Relativistic calculation of NMR and EPR parameters

Vladimir Malkin

Department of theoretical chemistry, Institute of Inorganic chemistry, Slovak Academy of Sciences, Bratislava, Slovakia
Magnetic interactions
Magnetic interactions

$\vec{B} \quad g$ – tenzor

$J$ – coupling

$A$ - HFS

$\sigma$ - chemical shielding
Relativity

Atomic and molecular properties caused by relativistic effects

Yellow colour of Au$^{[1]}$

Liquid state of Hg$^{[2]}$


Dirac equation (4-component scheme)

\[
H_D \begin{pmatrix} \Psi_L \\ \Psi_S \end{pmatrix} = \begin{pmatrix} V + c^2 & c\vec{\sigma} \cdot \vec{p} \\ c\vec{\sigma} \cdot \vec{p} & V - c^2 \end{pmatrix} \begin{pmatrix} \Psi_L \\ \Psi_S \end{pmatrix} = E \begin{pmatrix} \Psi_L \\ \Psi_S \end{pmatrix}
\]

Terminology

2-component scheme

\[
\begin{pmatrix} F^{\alpha\alpha} & F^{\alpha\beta} \\ F^{\beta\alpha} & F^{\beta\beta} \end{pmatrix}
\]

1-component scheme

\[
\begin{pmatrix} F^{\alpha\alpha} & 0 \\ 0 & F^{\beta\beta} \end{pmatrix}
\]

Pauli matrices

\[
\sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \quad \sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \quad \sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}
\]
Relativistic Effects on Atomic Valence Energy Levels

\[ E = (n-1)d^{3/2} + \text{spin-orbit coupling} (n-1)d^{5/2} \]

\[ np \quad \text{- spin-free relativistic effects} \]

\[ np_{1/2} \quad np_{3/2} \]

\[ ns \quad \text{nonrelativistic limit} \]

\[ ns \]

\[ (n-1)d_{5/2} \quad (n-1)d_{3/2} \]
1s orbital of Hg atom

- Non-relativistic Hartree-Fock
- Relativistic Dirac-Hartree-Fock
Breit type corrections

\[ B(n, Z) = \frac{\langle \Psi_{rel} | \hat{H}_{rel}^{hfs} | \Psi_{rel} \rangle}{\langle \Psi_{nonrel} | \hat{H}_{nonrel}^{hfs} | \Psi_{nonrel} \rangle} \]

Comparison of results for $^{127}$I Nuclear Quadruple Coupling Constants (in MHz) calculated with DFT (NR + NR and DKH2 + DKH2) method in comparison to experimental data.

Finite size of nucleus

Point nucleus

Charge distribution

Magnetic moment distribution


Calculated and experimental isotropic $^{199}$Hg HFCs

The solid line corresponds to ideal agreement with experiment.
Spin-Orbit interaction

\[ H = \vec{S} \cdot g \cdot \vec{B} \]

\[ g = 2.00231930 \]

\[
g = \left. \frac{\partial^2 E (\vec{S}, \vec{B})}{\partial \vec{S} \partial \vec{B}} \right|_{\vec{B}=0, \vec{S}=\vec{S}_{\text{eff}}} \]
**SO correction to chemical shift**

Definition:

\[
\sigma_{uv}^{SO}(N) = \sigma_{uv}(N, SO) - \sigma_{uv}(N, 0) \quad (9)
\]

A formal expression:

\[
\sigma_{uv}^{SO}(N) = \frac{\partial^3 E}{\partial \lambda_N \partial \lambda_{Bu} \partial \lambda_{S,v}} \quad (10)
\]

The Hamiltonian may be written as:

\[
H(\lambda) = H^{(0)} + \lambda_N H_{FC} + \lambda_{Bu} H_{O} + \lambda_S H_{SO}
\]
Spin-orbit correction to chemical shift (SO-CS)

\[ H^\alpha_{v\mu}(\lambda_N) = H^\alpha_{v\mu}(0) + \lambda_N \left\langle \chi_v \left| \delta(r_N) \right| \chi_\mu \right\rangle \]

\[ H^\beta_{v\mu}(\lambda_N) = H^\beta_{v\mu}(0) - \lambda_N \left\langle \chi_v \left| \delta(r_N) \right| \chi_\mu \right\rangle \]

\[
\sigma^p_{v\mu}(N) = \frac{1}{\lambda_N} \left[ \frac{e\hbar}{2mc} \sum \sum_{k,a} \left\langle \phi^\alpha_k(\lambda_N) \left| L_v \left| \phi^\alpha_a(\lambda_N) \right\rangle \left\langle \phi^\alpha_a(\lambda_N) \left| H^SO_u \left| \phi^\alpha_k(\lambda_N) \right\rangle \right\rangle \right) \varepsilon_k - \varepsilon_a \right] \]
\]

for \( \alpha \) spin

\[
- \frac{1}{\lambda_N} \left[ \frac{e\hbar}{2mc} \sum \sum_{k,a} \left\langle \phi^\beta_k(\lambda_N) \left| L_v \left| \phi^\beta_a(\lambda_N) \right\rangle \left\langle \phi^\beta_a(\lambda_N) \left| H^SO_u \left| \phi^\beta_k(\lambda_N) \right\rangle \right\rangle \right) \varepsilon_k - \varepsilon_a \right] \]
\]

for \( \beta \) spin
Spin-orbit corrections to NMR chemical shift
Spin-orbit corrections to NMR chemical shift

M. Kaupp, O.L. Malkina, V.G. Malkin,
How Do Spin-Orbit Induced Heavy-Atom Effects on NMR Chemical Shifts Work?

Olga L. Malkina$^{1,2}$, Vladimir G. Malkin$^2$, Martin Kaupp$^3$ and Pekka Pyykö$^4$

$^1$Computing Center, and $^2$Institute of Inorganic Chemistry, Slovak Academy of Sciences, Bratislava, Slovakia;
$^3$Max-Planck-Institut für Festkörperforschung, Stuttgart, Germany;
$^4$Department of Chemistry, University of Helsinki, Finland
Correlation between $^{13}\text{C}$ "SO Shifts" and Reduced Coupling Constants

\[ 1^\text{K}_{\text{FC}}(\text{C,I}) \]

"SO shift"

\[ \text{H}_3\text{C}-\text{CH}_2-\text{I} \quad \text{H}_2\text{C}=\text{CH}-\text{I} \quad \text{HC}≡\text{C}-\text{I} \]

IGLO-II basis, common gauge on iodine
A Karplus-Type Relation for Spin-Orbit Shifts in Iodoethane

$^1$H "SO shift"

$^3K_{FC}(H,I)$

Available approaches

Calculations of the EPR g-tensor

- 1-component unrestricted
- 2-component restricted
- 2-component unrestricted
- 4-component unrestricted

There are specific problems associated with any of listed above approaches
Performance for $\Delta g_{||}$ in $^2\Sigma$ Radicals

- PdH
- HgH
- HgAg
- CdH
- LaO
- RhC

Methods:
- BP 1-comp. (unrestricted)
- BP 1-comp. (this work, unrestricted)
- ZORA 2-comp. (restricted)
- DKH 2-comp. (this work, unrestricted)
FIG. 1. Comparison of the computed $g$-shift tensor components (in ppm) for different one- and two-component approaches with experiment for light-atom radicals (cf. Table I for numerical data). Crosses: two-component DKH results (this work); squares: one-component BP results (this work); upward triangles: two-component ZORA results; and downward triangles: one-component BP results with the Schreckenbach-Ziegler implementation.
2-component approaches for calculations of g-tensor

Density functional calculations of molecular $g$-tensors in the zero-order regular approximation for relativistic effects

Erik van Lenthe, Paul E. S. Wormer, and Ad van der Avoird
Institute of Theoretical Chemistry, NSR Center, University of Nijmegen, Toernooiveld, 6525 ED Nijmegen, The Netherlands

(Received 25 February 1997; accepted 16 May 1997


Electron spin resonance $g$ tensors from general Hartree–Fock calculations

Dylan Jayatillaka
Department of Chemistry, The University of Western Australia, Nedlands 6009, Australia

(Received 6 November 1997; accepted 30 January 1998)

Note: in a spin-orbit coupled spin restricted relativistic ZORA calculation and the ESR block key, ADF will also calculate and print the nuclear magnetic dipole hyperfine interaction, but the terms due to the spin-polarization density at the nucleus are absent. Furthermore, if there is more than one unpaired electron, the computed results will simply be incorrect, without any warning from the program.
Expression based on Kramer’s pair formalism

\[ g_{ux} = 4c \cdot \text{Re} \left\langle \Phi_1 \left| \frac{\partial}{\partial B_u} H^z \right| \Phi_2 \right\rangle \]

\[ g_{uy} = -4c \cdot \text{Im} \left\langle \Phi_1 \left| \frac{\partial}{\partial B_u} H^z \right| \Phi_2 \right\rangle \]

\[ g_{uz} = 4c \cdot \text{Re} \left\langle \Phi_1 \left| \frac{\partial}{\partial B_u} H^z \right| \Phi_1 \right\rangle \]

3-SCF calculations
Scaling the speed of the light!

Using 2-Component Treatment to Evaluate Importance of Higher-Order Terms

\[
y = -0.0293x^2 + 0.1884x + 2.0023 \\
R^2 = 1.0000
\]

\[
y = -0.0184x^2 - 0.0014x + 2.0023 \\
R^2 = 1.0000
\]

\[
y = -0.113x^2 + 0.3279x + 2.0024 \\
R^2 = 1.0000
\]

\[
y = -0.0584x^2 - 0.0128x + 2.0024 \\
R^2 = 0.9997
\]

Quadratic spin-orbit contributions dominate \(g_\parallel\) for both systems and become very important also for \(g_\perp\) of \(I_2^-\)!

DKH-BP86 results with Hirao basis set
Benchmark calculations ...

<table>
<thead>
<tr>
<th>Radical</th>
<th>1-comp.</th>
<th>2-comp.</th>
<th>Exp.</th>
</tr>
</thead>
<tbody>
<tr>
<td>O2</td>
<td>2.7</td>
<td>2.3</td>
<td>2.9</td>
</tr>
<tr>
<td>SO</td>
<td>4.8</td>
<td>3.9</td>
<td>3.6</td>
</tr>
<tr>
<td>S2</td>
<td>13.3</td>
<td>11.2</td>
<td>14.5</td>
</tr>
<tr>
<td>SeO</td>
<td>15.3</td>
<td>2.2</td>
<td>32.7</td>
</tr>
<tr>
<td>NF</td>
<td>1.8</td>
<td>1.6</td>
<td>2.0</td>
</tr>
<tr>
<td>NCl</td>
<td>5.4</td>
<td>5.0</td>
<td>5.4</td>
</tr>
</tbody>
</table>

Comparison of different approaches for the calculation of $\Delta g_\perp$ in triplet radicals (in ppt)

"We have found a number of lines in the field region expected for SeO but have not yet carried out accurate measurements. Two series of experiments have been terminated by violent explosions in the liquid nitrogen trap, with the subsequent release of hydrogen selenide into the laboratory atmosphere; accurate measurements will require some degree of patience!"  
(Alan Carrington and Donald H. Levy, J. Phys. Chem, 71 (1967) 2-12)
Dramatic spin-orbit effects on hydride $^1H$ shifts

The important role of higher-order spin-orbit contributions. Calculation of $\Delta g$-tensors (in ppt) at 1-, 2- and 4-comp. level of theory using BP86 functional. (2-comp.: SO-ECP on metal/IGLO-II/CGO; 4-comp.: all electron DKS)

![Diagram of tungsten complex]

<table>
<thead>
<tr>
<th>Complex</th>
<th>Method</th>
<th>$\Delta g_{11}$</th>
<th>$\Delta g_{22}$</th>
<th>$\Delta g_{33}$</th>
<th>$\Delta g_{iso}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-comp.</td>
<td></td>
<td>53</td>
<td>-32</td>
<td>-51</td>
<td>-10</td>
</tr>
<tr>
<td>2-comp.</td>
<td></td>
<td>46</td>
<td>-48</td>
<td>-65</td>
<td>-22</td>
</tr>
<tr>
<td>4-comp.</td>
<td></td>
<td>46</td>
<td>-58</td>
<td>-79</td>
<td>-30</td>
</tr>
<tr>
<td>[WO(bdt)$_2$]$^-$</td>
<td>Exp.</td>
<td>42</td>
<td>-71</td>
<td>-91</td>
<td>-40</td>
</tr>
</tbody>
</table>

Demonstration of 4-c calculations for larger, biologically relevant models

<table>
<thead>
<tr>
<th>Method</th>
<th>$\Delta g_{11}$</th>
<th>$\otimes g_{22}$</th>
<th>$\otimes g_{33}$</th>
<th>$\otimes g_{is}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-c DKH</td>
<td>-32</td>
<td>-10</td>
<td>-8</td>
<td>-17</td>
</tr>
<tr>
<td>Exp.</td>
<td>-82</td>
<td>-20</td>
<td>-20</td>
<td>-41</td>
</tr>
</tbody>
</table>

BP86 results.

Evaluation of g-tensor and Zero-Field-Splitting (D) for GdH₃

Calculated $g_\perp = 2.023$
2-Component Calculations of ZFS in GdH₃

In cm⁻¹; 2-component calculations (DFT with B3PW91).
Thank you!