

Magnetic Properties: NMR, EPR, Susceptibility

Part 1: Theory

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Heavy elements require **relativistic** quantum chemistry:

'The classic': P. Pyykkö. *Chem. Rev.* 88 (1988), 563 - 594.

Recent textbooks: Reiher & Wolf (2009), Dyllal & Fægri (2007)

Short review: T. Saue, *ChemPhysChem* 12 (2011), 3077 - 3094

By yours truly:

J. Chem. Phys. 136 (2012), 150902:

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Perspective: Relativistic effects

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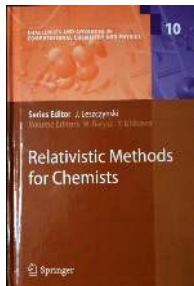
This perspective article discusses some broadly-known and some less broadly-known consequences of Einstein's special relativity in quantum chemistry, and provides a brief outline of the theoretical methods currently in use, along with a discussion of recent developments and selected applications. The treatment of the electron correlation problem in relativistic quantum chemistry methods, and expanding the reach of the available relativistic methods to calculate all kinds of energy derivative properties, in particular spectroscopic and magnetic properties, requires on-going efforts. © 2012 *American Institute of Physics*. [<http://dx.doi.org/10.1063/1.3702628>]

Annu. Rep. NMR Spectroscop. 67 (2009), 1-95.

Coord. Chem. Rev. 238/239 (2002), 83-126 and 251

(2007), 1796-1821.

Chapter 12 in:



- Some molecular derivative properties of interest
- Internal and external fields
- Field-dependent terms in the Hamiltonian: $4c$, $2c$, $nrel$.
- NMR shielding and J -coupling
- Magnetizability
- EPR g -shift and hyperfine coupling

Outline

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Molecular energy $E = \langle \Psi | H | \Psi \rangle$ or $E[\rho]$

Static molecular properties via derivatives wrt generalized field amplitudes \mathcal{F}_i

$$\frac{d\tilde{E}}{d\mathcal{F}_1} ; \frac{d^2\tilde{E}}{d\mathcal{F}_1 d\mathcal{F}_2} ; \dots$$

Quasi-energy $Q(t) = \langle \Phi | H - i\frac{\partial}{\partial t} | \Phi \rangle$ where $(H - i\frac{\partial}{\partial t}) | \Phi \rangle = | \Phi \rangle Q(t)$

Dynamic molecular properties via ¹

$$\frac{d\{\tilde{Q}\}_T}{d\mathcal{F}_1(\omega_1)} ; \frac{d^2\{\tilde{Q}\}_T}{d\mathcal{F}_1(\omega_1)d\mathcal{F}_2(\omega_2)} ; \dots$$

Time-averaged quasi-energy: $\{\tilde{Q}(t)\}_T = \frac{1}{T} \int_{-T/2}^{T/2} \tilde{Q}(t) dt$

Normalization: $\tilde{E} = E - \lambda[\langle \psi | \psi \rangle - 1]$; $\tilde{Q} = Q - \lambda \partial \langle \psi | \psi \rangle / \partial t$

¹Christiansen et al., IJQC 68 (1998), 68. For DFT, see Aiga et al., JCP 111 (1999), 2878, and Krykunov & JA, JCP 123 (2005), 114103

Usually, derivatives are taken around the expansion point = unperturbed stationary ground state, all $\mathcal{F}_i = 0$.

Notation:

$$A^{(0)} = A(\mathcal{F}) \Big|_{\mathcal{F}=0} ; \quad A^{(\mathcal{F}_i)} = \frac{\partial A(\mathcal{F})}{\partial \mathcal{F}_i} \Big|_{\mathcal{F}=0} ; \quad A^{(\mathcal{F}_i, \mathcal{F}_j)} = \frac{\partial^2 A(\mathcal{F})}{\partial \mathcal{F}_i \partial \mathcal{F}_j} \Big|_{\mathcal{F}=0}$$

where A is one of H , Ψ , E , Q , or some other quantity / operator.

Notation with $\mathcal{F} = 0$ is implicit from here on

If E or Q are calculated from a relativistic theory



Relativistic properties

If E or Q are calculated from nonrelativistic theory



Nonrelativistic properties

Or start with nonrelativistic E , Q , Ψ and introduce relativistic effects via perturbation theory

Beware picture-change effects (4-component vs. 2-component)

Focus here on **static** 1st and 2nd order magnetic properties and the associated operators in nrel., 2c, and 4c theory

1st order – expectation-value like (but see details later re. EPR parameters):

$$E_n^{(\mathcal{F}_i)} = \langle n | H^{(\mathcal{F}_i)} | n \rangle$$

2nd order – Sum-over-states (SOS) with $|n\rangle, |k\rangle =$ unperturbed states:

$$E_n^{(\mathcal{F}_i, \mathcal{F}_j)} = \underbrace{\langle n | H^{(\mathcal{F}_i, \mathcal{F}_j)} | n \rangle}_{\text{Diamagnetic}} + 2 \operatorname{Re} \underbrace{\sum_{k \neq n} \frac{\langle n | H^{(\mathcal{F}_j)} | k \rangle \langle k | H^{(\mathcal{F}_i)} | n \rangle}{E_n - E_k}}_{\text{Paramagnetic contrib. for mag. prop.}}$$

- Needs complete spectrum. Finite basis \Rightarrow finite number of non-continuum states.
- Explicit calculation of excited states not needed. Solve linear response equations instead: start with $H^{(0)}, \Psi^{(0)}$ given suitable approximations. Calculate $E_0^{(\mathcal{F}_i, \mathcal{F}_j)}$ for given $H^{(\mathcal{F}_i, \mathcal{F}_j)}, H^{(\mathcal{F}_i)}, H^{(\mathcal{F}_j)}$
- T -independent. For degenerate states the formulation is somewhat different ...

Suppose state n has degeneracy of d_n , and that we have several states that are thermally accessible.

Components of state n are: $|n, a\rangle$. Further, $\beta = 1/(k_B T)$.

$$\begin{aligned}
 E^{(\mathcal{F}_i, \mathcal{F}_j)}(T) = \frac{1}{Q} \sum_n e^{-\beta E_n} & \left[\sum_{a=1}^{d_n} \langle n, a | H^{(\mathcal{F}_i, \mathcal{F}_j)} | n, a \rangle \right. \\
 & + \beta \sum_{a=1}^{d_n} \sum_{a'=1}^{d_n} \langle n, a | H^{(\mathcal{F}_i)} | n, a' \rangle \langle n, a' | H^{(\mathcal{F}_j)} | n, a \rangle \\
 & \left. + 2 \operatorname{Re} \sum_{k \neq n} \sum_{a=1}^{d_n} \sum_{b=1}^{d_k} \frac{\langle n, a | H^{(\mathcal{F}_i)} | k, b \rangle \langle k, b | H^{(\mathcal{F}_j)} | n, a \rangle}{E_n - E_k} \right]
 \end{aligned}$$

Q is the partition function

$$Q = \sum_n d_n e^{-\beta E_n}$$

Soncini & van den Heuvel, J. Chem. Phys. 138 (2013), 021103.

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- **Internal and external fields**
- Field-dependent terms in the Hamiltonian: $4c$, $2c$, nrel.
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Electric and magnetic fields

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

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

where \mathbf{A} is the vector potential. Gauge-freedom:

$$\mathbf{A}' = \mathbf{A} + \nabla f(\mathbf{r}, t)$$

$$\phi' = \phi - \frac{\partial f}{\partial t}$$

such that

$$\mathbf{E}' = -\nabla\left(\phi - \frac{\partial f}{\partial t}\right) - \frac{\partial}{\partial t}(\mathbf{A} + \nabla f) = \mathbf{E}$$

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

Gauge freedom allows to make the choice $\nabla \cdot \mathbf{A} = 0$ (Coulomb gauge)

Some useful expressions:

- Static homogeneous magnetic field: $\mathbf{A}^B = \frac{1}{2} \mathbf{B} \times \mathbf{r}$

- Static magnetic field of a point magnetic dipole: $\mathbf{A}^m = \frac{\mu_0}{4\pi} \frac{\mathbf{m} \times \mathbf{r}}{r^3}$
(dipole \mathbf{m} at coordinate origin)

- Associated \mathbf{B} -field: $\mathbf{B}^m = \nabla \times \mathbf{A}^m = \frac{\mu_0}{4\pi} \left[\frac{3\mathbf{r}(\mathbf{m} \cdot \mathbf{r})}{r^5} - \frac{\mathbf{m}}{r^3} - \frac{8\pi}{3} \mathbf{m} \delta(\mathbf{r}) \right]$

Note: $\mu_0 \epsilon_0 = c^{-2} \Rightarrow$ in atomic units $\frac{\mu_0}{4\pi} \rightarrow \frac{1}{c^2}$

How to get the fields into quantum theory?

Classical Lagrangian $L(\mathbf{r}, \dot{\mathbf{r}})$, equation of motion $\nabla L - \frac{\partial}{\partial t} \frac{\partial L}{\partial \dot{\mathbf{r}}} = 0$

assume $L = \frac{1}{2}m\dot{\mathbf{r}}^2 - V(\mathbf{r}) = T - V$ then

$\nabla L = -\nabla V = \mathbf{F}$ Force equals

$$\frac{\partial}{\partial t} \frac{\partial L}{\partial \dot{\mathbf{r}}} = \frac{\partial}{\partial t} m\dot{\mathbf{r}} = m\ddot{\mathbf{r}} \text{ mass x acceleration (Newton II)}$$

With fields, the Lagrangian for a particle of charge q is (ignore V for now)

$$L = \frac{1}{2}m\dot{\mathbf{r}}^2 - q\Phi + q\dot{\mathbf{r}} \cdot \mathbf{A}$$

Equation of motion gives $m\ddot{\mathbf{r}} = q(\mathcal{E} + \dot{\mathbf{r}} \times \mathcal{B})$

(Coulomb & Lorentz force)

Canonical momentum: $\mathbf{p} = \frac{\partial L}{\partial \dot{\mathbf{r}}} = m\dot{\mathbf{r}} + q\mathbf{A} \Rightarrow \dot{\mathbf{r}} = \frac{1}{m}(\mathbf{p} - q\mathbf{A})$

Hamiltonian: $H = \mathbf{p}\dot{\mathbf{r}} - L = \frac{1}{2m}(\mathbf{p} - q\mathbf{A})^2 + q\Phi$

without fields: $H = \frac{1}{2m}\mathbf{p}^2$



The substitutions

$$\mathbf{p} \rightarrow \boldsymbol{\pi} = \mathbf{p} - q\mathbf{A} ; H \rightarrow H - q\Phi$$

turn the field-free Hamiltonian into the Hamiltonian that takes the presence of the fields into account.

We'll use this approach in the following.

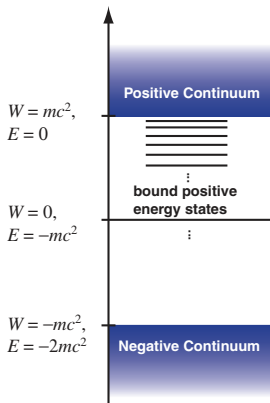
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Field-free Dirac Equation

$$h^D \psi^D = \psi^D W$$

$$h^D = c^2 \beta + c \boldsymbol{\alpha} \cdot \mathbf{p} = \begin{bmatrix} c^2 & c \boldsymbol{\sigma} \cdot \mathbf{p} \\ c \boldsymbol{\sigma} \cdot \mathbf{p} & -c^2 \end{bmatrix}$$



$$\beta = \begin{pmatrix} 1_2 & 0_2 \\ 0_2 & -1_2 \end{pmatrix}$$

$$\boldsymbol{\alpha} = \begin{pmatrix} 0_2 & \boldsymbol{\sigma} \\ \boldsymbol{\sigma} & 0_2 \end{pmatrix}$$

Pauli Matrices $\boldsymbol{\sigma}$:

$$\sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}$$

$$\sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}$$

$$\sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

With fields, for an electron with $q = -e$; $q\Phi = -e\Phi = V$, in a.u.:
 $\boldsymbol{\pi} = \mathbf{p} + \mathbf{A}$, $W \rightarrow W - V$, after shifting the energy origin:

$$[c^2\beta' + c\boldsymbol{\alpha} \cdot \boldsymbol{\pi} + V - E]\psi^D = \begin{bmatrix} V - E & c\boldsymbol{\sigma} \cdot \boldsymbol{\pi} \\ c\boldsymbol{\sigma} \cdot \boldsymbol{\pi} & V - E - 2c^2 \end{bmatrix} \psi^D = 0$$

For magnetic fields, the perturbation Hamiltonian is

$$h_{\text{mag}}^D = c\boldsymbol{\alpha} \cdot \mathbf{A}$$

In nonrelativistic and quasi-relativistic theory, the perturbation Hamiltonian also has a 'diamagnetic' term proportional to \mathbf{A}^2 . Let's see how that arises.

FW transformation up to $\mathcal{O}(c^{-2})$

$$h^{\text{FW}} = U^\dagger h^D U = \begin{pmatrix} \mathcal{O}(c^{-2}) & \bullet \\ \bullet & \bullet \end{pmatrix}$$

$$U = U^d U^n = \begin{pmatrix} 1 & -X^\dagger \\ X & 1 \end{pmatrix} \begin{pmatrix} A & 0 \\ 0 & B \end{pmatrix} = \begin{pmatrix} A & -BX^\dagger \\ AX & B \end{pmatrix}$$

with $A = 1/\sqrt{1 + X^\dagger X}$ and $B = 1/\sqrt{1 + XX^\dagger}$.

The approximations

- $X \approx \frac{1}{2c}(\varphi \cdot \boldsymbol{\pi})$
- $A \approx 1 - \frac{1}{2}XX^\dagger$
- $B \approx 1 - \frac{1}{2}X^\dagger X$
- $AX \approx X$; $BX^\dagger \approx X^\dagger$

give

$$U = \begin{pmatrix} 1 - \frac{1}{8c^2}(\varphi \cdot \boldsymbol{\pi})^2 & \frac{1}{2c}(\varphi \cdot \boldsymbol{\pi}) \\ -\frac{1}{2c}(\varphi \cdot \boldsymbol{\pi}) & 1 - \frac{1}{8c^2}(\varphi \cdot \boldsymbol{\pi})^2 \end{pmatrix}$$

Using the transformation matrix from the previous slide gives for the upper-upper part in $\mathcal{O}(c^{-2})$:

$$h^{\text{FW}} = V + \frac{1}{2}(\boldsymbol{\sigma} \cdot \boldsymbol{\pi})^2 - \frac{1}{8c^2} V(\boldsymbol{\sigma} \cdot \boldsymbol{\pi})^4 \\ - \frac{1}{8c^2} [(\boldsymbol{\sigma} \cdot \boldsymbol{\pi})^2 V + V(\boldsymbol{\sigma} \cdot \boldsymbol{\pi})^2] + \frac{1}{4c^2} (\boldsymbol{\sigma} \cdot \boldsymbol{\pi}) V(\boldsymbol{\sigma} \cdot \boldsymbol{\pi})$$

Note: $(\boldsymbol{\sigma} \cdot \mathbf{p})^2 = \mathbf{p}^2$ and

$$(\boldsymbol{\sigma} \cdot \boldsymbol{\pi})^2 = \mathbf{p}^2 + (\mathbf{p} \cdot \mathbf{A} + \mathbf{A} \cdot \mathbf{p}) + i\boldsymbol{\sigma} \cdot (\mathbf{p} \times \mathbf{A} + \mathbf{A} \times \mathbf{p}) + \mathbf{A}^2$$

In the absence of a vector potential, $\mathbf{A} = 0$,

$$h^{\text{FW}} = V + \frac{1}{2}(\boldsymbol{\sigma} \cdot \mathbf{p})^2 - \frac{1}{8c^2} V(\boldsymbol{\sigma} \cdot \mathbf{p})^4 \\ - \frac{1}{8c^2} [(\boldsymbol{\sigma} \cdot \mathbf{p})^2 V + V(\boldsymbol{\sigma} \cdot \mathbf{p})^2] + \frac{1}{4c^2} (\boldsymbol{\sigma} \cdot \mathbf{p}) V(\boldsymbol{\sigma} \cdot \mathbf{p})$$

$$\begin{aligned}
 h^{\text{FW}} &= V \\
 &+ \frac{1}{2}(\boldsymbol{\sigma} \cdot \mathbf{p})^2 \rightarrow \frac{1}{2}\mathbf{p}^2 \\
 &- \frac{1}{8c^2}V(\boldsymbol{\sigma} \cdot \mathbf{p})^4 \rightarrow -\frac{1}{8c^2}\mathbf{p}^4 \\
 &- \frac{1}{8c^2}(\boldsymbol{\sigma} \cdot \mathbf{p})^2 V \rightarrow -\frac{1}{8c^2}\mathbf{p}^2 V - \cancel{\frac{i}{8c^2}\boldsymbol{\sigma} \cdot \mathbf{p} \times \mathbf{p} V} \\
 &- \frac{1}{8c^2}V(\boldsymbol{\sigma} \cdot \mathbf{p})^2 \rightarrow -\frac{1}{8c^2}V\mathbf{p}^2 - \cancel{\frac{i}{8c^2}V\boldsymbol{\sigma} \cdot \mathbf{p} \times \mathbf{p}} \\
 &+ \frac{1}{4c^2}(\boldsymbol{\sigma} \cdot \mathbf{p})V(\boldsymbol{\sigma} \cdot \mathbf{p}) \rightarrow \frac{1}{4c^2}\mathbf{p}V \cdot \mathbf{p} + \frac{i}{4c^2}\boldsymbol{\sigma} \cdot \mathbf{p}V \times \mathbf{p}
 \end{aligned}$$

Line 4: $-\mathbf{p}^2 V = -\{\mathbf{p}^2 V\} - 2\{\mathbf{p}V\} \cdot \mathbf{p} - V\mathbf{p}^2$ + Line 5: $-V\mathbf{p}^2$, cancel
 Line 6: $\mathbf{p}V \cdot \mathbf{p} = \{\mathbf{p}V\} \cdot \mathbf{p} + V\mathbf{p}^2$ except for $-\{\mathbf{p}^2 V\}$

What remains is the field-free Pauli Operator

$$h^{\text{Pauli}} = V + \frac{1}{2}\mathbf{p}^2 - \frac{\mathbf{p}^4}{8c^2} - \frac{\{\mathbf{p}^2 V\}}{8c^2} + \frac{i}{4c^2}\boldsymbol{\sigma} \cdot [\mathbf{p}V \times \mathbf{p}]$$

After some straightforward manipulations, the one-electron operator in the presence of a field reads

$$\begin{aligned}
 h^{\text{FW}} &= V + \frac{1}{2}\boldsymbol{\pi}^2 && \text{nrel. Hamiltonian w/ fields (no spin)} \\
 &+ \frac{1}{2}\boldsymbol{\sigma} \cdot \boldsymbol{\mathcal{B}} && \text{nrel. spin-Zeeman} \\
 &- \frac{1}{8c^2}\boldsymbol{\pi}^4 - \frac{1}{4c^2}\boldsymbol{\sigma} \cdot \boldsymbol{\mathcal{B}} \boldsymbol{\pi}^2 && \text{rel. corrections of } T \text{ and of spin-Zeeman} \\
 &- \frac{1}{8c^2}\{\boldsymbol{p}^2 V\} && \text{Darwin term} \\
 &+ \frac{i}{4c^2}\boldsymbol{\sigma} \cdot [\boldsymbol{p}V \times \boldsymbol{\pi}] && \text{SO coupling + rel. spin-field interactions}
 \end{aligned}$$

with the replacement $\{\boldsymbol{p} \times \boldsymbol{A}\} = -i\boldsymbol{\mathcal{B}}$.

In the books by Moss² and Harriman³ the last term is written as

$\frac{1}{8c^2}\boldsymbol{\sigma} \cdot [\boldsymbol{\pi} \times \boldsymbol{\mathcal{E}} - \boldsymbol{\mathcal{E}} \times \boldsymbol{\pi}]$ where $\boldsymbol{\mathcal{E}} = \boldsymbol{\nabla}V = i\boldsymbol{p}V$ is the electric field

² R. E. Moss, Advanced Molecular Quantum Mechanics, 1973, Chapman & Hall, London.

³ J. E. Harriman, Theoretical Foundations of Electron Spin Resonance, 1978, Academic Press, New York

Example: In NMR calculations one considers a homogeneous \mathcal{B}^{ext} (from spectrometer) and the field \mathcal{B}^N from the nuclear spin magnetic dipoles located at \mathbf{r}_A (or a probe magnetic dipole at a nuclear position or elsewhere (NICS)).

Nonrelativistic limit (incl. spin-dependent terms)

$$h_{\text{mag}}^{\text{nrel}} = \frac{1}{2} \left([\mathbf{p} \cdot \mathbf{A} + \mathbf{A} \cdot \mathbf{p}] + i\sigma \cdot [\mathbf{p} \times \mathbf{A} + \mathbf{A} \times \mathbf{p}] + \mathbf{A}^2 \right)$$

With (see Slide 13, \mathbf{A}^N for point nuclei):

$$\mathbf{A} = \mathbf{A}^{\text{ext}} + \mathbf{A}^N = \frac{1}{2} \mathcal{B} \times \mathbf{r} + \frac{\mu_0}{4\pi} \sum_A \frac{\mathbf{m}_A \times \mathbf{r}_A}{r_A^3}$$

one obtains the operators (next slide):

$$h_{\text{mag}}^{\text{nrel}} = h^{\text{DM}} + h^{\text{OZ}} + h^{\text{SZ}} + h^{\text{OP}} + h^{\text{DS}} + h^{\text{FC}} + h^{\text{SD}} + h^{\text{OD}}$$

with

$$h^{\text{DM}} = \frac{1}{4} (\mathbf{r} \times \mathcal{B}^{\text{ext}}) \cdot (\mathbf{r} \times \mathcal{B}^{\text{ext}})$$

$$h^{\text{OZ}} = -\frac{1}{2} (\mathbf{r} \times \mathbf{p}) \cdot \mathcal{B}^{\text{ext}}$$

$$h^{\text{SZ}} = \frac{1}{2} \varphi \cdot \mathcal{B}^{\text{ext}}$$

$$h^{\text{OP}} = \frac{1}{c^2} \sum_A \mathbf{m}_A \cdot \left(\frac{\mathbf{r}_A}{r_A^3} \times \mathbf{p} \right)$$

$$h^{\text{DS}} = \frac{1}{2c^2} \sum_A \left[(\mathbf{m}_A \cdot \mathcal{B}^{\text{ext}}) \left(\frac{\mathbf{r}_A}{r_A^3} \cdot \mathbf{r} \right) - (\mathbf{m}_A \cdot \mathbf{r}) \left(\mathcal{B}^{\text{ext}} \cdot \frac{\mathbf{r}_A}{r_A^3} \right) \right]$$

$$h^{\text{FC}} + h^{\text{SD}} = \frac{1}{2} \varphi \cdot \mathcal{B}^{\text{nuc}} = \frac{1}{2c^2} \sum_A \varphi \cdot \left\{ \mathbf{m}_A \left(\nabla \cdot \frac{\mathbf{r}_A}{r_A^3} \right) - (\mathbf{m}_A \cdot \nabla) \frac{\mathbf{r}_A}{r_A^3} \right\}$$

$$h^{\text{OD}} = \frac{1}{2c^4} \sum_{B \neq A} \frac{(\mathbf{m}_A \cdot \mathbf{m}_B)(\mathbf{r}_A \cdot \mathbf{r}_B) - (\mathbf{m}_A \cdot \mathbf{r}_B)(\mathbf{m}_B \cdot \mathbf{r}_A)}{r_A^3 r_B^3}$$

Deriving the FC + SD terms

Consider: $\nabla \times \mathbf{A} + \mathbf{A} \times \nabla = \underbrace{\{\nabla \times \mathbf{A}\}}_{\nabla \text{ acts only on } \mathbf{A}} \quad \underbrace{-\mathbf{A} \times \nabla}_{\text{switch order}} + \mathbf{A} \times \nabla$

With $\mathbf{A} = \frac{\mu_0}{4\pi} \frac{\mathbf{m}_A \times \mathbf{r}_A}{r_A^3}$ and

$$\nabla \times \mathbf{m}_A \times \frac{\mathbf{r}_A}{r_A^3} = \mathbf{m}_A (\nabla \cdot \frac{\mathbf{r}_A}{r_A^3}) - (\mathbf{m}_A \cdot \nabla) \frac{\mathbf{r}_A}{r_A^3} \quad (+ \mathbf{m}_A \text{ derivatives} = 0)$$

one obtains the operators FC and SD on slide 24 where the derivative only acts on $\frac{\mathbf{r}_A}{r_A^3}$. Applying the derivatives gives

$$h^{FC} + h^{SD} = \underbrace{\frac{4\pi}{3c^2} \delta(r_A) \mathbf{m}_A \cdot \boldsymbol{\sigma}}_{\text{'contact' term}} + \frac{1}{2c^2} \frac{3(\boldsymbol{\sigma} \cdot \mathbf{r}_A)(\mathbf{m}_A \cdot \mathbf{r}_A) - r_A^2 \mathbf{m}_A \cdot \boldsymbol{\sigma}}{r_A^5}$$

in a.u.

ZORA as an example for a variationally stable quasi-relativistic method

$$h^{\text{FW}} = U^\dagger h^D U = \begin{pmatrix} h^{\text{QR}} & \bullet \\ \bullet & \bullet \end{pmatrix}$$

$$U = U^d U^n = \begin{pmatrix} 1 & -X^\dagger \\ X & 1 \end{pmatrix} \begin{pmatrix} A & 0 \\ 0 & B \end{pmatrix} = \begin{pmatrix} A & -BX^\dagger \\ AX & B \end{pmatrix}$$

with $A = 1/\sqrt{1 + X^\dagger X}$ and $B = 1/\sqrt{1 + XX^\dagger}$.

The approximations

- $X \approx \frac{1}{2c} \frac{2c^2}{2c^2 - V} \sigma \cdot \pi$
- $A = B \approx 1$
- $AX \approx X$; $BX^\dagger \approx X^\dagger$

give the ZORA Hamiltonian in the presence of fields

Alternatively, obtain the operator from the ESC equation

$$h^{\text{ESC}} = \left[V + \frac{1}{2}(\boldsymbol{\sigma} \cdot \boldsymbol{\pi})k(\boldsymbol{\sigma} \cdot \boldsymbol{\pi}) \right]$$

$$k = \left(1 - \frac{V - E}{2c^2} \right)^{-1} = \frac{2c^2}{2c^2 - V} \left(1 + \frac{E}{2c^2 - V} \right)^{-1}$$

Then expand the rhs into a power series in $E/(2c^2 - V)$. In zeroth order,

$$h^{\text{ZORA}} = V + \frac{1}{2}(\boldsymbol{\sigma} \cdot \boldsymbol{\pi})\mathcal{K}(\boldsymbol{\sigma} \cdot \boldsymbol{\pi})$$

$$= V + \frac{1}{2}\boldsymbol{\pi} \cdot \mathcal{K}\boldsymbol{\pi} + \frac{i}{2}\boldsymbol{\sigma} \cdot [\boldsymbol{\pi}\mathcal{K} \times \boldsymbol{\pi}]$$

where $\mathcal{K} = \frac{2c^2}{2c^2 - V} = \frac{1}{1 - V/(2c^2)}$. Nrel. limit for $\mathcal{K} \rightarrow 1$

A number of perturbation operators are obtained in $\mathcal{O}(c^{-2})$, incl. additional 2-electron terms. We will not list them all here.*

Compare different magnetic one-electron perturbation operators:

$$h_{\text{mag}}^{\text{nrel}} = \frac{1}{2} \left([\mathbf{p} \cdot \mathbf{A} + \mathbf{A} \cdot \mathbf{p}] + i\sigma \cdot [\mathbf{p} \times \mathbf{A} + \mathbf{A} \times \mathbf{p}] + \mathbf{A}^2 \right)$$

$$h_{\text{mag}}^{\text{ZORA}} = \frac{1}{2} \left([\mathbf{p} \cdot \mathcal{K}\mathbf{A} + \mathbf{A}\mathcal{K} \cdot \mathbf{p}] + i\sigma \cdot [\mathbf{p} \times (\mathcal{K}\mathbf{A}) + \mathbf{A} \times (\mathcal{K}\mathbf{p})] + \mathcal{K}\mathbf{A}^2 \right)$$

$$\text{where } \mathcal{K} = 2c^2 / (2c^2 - V)$$

$$h_{\text{mag}}^{\text{DKH1}} = c \left(\mathbf{K}[\mathbf{R}\mathbf{p} \cdot \mathbf{A} + \mathbf{p} \cdot \mathbf{A}\mathbf{R}]\mathbf{K} + i\sigma \cdot \mathbf{K}[\mathbf{R}\mathbf{p} \times \mathbf{A} + \mathbf{p} \times \mathbf{A}\mathbf{R}]\mathbf{K} \right)^{**}$$

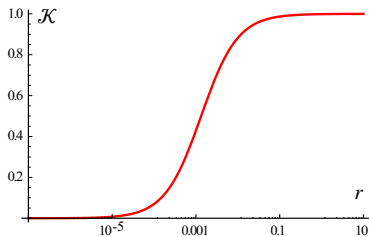
$$\text{with } E_p = \sqrt{\mathbf{p}^2 c^2 + c^4}; \quad \mathbf{K} = \sqrt{\frac{E_p + c^2}{2E_p}}; \quad \mathbf{R} = \frac{c\sigma \cdot \mathbf{p}}{E_p + c^2}$$

$$h_{\text{mag}}^{\text{D}} = c\alpha \cdot \mathbf{A}$$

* See, for example, Manninen et al., JCP 122 (2005), 114107

** Melo et al., JCP 123 (2005), 204112. The DKH2 expression affords an \mathbf{A}^2 term but it is less compact

Nonrelativistic hyperfine terms versus ZORA:



\mathcal{K} for $V = -50/r$

$$\begin{aligned}
 h_{\text{nrel}}^{\text{FC}+\text{SD}} &= \frac{1}{2c^2} \sum_A \boldsymbol{\sigma} \cdot \left[\mathbf{m}_A \left(\nabla \cdot \frac{\mathbf{r}_A}{r_A^3} \right) - (\mathbf{m}_A \cdot \nabla) \frac{\mathbf{r}_A}{r_A^3} \right] \\
 &= \frac{4\pi}{3c^2} \delta(\mathbf{r}_A) \mathbf{m}_A \cdot \boldsymbol{\sigma} + \frac{1}{2c^2} \frac{3(\boldsymbol{\sigma} \cdot \mathbf{r}_A)(\mathbf{m}_A \cdot \mathbf{r}_A) - r_A^2 \mathbf{m}_A \cdot \boldsymbol{\sigma}}{r_A^5}
 \end{aligned}$$

$$h_{\text{ZORA}}^{\text{FC}+\text{SD}} = \frac{1}{2c^2} \sum_A \boldsymbol{\sigma} \left[\mathbf{m}_A \left(\nabla \cdot \left[\mathcal{K} \frac{\mathbf{r}_A}{r_A^3} \right] \right) - (\mathbf{m}_A \cdot \nabla) \left[\mathcal{K} \frac{\mathbf{r}_A}{r_A^3} \right] \right]$$

$$\mathcal{K} = 2c^2 / (2c^2 - V)$$

Is there a 'contact' term in the ZORA hyperfine operator?

Formally it contains a term $\mathcal{K} \sigma \cdot \mathcal{B}$ with the nuclear magnetic field \mathcal{B} from Slide 13, so there is a $\mathcal{K} \delta(\mathbf{r}_A)$ term.

Consider a 1-electron atom:

ZORA 2c density = scaled 4c density (van Lenthe, 1993)

$$g_{1s} \propto (Zr)^{\gamma-1} e^{-Zr} \text{ with } \gamma = \sqrt{1 - Z^2/c^2}$$



2c density $\rho_{1s} \propto (Zr)^{2\gamma-2} \exp(-2Zr)$ upon integration over the angular variables, with r scaled.

$V = -Z/r \Rightarrow \mathcal{K}$ goes as $(2c^2/Z)r$ for very small r .

Thus, $\rho_{1s} \mathcal{K} \propto r^{2\gamma-1}$ for small r . No 'contact' term for $\gamma > 1/2$

but

$r^{2\gamma-1}$ diverges for $r \rightarrow 0$ if $\gamma < 0.5$, corresponding to $Z > 118$. Break-down of ZORA calculations with point-nucleus hyperfine operator expected for $Z \approx 118$ or higher (basis set permitting).

Finite nuclei:

Near finite nucleus Gaussian basis fcts. are good.

Gaussian nuclear model:

$$\rho_A^{\text{Gauss}}(\mathbf{R}) = Z_A \left(\frac{\xi_A}{\pi} \right)^{3/2} e^{-\xi_A |\mathbf{R} - \mathbf{R}_A|^2}$$

Potential: $-Z/r_A \rightarrow$

$$V_A^{\text{Gauss}}(\mathbf{r}) = -\frac{Z_A}{r_A} P\left(\frac{1}{2}, \tilde{r}_A^2\right) = -\frac{Z_A}{r_A} \text{erf}(\tilde{r}_A)$$

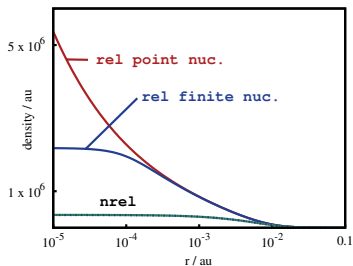
with $\tilde{r}_A = \sqrt{\xi} r_A$ and $P(a, x) = \frac{1}{\Gamma(a)} \int_0^x dt t^{a-1} e^{-t}$

$$\mathbf{A}_A^{\text{nuc}}(\mathbf{r}) = -\frac{1}{c^2} \mathbf{m}_A \times \nabla \int d^3R \cdot \frac{\rho_A^{\text{nuc}}(\mathbf{R})/Z_A}{|\mathbf{r} - \mathbf{R}|}$$

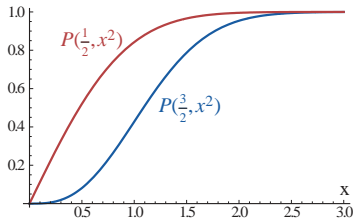
$$\text{Gaussian model: } \mathbf{A}_A^{\text{Gauss}} = \frac{1}{c^2} \frac{\mathbf{m}_A \times \mathbf{r}_A}{r_A^3} P\left(\frac{3}{2}, \tilde{r}_A^2\right)$$

Visser & Dyall, At. Data Nucl. Data Tabs. 67 (1997), 207.

Hennum et al., JCP 115 (2001), 7356. JA, ChemPhysChem 10 (2009), 2274.



Top: Gold atom, 4c X α



Outline

- Some molecular derivative properties of interest
- Internal and external fields
- Field-dependent terms in the Hamiltonian: $4c$, $2c$, $nrel$.
- NMR shielding and J -coupling
- Magnetizability
- EPR g -shift and hyperfine coupling

Example: NMR shielding and J -coupling

Phenomenological Spin-Hamiltonians: external static magnetic field \mathcal{B} and internal magnetic fields from nuclear spin magnetic moments $\mathbf{m}_A, \mathbf{m}_B, \dots$

$$H = -\mathbf{m}_A(1 - \sigma_A)\mathcal{B} \quad \text{Shielding tensor}$$

$$H = \mathbf{m}_A K_{AB} \mathbf{m}_B \quad \text{Reduced spin-spin coupling tensor}$$

It follows ($-\mathbf{m}_A \cdot \mathcal{B}$ not included in electronic energy)

$$\sigma_A = E^{(\mathbf{m}_A, \mathcal{B})} = \frac{d^2 E}{d\mathbf{m}_A d\mathcal{B}} \quad ; \quad K_{AB} = E^{(\mathbf{m}_A, \mathbf{m}_B)} = \frac{d^2 E}{d\mathbf{m}_A d\mathbf{m}_B}$$

Isotropic shielding constant: σ_A , isotropic reduced coupling: K_{AB} . Further,

$$\delta = \frac{\sigma^{\text{ref}} - \sigma}{1 - \sigma^{\text{ref}}} 10^6 \quad ; \quad J_{AB} = \frac{\hbar}{2\pi} \gamma_A \gamma_B K_{AB}$$

One-electron operators relevant for $\sigma_A = E^{(m_A, \mathcal{B})} = \frac{d^2 E}{dm_A d\mathcal{B}}$

$$E_n^{(\mathcal{B}, m_A)} = \langle \Psi_n^{(0)} | H^{(\mathcal{B}, m_A)} | \Psi_n^{(0)} \rangle + 2 \operatorname{Re} \sum_{k \neq n} \frac{\langle \Psi_n^{(0)} | H^{(\mathcal{B})} | \Psi_k^{(0)} \rangle \langle \Psi_k^{(0)} | H^{(m_A)} | \Psi_n^{(0)} \rangle}{E_n - E_k}$$

(assuming no degeneracy. see Slide 24 for nrel. operators)

operator	nrel.	Dirac
$h^{(\mathcal{B})}$	$\frac{\partial}{\partial \mathcal{B}} (\text{OZ} + \text{SZ})$	$-\frac{1}{2} (\boldsymbol{\alpha} \times \mathbf{r})$
$h^{(m_A)}$	$\frac{\partial}{\partial m_A} (\text{OP} + \text{FC} + \text{SD})$	$-\frac{1}{c} (\boldsymbol{\alpha} \times \frac{\mathbf{r}_A}{r_A^3})$
$h^{(\mathcal{B}, m_A)}$	$\frac{\partial^2}{\partial \mathcal{B} \partial m_A} (\text{DS})$	none *

(green = spin-dependent nrel. operators)

Nonrelativistic $\Psi^{(0)}$: SZ terms vanish, **no cross terms** between spin-dependent and spin-independent operators

* Role of negative energy states & diamagnetism: P. Pyykkö, Chem. Phys. 74 (1983), 1. G. Aucar et al., JCP 110 (1999), 6208. W. Kutzelnigg, W. Liu, et al., e.g. JCP 126 (2007), 081101 & 214101.

In the 'paramagnetic' terms on the previous slide, in nonrelativistic theory with spin-eigenfunctions,

$$\langle \Psi_n^{(0)} | \frac{\partial}{\partial \mathbf{B}} (\text{OZ} + \text{SZ}) | \Psi_k^{(0)} \rangle \langle \Psi_k^{(0)} | \frac{\partial}{\partial \mathbf{m}_A} (\text{OP} + \text{FC} + \text{SD}) | \Psi_n^{(0)} \rangle$$

OZ–OP paramagnetic shielding, c.f. Ramsey's equation

OZ–(FC+SD) spatial – spin cross terms vanish

SZ–anything $\langle \Psi_n^{(0)} | \frac{\partial}{\partial \mathbf{B}} (\text{SZ}) | \Psi_k^{(0)} \rangle$ vanishes b/c of orthogonality

Relativistic effects:

- OZ–(FC+SD) spin-orbit cross terms if SO coupling is included in $\Psi^{(0)}$ (or via additional perturbation treatment)
- OP operators are large near the nuclei \rightarrow sensitive to scalar rel. effects (also: SO coupling)

For degenerate states, the 'Curie term' from slide 10, written here for the NMR shielding contribution from state n ,

$$\beta \sum_{a=1}^{d_n} \sum_{a'=1}^{d_n} \langle n, a | H^{(B)} | n, a' \rangle \langle n, a' | H^{(m_A)} | n, a \rangle$$

becomes extremely important. In terms of eigenfunctions of an EPR pseudo-spin Hamiltonian (see below) for pseudo-spin S , one can write the Curie term for NMR shielding as

$$\frac{S(S+1)}{3k_B T} g a_A$$

Here, g is the EPR Zeeman coupling matrix (' g -tensor'), and a_A is the hyperfine coupling matrix for nucleus A .

Example: ^{13}C NMR shifts of spin-triplet **nickelocene** (NiCp_2) are ca. 1600 ppm b/c of large carbon hyperfine coupling.

One-electron operators relevant for $K_{AB} = E^{(m_A, m_B)} = \frac{d^2 E}{dm_A dm_B}$

$$E_n^{(m_A, m_B)} = \langle \Psi_n^{(0)} | H^{(m_A, m_B)} | \Psi_n^{(0)} \rangle + 2 \operatorname{Re} \sum_{k \neq n} \frac{\langle \Psi_n^{(0)} | H^{(m_A)} | \Psi_k^{(0)} \rangle \langle \Psi_k^{(0)} | H^{(m_B)} | \Psi_n^{(0)} \rangle}{E_n - E_k}$$

(see Slide 24 for nrel. operators)

operator	nrel.	Dirac
$h^{(m_A)}$	$\frac{\partial}{\partial m_A} (\text{OP} + \text{FC} + \text{SD})$	$-\frac{1}{c} (\boldsymbol{\alpha} \times \frac{\mathbf{r}_A}{r_A^3})$
$h^{(m_B)}$	$\frac{\partial}{\partial m_B} (\text{OP} + \text{FC} + \text{SD})$	$-\frac{1}{c} (\boldsymbol{\alpha} \times \frac{\mathbf{r}_B}{r_B^3})$
$h^{(m_A, m_B)}$	$\frac{\partial^2}{\partial \mathcal{B} \partial m_A} (\text{OD})$	none

(green = spin-dependent nrel. operators)

Nonrelativistic $\Psi^{(0)}$: no cross terms between spin-dependent and spin-independent operators

In the 'paramagnetic' terms on the previous slide, in nonrelativistic theory with spin-eigenfunctions,

$$\langle \Psi_n^{(0)} | \frac{\partial}{\partial m_A} (\text{OP} + \text{FC} + \text{SD}) | \Psi_k^{(0)} \rangle \langle \Psi_k^{(0)} | \frac{\partial}{\partial m_B} (\text{OP} + \text{FC} + \text{SD}) | \Psi_n^{(0)} \rangle$$

OP-OP	PSO mechanism of J -coupling
FC-FC	FC mechanism
SD-SD	SD mechanism
FC-SD	spin-dependent cross terms
OP-(FC+SD)	spatial – spin cross terms vanish

Relativistic effects:

- OP-(FC+SD) spin-orbit cross terms if SO coupling is included in $\Psi^{(0)}$ (or via additional perturbation treatment)
- Operators are large near the nuclei → **very** sensitive to scalar rel. effects (in particular FC)
- For degenerate states there is also a Curie term $\propto 1/(k_B T)$

Outline

- Some molecular derivative properties of interest
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- EPR g -shift and hyperfine coupling

One-electron operators relevant for $\chi = E^{(\mathcal{B}, \mathcal{B})} = \frac{d^2 E}{d\mathcal{B}d\mathcal{B}}$

The relevant expression is on slide 10, where one needs to substitute:
 $H^{(\mathcal{F}_i, \mathcal{F}_j)} \rightarrow H^{(\mathcal{B}_i, \mathcal{B}_j)}$; $H^{(\mathcal{F}_i)} \rightarrow H^{(\mathcal{B}_i)}$; $H^{(\mathcal{F}_j)} \rightarrow H^{(\mathcal{B}_j)}$

(see Slide 24 for nrel. operators)

operator	nrel.	Dirac
$h^{(\mathcal{B})}$	$\frac{\partial}{\partial \mathcal{B}}(\text{OZ} + \text{SZ})$	$-\frac{1}{2}(\alpha \times \mathbf{r})$
$h^{(\mathcal{B}, \mathcal{B})}$	$\frac{\partial^2}{\partial \mathcal{B} \partial \mathcal{B}}(\text{DM})$	none

(green = spin-dependent nrel. operators)

Nonrelativistic $\Psi^{(0)}$: no cross terms between spin-dependent and spin-independent operators

For degenerate ground states or low-energy excited states, the Curie term $\propto 1/(k_B T)$ causes T -dependent magnetism.

Outline

- Some molecular derivative properties of interest
- Internal and external fields
- Field-dependent terms in the Hamiltonian: $4c$, $2c$, nrel.
- NMR shielding and J -coupling
- Magnetizability
- EPR g -shift and hyperfine coupling

Example: g -shift and hyperfine coupling:

Phenomenological Spin-Hamiltonians: external static magnetic field \mathbf{B} and nuclear spin magnetic moments $\mathbf{m}_A, \mathbf{m}_B, \dots$, pseudo-spin S

$$\mathbf{m}_A = \hbar\gamma_A \underbrace{\mathbf{I}_A}_{\text{nuclear spin}} = \underbrace{g_A}_{\text{nuc. } g\text{-factor}} \beta_N \mathbf{I}_A$$

$$H = \beta_e \mathbf{S} g \mathbf{B} \quad g\text{-values. } g\text{-shift } \Delta g = g - g_e$$

$$H = \mathbf{I}_A a_A \mathbf{S} \quad \text{Hyperfine coupling (HFC)}$$

If SO coupling is treated as a perturbation (starting with a scalar relativistic calculation), no orbital degeneracy:

$$g_{uv} = \frac{1}{\beta_e} \frac{\partial^2 E}{\partial B_u \partial S_v}$$

$$a_{A,uv} = \frac{\partial^2 E}{\partial I_{A,u} \partial S_v} = g_A \beta_N \frac{\partial^2 E}{\partial m_{N,u} \partial S_v}$$

Derivative techniques for calculating EPR parameters, similar to NMR

One-electron operators relevant for (see Slide 24 for nrel. operators)

$$g_{uv} = \frac{1}{\beta_e} \frac{\partial^2 E}{\partial B_u \partial S_v}$$

$$a_{A,uv} = \frac{\partial^2 E}{\partial I_{A,u} \partial S_v} = g_A \beta_N \frac{\partial^2 E}{\partial m_{A,u} \partial S_v}$$

operator	nrel. or 2c
$h(\sigma)$	SO
$h(\mathcal{B})$	OZ
$h(\sigma, \mathcal{B})$	SZ \mathcal{B} -field pert. in SO*

operator	nrel. or 2c
$h(\sigma)$	SO
$h(\mathbf{m}_A)$	OP
$h(\sigma, \mathbf{m}_A)$	FC, SD \mathbf{m}_A pert. in SO*

In methods where SO coupling is included in the unperturbed wavefunction / density calculation, the EPR parameters can be calculated via expectation values (see following slides)

* in the Pauli operator, for example, from $\frac{i}{4c^2} \sigma \cdot [\mathbf{p}V \times \mathbf{A}]$, see Slide 22.

Ab-initio route using SO wavefunctions^a, for a Kramers doublet with components ψ_1 and ψ_2 :

Define Zeeman operator $-\beta_e \mathbf{h}^{(B)} \cdot \mathbf{B}$, then:

$$G_{uv} = (g g^T)_{uv} = 2 \sum_{a=1}^2 \sum_{b=1}^2 \langle \psi_a | H^{(B_u)} | \psi_b \rangle \langle \psi_b | H^{(B_v)} | \psi_a \rangle$$

Then the principal g -factors are the square roots of the eigenvalues of G . Similar strategy for hyperfine coupling.

Define a hyperfine operator $g_A \beta_N \mathbf{h}^{(m_A)} \cdot \mathbf{m}_A$, then:

$$A_{A,uv} = (a_A a_A^T)_{uv} = \frac{2}{(g_A \beta_N)^2} \sum_{a=1}^2 \sum_{b=1}^2 \langle \psi_a | H^{(m_{A,u})} | \psi_b \rangle \langle \psi_b | H^{(m_{A,v})} | \psi_a \rangle$$

^a g -factors: H. Bolvin et al., PRL 101 (2008), 033003; ChemPhysChem 7 (2006), 1575. Hyperfine coupling: K. Sharkas & JA, manuscript submitted.

With DFT, van Lenthe, Wormer, and van der Avoird (LWA) used a similar strategy by creating a Kramers pair of Kohn-Sham orbitals from a quasi spin-restricted calculation with 0.5 / 0.5 occupations in the 'unpaired' orbitals and its counterpart:

$$\frac{\partial}{\partial B_u} \begin{bmatrix} \langle \phi_1 | h^{(B)} | \phi_1 \rangle & \langle \phi_1 | h^{(B)} | \phi_2 \rangle \\ \langle \phi_2 | h^{(B)} | \phi_1 \rangle & \langle \phi_2 | h^{(B)} | \phi_2 \rangle \end{bmatrix} = \frac{1}{4} \sum_v g_{uv} \sigma_v$$

with g_{uv} real; then form a proper tensor, $\mathcal{G} = \mathcal{g} \mathcal{g}^T$, eigenvalues G_i .

Define $|g_i| = \sqrt{G_i}$, in the PAS of \mathcal{G} . Sign information is lost.

Assume a similarity transformation $\mathcal{T}^{-1} \mathcal{g} \mathcal{T} = \begin{pmatrix} g_1 & 0 & 0 \\ 0 & g_2 & 0 \\ 0 & 0 & g_3 \end{pmatrix}$, it leaves

$\det(\mathcal{g}) = g_1 g_2 g_3$ invariant.

⇒ Sign of the product of the g_i .

Non-vanishing g -shift when SO coupling is included when the Zeeman Hamiltonian matrix is calculated, or with orbital degeneracies

Similar strategy for hyperfine coupling

Another DFT approach, including SO coupling variationally as well as spin polarization^a (we call it the **MA** approach^b):

Perform three SCF cycles, with different directions $u = x, y, z$ of the spin quantization axis, to get orbitals φ_i^u , occupations n_i .

$$g_{uv} = -\frac{1}{S} \sum_i n_i \langle \varphi_i^u | h_v^{(\mathcal{B})} | \varphi_i^u \rangle$$

$$a_{A,uv} = \frac{g_A \beta_N}{S} \sum_i n_i \langle \varphi_i^u | h_v^{(m_A)} | \varphi_i^u \rangle$$

Here, S is the value of the pseudo-spin.

^a P. Verma, JA, JCTC 9 (2013), 1052 & 1932. ^b **Magnetic anisotropy** calculated via generalized-collinear DFT: Ch. van Wüllen, JCP 130 (2009), 194109.

Second-order approach in HF or DFT for

$$g_{uv} = \frac{1}{\beta_e} \frac{\partial^2 E}{\partial B_u \partial S_v}$$

in a scalar relativistic framework. Formally:

$$g_{uv} = \beta_e^{-1} \left\{ \sum_i^{\text{occ}} \langle \varphi_i^{(0)} | h^{(u,v)} | \varphi_i^{(0)} \rangle + 2 \operatorname{Re} \sum_i^{\text{occ}} \underbrace{\langle \varphi_i^{(u)} | h^{(v)} | \varphi_i^{(0)} \rangle}_{\text{OZ-SO terms}} \right\}$$

'Spin derivative' for spin-dependent operators, using $S_z = \frac{n_\alpha - n_\beta}{2}$, via

$$\frac{\partial}{\partial S_v} \sum_i^{\text{all}} \langle \varphi_i^{(0)} | X_v \sigma_v | \varphi_i^{(0)} \rangle = S_z^{-1} \left\{ \sum_i^{\alpha \text{ spin}} \langle \varphi_i^{(0)} | X_v | \varphi_i^{(0)} \rangle - \sum_i^{\beta \text{ spin}} \langle \varphi_i^{(0)} | X_v | \varphi_i^{(0)} \rangle \right\}$$

along with an equivalent expression involving $\varphi_i^{(u)}$

Similar approach for HFC

For example, with ZORA we have

$$h^{(u)} = -\frac{i}{4} [\mathcal{K}(\mathbf{r} \times \nabla_u) + (\mathbf{r} \times \nabla_u)\mathcal{K}]$$

$$h^{(v)} = \frac{i}{2} (\mathbf{p}\mathcal{K} \times \mathbf{p})_v$$

$$h^{(u,v)} = \frac{1}{4} \{ \delta_{uv} \nabla \cdot (\mathcal{K}\mathbf{r}) - \nabla_u (\mathcal{K}r_v) \}$$

The nonrelativistic limit, $\mathcal{K} \rightarrow 1$, of $h^{(v)}$ vanishes. For the bilinear operator $h^{(u,v)}$ one gets the spin-Zeeman spin derivative

$$h_{\text{nrrel}}^{(u,v)} = \frac{1}{4} [\delta_{uv} \cdot 3 - \delta_{uv}] = \frac{1}{2} \delta_{uv}$$

The expectation value taken in the way as shown on prev. slide gives

$$g_{\text{nrrel}} = \frac{1}{\beta_e} \langle h^{(u,v)} \rangle = \delta_{uv} \frac{1}{\beta_e} \cdot \frac{1}{2} \cdot \left(\frac{n_\alpha - n_\beta}{2} \right)^{-1} (n_\alpha - n_\beta) = 2\delta_{uv}$$

⇒ isotropic g -value of 2

Note that g -shifts from relativistic corrections to $h^{(u,v)}$ tend to be small. The dominant contributions are from the OZ–SO linear response terms. Consider (ZORA)

$$h^{(u)} = -\frac{i}{4} [\mathcal{K}(\mathbf{r} \times \nabla_u) + (\mathbf{r} \times \nabla_u)\mathcal{K}]$$

Perturbed orbitals (uncoupled): $\varphi_i^{(u)} = \sum_{a \neq i} \varphi_a^{(0)} \frac{\langle \varphi_a^{(0)} | h^{(u)} | \varphi_i^{(0)} \rangle}{\varepsilon_i^{(0)} - \varepsilon_a^{(0)}}$ Nonrelativistic

limit of $h^{(u)}$: $\frac{1}{2}(\mathbf{r} \times \mathbf{p})_u = L_u$

For linear molecules, with eigenfunctions of L_u , the terms $\langle \varphi_a^{(0)} | L_u | \varphi_i^{(0)} \rangle$ vanish.



Strongly suppressed g_{\parallel} (along molecular axis) in second-order g -shift calculations

Hyperfine coupling:

Non-vanishing nonrelativistic limit. Extremely large relativistic effects.

For example, with ZORA the perturbation operators are

$$h^{(u)} = -\frac{i}{2} [\mathcal{K}(\mathbf{U}_A \times \nabla)_u + (\mathbf{U}_A \times \nabla)_u \mathcal{K}]$$

$$h^{(v)} = \frac{i}{2} (\mathbf{p} \mathcal{K} \times \mathbf{p})_v$$

$$h^{(u,v)} = \frac{1}{2} \{ \delta_{uv} \nabla \cdot (\mathcal{K} \mathbf{U}_A) - \nabla_u (\mathcal{K} U_{A,v}) \}$$

with $\mathbf{U}_A = c^{-2} \frac{\mathbf{r}_A}{r_A^3}$ for a point nucleus

Nrel. limit ($\mathcal{K} \rightarrow 1$): $h^{(v)} \rightarrow 0 \Rightarrow$ OP–SO term vanishes,

$$h^{(u,v)}(\text{nrel}) = \frac{1}{2c^2} \left(\frac{8\pi}{3} \delta_{uv} \delta(\mathbf{r}_N) - \left[\frac{\delta_{uv}}{r_N^3} - 3 \frac{r_{N,u} r_{N,v}}{r_N^5} \right] \right)$$

FC+SD operator derivative, samples spin-density at the nucleus