Doing calculations with ReSpect

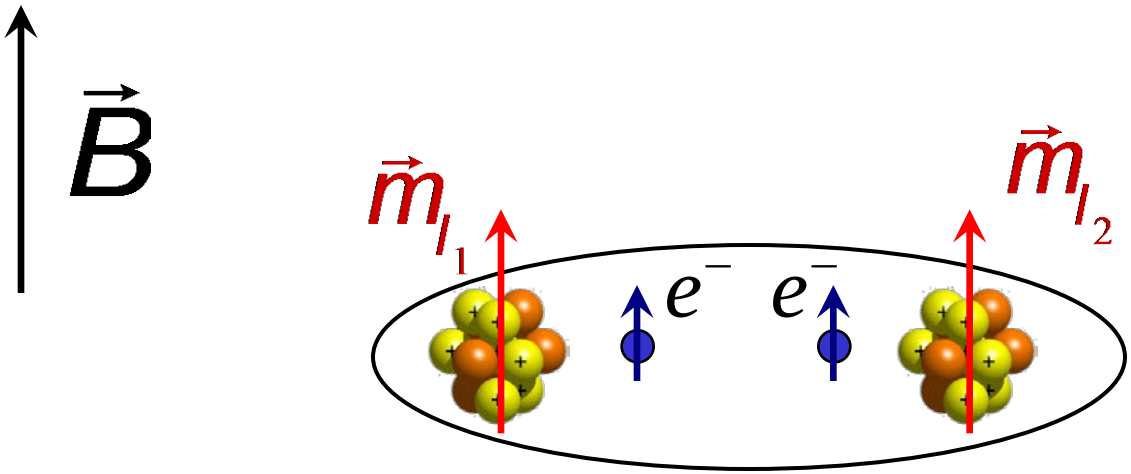
Relativistic calculation of NMR and EPR parameters

Vladimir Malkin

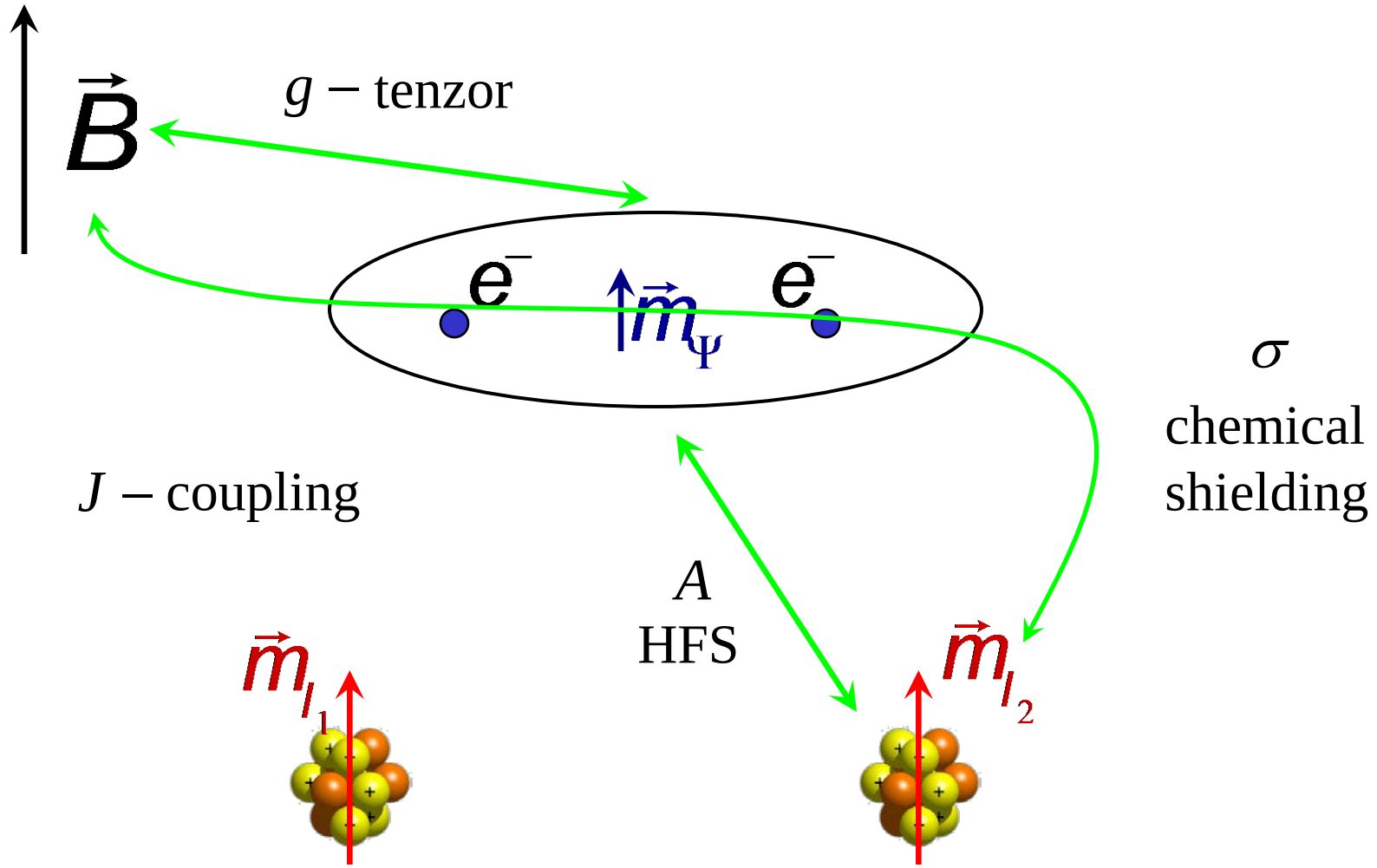
Department of theoretical chemistry, Institute of Inorganic chemistry, Slovak Academy of Sciences, Bratislava, Slovakia

Mariapfarr February 24, 2014

Magnetic interactions



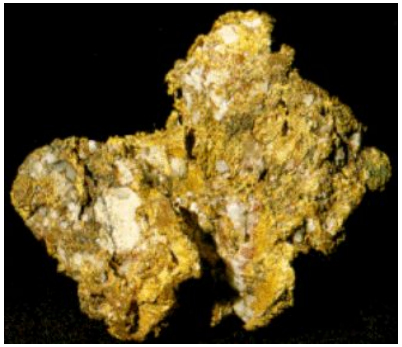
Magnetic interactions



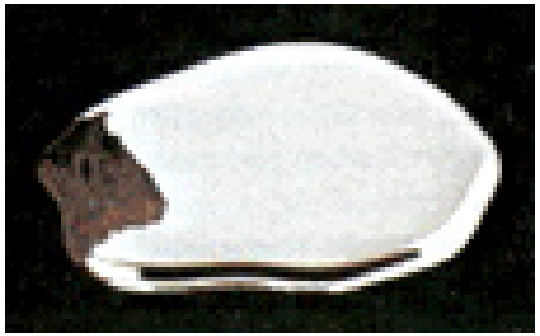
Motivation

Relativity

Atomic and molecular properties caused by relativistic effects



Yellow colour of Au[1]



Liquid state of Hg[2]

[1] N. Bartlett, *Gold Bull*. **1998**, *31*, 22

[2] L. J. Norrby, *J. Chem. Edu.* **1991**, *68*, 110

Terminology

Dirac equation (4-component scheme)

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

α
β
α
β

2-component scheme

$$\begin{pmatrix} F^{\alpha\alpha} & F^{\alpha\beta} \\ F^{\beta\alpha} & F^{\beta\beta} \end{pmatrix}$$

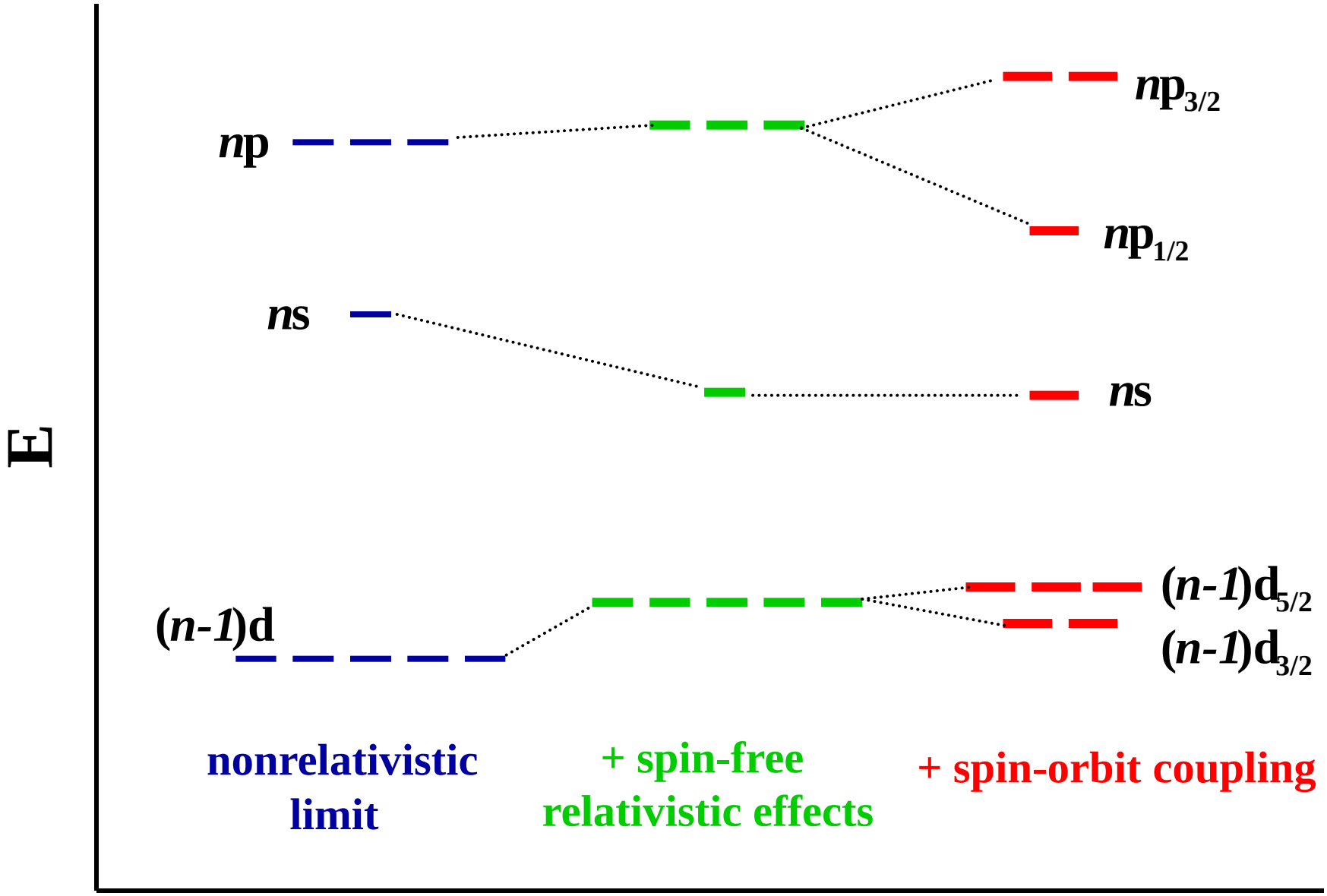
1-component scheme

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

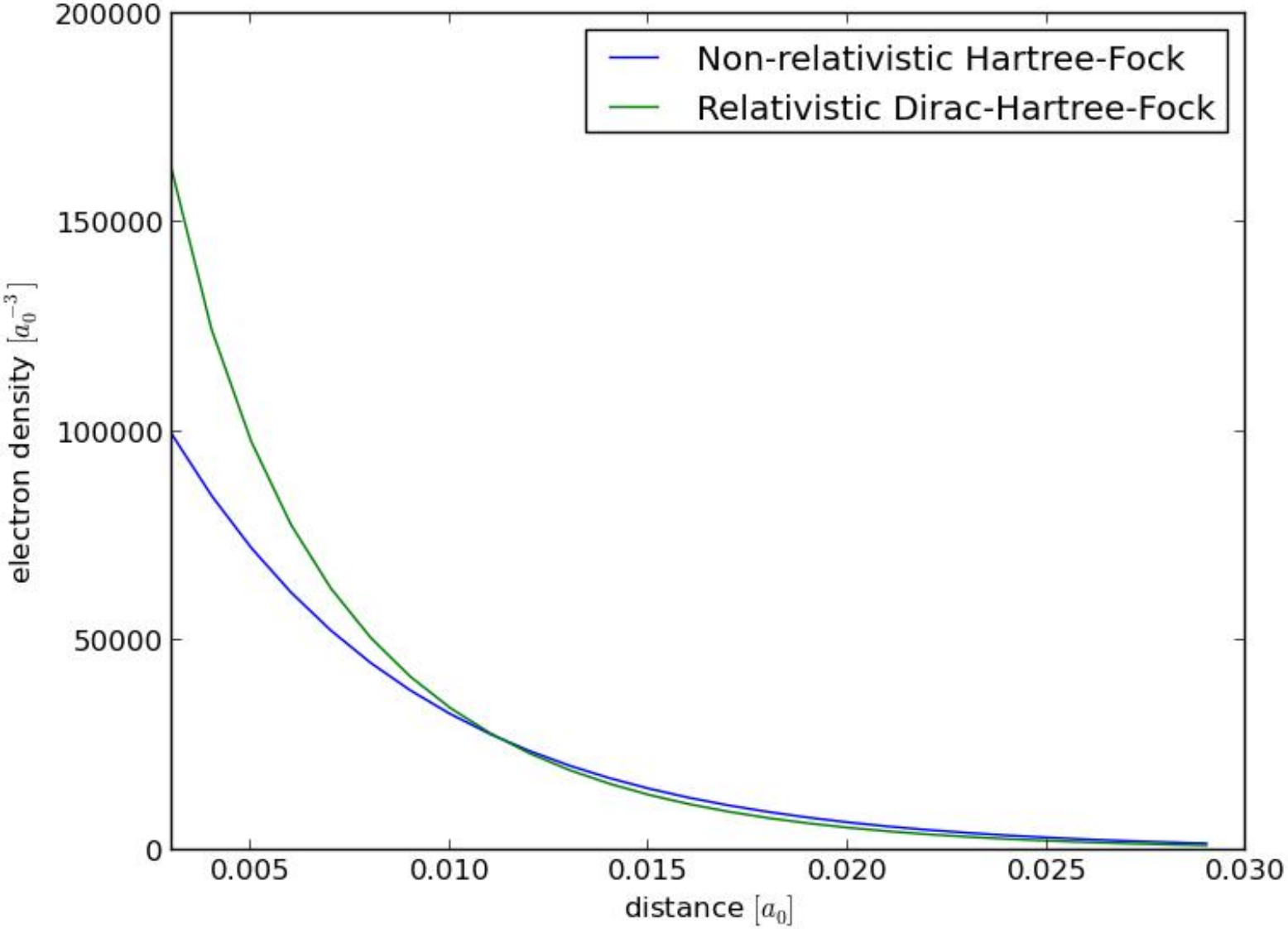
Pauli matrices

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

Relativistic Effects on Atomic Valence Energy Levels

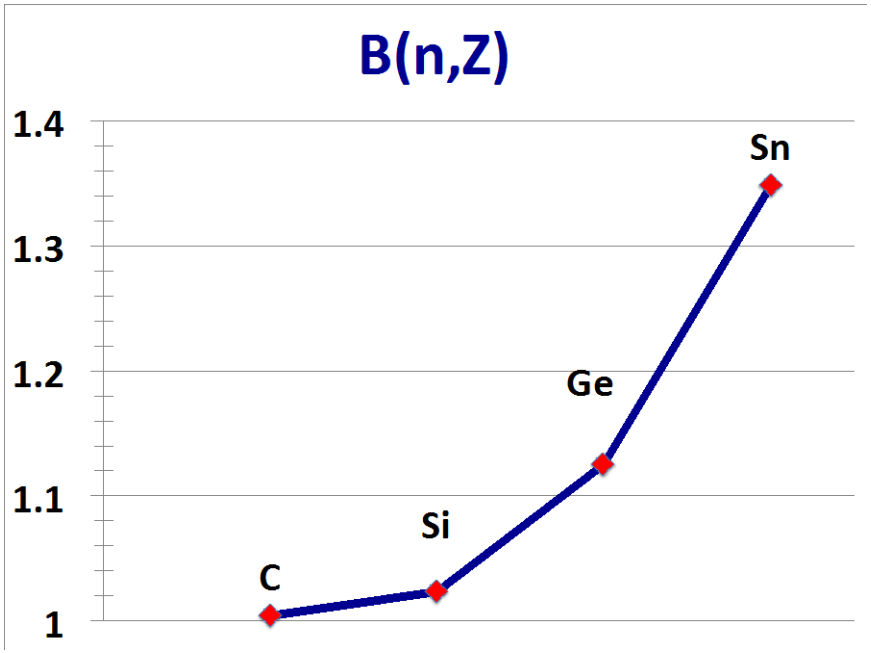


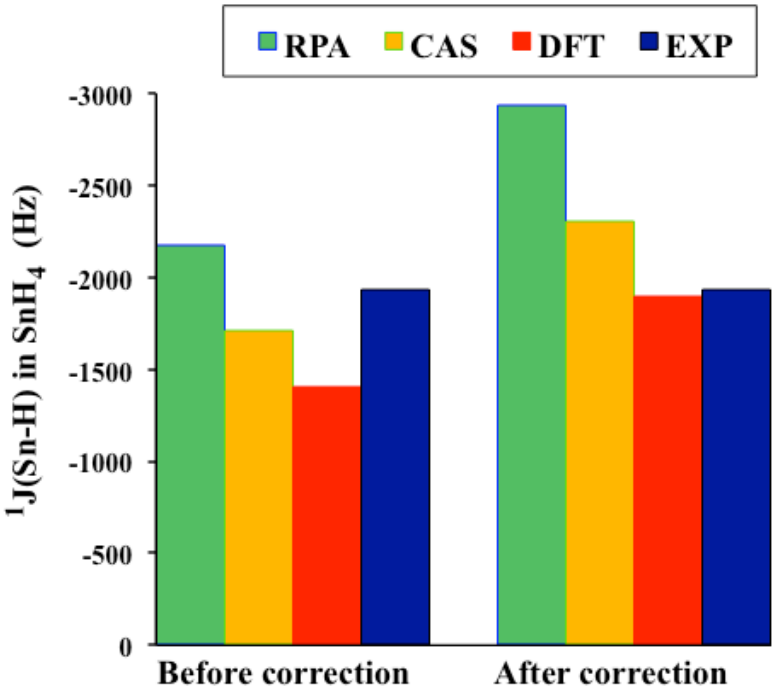
1s orbital of Hg atom



Breit type corrections

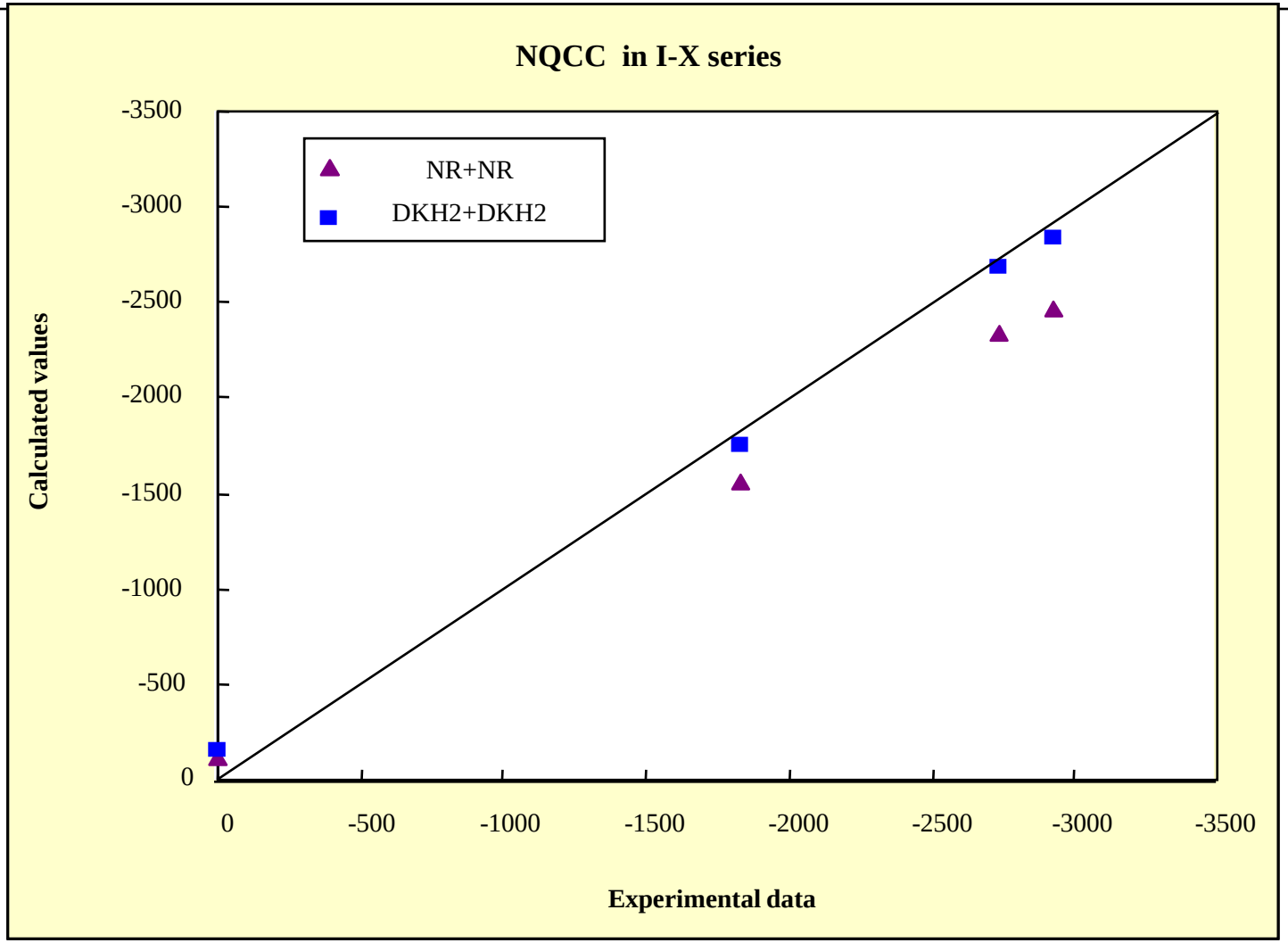
$$B(n,Z) = \frac{\left\langle \Psi_{rel} \left| H_{rel}^{hfs} \right| \Psi_{rel} \right\rangle}{\left\langle \Psi_{nonrel} \left| H_{nonrel}^{hfs} \right| \Psi_{nonrel} \right\rangle}$$





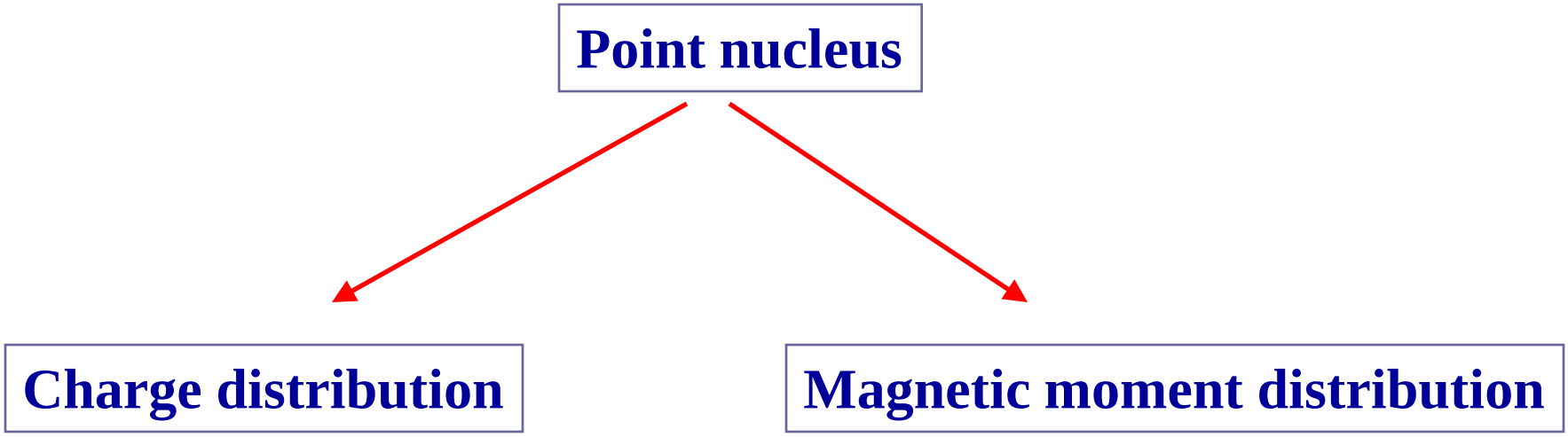
P. Pyykko, E. Pajanne, Int. J. Quant. Chem., v. VII, 785-806, (1973),
"Hydrogen-like relativistic corrections for electric and magnetic hyperfine integrals.

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



I. Malkin, O.L. Malkina, V.G. Malkin, *Chem. Phys. Lett.*, *361* **2002**, *231*

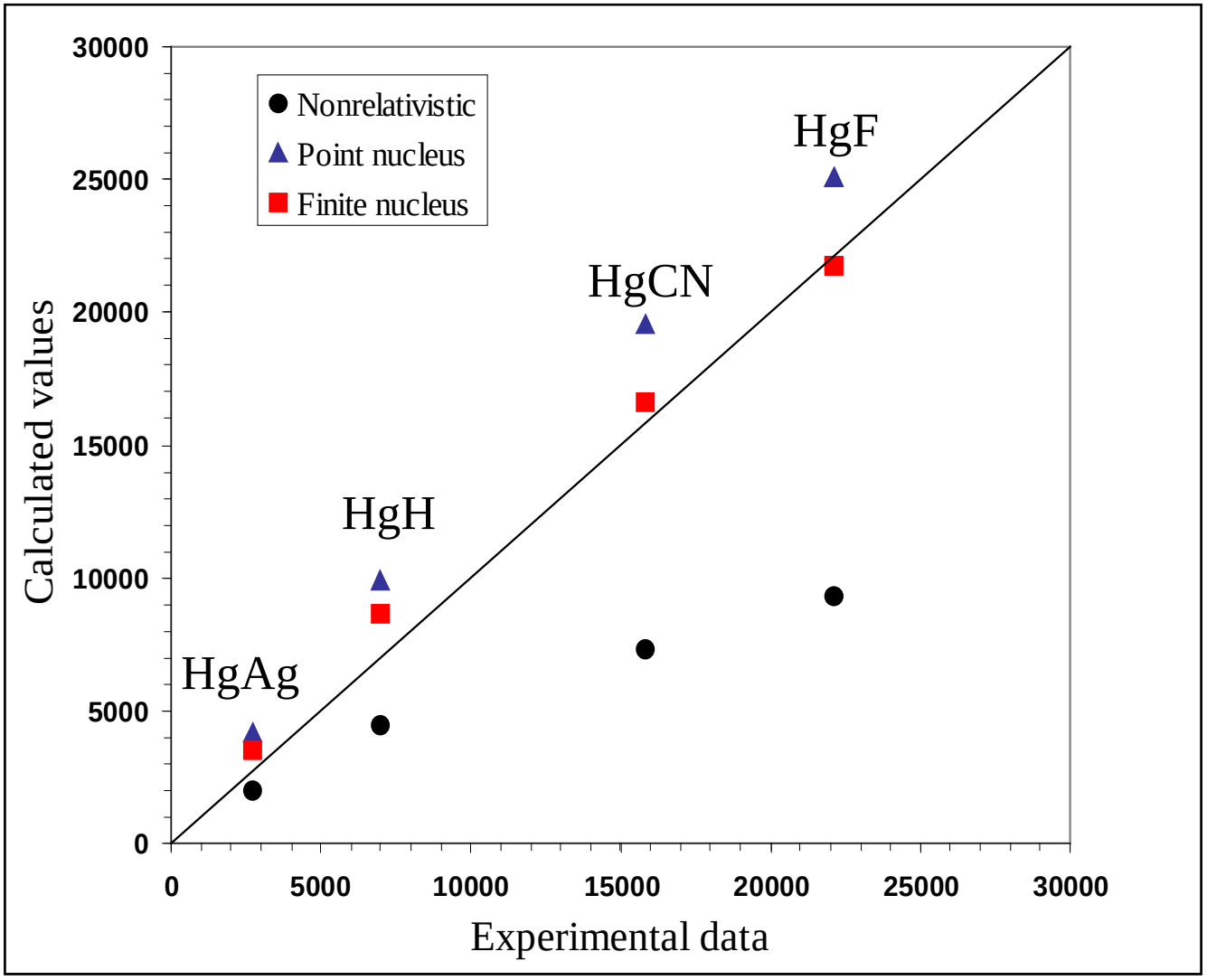
Finite size of nucleus



D. Andrae, *Phys. Rep.*,
2000 , **336**, 413-525

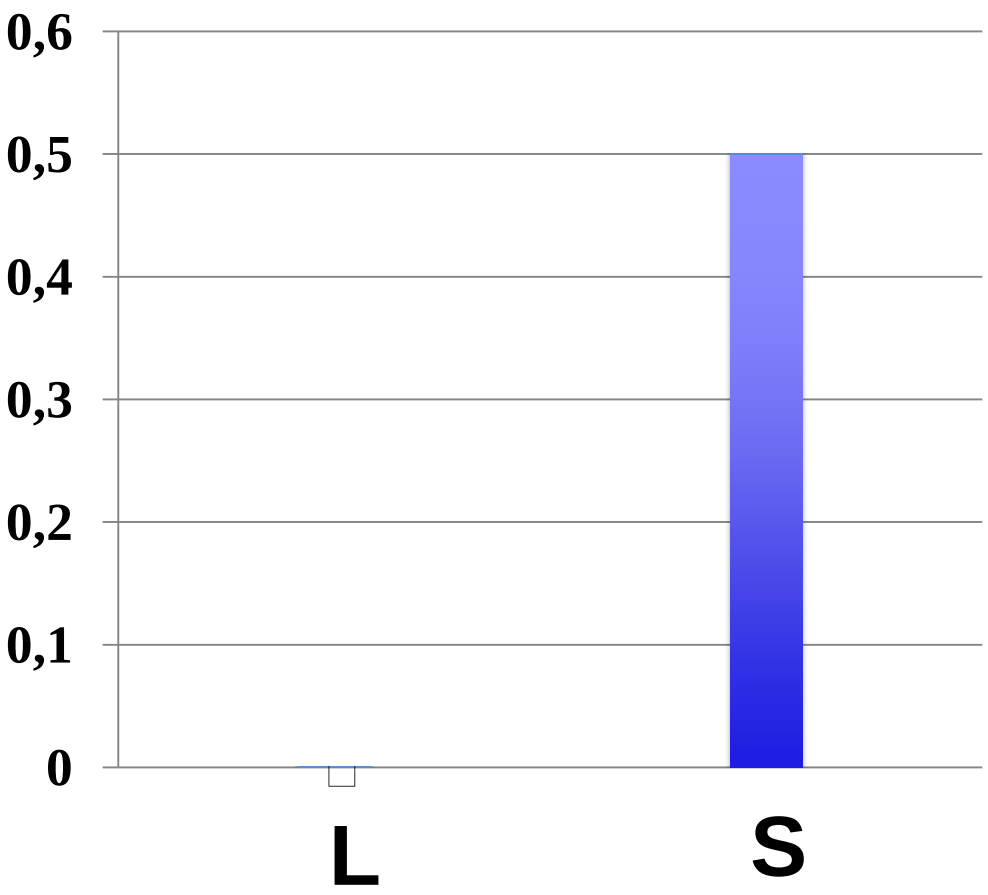
E. Malkin, I. Malkin, O.L. Malkina, V.G. Malkin, M. Kaupp,
Phys. Chem. Chem. Phys., 2006, 8, 4079 – 4085.

Calculated and experimental isotropic ^{199}Hg HFCs



The solid line corresponds to ideal agreement with experiment.

Spin-Orbit interaction



$$\mathbf{H} = \vec{\mathbf{S}} \cdot \mathbf{g} \cdot \vec{\mathbf{B}}$$

$$\mathbf{g} = 2.00231930$$

$$\mathbf{g} = \left. \frac{\partial^2 \mathbf{E}(\vec{\mathbf{S}}, \vec{\mathbf{B}})}{\partial \vec{\mathbf{S}}\, \partial \vec{\mathbf{B}}} \right|_{\substack{\vec{\mathbf{B}}=\mathbf{0} \\ \vec{\mathbf{S}}=\vec{\mathbf{S}}_{\mathbf{eff}}}}$$

SO correction to chemical shift

Definition:

$$\sigma_{uv}^{SO}(N) = \sigma_{uv}(N, SO) - \sigma_{uv}(N, 0) \tag{9}$$

A formal expression:

$$\sigma_{uv}^{SO}(N) = \frac{\partial^3 E}{\partial\lambda_N \partial\lambda_{B_u} \partial\lambda_{S,v}} \tag{10}$$

The Hamiltonian may be written as:

$$H(\lambda) \;=\; H^{(0)} + \lambda_N H_{FC} + \lambda_{B_u} H_O + \lambda_S H_{SO}$$

Spin-orbit correction to chemical shift (SO-CS)

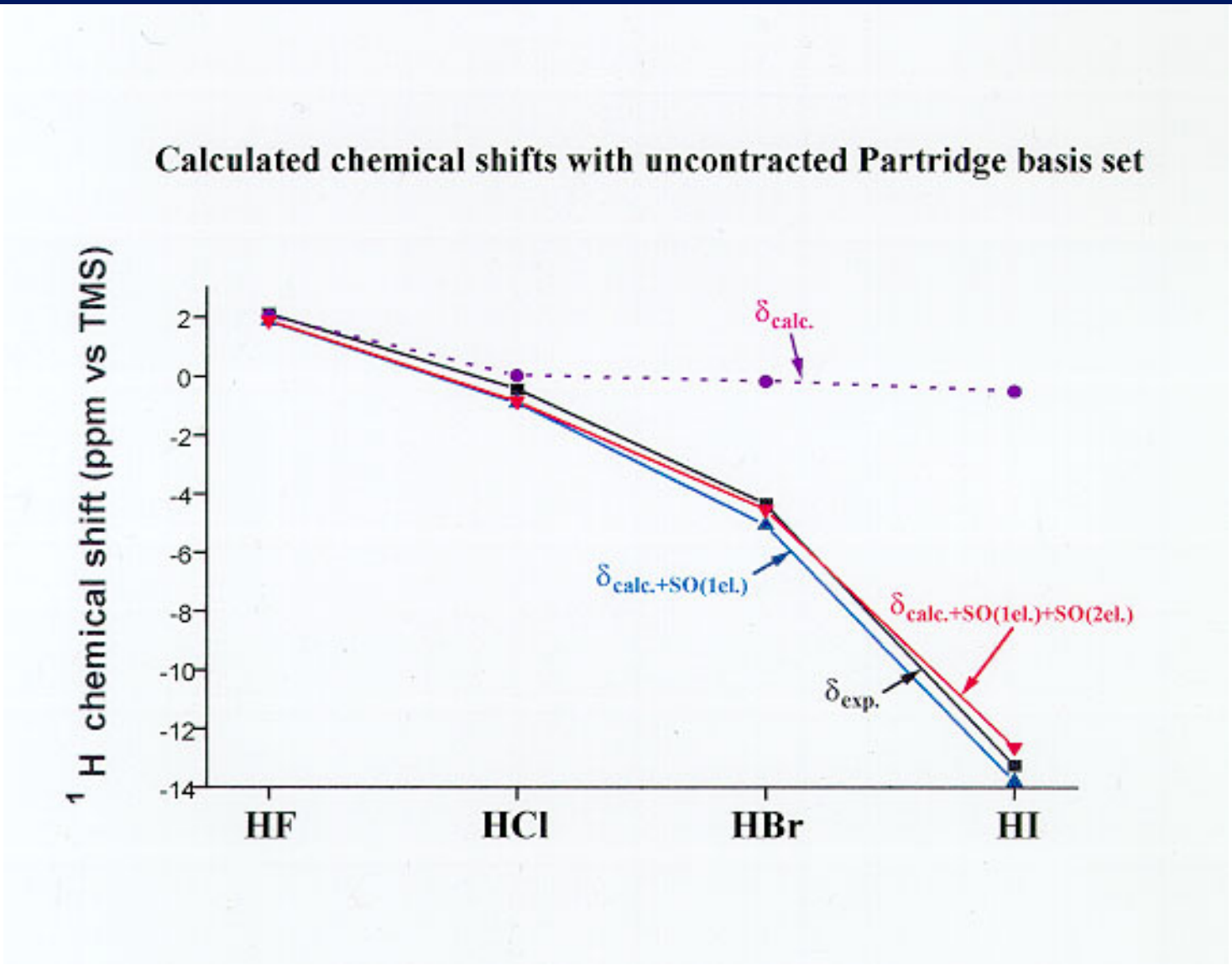
$$H^{\alpha}_{\nu\mu}(\lambda_N) = H^{\alpha}_{\nu\mu}(0) + \lambda_N \left\langle \chi_\nu \middle| \delta(r_N) \middle| \chi_\mu \right\rangle$$

$$H^{\beta}_{\nu\mu}(\lambda_N) = H^{\beta}_{\nu\mu}(0) - \lambda_N \left\langle \chi_\nu \middle| \delta(r_N) \middle| \chi_\mu \right\rangle$$

$$\sigma^{p}_{vu}(N) = \frac{1}{\lambda_N}\left[\frac{e\hbar}{2mc}\sum_{k}^{occ}\sum_{a}^{vac}\frac{\left\langle \phi^{\alpha}_{k}(\lambda_N)\middle|L_v\middle|\phi^{\alpha}_{a}(\lambda_N)\right\rangle\left\langle \phi^{\alpha}_{a}(\lambda_N)\middle|H^{SO}_{u}\middle|\phi^{\alpha}_{k}(\lambda_N)\right\rangle}{\varepsilon_k - \varepsilon_a}\right] \quad \text{for} \quad \alpha \text{ spin}$$

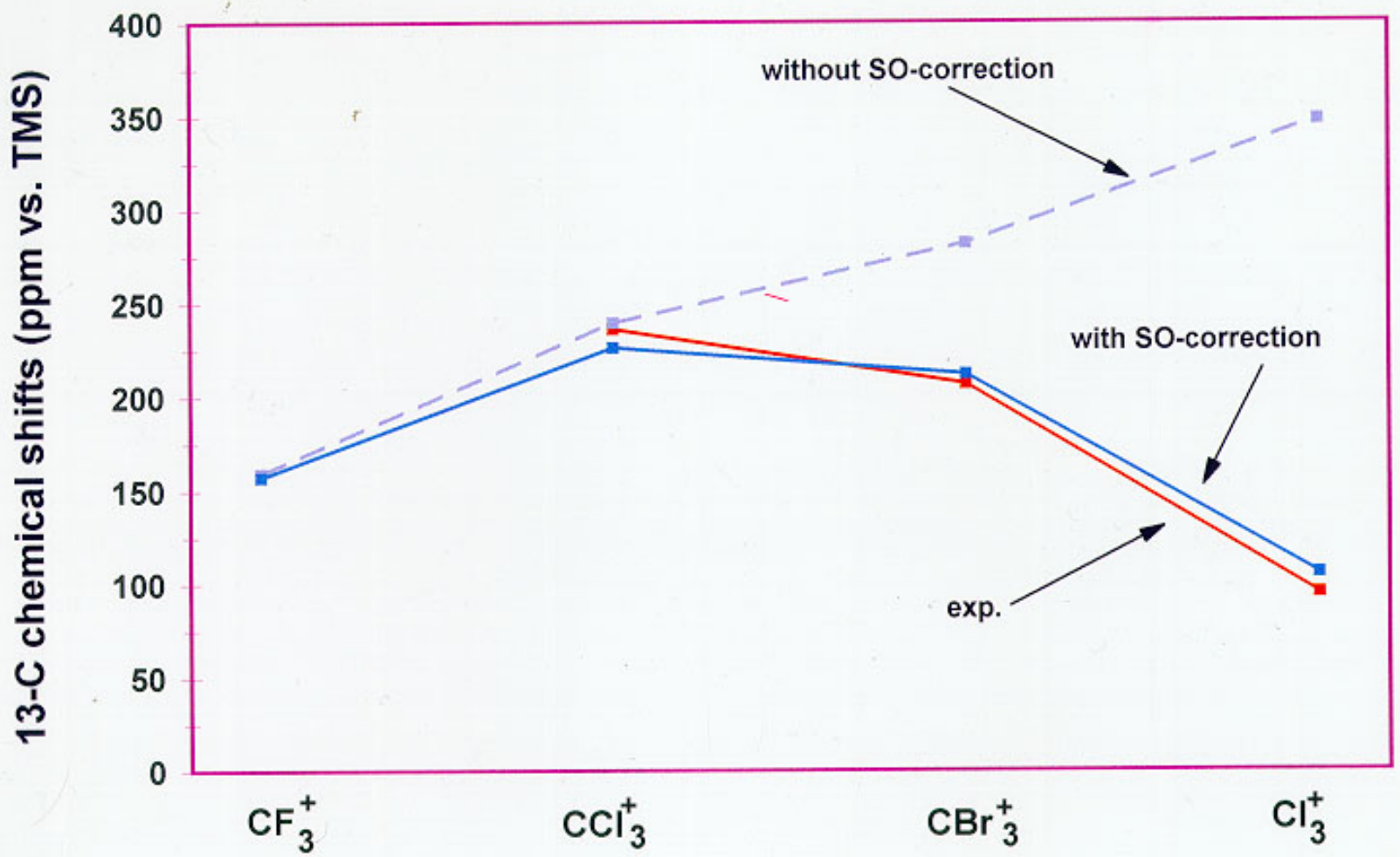
$$-\frac{1}{\lambda_N}\left[\frac{e\hbar}{2mc}\sum_{k}^{occ}\sum_{a}^{vac}\frac{\left\langle \phi^{\beta}_{k}(\lambda_N)\middle|L_v\middle|\phi^{\beta}_{a}(\lambda_N)\right\rangle\left\langle \phi^{\beta}_{a}(\lambda_N)\middle|H^{SO}_{u}\middle|\phi^{\beta}_{k}(\lambda_N)\right\rangle}{\varepsilon_k - \varepsilon_a}\right] \quad \text{for} \quad \beta \text{ spin}$$

Spin-orbit corrections to NMR chemical shift



Spin-orbit corrections to NMR chemical shift

M. Kaupp, O.L. Malkina, V.G. Malkin,
Chem. Phys. Lett., 265 (1997) 55.

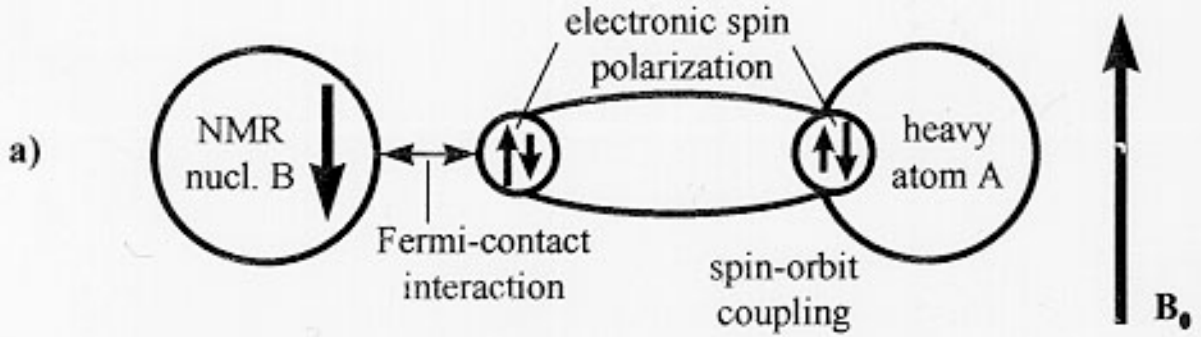


How Do Spin-Orbit Induced Heavy-Atom Effects on NMR Chemical Shifts Work?

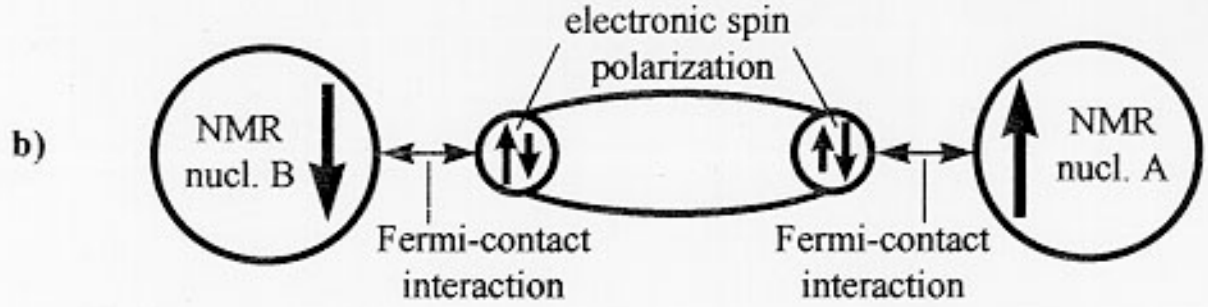
Olga L. Malkina[1,2], Vladimir G. Malkin[2], Martin Kaupp[3] and Pekka Pyykkö[4]

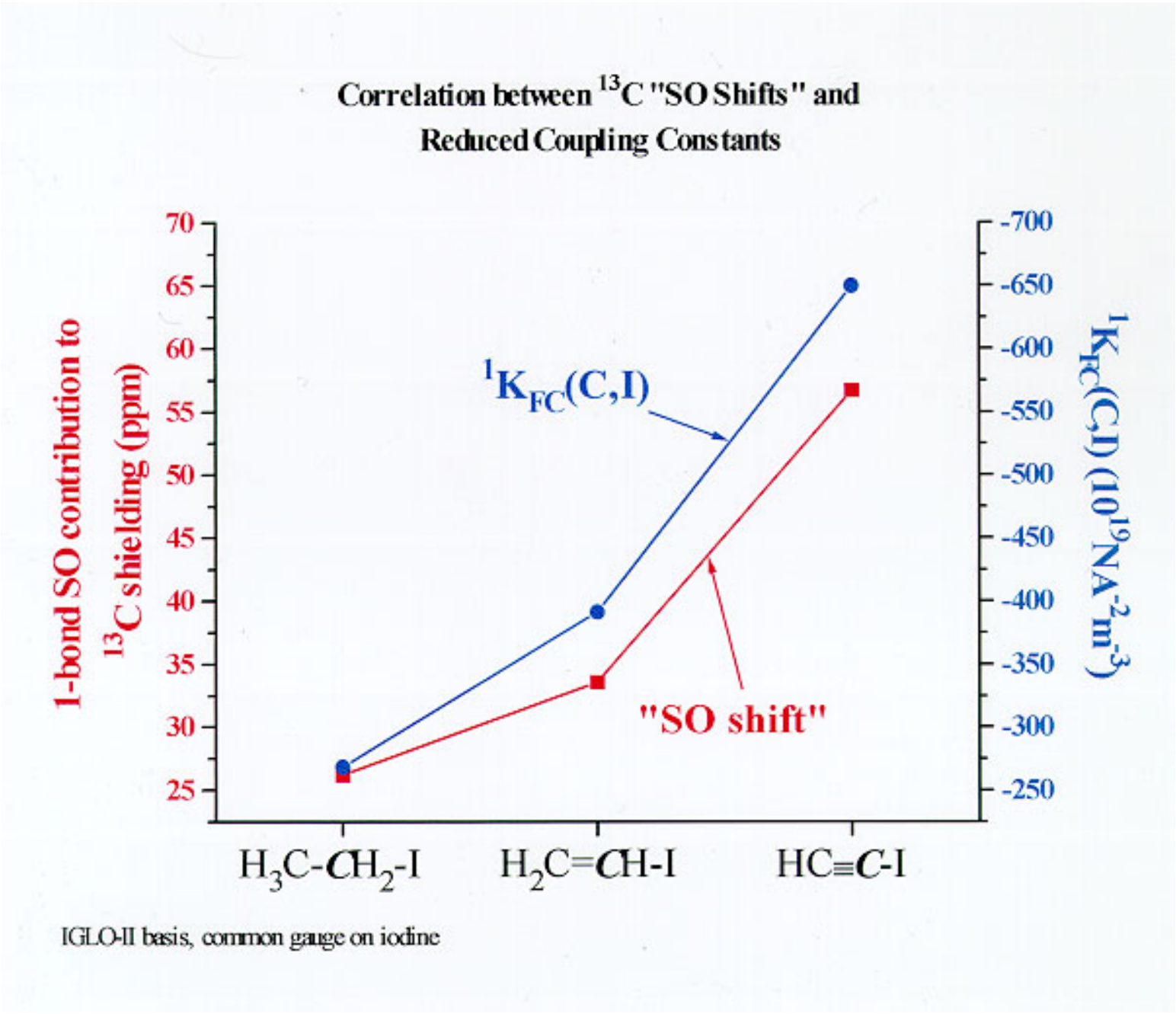
[1]Computing Center, and [2]Institute of Inorganic Chemistry, Slovak Academy of Sciences, Bratislava, Slovakia;
[3]Max-Planck-Institut für Festkörperforschung, Stuttgart, Germany;
[4]Department of Chemistry, University of Helsinki, Finland

Spin-Orbit Chemical Shifts

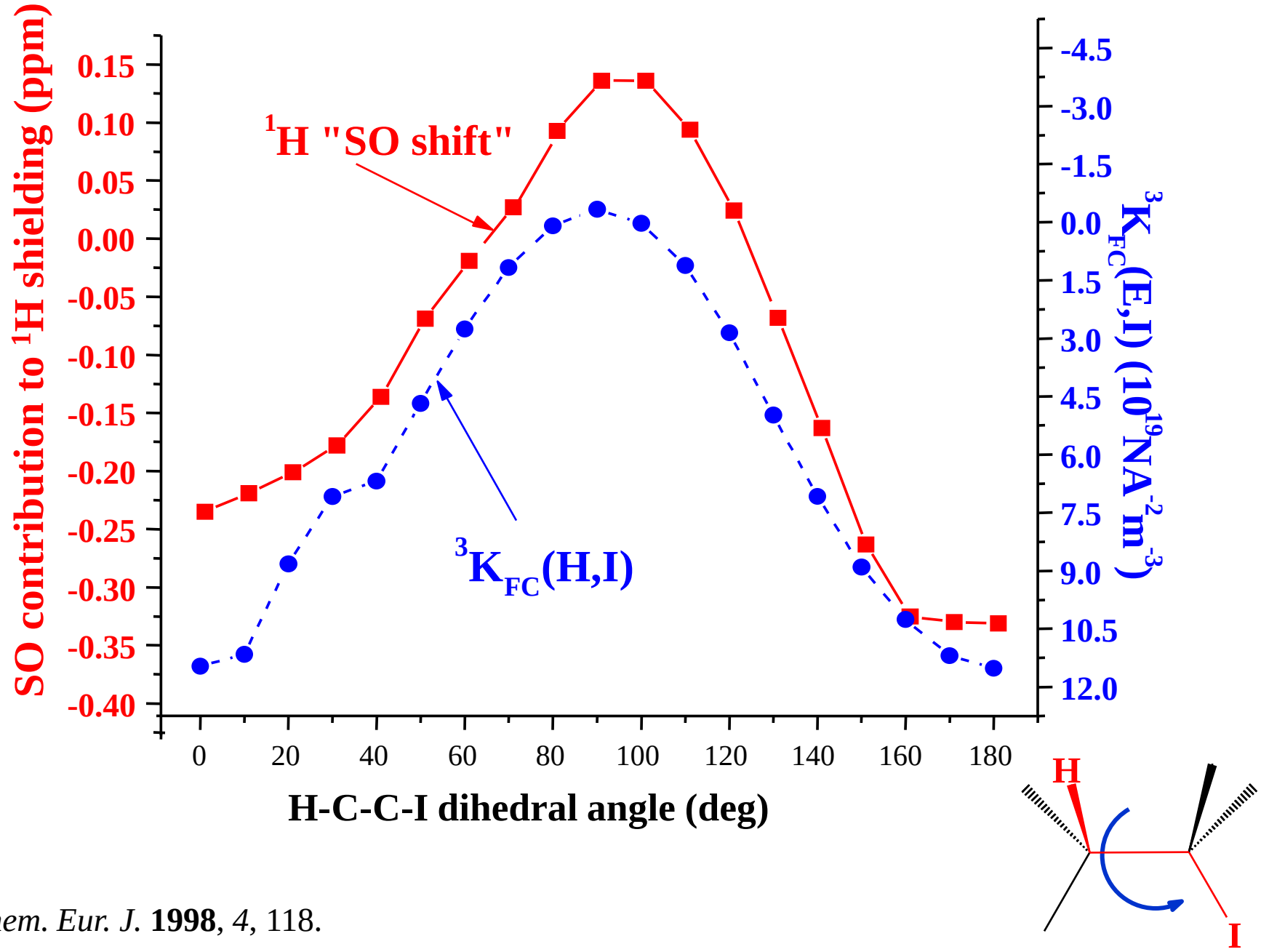


Fermi-Contact Spin-Spin Coupling




Correlation between ^{13}C "SO Shifts" and
Reduced Coupling Constants
1-bond SO contribution to ^{13}C shielding (ppm)
$^{1}K_{FC}(C,I)$ $(10^{19}NA^{-2}m^{-3})$
$^{1}K_{FC}(C,I)$
"SO shift"
70
65
60
55
50
45
40
35
30
25
-700
-650
-600
-550
-500
-450
-400
-350
-300
-250
H_3C-CH_2-I
H_2C=CH-I
HC≡C-I
IGLO-II basis, common gauge on iodine

A Karplus-Type Relation for Spin-Orbit Shifts in Iodoethane



Chem. Eur. J. **1998**, *4*, 118.

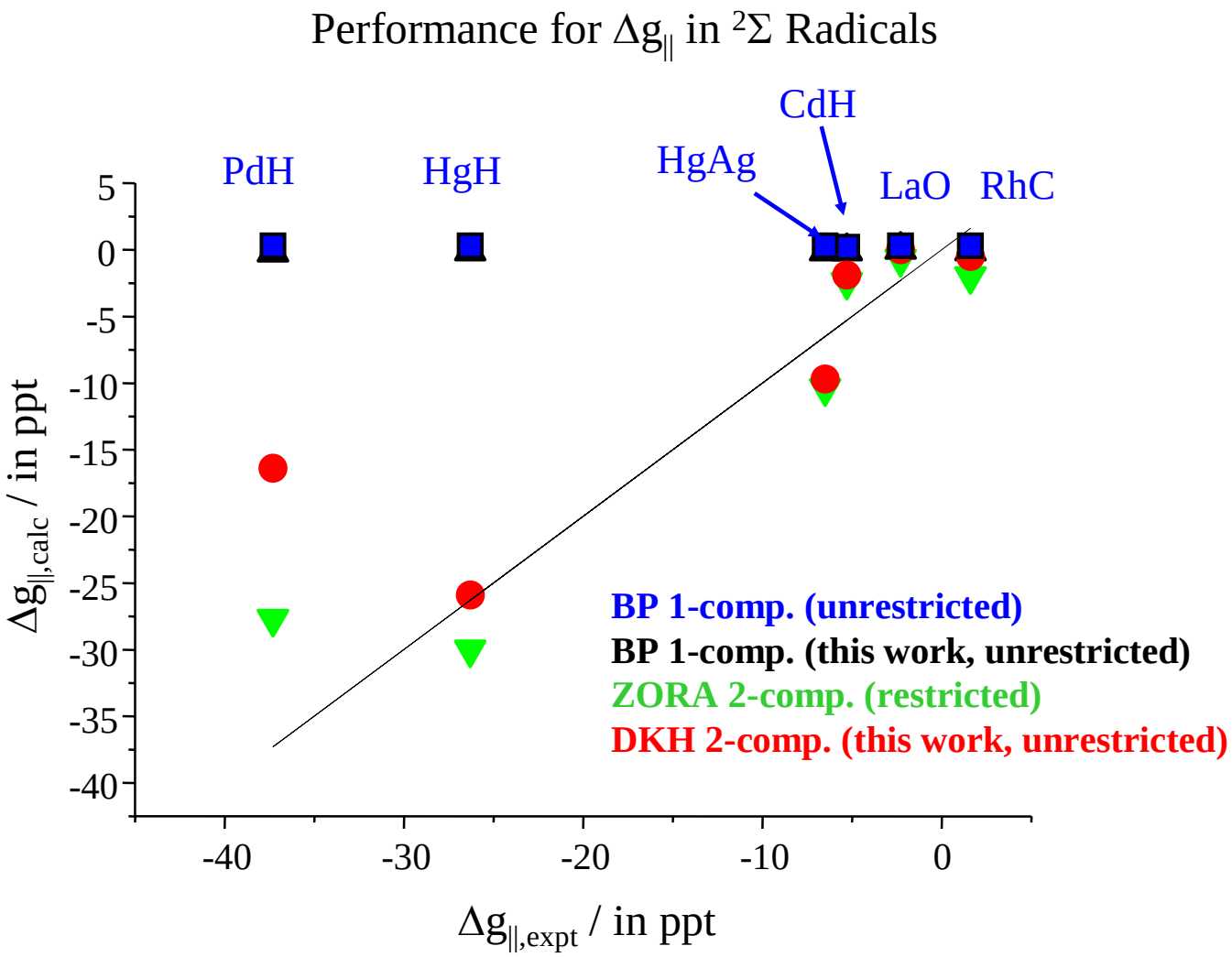
Available approaches

Calculations of the EPR g-tensor

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

There are specific problems associated with any of listed above approaches

1-component or 2-component ?



Restricted or unrestricted ?

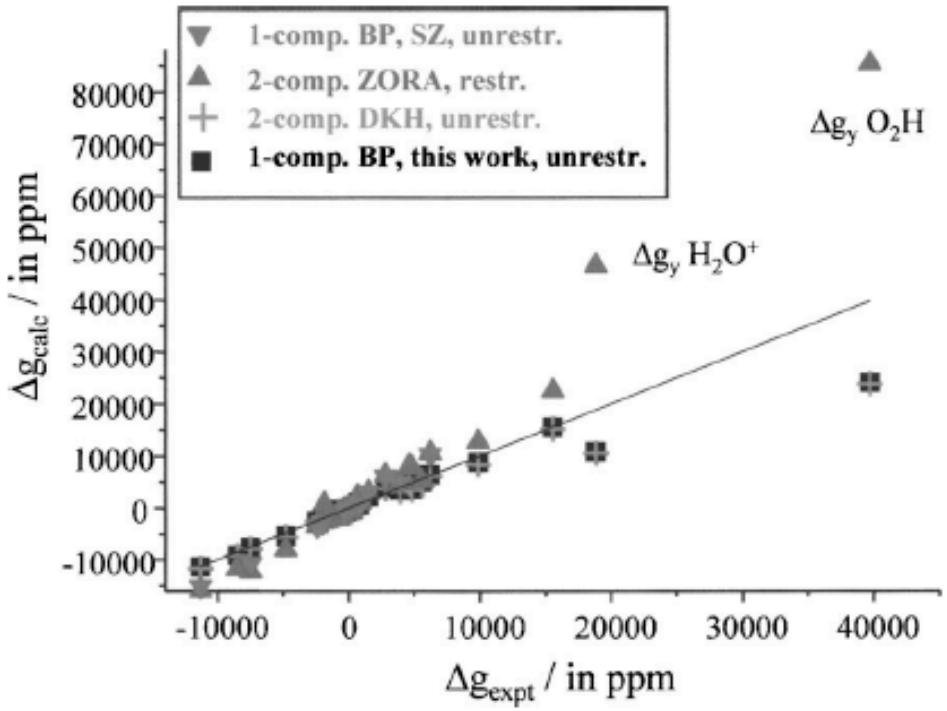


FIG. 1. Comparison of the computed *g*-shift tensor components (in ppm) for different one- and two-component approaches with experiment for light-atom radicals (cf. Table I for numerical data). Crosses: two-component DKH results (this work); squares: one-component BP results (this work); upward triangles: 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)

JOURNAL OF CHEMICAL PHYSICS VOLUME 108, NUMBER 18 8 MAY 1998

Electron spin resonance g tensors from general Hartree–Fock calculations

Dylan Jayatilaka
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

$$g_{ux} = 4c \cdot \mathrm{Re}\left\langle \Phi_1 \left| \frac{\partial}{\partial B_u} H^Z \right| \Phi_2 \right\rangle$$

$$g_{uy} = -4c \cdot \mathrm{Im}\left\langle \Phi_1 \left| \frac{\partial}{\partial B_u} H^Z \right| \Phi_2 \right\rangle$$

$$g_{uz} = 4c \cdot \mathrm{Re}\left\langle \Phi_1 \left| \frac{\partial}{\partial B_u} H^Z \right| \Phi_1 \right\rangle$$

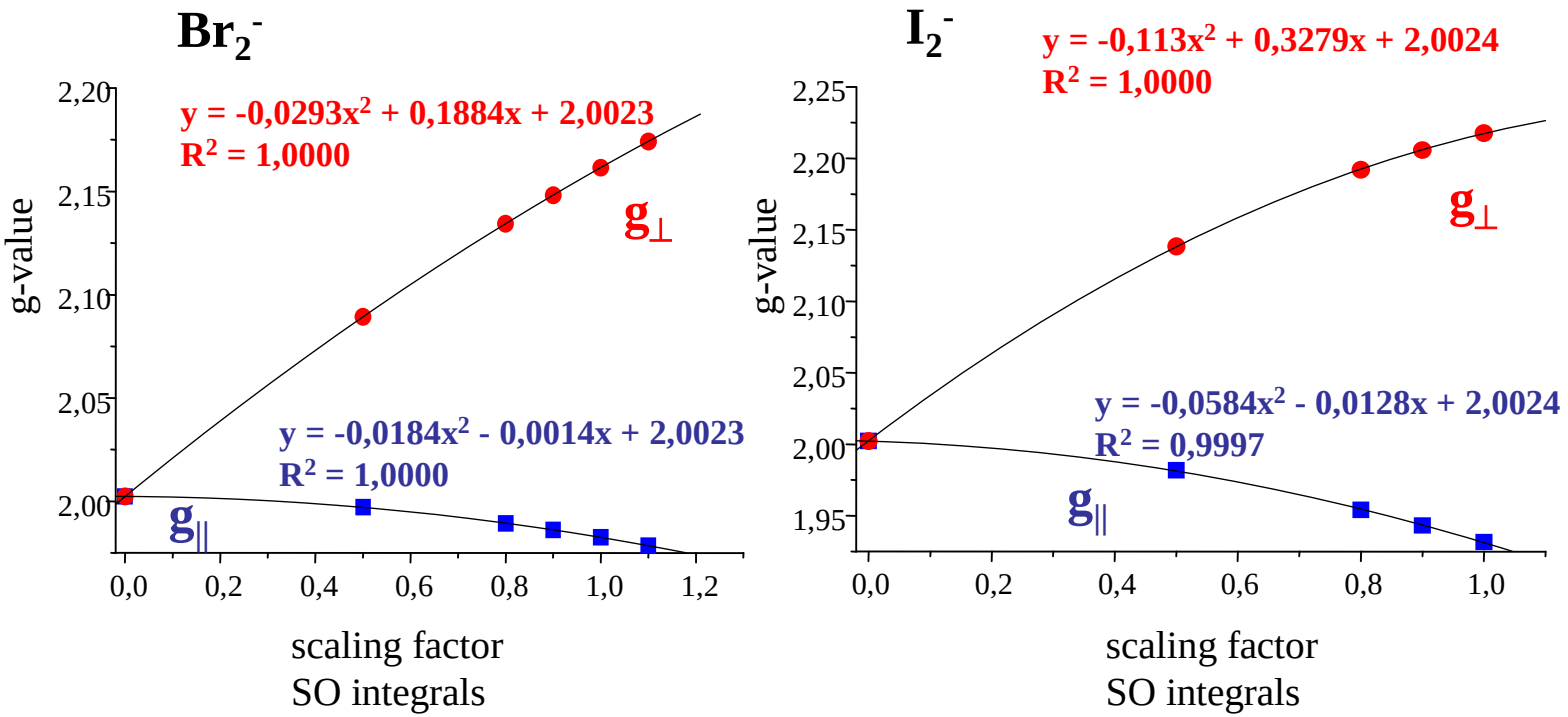
3-SCF calculations

Scaling the speed of the light …

I. Malkin, O.L. Malkina, V.G. Malkin, and
M. Kaupp, J. Chem. Phys., 123 (2005) 244103

Scaling the speed of the light !

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

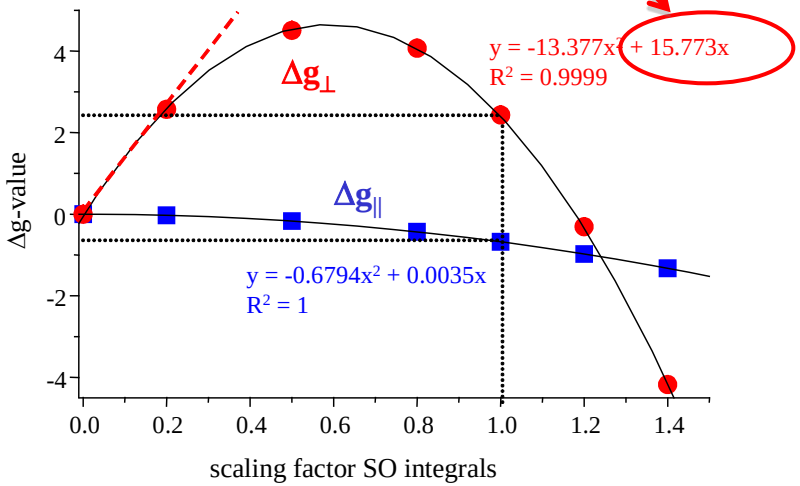


quadratic spin-orbit contributions dominate $g_{||}$ for both systems and become very important also for $g_{\perp}$ of I_2^- !

DKH-BP86 results with Hirao basis set

Benchmark calculations …

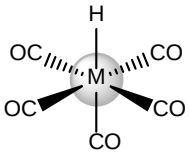
Radical	1-comp.	2-comp.	Exp.
O_2	2.7	2.3	2.9
SO	4.8	3.9	3.6
S_2	13.3	11.2	14.5
SeO	15.3	2.2	32.7
NF	1.8	1.6	2.0
NCl	5.4	5.0	5.4



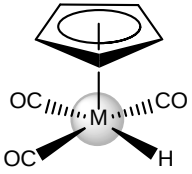
Comparison of different approaches for the calculation of $\Delta g_\perp$ in triplet radicals (in ppt)

"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)

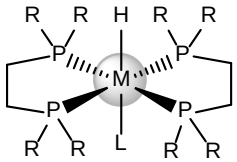
Dramatic spin-orbit effects on hydride ^1H shifts



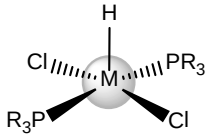
$[HM(CO)_5]^q$
M = Cr, Mo, W (q=-1)
M = Mn, Tc, Re (q=0)



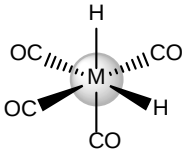
$[HMCp(CO)_3]$
M = Cr, Mo, W



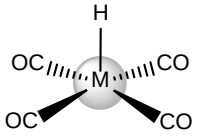
$[HM(L)(dhpe)_2]$
M = Fe, Ru, Os
L = Cl, CN



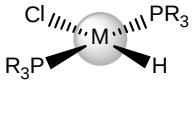
$[HMCl_2(PR_3)_2]$
M = Co, Rh, Ir



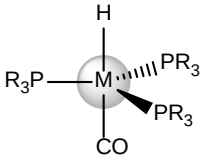
$[H_2M(CO)_4]$
M = Fe, Ru, Os



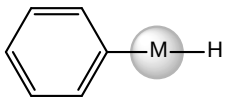
$[HM(CO)_4]$
M = Co, Rh, Ir



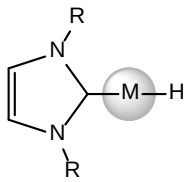
$[HMCl(PR_3)_2]$
M = Ni, Pd, Pt



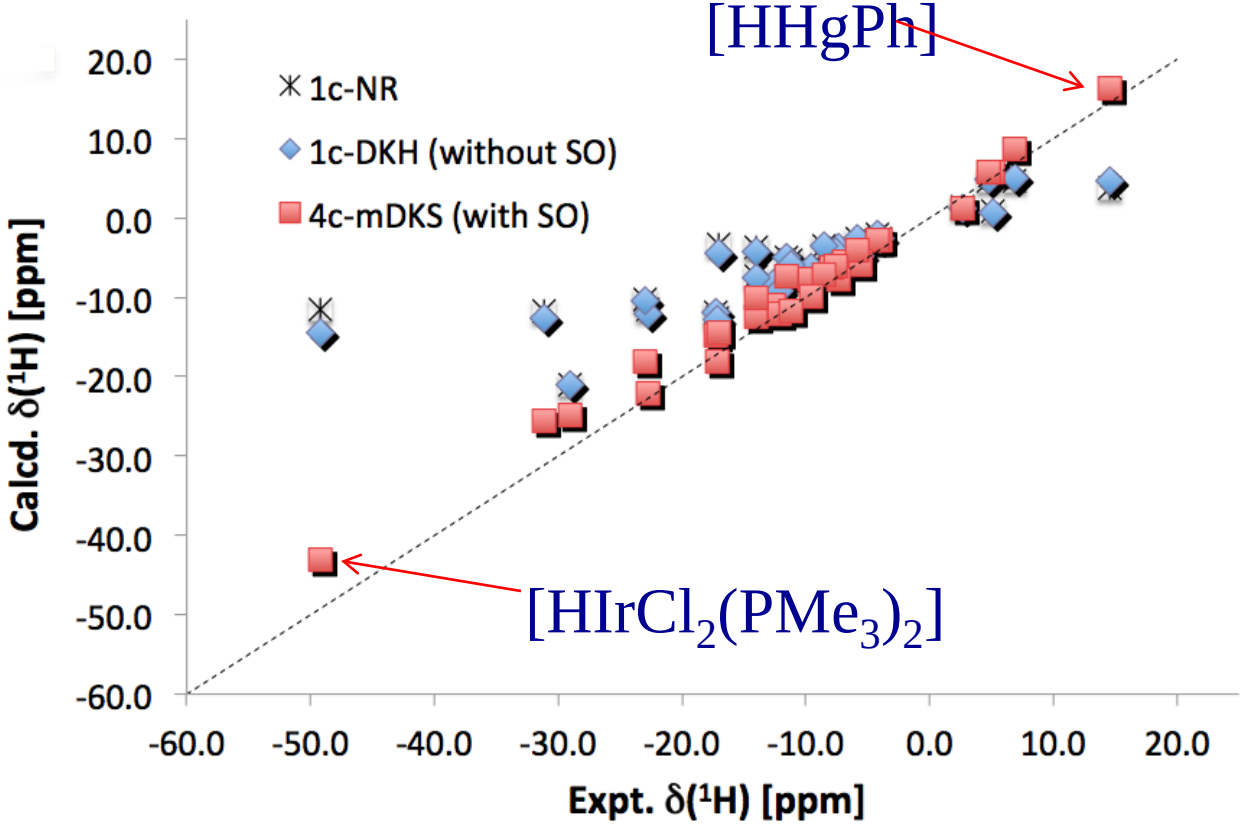
$[HM(CO)(PR_3)_3]$
M = Co, Rh, Ir



[HMPh]
M = Zn, Cd, Hg



[HM(NHC)]
M = Cu, Ag, Au

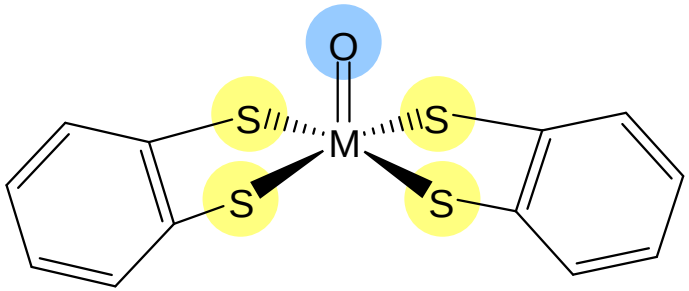


P. Hrobárik, V. Hrobáriková, F. Meier, M. Repiský, S. Komorovský, M. Kaupp J. Phys. Chem. A ***2011****, 115, 5654.*

EPR Parameters in Tungsten(V) Complexes

The important role of higher-order spin-orbit contributions.

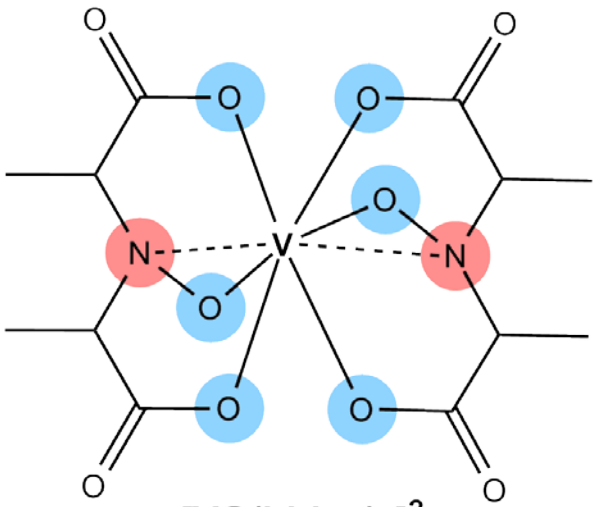
Calculation of Δg-tensors (in ppt) at 1-, 2- and 4-comp. level of theory using BP86 functional. (2-comp.: SO-ECP on metal/IGLO-II/CGO; 4-comp.: all electron DKS)



Complex	Method	Δg_{11}	Δg_{22}	Δg_{33}	Δg_{iso}
$[WO(bdt)_2]^-$	1-comp.[a]	53	-32	-51	-10
	2-comp.[a]	46	-48	-65	-22
	4-comp.	46	-58	-79	-30
	Exp.	42	-71	-91	-40

[a] P. Hrobárik, O. L. Malkina, V. G. Malkin, and M. Kaupp *Chem. Phys.* **356**, 229 (2009).

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

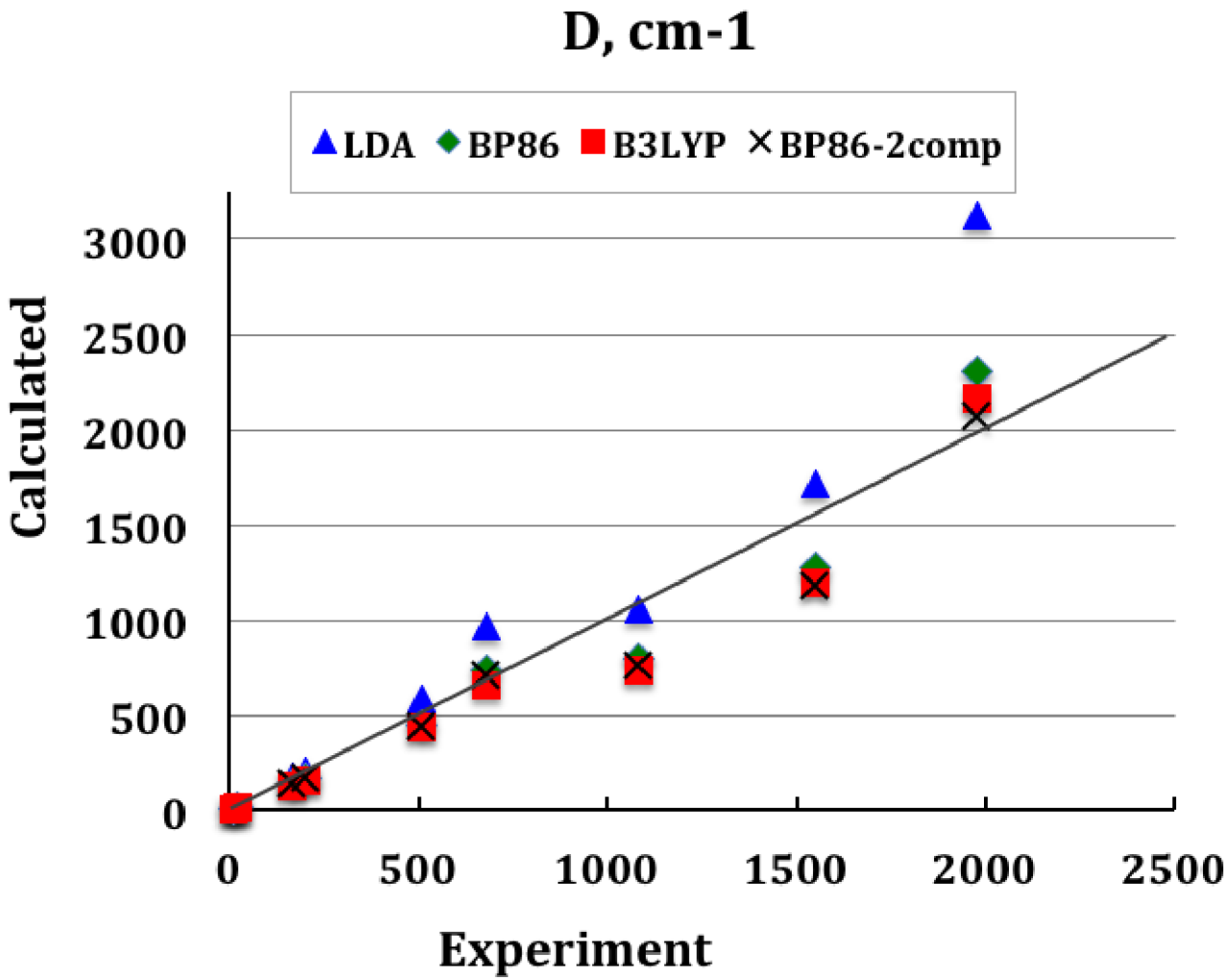


$[VO(hidpa)_2]^{2-}$
"*amavadin*"

Method	Δg_{11} [ppt]	$\otimes g_{22}$ [ppt]	$\otimes g_{33}$ [ppt]	$\otimes g_{is}$ [ppt]
1-c DKH	-32	-10	-8	-17
Exp.	-82	-20	-20	-41

BP86 results.

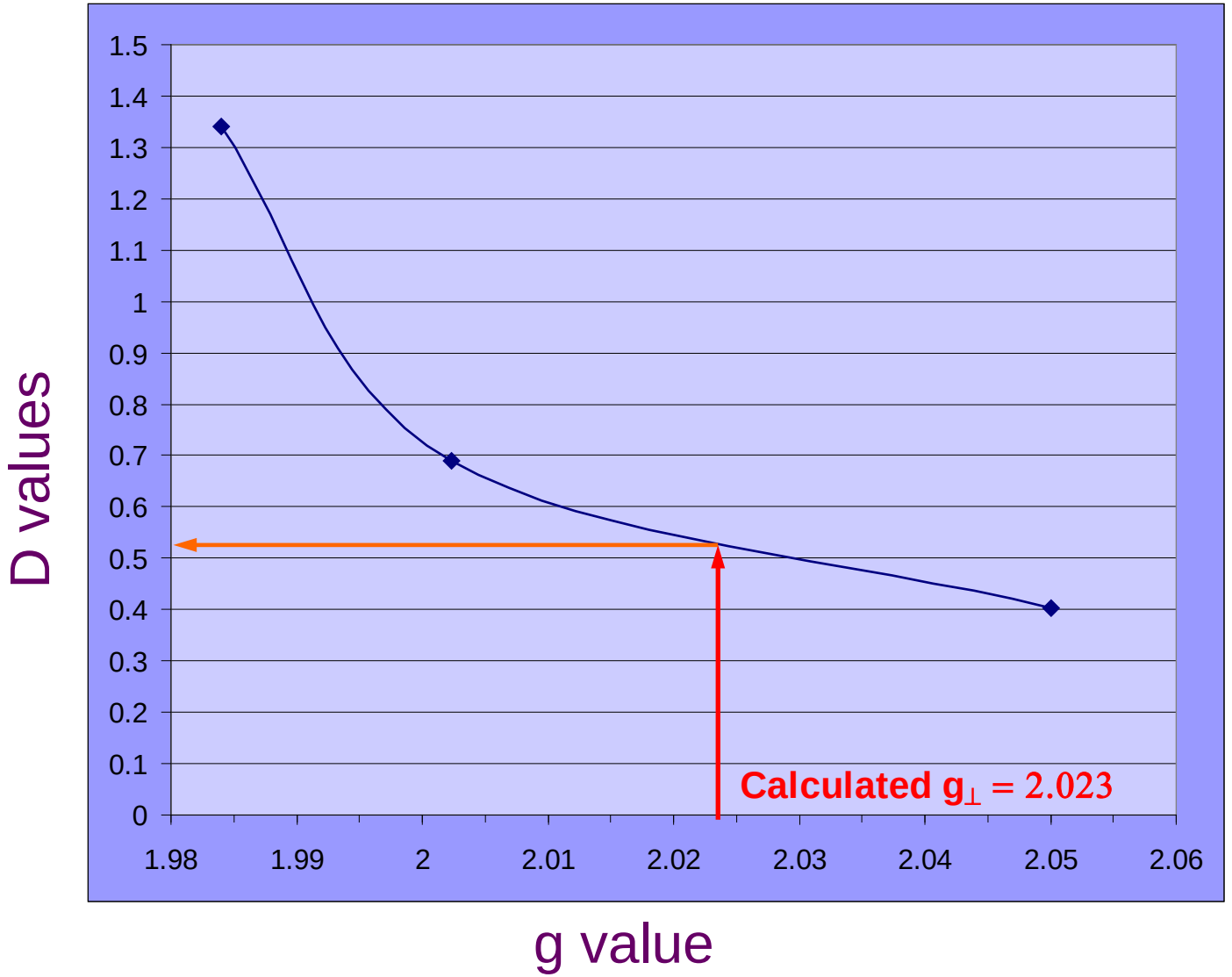
P. Hrobárik, M. Repiský, V. Hrobáriková, M. Kaupp Theor. Chem. Acc. ***2011,*** *129, 715.*



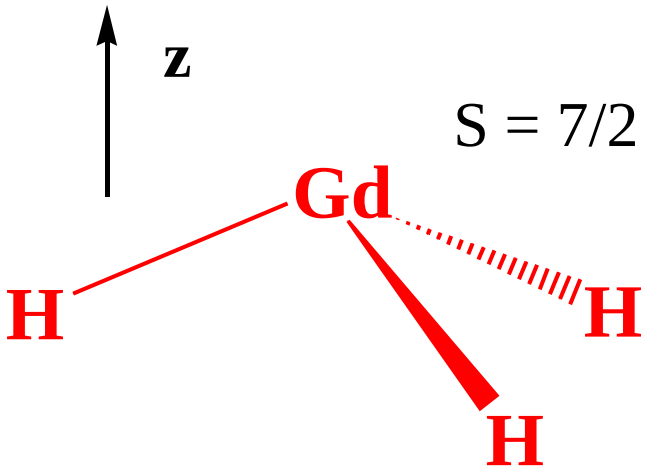
SO
S_2
SeO
SeS
Se_2
TeO
TeS
TeSe
Te_2

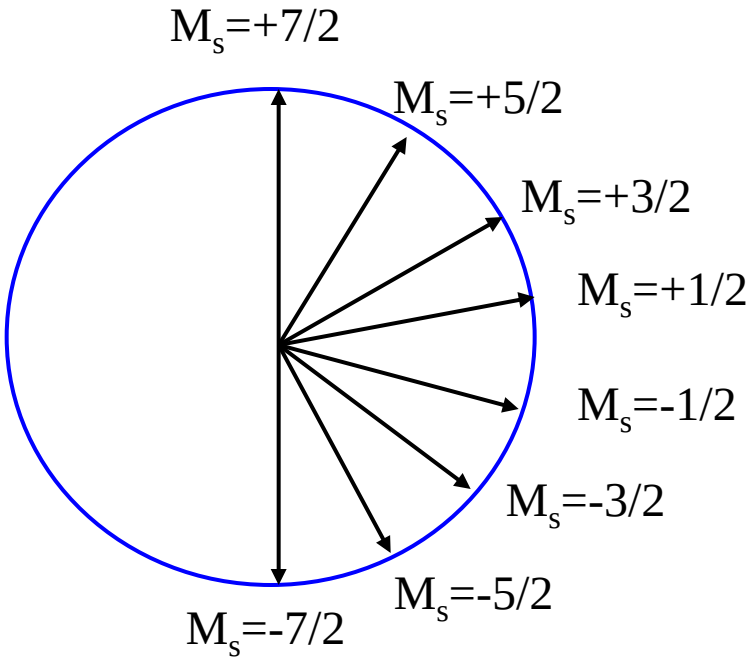
J. Chem. Phys. 125, 054110 (2006)

Evaluation of g-tensor and Zero-Field-Splitting (D) for GdH_3



2-Component Calculations of ZFS in GdH_3





D	1/6[E(7/2) – E(5/2)]	1/4[E(5/2) – E(3/2)]	1/2[E(3/2) – E(1/2)]
All-electron	0.22	0.22	0.22
ECP	0.23	0.23	0.23

In cm^{-1}; 2-component calculations (DFT with B3PW91).


REHE-2014 conference
"Relativistic effects in heavy element chemistry and physics”
Smolenice congress centrum, Slovakia,
September 20-25, 2014
Thank you!