Magnetic Properties: NMR, EPR, Susceptibility

Part 1: Theory

Jochen Autschbach, University at Buffalo, jochena@buffalo.edu
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Perspective: Relativistic effects

Jochen Autschbach
Department of Chemistry, State University of New York at Buffalo, New York 14260-3000, USA
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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.
• 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 $F_i$

$$\frac{d\tilde{E}}{dF_1} ; \quad \frac{d^2\tilde{E}}{dF_1 dF_2} ; \quad \cdots$$

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 $^1$

$$\frac{d\{\tilde{Q}\}_T}{dF_1(\omega_1)} ; \quad \frac{d^2\{\tilde{Q}\}_T}{dF_1(\omega_1) dF_2(\omega_2)} ; \quad \cdots$$

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

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

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$^1$ Christiansen et al., IJQC 68 (1998), 68. For DFT, see Aiga et al., JCP 111 (1999), 2878, and Krykunov & JA, JCP 123 (2005), 114103
Some molecular derivative properties of interest

Usually, derivatives are taken around the expansion point = unperturbed stationary ground state, all $F_i = 0$.

Notation:

$$A^{(0)} = A(F) \bigg|_{F=0} ; \quad A^{(F_i)} = \frac{\partial A(F)}{\partial F_i} \bigg|_{F=0} ; \quad A^{(F_i,F_j)} = \frac{\partial^2 A(F)}{\partial F_i \partial F_j} \bigg|_{F=0}$$

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

Notation with $F = 0$ is implicit from here on.
If $E$ or $Q$ are calculated from a relativistic theory

\[ \Downarrow \]

Relativistic properties

If $E$ or $Q$ are calculated from nonrelativistic theory

\[ \Downarrow \]

Nonrelativistic properties

Or start with nonrelativistic $E$, $Q$, $\Psi$ 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):

$$E_n^{(F_i)} = \langle n | H^{(F_i)} | n \rangle$$

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

$$E_n^{(F_i, F_j)} = \langle n | H^{(F_i, F_j)} | n \rangle + 2 \text{ Re} \sum_{k \neq n} \frac{\langle n | H^{(F_j)} | k \rangle \langle k | H^{(F_i)} | n \rangle}{E_n - E_k}$$

- **Diamagnetic**
- **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 \( E_0^{(F_i, F_j)} \) for given \( H^{(F_i, F_j)}, H^{(F_i)}, H^{(F_j)} \)
- \( T \)-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, \( \beta = 1/(k_B T) \).

\[
E(F_i,F_j)(T) = \frac{1}{Q} \sum_n d_n e^{-\beta E_n} \left[ \sum_{a=1}^{d_n} \langle n, a|H(F_i,F_j)|n, a\rangle + \beta \sum_{a=1}^{d_n} \sum_{a'=1}^{d_n} \langle n, a|H(F_i)|n, a'\rangle \langle n, a'|H(F_j)|n, a\rangle + 2 \text{Re} \sum_{k \neq n} \sum_{a=1}^{d_n} \sum_{b=1}^{d_k} \frac{\langle n, a|H(F_i)|k, b\rangle \langle k, b|H(F_j)|n, a\rangle}{E_n - E_k} \right]
\]

\( Q \) is the partition function

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

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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:**

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

\[ \Phi' = \Phi - \frac{\partial f}{\partial t} \]

such that

\[ \mathbf{E}' = -\nabla (\Phi - \frac{\partial f}{\partial t}) - \frac{\partial}{\partial t} (\mathbf{A} + \nabla f) = \mathbf{E} \]

\[ \mathbf{B}' = \nabla \times \mathbf{A} + \nabla \times \nabla f = \mathbf{B} \]
Gauge freedom allows to make the choice $\nabla \cdot A = 0$ (Coulomb gauge)

Some useful expressions:

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

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

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

Note: $\mu_0 \varepsilon_0 = c^{-2} \Rightarrow$ in atomic units $\frac{\mu_0}{4\pi} \to \frac{1}{c^2}$
How to get the fields into quantum theory?

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

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

$\nabla L = -\nabla V = F$  Force equals

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

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

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

Equation of motion gives

$m \ddot{r} = q(E + \dot{r} \times B)$

(Coulomb & Lorentz force)
Canonical momentum: \[ p = \frac{\partial L}{\partial \dot{r}} = m\dot{r} + qA \Rightarrow \dot{r} = \frac{1}{m}(p - qA) \]

Hamiltonian: \[ H = p\dot{r} - L = \frac{1}{2m}(p - qA)^2 + q\Phi \]

without fields: \[ H = \frac{1}{2m}p^2 \]

\[ \downarrow \]

The substitutions

\[ p \rightarrow \pi = p - qA ; \ H \rightarrow H - q\Phi \]

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

\[ h^D \psi^D = \psi^D W \]

\[ h^D = c^2 \beta + c \alpha \cdot p = \begin{bmatrix} c^2 & c \varphi \cdot p \\ c \varphi \cdot p & -c^2 \end{bmatrix} \]

Pauli Matrices \( \varphi \):

\[ \sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \]

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

\[ \sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \]
With fields, for an electron with $q = -e; q\Phi = -e\Phi = V$, in a.u.:

$$\pi = p + A, \ W \to W - V,$$

after shifting the energy origin:

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

For magnetic fields, the perturbation Hamiltonian is

$$h_{\text{mag}}^D = c^2 \alpha \cdot A$$

In nonrelativistic and quasi-relativistic theory, the perturbation Hamiltonian also has a ‘diamagnetic’ term proportional to $A^2$. Let’s see how that arises.
FW transformation up to $O(c^{-2})$

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

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

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

The approximations

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

give

$$U = \begin{pmatrix} 1 - \frac{1}{8c^2} (\varphi \cdot \pi)^2 & \frac{1}{2c} (\varphi \cdot \pi) \\ -\frac{1}{2c} (\varphi \cdot \pi) & 1 - \frac{1}{8c^2} (\varphi \cdot \pi)^2 \end{pmatrix}$$
Using the transformation matrix from the previous slide gives for the upper-upper part in $O(c^{-2})$:

$$h_{FW} = V + \frac{1}{2} (\varphi \cdot \pi)^2 - \frac{1}{8c^2} V(\varphi \cdot \pi)^4$$

$$- \frac{1}{8c^2} [(\varphi \cdot \pi)^2 V + V(\varphi \cdot \pi)^2] + \frac{1}{4c^2} (\varphi \cdot \pi) V(\varphi \cdot \pi)$$

Note: $(\varphi \cdot p)^2 = p^2$ and $(\varphi \cdot \pi)^2 = p^2 + (p \cdot A + A \cdot p) + i\varphi \cdot (p \times A + A \times p) + A^2$

In the absence of a vector potential, $A = 0$,

$$h_{FW} = V + \frac{1}{2} (\varphi \cdot p)^2 - \frac{1}{8c^2} V(\varphi \cdot p)^4$$

$$- \frac{1}{8c^2} [(\varphi \cdot p)^2 V + V(\varphi \cdot p)^2] + \frac{1}{4c^2} (\varphi \cdot p) V(\varphi \cdot p)$$
Field-dependent terms in the Hamiltonian: 4c, 2c, nrel.

\[ h^{FW} = V^{2\sigma} + \frac{1}{2}(\sigma \cdot p)^2 \rightarrow \frac{1}{2}p^2 \]

\[ -\frac{1}{8c^2} V(\sigma \cdot p)^4 \rightarrow -\frac{1}{8c^2}p^4 \]

\[ -\frac{1}{8c^2}(\sigma \cdot p)^2 V \rightarrow -\frac{1}{8c^2}p^2 V - \frac{i}{8c^2}p \times pV \]

\[ -\frac{1}{8c^2} V(\sigma \cdot p)^2 \rightarrow -\frac{1}{8c^2}Vp^2 - \frac{i}{8c^2}V\sigma \cdot p \times p \]

\[ +\frac{1}{4c^2}(\sigma \cdot p) V(\sigma \cdot p) \rightarrow \frac{1}{4c^2}pV \cdot p + \frac{i}{4c^2}\sigma \cdot pV \times p \]

Line 4: \(-p^2 V = -\{p^2 V\} - 2\{p V\} \cdot p - Vp^2 + \) Line 5: \(-Vp^2\), cancel

Line 6: \(pV \cdot p = \{p V\} \cdot p + Vp^2\) except for \(-\{p^2 V\}\)

What remains is the field-free Pauli Operator

\[ h^{\text{Pauli}} = V + \frac{1}{2}p^2 - \frac{p^4}{8c^2} - \frac{\{p^2 V\}}{8c^2} + \frac{i}{4c^2}\sigma \cdot [pV \times p] \]
After some straightforward manipulations, the one-electron operator in the presence of a field reads

\[
\hat{h}^{\text{FW}} = V + \frac{1}{2} \pi^2 + \frac{1}{2} \varphi \cdot \mathbf{B} - \frac{1}{8c^2} \pi^4 - \frac{1}{4c^2} \varphi \cdot \mathbf{B} \pi^2 - \frac{1}{8c^2} \{ \mathbf{p}^2 V \} + \frac{i}{4c^2} \varphi \cdot [\mathbf{p} V \times \pi]
\]

nrel. Hamiltonian w/ fields (no spin)
nrel. spin-Zeeman
rel. corrections of $T$ and of spin-Zeeman
Darwin term
SO coupling + rel. spin-field interactions

with the replacement \( \{ \mathbf{p} \times \mathbf{A} \} = -i \mathbf{B} \).

In the books by Moss \(^2\) and Harriman \(^3\) the last term is written as

\[
\frac{1}{8c^2} \varphi \cdot [\pi \times \mathbf{E} - \mathbf{E} \times \pi]
\]

where \( \mathbf{E} = \nabla V = i \mathbf{p} V \) is the electric field

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

Nonrelativistic limit (incl. spin-dependent terms)

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

With (see Slide 13, $A^N$ for point nuclei):

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

one obtains the operators (next slide):
Field-dependent terms in the Hamiltonian: 4c, 2c, nrel.

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

with

\[ h^{DM} = \frac{1}{4} (r \times B^{\text{ext}}) \cdot (r \times B^{\text{ext}}) \]

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

\[ h^{SZ} = \frac{1}{2} \varphi \cdot B^{\text{ext}} \]

\[ h^{OP} = \frac{1}{c^2} \sum_A m_A \cdot \left( \frac{r_A}{r_A^3} \times p \right) \]

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

\[ h^{FC} + h^{SD} = \frac{1}{2} \varphi \cdot B^{\text{nuc}} = \frac{1}{2c^2} \sum_A \varphi \cdot \left\{ m_A (\nabla \cdot \frac{r_A}{r_A^3}) - (m_A \cdot \nabla) \frac{r_A}{r_A^3} \right\} \]

\[ h^{OD} = \frac{1}{2c^4} \sum_{B \neq A} \frac{(m_A \cdot m_B)(r_A \cdot r_B) - (m_A \cdot r_B)(m_A \cdot r_A)}{r_A^3 r_B^3} \].
Deriving the FC + SD terms

Consider: $\nabla \times \mathbf{A} + \mathbf{A} \times \nabla = \{ \nabla \times \mathbf{A} \} + \mathbf{A} \times \nabla$

\nabla \text{ acts only on } \mathbf{A} \quad \text{switch order}

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

$$h^{FC} + h^{SD} = \frac{4\pi}{3c^2} \delta(\mathbf{r}_A) \mathbf{m}_A \cdot \varphi + \frac{1}{2c^2} \frac{3(\varphi \cdot \mathbf{r}_A) (\mathbf{m}_A \cdot \mathbf{r}_A) - r_A^2 \mathbf{m}_A \cdot \varphi}{r_A^5}$$

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

\[ h^{FW} = U^\dagger h^D U = \begin{pmatrix} h^{QR} \\ \vdots \end{pmatrix} \]

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

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

The approximations

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

give the ZORA Hamiltonian in the presence of fields.
Alternatively, obtain the operator from the ESC equation

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

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

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

\[ h^{\text{ZORA}} = V + \frac{1}{2} (\mathbf{\sigma} \cdot \mathbf{\pi}) \mathbf{K} (\mathbf{\sigma} \cdot \mathbf{\pi}) \]

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

where \( \mathbf{K} = \frac{2c^2}{2c^2 - V} = \frac{1}{1 - V/(2c^2)} \). Nrel. limit for \( \mathbf{K} \rightarrow 1 \)
A number of perturbation operators are obtained in $O(c^{-2})$, incl. additional 2-electron terms. We will not list them all here.*

Compare different magnetic one-electron perturbation operators:

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

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

where $K = 2c^2 / (2c^2 - V)$

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

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

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

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* See, for example, Manninen et al., JCP 122 (2005), 114107
** Melo et al., JCP 123 (2005), 204112. The DKH2 expression affords an $A^2$ term but it is less compact
Nonrelativistic hyperfine terms versus ZORA:

\[
\mathcal{K} = \frac{2c^2}{(2c^2 - V)}
\]

\[
h_{\text{nrel}}^{FC+SD} = \frac{1}{2c^2} \sum_A \varphi \cdot \left[ m_A (\nabla \cdot \frac{r_A}{r_A^3}) - (m_A \cdot \nabla) \frac{r_A}{r_A^3} \right]
\]

\[
h_{\text{ZORA}}^{FC+SD} = \frac{1}{2c^2} \sum_A \varphi \left[ m_A (\nabla \cdot \left[ \mathcal{K} \frac{r_A}{r_A^3} \right]) - (m_A \cdot \nabla) \left[ \mathcal{K} \frac{r_A}{r_A^3} \right] \right]
\]
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 $\mathcal{K}\delta(r_A)$ term.

Consider a 1-electron atom:
ZORA 2c density = scaled 4c density (van Lenthe, 1993)

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

$\downarrow$

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 $r \to 0$ 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:

\[ \rho_{A}^{\text{Gauss}}(R) = Z_{A} \left( \frac{\xi_{A}}{\pi} \right)^{3/2} e^{-\xi_{A}|R-R_{A}|^{2}} \]

Potential: \(-Z/r_{A} \rightarrow \)

\[ V_{A}^{\text{Gauss}}(r) = -\frac{Z_{A}}{r_{A}} P\left(\frac{1}{2}, \tilde{r}_{A}^{2}\right) = -\frac{Z_{A}}{r_{A}} \text{erf}(\tilde{r}_{A}) \]

with \(\tilde{r}_{A} = \sqrt{\xi} r_{A}\) and \(P(a, x) = \frac{1}{\Gamma(a)} \int_{0}^{x} dt t^{a-1} e^{-t}\)

\[ A_{A}^{\text{nuc}}(r) = -\frac{1}{c^{2}} m_{A} \times \nabla \int d^{3}R \frac{Q_{A}^{\text{nuc}}(R)/Z_{A}}{|r-R|} \]

Gaussian model: \(A_{A}^{\text{Gauss}} = \frac{1}{c^{2}} \frac{m_{A} \times r_{A}}{r_{A}^{3}} P\left(\frac{3}{2}, \tilde{r}_{A}^{2}\right) \)

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Example: NMR shielding and $J$-coupling

Phenomenological Spin-Hamiltonians: external static magnetic field $\mathcal{B}$ and internal magnetic fields from nuclear spin magnetic moments $m_A, m_B, \ldots$

\[ H = -m_A (1 - \sigma_A) \mathcal{B} \quad \text{Shielding tensor} \]

\[ H = m_A \mathcal{K}_{AB} m_B \quad \text{Reduced spin-spin coupling tensor} \]

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

\[ \sigma_A = E^{(m_A, \mathcal{B})} = \frac{d^2 E}{dm_A d\mathcal{B}} ; \quad \mathcal{K}_{AB} = E^{(m_A, m_B)} = \frac{d^2 E}{dm_A dm_B} \]

Isotropic shielding constant: $\sigma_A$, isotropic reduced coupling: $\mathcal{K}_{AB}$. Further,

\[ \delta = \frac{\sigma^{\text{ref}} - \sigma}{1 - \sigma^{\text{ref}}} 10^6 ; \quad J_{AB} = \frac{\hbar}{2\pi} \gamma_A \gamma_B \mathcal{K}_{AB} \]
One-electron operators relevant for \( \varphi_A = E^{(m_A, B)} = \frac{d^2 E}{d m_A d' B} \)

\[
E_n^{(B,m_A)} = \langle \psi_n^{(0)} | H^{(B,m_A)} | \psi_n^{(0)} \rangle + 2 \text{Re} \sum_{k \neq n} \frac{\langle \psi_n^{(0)} | H^{(B)} | \psi_k^{(0)} \rangle \langle \psi_k^{(0)} | H^{(m_A)} | \psi_n^{(0)} \rangle}{E_n - E_k}
\]

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

<table>
<thead>
<tr>
<th>operator</th>
<th>nrel.</th>
<th>Dirac</th>
</tr>
</thead>
<tbody>
<tr>
<td>( h^{(B)} )</td>
<td>( \frac{\partial}{\partial B} ) (OZ + SZ)</td>
<td>( -\frac{1}{2} (\alpha \times r) )</td>
</tr>
<tr>
<td>( h^{(m_A)} )</td>
<td>( \frac{\partial}{\partial m_A} ) (OP + FC + SD)</td>
<td>( -\frac{1}{c} (\alpha \times \frac{r_A}{r_A^3}) )</td>
</tr>
<tr>
<td>( h^{(B,m_A)} )</td>
<td>( \frac{\partial^2}{\partial B \partial m_A} ) (DS)</td>
<td>none *</td>
</tr>
</tbody>
</table>

(green = spin-dependent nrel. operators)

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


J. Autschbach
In the ‘paramagnetic’ terms on the previous slide, in nonrelativistic theory with spin-eigenfunctions,

$$\langle \psi_{n}^{(0)} | \frac{\partial}{\partial B} (OZ + SZ) | \psi_{k}^{(0)} \rangle \langle \psi_{k}^{(0)} | \frac{\partial}{\partial m_{A}} (OP + FC + SD) | \psi_{n}^{(0)} \rangle$$

| OZ–OP | paramagnetic shielding, c.f. Ramsey’s equation |
| OZ–(FC+SD) | spatial – spin cross terms vanish |
| SZ–anything | $\langle \psi_{n}^{(0)} | \frac{\partial}{\partial B} (SZ) | \psi_{k}^{(0)} \rangle$ 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: $^{13}\text{C}$ NMR shifts of spin-triplet nickelocene ($\text{NiCp}_2$) are ca. 1600 ppm b/c of large carbon hyperfine coupling.
NMR shielding and $J$-coupling

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

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

(see Slide 24 for nrel. operators)

<table>
<thead>
<tr>
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<th>Dirac</th>
</tr>
</thead>
<tbody>
<tr>
<td>$h^{(m_A)}$</td>
<td>$\frac{\partial}{\partial m_A} (\text{OP} + \text{FC} + \text{SD})$</td>
<td>$-\frac{1}{c} (\alpha \times \frac{r_A}{r_A^3})$</td>
</tr>
<tr>
<td>$h^{(m_B)}$</td>
<td>$\frac{\partial}{\partial m_B} (\text{OP} + \text{FC} + \text{SD})$</td>
<td>$-\frac{1}{c} (\alpha \times \frac{r_B}{r_B^3})$</td>
</tr>
<tr>
<td>$h^{(m_A, m_B)}$</td>
<td>$\frac{\partial^2}{\partial B \partial m_A} (\text{OD})$</td>
<td>none</td>
</tr>
</tbody>
</table>

(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,

\[
\langle \psi_{n}^{(0)} \partial_{m_{A}} (\text{OP} + \text{FC} + \text{SD}) \psi_{k}^{(0)} \rangle \langle \psi_{k}^{(0)} \partial_{m_{B}} (\text{OP} + \text{FC} + \text{SD}) \psi_{n}^{(0)} \rangle
\]

<table>
<thead>
<tr>
<th>OP–OP</th>
<th>PSO mechanism of J-coupling</th>
</tr>
</thead>
<tbody>
<tr>
<td>FC–FC</td>
<td>FC mechanism</td>
</tr>
<tr>
<td>SD–SD</td>
<td>SD mechanism</td>
</tr>
<tr>
<td>FC–SD</td>
<td>spin-dependent cross terms</td>
</tr>
<tr>
<td>OP–(FC+SD)</td>
<td>spatial – spin cross terms vanish</td>
</tr>
</tbody>
</table>

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 \( \alpha 1/(k_{B} T) \)
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
One-electron operators relevant for \( \chi = E^{(B,B)} = \frac{d^2E}{dB dB} \)

The relevant expression is on slide 10, where one needs to substitute:
\[
H^{(F_i,F_j)} \rightarrow H^{(B_i,B_j)}, \quad H^{(F_i)} \rightarrow H^{(B_i)}, \quad H^{(F_j)} \rightarrow H^{(B_j)}
\]

(see Slide 24 for nrel. operators)

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<td>( -\frac{1}{2} (\alpha \times r) )</td>
</tr>
<tr>
<td>( h^{(B,B)} )</td>
<td>( \frac{\partial^2}{\partial B \partial B} \text{(DM)} )</td>
<td>none</td>
</tr>
</tbody>
</table>

(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 $\mathcal{B}$ and nuclear spin magnetic moments $m_A, m_B, \ldots$, pseudo-spin $S$

$$m_A = \hbar \gamma_A \mathbf{l}_A = g_A \beta_N \mathbf{l}_A$$

nuclear spin  

nuc. g-factor

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

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

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

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

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

Derivative techniques for calculating EPR parameters, similar to NMR
One-electron operators relevant for (see Slide 24 for nrel. operators)

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

<table>
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<tr>
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</thead>
<tbody>
<tr>
<td>( h(\varphi) )</td>
<td>SO</td>
</tr>
<tr>
<td>( h(\mathcal{B}) )</td>
<td>OZ</td>
</tr>
<tr>
<td>( h(\varphi, \mathcal{B}) )</td>
<td>SZ</td>
</tr>
</tbody>
</table>

\( \mathcal{B} \)-field pert. in SO*

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

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<tr>
<td>( h(\varphi) )</td>
<td>SO</td>
</tr>
<tr>
<td>( h(\mathbf{m}_A) )</td>
<td>OP</td>
</tr>
<tr>
<td>( h(\varphi, \mathbf{m}_A) )</td>
<td>FC, SD</td>
</tr>
</tbody>
</table>

\( \mathbf{m}_A \) 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 \( \frac{i}{4c^2} \varphi \cdot [\mathbf{p} \mathbf{V} \times \mathbf{A}] \), see Slide 22.
Ab-initio route using SO wavefunctions, for a Kramers doublet with components $\psi_1$ and $\psi_2$:

Define Zeeman operator $-\beta_e \hbar^{(B)} \cdot B$, 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 $g_A \beta_N \hbar^{(m_A)} \cdot m_A$, then:

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

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, \( G = g g^T \), eigenvalues \( G_i \).

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

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

\[ \det(g) = g_1 g_2 g_3 \] invariant.

\( \Rightarrow \) 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

E. van Lenthe et al., JCP 107, 1997, 2488.
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 $\varphi_i^u$, occupations $n_i$.

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

$$
a_{A,uv} = \frac{g_A \beta N}{S} \sum_i n_i \langle \varphi_i | h_{v}^{(m_A)} | \varphi_i \rangle$$

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

---

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:

\[
g_{uv} = \beta_e^{-1} \left\{ \sum_{i}^{\text{occ}} \langle \phi_i^{(0)} | h^{(u,v)} | \phi_i^{(0)} \rangle + 2 \text{Re} \sum_{i}^{\text{occ}} \langle \phi_i^{(u)} | h^{(v)} | \phi_i^{(0)} \rangle \right\}
\]

‘Spin derivative’ for spin-dependent operators, using \( S_z = \frac{n_\alpha - n_\beta}{2} \), via

\[
\frac{\partial}{\partial S_v} \sum_{i}^{\text{all}} \langle \phi_i^{(0)} | X_v \sigma_v | \phi_i^{(0)} \rangle = S_z^{-1} \left\{ \sum_{i}^{\alpha \text{ spin}} \langle \phi_i^{(0)} | X_v | \phi_i^{(0)} \rangle - \sum_{i}^{\beta \text{ spin}} \langle \phi_i^{(0)} | X_v | \phi_i^{(0)} \rangle \right\}
\]

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

Similar approach for HFC
For example, with ZORA we have

\[
\begin{align*}
    h^{(u)} &= -\frac{i}{4} \left[ \mathcal{K}(r \times \nabla u) + (r \times \nabla u) \mathcal{K} \right] \\
    h^{(v)} &= \frac{i}{2} (p \mathcal{K} \times p)_v \\
    h^{(u,v)} &= \frac{1}{4} \left\{ \delta_{uv} \nabla \cdot (\mathcal{K} r) - \nabla_u (\mathcal{K} r_v) \right\}
\end{align*}
\]

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

\[
h_{nrel}^{(u,v)} = \frac{1}{4} \left[ \delta_{uv} \cdot 3 - \delta_{uv} \right] = \frac{1}{2} \delta_{uv}
\]

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

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

\( \Rightarrow \) isotropic \( g \)-value of 2
Note that \textit{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)

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

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

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

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

\[
\downarrow
\]

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

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

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

\[ h^{(u,v)} = \frac{1}{2} \left\{ \delta_{uv} \nabla \cdot (\mathcal{K} \mathbf{U}_A) - \nabla_u (\mathcal{K} \mathbf{U}_{A,v}) \right\} \]

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

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

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

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