, any method based on the RHF reference state may have problems:
  - $^1J_{CN}$ in HCN [Auer and Gauss, JCP 115 (2001) 1619]

Hz	RHF	CCSD	CCSD(T)	CC3	CCSDT
relaxed	−92.0	−8.1	7.4	−2.6	−14.5
unrelaxed		−15.0		−14.7	−14.6

  - in CC theory, orbital relaxation should be treated through singles amplitudes
  - noniterative CCSD(T) cannot be used; iterative CC3 must be used instead
  - all electrons must be correlated in unrelaxed CC calculations

Reduced spin–spin coupling constants (10^{19}kg m^{-2} s^{-2}Å^{-2})

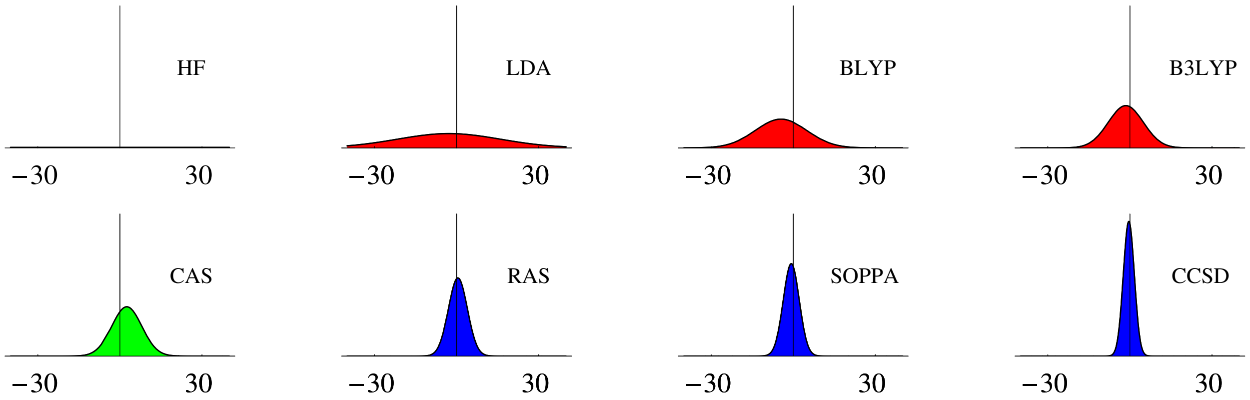
		RHF	CAS	RAS	SOPPA	CCSD	CC3	exp*	vib
HF	$^1J_{HF}$	59.2	48.0	48.1	46.8	46.1	46.1	47.6	−3.4
CO	$^1J_{CO}$	13.4	−28.1	−39.3	−45.4	−38.3	−37.3	−38.3	−1.7
N_2	$^1J_{NN}$	175.0	−5.7	−9.1	−23.9	−20.4	−20.4	−19.3	−1.1
H_2O	$^1J_{OH}$	63.7	51.5	47.1	49.5	48.4	48.2	52.8	−3.3
	$^2J_{HH}$	−1.9	−0.8	−0.6	−0.7	−0.6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

Reduced spin–spin coupling constants (10^{19}kg m^{-2} s^{-2}Å^{-2})

		RHF	LDA	BLYP	B3LYP	RAS	exp*	vib
HF	$^1J_{HF}$	59.2	35.0	34.5	36.8	48.1	47.6	−3.4
CO	$^1J_{CO}$	13.4	−65.4	−55.7	−44.9	−39.3	−38.3	−1.7
N_2	$^1J_{NN}$	175.0	32.9	−46.6	−32.9	−9.1	−19.3	−1.1
H_2O	$^1J_{OH}$	63.7	40.3	44.6	46.6	47.1	52.8	−3.3
	$^2J_{HH}$	−1.9	−0.3	−0.9	−0.6	−0.6	−0.7	0.1
NH_3	$^1J_{NH}$	61.4	41.0	49.6	52.6	50.2	50.8	−0.3
	$^2J_{HH}$	−1.9	−0.4	−0.7	−0.8	−0.9	−0.9	0.1
C_2H_4	$^1J_{CC}$	1672.0	66.6	90.3	98.3	90.5	87.8	1.2
	$^1J_{CH}$	249.7	42.5	55.3	54.7	50.2	50.0	1.7
	$^2J_{CH}$	−189.3	0.4	0.0	−0.4	−0.5	−0.4	−0.4
	$^2J_{HH}$	−28.7	0.4	0.4	0.2	0.1	0.2	0.0
	$^3J_{cis}$	30.0	0.8	1.1	1.1	1.0	0.9	0.1
	$^3J_{tns}$	33.3	1.2	1.7	1.7	1.5	1.4	0.2
$\lvert\bar{\Delta}\rvert$	abs.	180.3	11.2	5.9	4.2	1.6	*at R_e	
	%	5709	72	48	20	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

DFT failures and successes

- DFT failures: couplings to electronegative and lone-pair atoms
  - fluorine couplings, in particular, are strongly underestimated:

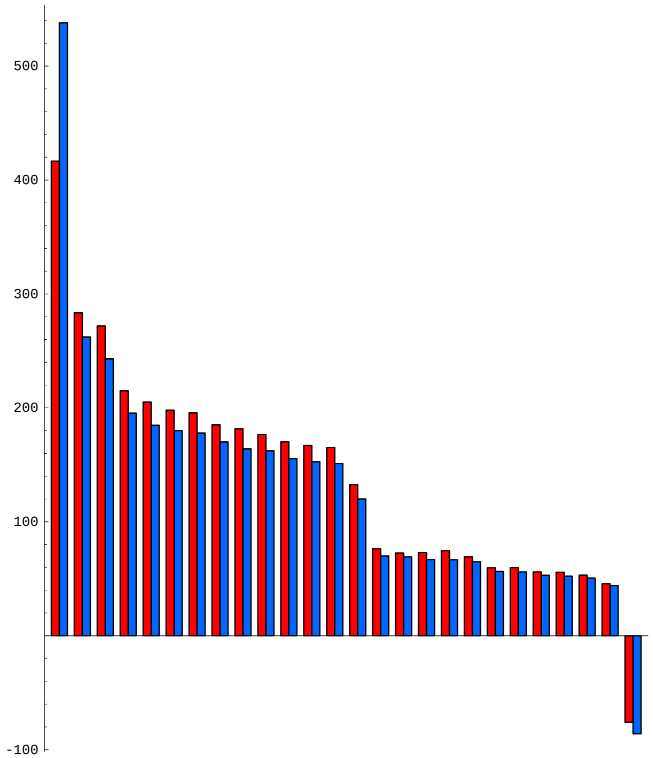
		RHF	LDA	BLYP	B3LYP	CCSD	exp
HF	$^1J_{\mathrm{HF}}$	669	396	390	417	522	538
FHF^-	$^2J_{\mathrm{FF}}$	657	−175	−113	25	439	≈ 274

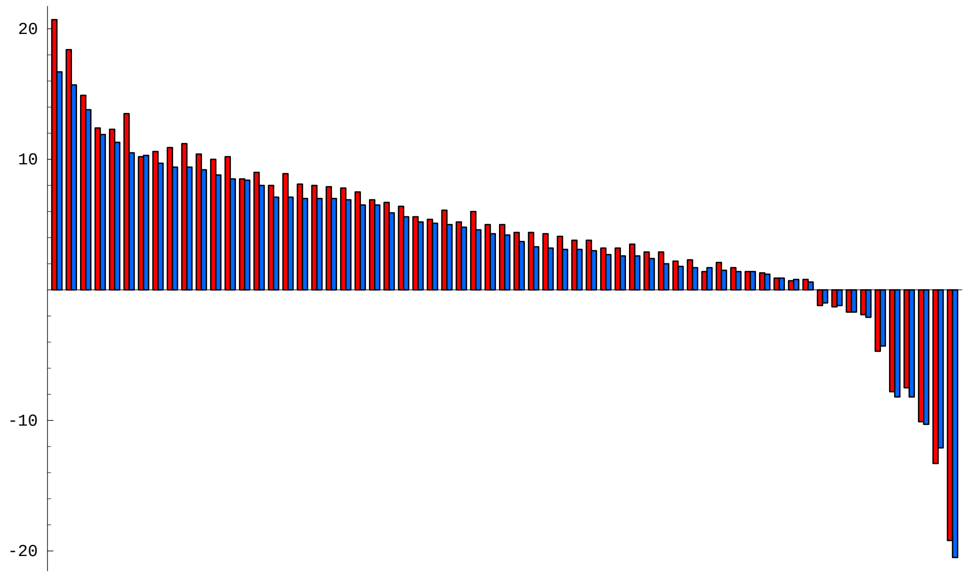
  - this is obviously a failure of the functionals rather than of DFT as such

- Successes of DFT:
  - trends are well reproduced
  - hydrocarbons are well reproduced (Malkin, Malkina, and Salahub) mean abs. err. 4 Hz and std. dev. 6 Hz (vs. 5 and 15 Hz in general) even better with small basis sets :)

Trends in spin–spin coupling constants

- comparison of calculated (red) and B3LYP (blue) spin–spin coupling constants
  - plotted in order of decreasing experimental value





- trends are quite well reproduced by B3LYP, in particular for large couplings

Spin–spin coupling constants of hydrocarbons

	B3LYP	emp		B3LYP	emp		B3LYP	emp
Benzene			$^2J_{C_2H_1}$	5.0	4.3	$^3J_{C_2H_4}$	7.5	6.5
$^3J_{HH}$	8.9	7.1	$^3J_{C_2H_5}$	6.9	6.5	$^1J_{C_2C_3}$	76.4	70.0
$^4J_{HH}$	1.3	1.2	$^3J_{C_3H_1}$	7.9	7.0	Thiophene		
$^5J_{HH}$	0.8	0.6	$^3J_{C_3H_5}$	8.0	7.0	$^3J_{H_2H_3}$	6.0	4.6
$^1J_{CH}$	167.1	152.7	$^3J_{C_2H_4}$	8.1	7.0	$^3J_{H_3H_4}$	4.4	3.3
$^2J_{CH}$	2.1	1.5	$^1J_{C_2C_3}$	73.0	66.9	$^4J_{H_2H_5}$	3.2	2.6
$^3J_{CH}$	8.0	7.1	$^1J_{NH_1}$	72.6	69.2	$^4J_{H_2H_4}$	0.9	0.9
$^4J_{CH}$	−1.2	−1.0	$^2J_{NH_2}$	3.8	3.1	$^1J_{C_2H_2}$	198.0	180.0
$^1J_{CC}$	59.9	56.0	$^3J_{NH_3}$	4.4	3.7	$^1J_{C_3H_3}$	176.7	162.3
$^2J_{CC}$	−1.7	−1.7	$^1J_{NC_2}$	10.2	10.3	$^2J_{C_2H_3}$	9.0	8.0
$^3J_{CC}$	11.2	9.4	$^2J_{NC_3}$	3.8	3.0	$^2J_{C_3H_2}$	5.4	5.1
Pyrrole			Furan			$^2J_{C_3H_4}$	6.7	5.9
$^3J_{H_1H_2}$	3.2	2.7	$^3J_{H_2H_3}$	2.3	1.7	$^3J_{C_2H_5}$	5.6	5.2
$^3J_{H_2H_3}$	3.5	2.6	$^3J_{H_3H_4}$	4.1	3.1	$^3J_{C_3H_5}$	10.4	9.2
$^3J_{H_3H_4}$	4.3	3.2	$^4J_{H_2H_5}$	1.7	1.4	$^3J_{C_2H_4}$	10.9	9.4
$^4J_{H_2H_5}$	2.2	1.8	$^4J_{H_2H_4}$	0.7	0.8	$^1J_{C_2C_3}$	69.3	64.9
$^4J_{H_1H_3}$	2.9	2.4	$^1J_{C_2H_2}$	215.0	195.4	Cyclopropane		
$^4J_{H_2H_4}$	1.4	1.4	$^1J_{C_3H_3}$	185.1	170.1	$^2J_{H,H}$	−4.7	−4.2
$^1J_{C_2H_2}$	195.6	177.9	$^2J_{C_2H_3}$	12.3	11.3	$^3J_{HH}^{cis}$	10.3	8.6
$^1J_{C_3H_3}$	181.6	164.0	$^2J_{C_3H_2}$	14.9	13.8	$^3J_{HH}^{trans}$	6.1	5.1
$^2J_{C_2H_3}$	10.0	8.8	$^2J_{C_3H_4}$	5.0	4.2	$^1J_{CH}$	170.3	156.0
$^2J_{C_3H_2}$	8.5	8.4	$^3J_{C_2H_5}$	7.8	6.9	$^2J_{CH}$	−1.9	−2.1
$^2J_{C_3H_4}$	5.2	4.8	$^3J_{C_3H_5}$	6.4	5.6	$^1J_{CC}$	12.4	11.9

Basis-set requirements

- Accurate spin–spin calculations require large basis sets, augmented with steep s functions
  - Huz-III-su0: [11s6p2d/6s2p]
  - Huz-III-su3: [14s6p2d/9s2p]

- B3LYP calculations on benzene with and without added s functions:

Hz	MCSCF	B3LYP-su3	B3LYP-su0	emp
${}^1J_{CC}$	70.9	60.0	56.7	56.1
${}^2J_{CC}$	−5.0	−1.8	−1.7	−1.7
${}^3J_{CC}$	19.1	11.2	10.7	9.4
${}^1J_{CH}$	176.7	166.3	151.7	152.7
${}^2J_{CH}$	−7.4	2.0	1.7	1.4
${}^3J_{CH}$	11.7	8.0	7.3	7.0
${}^4J_{CH}$	−1.3	−1.2	−1.3	−1.0
${}^3J_{HH}$		8.7	7.6	7.0
${}^4J_{HH}$		1.3	1.1	1.2
${}^5J_{HH}$		0.8	0.7	0.6

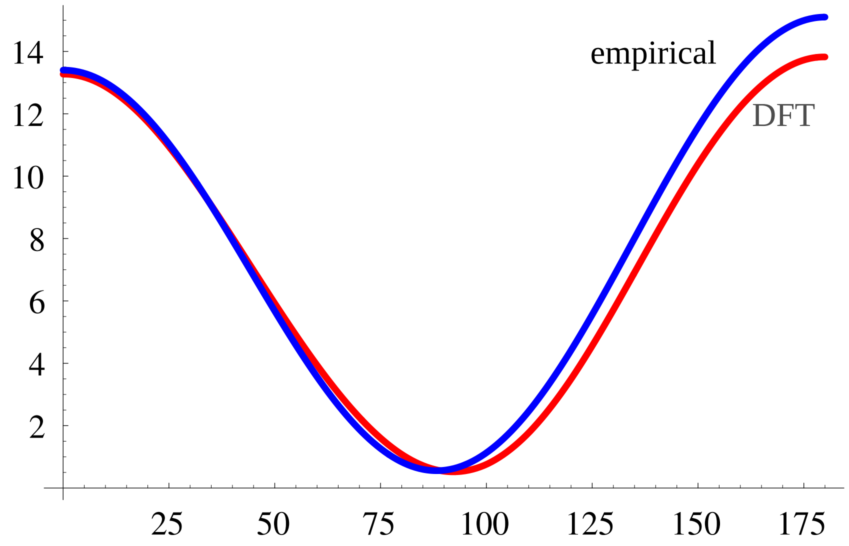
- Cancellation of errors gives excellent agreement without added steep functions :)

The Karplus curve

- Vicinal couplings depend critically on the dihedral angle:

  – $^3J_{\mathrm{HH}}$ in ethane as a function of the dihedral angle:

  – The agreement with the empirical Karplus curve is good.

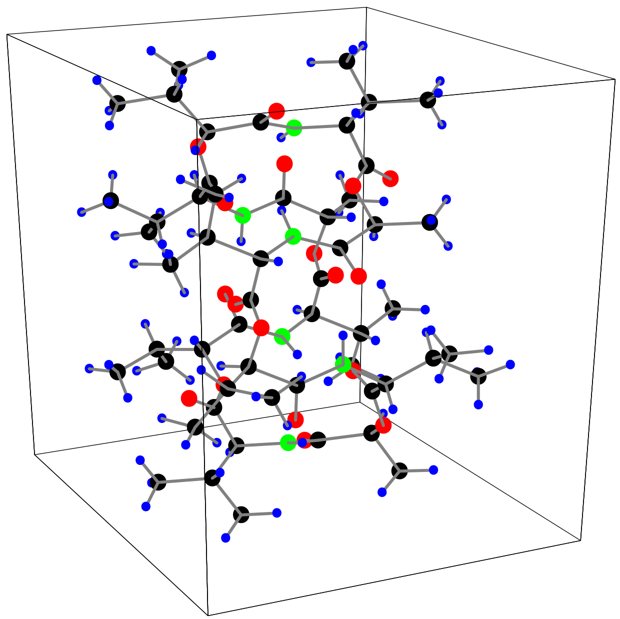


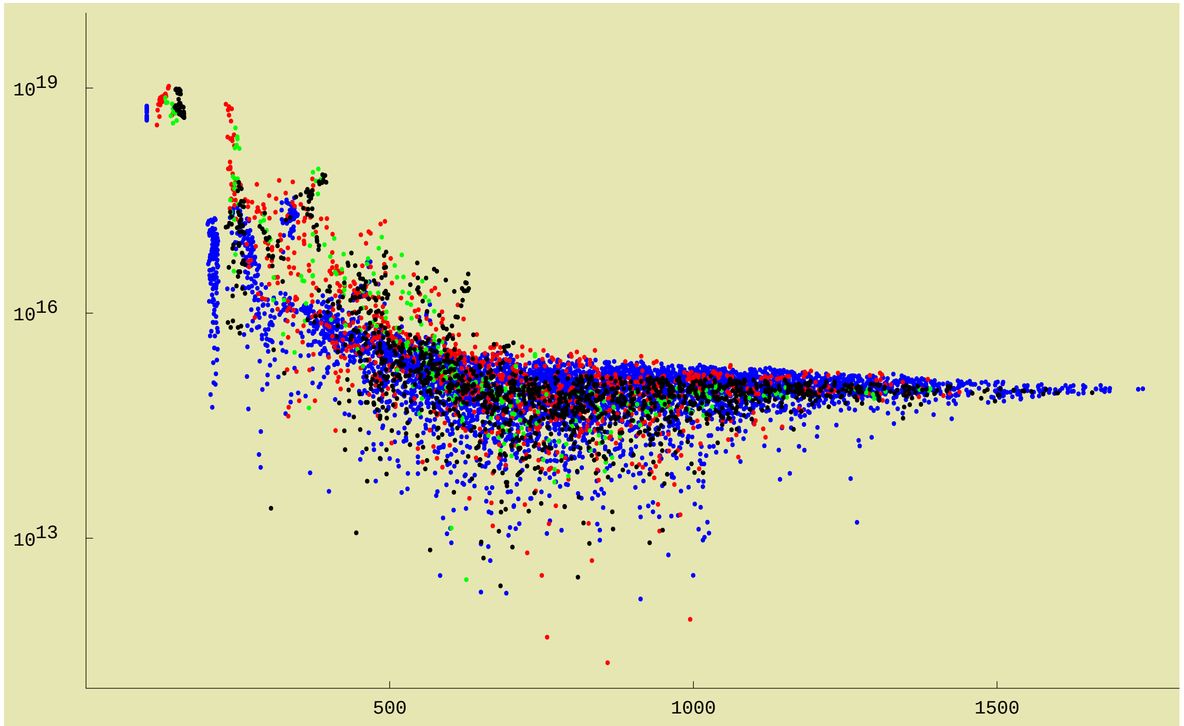
NMR spin–spin coupling constants in C_{60}

- For the spin–spin coupling constants in C_{60}, we find (at the B3LYP level):
  – ^1J couplings within one pentagon and between two pentagons are 62 and 77 Hz.
  – ^2J couplings within one pentagon and between two pentagons are 7 and 1 Hz.
  – ^3J couplings are 4 Hz.
  – ^4J couplings and all other couplings are smaller than 1 Hz.

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

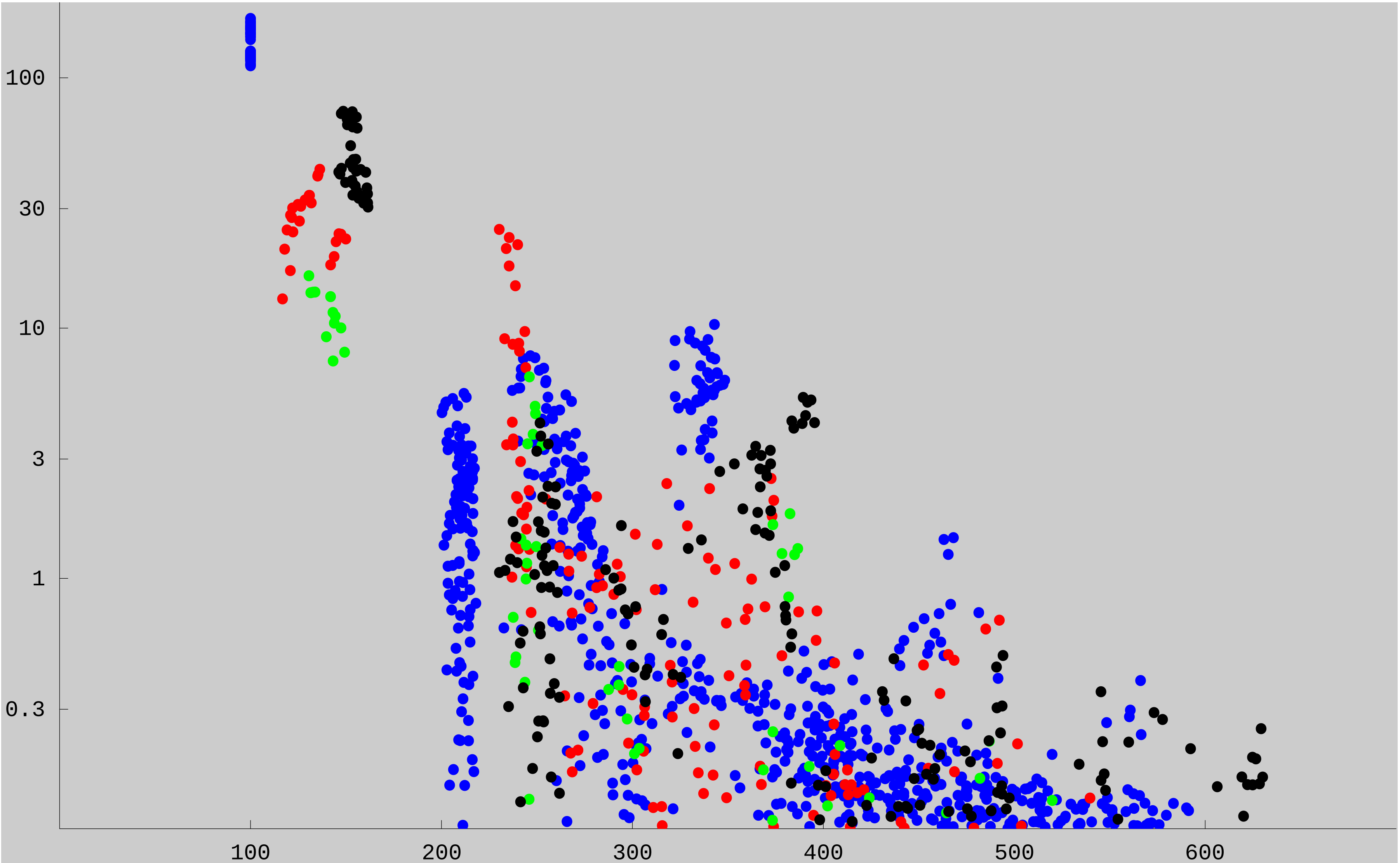
- DFT can be applied to large molecular systems such as valinomycin (168 atoms)
  - there are a total of 7587 spin–spin couplings to the carbon atoms in valinomycin
  - below, we have plotted the magnitude of the reduced LDA/6-31G coupling constants on a logarithmic scale, as a function of the internuclear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





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

Valinomycin LDA/6-31G spin–spin couplings to CH, CO, CN, CC greater than 0.1 Hz



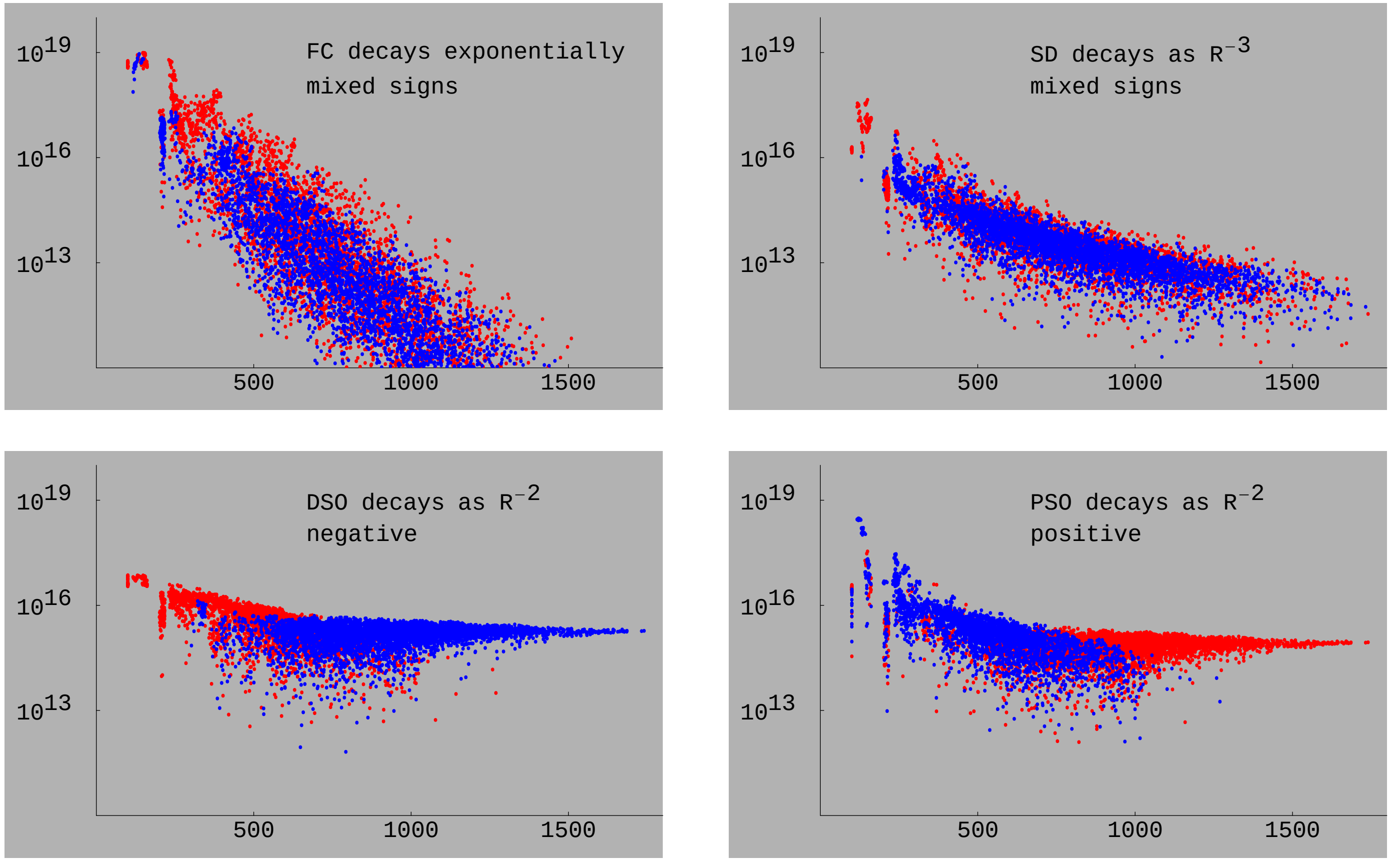
The different long-range decays of the Ramsey terms

- Letting M be the center of the product Gaussian $G_a G_b$, we obtain

$$\left\langle G_a \left| h_K^{\mathrm{FC}} \right| G_b \right\rangle \propto \exp\left(-\mu R_{KM}^2\right), \qquad \left\langle G_a \left| h_K^{\mathrm{SD}} \right| G_b \right\rangle \propto R_{KM}^{-3},$$

$$\left\langle G_a \left| h_{KL}^{\mathrm{DSO}} \right| G_b \right\rangle \propto R_{KM}^{-2} R_{LM}^{-2}, \qquad \left\langle G_a \left| h_K^{\mathrm{PSO}} \right| G_b \right\rangle \propto R_{KM}^{-2}$$

- Insertion in Ramsey's expression gives (red positive, blue negative)



The long-range orbital contributions

- At large separations, the couplings are dominated by the orbital contributions:

$$\mathbf{J}_{PQ}^{\mathrm{DSO}} \propto R_{PQ}^{-2}, \quad \mathbf{J}_{PQ}^{\mathrm{PSO}} \propto R_{PQ}^{-2} \qquad \leftarrow \text{large separations}$$

- Moreover, in this limit, the DSO contributions all become negative:

$$K_{PQ}^{\mathrm{DSO}} = \frac{2\alpha^4}{3} \left\langle 0 \left| r_P^{-3} r_Q^{-3} \, \mathbf{r}_P \cdot \mathbf{r}_Q \right| 0 \right\rangle < 0 \qquad \leftarrow \text{large separations}$$

- Also, the PSO contributions become positive, nearly cancelling the DSO contributions.
  - use of Taylor expansion, the virial theorem, and the resolution of identity give:

$$\mathbf{J}_{PQ}^{\mathrm{DSO}} + \mathbf{J}_{PQ}^{\mathrm{PSO}} \propto R_{PQ}^{-3} \qquad \leftarrow \text{large separations, large basis}$$

- However, the PSO contributions converge very slowly to the basis-set limit: