

A Short Introduction into Quantum Chemical Calculations of NMR and EPR Parameters



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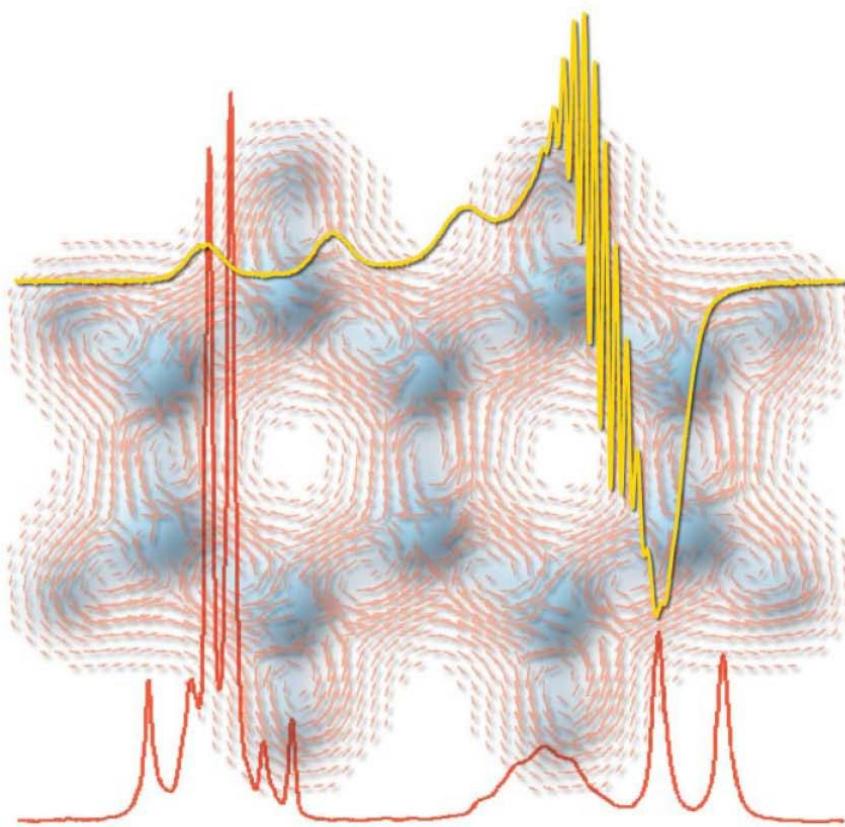
- Part I: Some basics on quantum chemical methods
- Part II: Basics on perturbation theory methods for the quantum-chemical calculation of NMR and EPR parameters
 - a) Rayleigh-Schrödinger perturbation theory
 - b) choice of Hamiltonian
 - c) nuclear shieldings (diamagnetic systems)
 - d) electronic g-tensor
 - e) hyperfine coupling
 - f) (zero-field splitting)

Edited by Martin Kaupp,
Michael Bühl, Vladimir G. Malkin

WILEY-VCH

Calculation of NMR and EPR Parameters

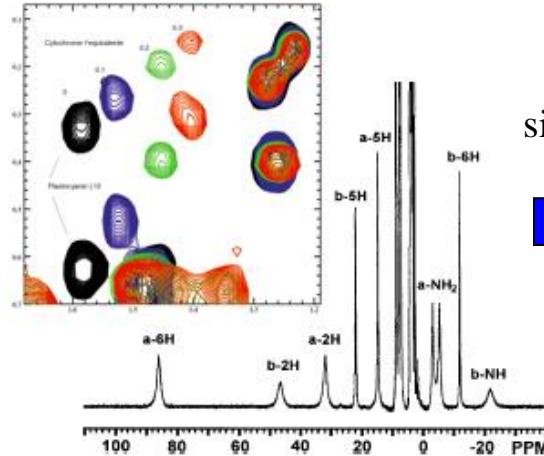
Theory and Applications



A comprehensive treatment,
Wiley-VCH 2004.

*With 36 chapters on methodology
and applications.*

The effective spin Hamiltonian



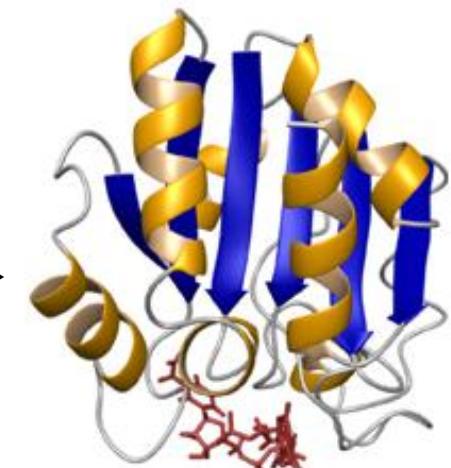
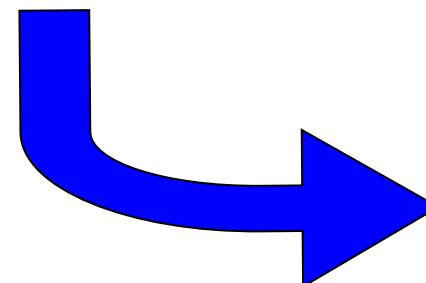
simulation

$$\hat{\mathcal{H}} \Psi = E \Psi$$

$\Psi \Rightarrow properties$

model
structure

spin Hamiltonian
parameters



comparison with model and/or
homologous systems (e.g. from
literature, database)

Applications to:

- spectra assignment
- structure elucidation
- interpretation
- dynamics

Introduction (1)

effective spin Hamiltonian provides link between magnetic resonance experiment and quantum mechanical treatment:

$$H = S \cdot g \cdot B + \sum_N S \cdot A_N \cdot I_N + S \cdot D \cdot S + \sum_{\mu,\nu} I_\mu q_{\mu\nu} I_\nu \\ + \sum_N I_N \cdot (1 - \sigma_N) \cdot B + \sum_{N,M} I_N \cdot (D_{NM} + K_{NM}) \cdot I_M$$

in most cases, property may be expressed as second derivative:

$$\langle X \rangle = \frac{\partial \langle H \rangle}{\partial a \partial b} = \frac{\partial E(a,b)}{\partial a \partial b} \quad (a = S, I; \quad b = B, S, I)$$

⇒ appropriately treated by second-order perturbation theory:

$$H|\Phi\rangle = (H_0 + V(a,b))|\Phi\rangle = E|\Phi\rangle$$

Introduction (2)

-relation between effective-spin Hamiltonian and quantum-chemical treatment requires appropriate Hamiltonian that takes care of spins and magnetic fields

⇒ starting point relativistic quantum mechanics (e.g. Dirac equation)
often transformation to quasi-nonrelativistic formalism
(e.g. Breit-Pauli Hamiltonian)

we will start by ignoring relativistic effects and magnetic interactions
⇒initially nonrelativistic quantum mechanics for \mathbf{H}_0

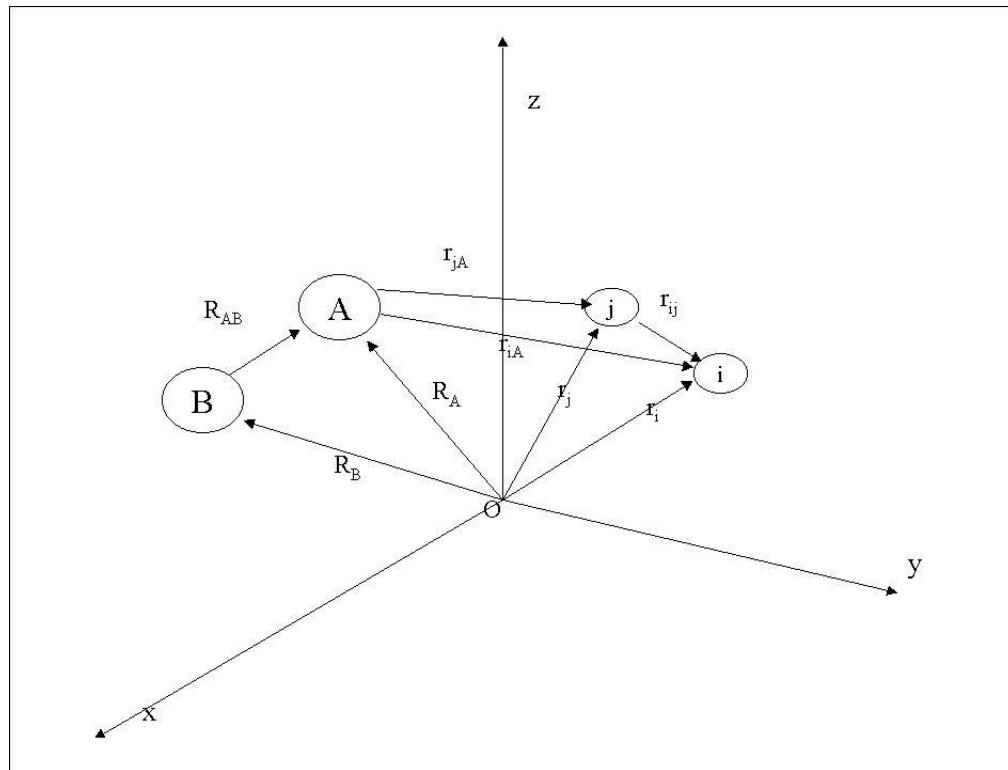
relativistic effects and magnetic interactions will be introduced later,
mainly by **perturbation theory**

Part I: Some Basics on Quantum Chemical Methods

H_0 : Nonrelativistic Quantum Mechanics (1)

The general (non-relativistic) Hamiltonian describing N electrons and M nuclei is given (in a.u.) by:

$$H = - \sum_{i=1,N} \frac{1}{2} \nabla_i^2 - \sum_{A=1,M} \frac{1}{2M_A} \nabla_A^2 - \sum_{i=1,N} \sum_{A=1,M} \frac{Z_A}{r_{iA}} + \sum_{i=1,N} \sum_{j>i} \frac{1}{r_{ij}} + \sum_{A=1,M} \sum_{B>A} \frac{Z_A Z_B}{R_{AB}}$$



H_0 : Nonrelativistic Quantum Mechanics (2)

after Born-Oppenheimer approximation (electronic Schrödinger equation):*

$$\hat{H}\Psi = E\Psi$$

electronic wave function

electronic Hamiltonian

one-electron Hamiltonian

operator of kinetic energy

operator of potential energy
(mainly el.-nuclear attraction)

electron-electron repulsion

$$\hat{H} = \sum_i \hat{h}(i) + \boxed{\frac{1}{2} \sum_{i \neq j} \frac{1}{r_{ij}}}$$
$$\hat{h}(i) = -\frac{1}{2} \hat{\nabla}^2(i) + V(i)$$

still missing: electronic spin (Pauli principle), *and time dependence removed

H₀: Nonrelativistic Quantum Mechanics (3)

energy expectation value:

$$E_0 = \frac{\langle \Psi | H | \Psi \rangle}{\langle \Psi | \Psi \rangle}$$

variational principle:

$$\tilde{E}_0 = \frac{\langle \tilde{\Psi} | H | \tilde{\Psi} \rangle}{\langle \tilde{\Psi} | \tilde{\Psi} \rangle} \geq E_0$$

exact ground-state solution provides lower bound to energies of approximate solutions!

H_0 : Nonrelativistic Quantum Mechanics (4)

in the absence of electron-electron interactions:

$$\Psi(1,2,3,4,\dots,n) = \varphi_1(1)\varphi_2(2)\varphi_3(3)\varphi_4(4)\dots\varphi_n(n)$$

Hartree product, independent-particle model, violates Pauli principle,
no correlation.

$$\Psi(1,2,3,4,\dots,n) = |\varphi_1(1)\varphi_2(2)\varphi_3(3)\varphi_4(4)\dots\varphi_n(n)|$$

Slater determinant (antisym. linear combination of product wavefunctions)

- $\varphi_i(i)$: one-electron wave functions (molecular orbitals)

- still no Coulomb correlation but Pauli exchange

insert as $\tilde{\Psi}$ into variational principle !

⇒ Hartee-Fock method

H_0 : Nonrelativistic Quantum Mechanics (5)

take trial wave function with free parameters q and minimize energy:*

$$\frac{\partial \tilde{E}_0}{\partial q} = \frac{\partial}{\partial q} \left[\frac{\langle \tilde{\Psi} | H | \tilde{\Psi} \rangle}{\langle \tilde{\Psi} | \tilde{\Psi} \rangle} \right] = 0$$

*Lagrange multipliers ε_a to account for constant N(electrons), and for orthogonality of MOs

for example: single Slater determinant \Rightarrow Hartree-Fock method

$$f(1)\varphi_a(1) = \varepsilon_a \varphi_a(1)$$

f depends on coordinates of all electrons (via ν_{HF}) \Rightarrow iterative solution

“self-consistent field” (SCF) method
 φ_i : molecular orbitals
 J_i : Coulomb op., K_i : exchange op.

$$f(1) = h(1) + \nu_{HF}(1)$$

$$h(1) = -\frac{1}{2} \nabla_1^2 + \sum_A \frac{Z_A}{r_{iA}}$$

$$\nu_{HF}(1) = \sum_b J_b - K_b$$

$$J_b(1) = \int dx_2 |\varphi_b(2)|^2 r_{12}^{-1}$$

$$K_b(1)\varphi_a(1) = \left[\int dx_2 \varphi_b^*(2) r_{12}^{-1} \varphi_a(2) \right] \varphi_b(1)$$

H_0 : Nonrelativistic Quantum Mechanics (6)

algebraic expansion of φ_i into basis set: Roothan-Hall method \Rightarrow matrix operations, linear algebra

$$\varphi_i = \sum_j c_{ij} \chi_j(A)$$

optimizable parameters!!!

χ : atomic orbital basis function with center on atom A \Rightarrow MO expanded in linear combination of AOs \Rightarrow MO-LCAO method

typical basis sets:

$$\chi = B g(r, \Phi, \Theta) e^{-\beta r}$$

$$\chi = A f(r, \Phi, \Theta) e^{-\alpha r^2}$$

Slater-type orbitals (STO)
fullfil cusp condition

Gaussian-type orbitals (GTO)
integrals more convenient

others: plane waves, numerical AOs, muffin-tin orbitals, etc.....*

*also for DFT etc.....

H_0 : Nonrelativistic Quantum Mechanics (7)

Hartree-Fock method accounts for Pauli exchange but not for Coulomb correlation \Rightarrow

$$\tilde{E}_0^{HF} \geq E_0$$

(even with infinite basis set!)

$$E_{corr} = E_0 - \tilde{E}_0^{HF}$$

Löwdin definition of correlation energy

\Rightarrow better methods (e.g. post-Hartree-Fock or DFT), to account for E_{corr}

post-HF methods:

- perturbation theory (MPn)
- configuration interaction (CI)
- coupled-cluster theory (CC)

size-consistent, not variational
not size-consistent, variational*
size-consistent, not variational

**in truncated form*

A Hierarchy of post-Hartree-Fock Theories

Semi-Empirical
MO-Theory

Density
Functional
Theory
(n^3-n^4)

Hartree-Fock (HF), SCF, MO-LCAO

$$\tilde{\Psi} = |\varphi_1(1)\varphi_2(2) \dots \varphi_{n-1}(n-1)\varphi_n(n)|$$

n^4

Perturbation Theory (MBPT)
(e.g. MP2: n^5 , MP3: n^6 , MP4: n^7)

Configuration Interaction (CI)

$$|\tilde{\Psi}\rangle = (C_0|\Psi_0\rangle + \sum_r C_a^r |\Psi_a^r\rangle + \sum_{r < s} C_{ab}^{rs} |\Psi_{ab}^{rs}\rangle + \dots)$$

(e.g. SDCI: n^6)

Coupled Cluster Methods (CC)

$$|\tilde{\Psi}\rangle = e^{\hat{T}}\Psi_0$$

($\hat{T} = \hat{T}_1 + \hat{T}_2 + \dots$)

(e.g. CCSD: n^6 ,
CCSD(T): n^7)

“Dressed CI Methods”
CPF, ACPF, MCPF, CEPA
typically n^6

Multiconfiguration SCF
(MCSCF, CASSCF, GVB)

Multireference
Perturbation Theory
(CASPT2, MR-MP2, MR-MPn?)

Multireference
Configuration Interaction
(e.g. MR-SDCI, MR-ACPF)

Multireference
Coupled Cluster Theory

n^m : formal scaling factors relative to system size n . Note that linear pre-factors are also important

Density Functional Theory (1)

basic idea: use $\rho(\mathbf{r})$ instead of the more complicated $\psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_n)$:

Hohenberg-Kohn Theorem (1963): $E = E[\rho]$

$$E[\rho] = T[\rho] + V_{\text{ne}}[\rho] + V_{ee}[\rho] =$$

$$\int \rho(\mathbf{r})v(\mathbf{r})d\mathbf{r} + F_{HK}[\rho] \quad \longleftarrow \text{Hohenberg-Kohn functional}$$

$$F_{HK}[\rho] = T[\rho] + V_{ee}[\rho]$$

Kohn-Sham Method (1964):

$$F[\rho] = T_s[\rho] + J[\rho] + E_{xc}[\rho] \quad \longleftarrow \text{exchange-correlation functional of the KS method}$$

$$E_{xc}[\rho] = T[\rho] - T_s[\rho] + V_{ee}[\rho] - J[\rho]$$

Density Functional Theory (2)

Kohn-Sham equations:

$$f(1)\varphi_a(1) = \varepsilon_a \varphi_a(1)$$

$$f(1) = h(1) + v_{xc}(1)$$

while formally similar to HF-SCF equations, KS method incorporates electron correlation via (unknown) v_{xc}

approximations to E_{xc} and v_{xc} :

$E_{xc}[\rho]$: local density approximation, LDA
(e.g. SVWN, X_a)

$E_{xc}[\rho, \nabla\rho]$: gen. gradient approximation, GGA
(e.g. BLYP, BP86, PW91, PBE,...)

$E_{xc}[\rho, \nabla\rho, \nabla^2\rho, \tau]$: meta-GGA
(e.g. PKZB, FT98,...)

hybrid functionals (with exact exchange)
(e.g. B3LYP, BHPW91, mPW1,...)

further: OEP, exact-exchange functionals....

Density Functional Theory (3)

See also: <https://sites.google.com/site/markcasida/dft>

Local Density Approximation (LDA)

$$\tilde{E}_x^{\text{LDA}} = \int \tilde{\epsilon}_x^{\text{LDA}} [\rho(\mathbf{r})] d\mathbf{r} = \int -\frac{3}{4} \left(\frac{3}{\pi} \right)^{1/3} \rho(\mathbf{r})^{4/3} d\mathbf{r}$$

E_c for homogeneous electron gas not known analytically but from very accurate fits to Quantum Monte Carlo simulations

Generalized Gradient Approximation (GGA)

$$\tilde{E}_{xc}^{\text{GGA}} = \int \tilde{\epsilon}_{xc}^{\text{LDA}} [\rho(\mathbf{r})] F_{xc}^{\text{GGA}} [\rho(\mathbf{r}), \nabla \rho(\mathbf{r})] d\mathbf{r}$$

(different functionals have been constructed).

Meta-Generalized Gradient Approximation (mGGA)

$$\tilde{E}_{xc}^{\text{mGGA}} = \int \tilde{\epsilon}_{xc}^{\text{mGGA}} [\rho(\mathbf{r}), \nabla \rho(\mathbf{r}), \nabla^2 \rho(\mathbf{r}), \tau(\mathbf{r})] d\mathbf{r}$$

$$\tau(\mathbf{r}) = \frac{1}{2} \sum_i^{\text{occ}} |\nabla \varphi_i(\mathbf{r})|^2$$

Density Functional Theory (4)

Type of xc-functional	Variables	Examples
local density appr. (LDA)	ρ_σ	SVWN, X _a
generalized gradient approximation (GGA)	ρ_σ , $ \nabla\rho_\sigma $	PP86, BP86, BLYP PW91, PBE
meta-GGA	ρ_σ , $ \nabla\rho_\sigma $, $\nabla^2\rho_\sigma$, τ_σ	FT98, PKZB, TPSS, BRx89, Bc88
hybrid functionals	GGA + exact (nonlocal) exchange	B3LYP, B3PW91 BHPW91, PBE0PBE

See also: <https://sites.google.com/site/markcasida/dft>

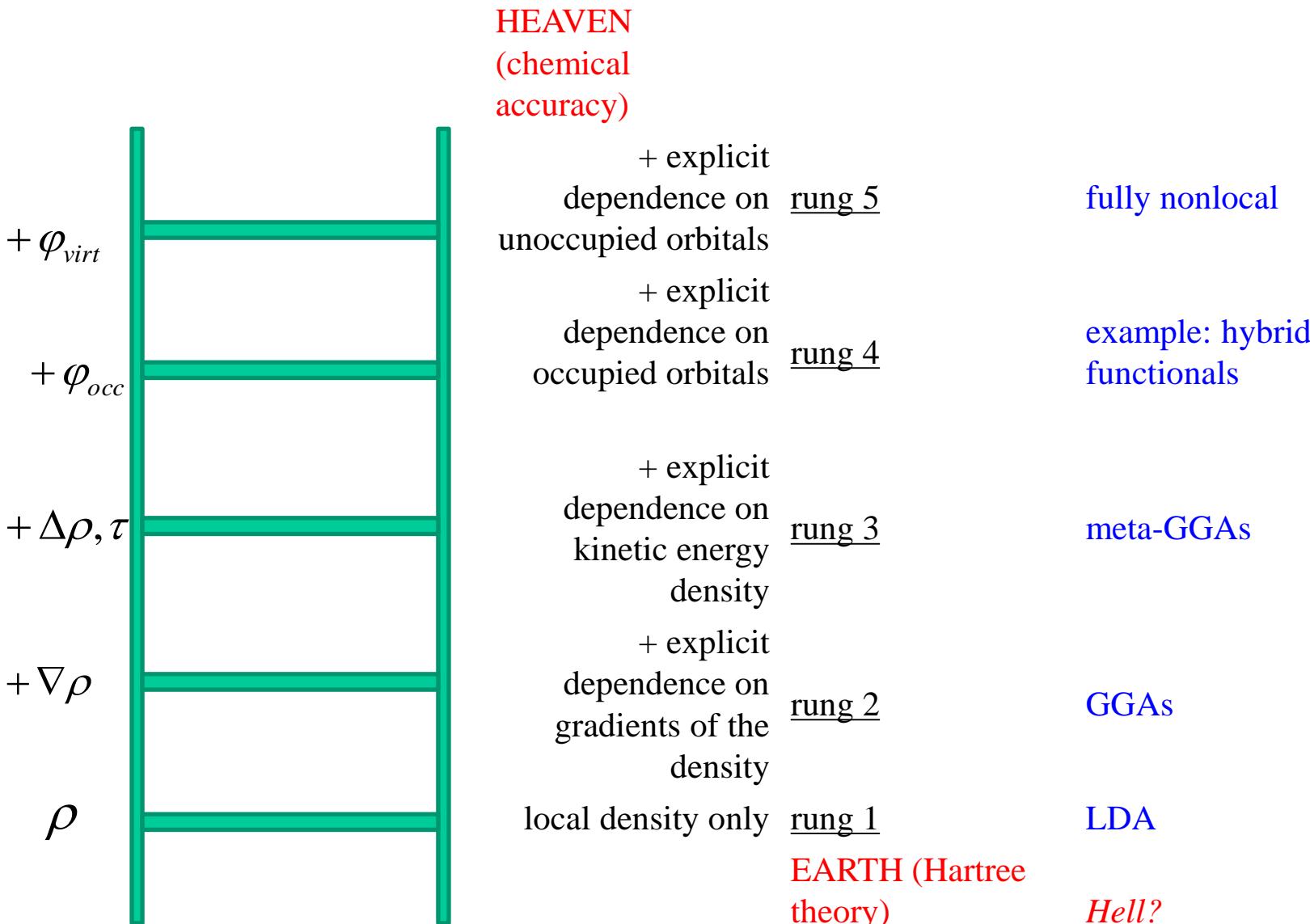
„classical“ hybrid functionals, e.g. B3LYP:

$$E_{xc}^{B3LYP} = E_{xc}^{LDA} + 0.20 \left(E_x^{exact} - E_x^{LDA} \right) + 0.72 \Delta E_x^{B88} + 0.81 \Delta E_c^{LYP}$$



nonlocal, nonmultiplicative exchange is not an explicit density functional,
 ⇒ complications

Jacob's Ladder to the heaven of chemical accuracy



A simpler hierarchy of exchange-correlation functionals

class	ingredients	examples
general nonlocal functionals	+ virtual-orbital dependent contributions	e.g. OEP2, B2PLYP
occupied-orbital dependent functionals	+ $\mathcal{E}_x, \tau, \dots$	τ -dependent meta-GGA, global hybrid, OEP, <u>local hybrid</u> , <u>B05-NDC model</u>
explicit density functionals	$\rho, \nabla\rho, \nabla^2\rho, \dots$	LDA, GGA, some meta-GGAs

Hybrid Functionals: Variation of Exact-Exchange Admixture

$$E_{\text{xc}}^{\text{hybrid}} = a_0 E_{\text{x}}^{\text{exact}} + \tilde{E}_{\text{xc}}^{\text{DFT}}; \quad \tilde{E}_{\text{xc}}^{\text{DFT}} = \tilde{E}_{\text{xc}}^{\text{DFT}} [\rho] \text{ (explicit)}$$

The most important parameter in „classical“ hybrid functionals is a_0 :

LDA or GGA functionals: $a_0 = 0.0$

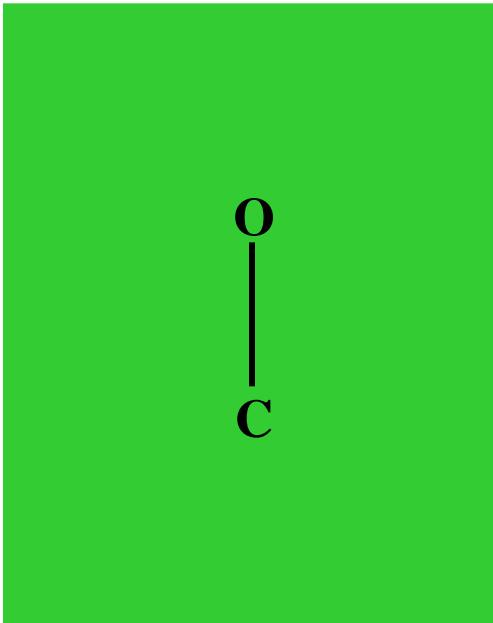
B3LYP: $a_0 = 0.20$

BHLYP: $a_0 = 0.50$

etc.....

The next natural step in DFT: local hybrid functionals

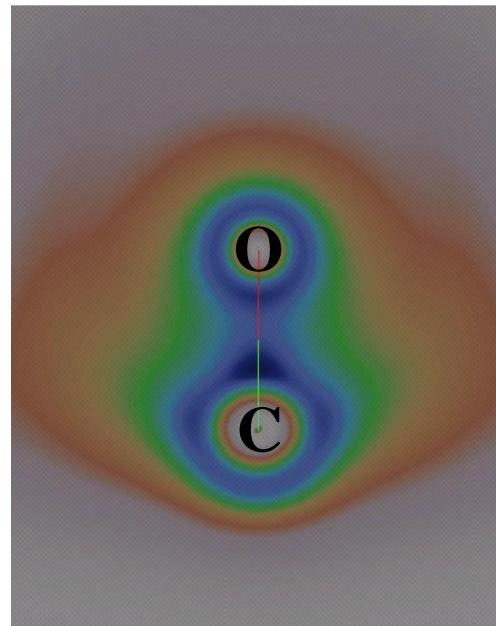
traditional (global) hybrid



admixture of exact
exchange within the
CO molecule

$$a_0 \rightarrow a(r)$$

local hybrid



$$E_X^{global\ hybrid} = a_0 \int \varepsilon_X^{exact}(r) dr + (1 - a_0) \int \varepsilon_X^{DFT}(r) dr$$

$$E_X^{local\ hybrid} = \int a(r) \varepsilon_X^{exact}(r) dr + \int [1 - a(r)] \varepsilon_X^{DFT}(r) dr$$

Local hybrid functional: J. Jaramillo, G. E. Scuseria, M. Ernzerhof *J. Chem. Phys.* **2003**, *118*, 1068
(first suggestion of principle by: F. G. Cruz, K.-C. Lam, K. Burke *J. Chem. Phys.* **1998**, *102*, 4911).

Part II:

**Basics on perturbation theory methods
for the quantum-chemical calculation of NMR
and EPR parameters**

Rayleigh-Schrödinger Perturbation Theory (1)

unknown eigenvalue problem:

$$H|\Phi\rangle = (H_0 + V)|\Phi\rangle = E|\Phi\rangle$$

with presumably known eigenvalue problem:

$$H_0|\psi^{(0)}\rangle = E^{(0)}|\psi^{(0)}\rangle$$

(solutions orthonormalized, i.e. $\langle \Psi_i^{(0)} | \Psi_j^{(0)} \rangle = \delta_{ij}$).

V is small. We want to derive Φ and E from $\Psi^{(0)}$ and $E^{(0)}$.

Introduce ordering parameter λ , which will transform H_0 into H :

$$H = H_0 + \lambda V$$

Rayleigh-Schrödinger Perturbation Theory (2)

Expansion into Taylor series:

$$E = E^{(0)} + \lambda E^{(1)} + \lambda^2 E^{(2)} \dots$$

$$\Phi = \psi^{(0)} + \lambda \psi^{(1)} + \lambda^2 \psi^{(2)} \dots$$

Task: express exact quantities only as a function of zero-order energies and matrix elements of the perturbation \mathcal{V} between the unperturbed wavefunctions $\langle \Psi_i^{(0)} | \mathcal{V} | \Psi_j^{(0)} \rangle$!

$$\begin{aligned} H|\Phi\rangle &= (H_0 + \lambda \mathcal{V})|\Phi\rangle = \\ &= (H_0 + \lambda \mathcal{V})(\psi^{(0)} + \lambda \psi^{(1)} + \lambda^2 \psi^{(2)} + \dots) = \\ &= (E^{(0)} + \lambda E^{(1)} + \lambda^2 E^{(2)} \dots)(\psi^{(0)} + \lambda \psi^{(1)} + \lambda^2 \psi^{(2)}) \end{aligned}$$

choose intermediate normalization: $\langle \Psi | \Phi \rangle = 1 \Rightarrow \langle \Psi^{(0)} | \Psi^{(n)} \rangle = 0$ (for $n \neq 0$)

Rayleigh-Schrödinger Perturbation Theory (3)

collect and equate coefficients for a given power n of λ^n :

$$H_0 |\psi^{(0)}\rangle = E^{(0)} |\psi^{(0)}\rangle$$

$$H_0 |\psi^{(1)}\rangle + V |\psi^{(0)}\rangle = E^{(0)} |\psi^{(1)}\rangle + E^{(1)} |\psi^{(0)}\rangle \quad (1), \text{ remember!}$$

$$H_0 |\psi^{(2)}\rangle + V |\psi^{(1)}\rangle = E^{(0)} |\psi^{(2)}\rangle + E^{(1)} |\psi^{(1)}\rangle + E^{(2)} |\psi^{(0)}\rangle$$

$$H_0 |\psi^{(3)}\rangle + V |\psi^{(2)}\rangle = E^{(0)} |\psi^{(3)}\rangle + E^{(1)} |\psi^{(2)}\rangle + E^{(2)} |\psi^{(1)}\rangle + E^{(3)} |\psi^{(0)}\rangle$$

multiply each of the equations by $\langle \Psi^{(0)} |$ and recall orthogonality relations:

$$E^{(0)} = \langle \psi^{(0)} | H_0 | \psi^{(0)} \rangle$$

$$E^{(1)} = \langle \psi^{(0)} | V | \psi^{(0)} \rangle$$

$$E^{(2)} = \langle \psi^{(0)} | V | \psi^{(1)} \rangle$$

$$E^{(3)} = \langle \psi^{(0)} | V | \psi^{(2)} \rangle$$

Rayleigh-Schrödinger Perturbation Theory (4)

For $E^{(2)}$ we need $\Psi^{(1)}$ \Rightarrow expand $\Psi^{(1)}$:

$$|\psi^{(1)}\rangle = \sum_{k \neq 0} c_k^{(1)} |\psi_k^{(0)}\rangle$$

recall (1):

$$H_0 |\psi^{(1)}\rangle + V |\psi^{(0)}\rangle = E^{(0)} |\psi^{(1)}\rangle + E^{(1)} |\psi^{(0)}\rangle$$

$$\Rightarrow H_0 |\psi^{(1)}\rangle - E^{(0)} |\psi^{(1)}\rangle = E^{(1)} |\psi^{(0)}\rangle - V |\psi^{(0)}\rangle$$

multiply by $\langle \Psi_k^{(0)} |$ and expand $|\Psi_0^{(1)}\rangle$:

$$\langle \psi_k^{(0)} | (H_0 - E_0) \sum_{k \neq 0} c_k^{(1)} |\psi_k^{(0)}\rangle = -\langle \psi_k^{(0)} | V |\psi_0^{(0)}\rangle$$

with hermiticity of H and intermediate normalization:

$$(E_k^0 - E_0) c_k^{(1)} = -\langle \psi_k^{(0)} | V |\psi_0^{(0)}\rangle$$

$$\Rightarrow c_k^{(1)} = -\frac{\langle \psi_k^{(0)} | V |\psi_0^{(0)}\rangle}{(E_k^0 - E_0)}$$

Rayleigh-Schrödinger Perturbation Theory (5)

recall:

$$E^{(2)} = \langle \psi_0^{(0)} | \mathcal{V} | \psi_0^{(1)} \rangle = \langle \psi_0^{(0)} | \mathcal{V} \sum_{k \neq 0} | \psi_k^{(0)} \rangle c_k^{(1)}$$

$$c_k^{(1)} = -\frac{\langle \psi_k^{(0)} | \mathcal{V} | \psi_0^{(0)} \rangle}{(E_k^{(0)} - E_0^{(0)})}$$

$$\Rightarrow E^{(2)} = \sum_{n \neq 0} \frac{\langle \psi_0^{(0)} | \mathcal{V} | \psi_n^{(0)} \rangle \langle \psi_n^{(0)} | \mathcal{V} | \psi_0^{(0)} \rangle}{E_0^{(0)} - E_n^{(0)}}$$

in case of one-electron operators and one-electron-type wavefunctions:

$$E = \sum_a \mathcal{E}_a^{(0)} + \sum_a v_{aa} + \sum_{ar} \frac{v_{ar} v_{ra}}{\mathcal{E}_a^{(0)} - \mathcal{E}_r^{(0)}}$$

$$(v_{ar} = \langle a | v | r \rangle)$$

a,r represent spin orbitals

Perturbation Theory Applied to MR Parameters (1)

$$\begin{aligned}
 H = & S \cdot g \cdot B + \sum_N S \cdot A_N \cdot I_N + S \cdot D \cdot S + \sum_{\mu,\nu} I_\mu q_{\mu\nu} I_\nu \\
 & + \sum_N I_N \cdot (1 - \sigma_N) \cdot B + \sum_{N,M} I_N \cdot (D_{NM} + K_{NM}) \cdot I_M
 \end{aligned}$$

$$\langle X \rangle = \frac{\partial \langle H \rangle}{\partial a \partial b} = \frac{\partial E(a, b)}{\partial a \partial b} \quad (a = S, I; \quad b = B, S, I)$$

$$\begin{aligned}
 E = & E^{ele} + E^{(1)} + E^{(2)} \\
 = & E^{ele} + \langle \Psi_0^{(0)} | V(a, b) | \Psi_0^{(0)} \rangle + \sum_{n \neq 0} \frac{\langle \Psi_0^{(0)} | V(a, b) | \Psi_n^{(0)} \rangle \langle \Psi_n^{(0)} | V(a, b) | \Psi_0^{(0)} \rangle}{E_o - E_n}
 \end{aligned}$$

$$\langle X \rangle = \frac{\partial E(a, b)}{\partial a \partial b} = \frac{\partial}{\partial a \partial b} \left[E^{ele} + \langle \Psi_0^{(0)} | V(a, b) | \Psi_0^{(0)} \rangle + \sum_{n \neq 0} \frac{\langle \Psi_0^{(0)} | V(a, b) | \Psi_n^{(0)} \rangle \langle \Psi_n^{(0)} | V(a, b) | \Psi_0^{(0)} \rangle}{E_o - E_n} \right]$$

note that only V depends on a and b !

Perturbation Theory Applied to MR Parameters (2)

carry out differentiation:

$$\langle X \rangle = \left\langle \Psi_0^{(0)} \left| \frac{\partial}{\partial a \partial b} V(a, b) \right| \Psi_0^{(0)} \right\rangle + \sum_{n \neq 0} \frac{\left\langle \Psi_0^{(0)} \left| \frac{\partial}{\partial a} V(a, b) \right| \Psi_n^{(0)} \right\rangle \left\langle \Psi_n^{(0)} \left| \frac{\partial}{\partial b} V(a, b) \right| \Psi_0^{(0)} \right\rangle}{E_o - E_n}$$
$$+ \sum_{n \neq 0} \frac{\left\langle \Psi_0^{(0)} \left| \frac{\partial}{\partial b} V(a, b) \right| \Psi_n^{(0)} \right\rangle \left\langle \Psi_n^{(0)} \left| \frac{\partial}{\partial a} V(a, b) \right| \Psi_0^{(0)} \right\rangle}{E_o - E_n}$$

simplification in case of “real” wavefunctions and operators:

$$\langle X \rangle = \frac{\partial E(a, b)}{\partial a \partial b} = \left\langle 0 \left| \frac{\partial H(a, b)}{\partial a \partial b} \right| 0 \right\rangle + 2 \sum_{n \neq 0} \frac{\left\langle 0 \left| \frac{\partial H(a, b)}{\partial a} \right| n \right\rangle \left\langle n \left| \frac{\partial H(a, b)}{\partial b} \right| 0 \right\rangle}{E_0 - E_n}$$

1. select appropriate Hamiltonian for both H_0 and V
2. work out second-order perturbation theory

The Breit-Pauli Hamiltonian (incl. ext. fields)

$$H_0 + V = H_e + H_N + H_{eN}$$

$$H_e = \sum_i H_{ei}$$

$$H_{e1} = \sum_i \frac{\pi_i^2}{2m_e}$$

kinetic energy

$$H_{e2} = -e \sum_i \phi_i$$

int. with external electric field

$$H_{e3} = g_e \beta_e \sum_i \left(1 - \frac{\pi_i^2}{2m_0 k_B c^2} \right) \mathbf{s}_i \cdot \mathbf{B}$$

electron Zeeman interaction

$$H_{e4} = -\sum_i \frac{\pi_i^2}{8m_e^3 c^2}$$

relativistic correction to kinetic energy

$$H_{e5} = -\frac{g_e \beta_e}{4m_e c^2} \sum_i (\mathbf{s}_i \pi_i \times \mathbf{E}_i - \mathbf{s}_i \mathbf{E}_i \times \pi_i)$$

1-elect. spin-orbit interaction

$$H_{e6} = -\frac{\hbar \beta e}{4m_e c^2} \sum_i \operatorname{div} \mathbf{E}_i$$

Darwin corr. to electric field int.

$$H_{e7} = -\frac{e^2}{2k_0} \sum_{ij} \frac{1}{r_{ij}}$$

Coulomb repulsion

$$H_{e8} = -\frac{2\pi\beta_e}{k_0 c^2} \sum_{ij} \delta(\mathbf{r}_i - \mathbf{r}_j)$$

2-elect. Darwin term

$$H_{e9} = -\frac{g_e \beta_e^2}{\hbar k_0 c^2} \sum_{ij} \frac{(2\mathbf{s}_i \cdot \mathbf{r}_{ij} \times \pi_j + \mathbf{s}_j \cdot \mathbf{r}_{ij} \times \pi_i)}{r_{ij}^3}$$

2-electr. spin-orbit interaction

$$H_{e10} = -\frac{\beta_e^2}{\hbar k_0 c^2} \sum_{ij} \frac{(\mathbf{r}_{ij}^2 \cdot \pi_i \times \mathbf{r}_j + \mathbf{r}_{ij} \cdot (\mathbf{r}_{ij} \times \pi_i) \cdot \pi_j)}{r_{ij}^3}$$

orbit-orbit interaction

$$H_{e11} = -\frac{g_e^2 \beta_e^2}{2k_0 c^2} \sum_{ij} \frac{((3\mathbf{s}_j \cdot \mathbf{r}_{ij})(\mathbf{s}_i \cdot \mathbf{r}_j) - \mathbf{r}_{ij}^2 (\mathbf{s}_i \cdot \mathbf{s}_j))}{r_{ij}^5}$$

electron-spin dipolar interaction

$$H_{e12} = -\frac{4\pi g_e^2 \beta_e^2}{2k_0 c^2} \sum_{ij} \mathbf{s}_i \mathbf{s}_j \delta(\mathbf{r}_i - \mathbf{r}_j)$$

electron spin-spin interaction

$$H_N = \sum_i H_{Ni}$$

$$H_{NI} = -e \sum_N Z_N \phi_N$$

int. with external electric field

$$H_{N2} = \beta_N \sum_N g_N I_N \cdot \mathbf{B}$$

nuclear Zeeman interaction

$$H_{N3} = \frac{e^2}{2k_0} \sum_{NM} \frac{Z_N Z_M}{R_{NM}}$$

nuclear-nuclear Coulomb interaction

$$H_{N4} = -\frac{\beta_N^2}{2k_0 c^2} \sum_{NM} g_N g_M \frac{((3I_N \cdot R_{NM})(I_M \cdot R_{NM}) - R_{NM}^2 (I_N \cdot I_M))}{R_{NM}^5}$$

nucl. dipole-dipole int

$$H_{eN} = \sum_i H_{eNi}$$

$$H_{eNI} = -\frac{e^2}{k_0} \sum_{i,N} \frac{Z_N}{r_{iN}}$$

electron-nuclear Coulomb interaction

$$H_{eN2} = \frac{g_e \beta_e \beta_N}{k_0 e^2} \sum_{i,N} g_N \frac{((3s_i \cdot r_{iN})(l_N \cdot r_{iN}) - r_{iN}^2 (s_i \cdot l_N))}{r_{iN}^5}$$

dipolar hyperfine int.

$$H_{eN3} = \frac{8\pi g_e}{3} \frac{\beta_e \beta_N}{2k_0 c^2} \sum_{i,N} g_N s_i \cdot l_N \delta(r_i - R_N)$$

Fermi contact term

$$H_{eN4} = \frac{2\beta_e \beta_N}{\hbar k_0 c^2} \sum_{i,N} g_N \frac{l_N \cdot r_{iN} \times \pi_i}{r_{iN}^3}$$

orbital hyperfine interaction

$$H_{eN5} = \frac{g_e \beta_e^2}{\hbar k_0 c^2} \sum_{i,N} Z_N \frac{s_i \cdot r_{iN} \times \pi_i}{r_{iN}^3}$$

electron-electron spin-orbit hyperfine int.

$$H_{eN6} = \frac{2\pi \beta_e^2}{k_0 c^2} \sum_{i,N} Z_N \delta(r_i - R_N)$$

electron-nuclear Darwin term

var. stable quasirelativistic Hamiltonians:
Douglas-Kroll-Hess, ZORA.
Or fully relativistic: Dirac-Coulomb-Breit

NMR/EPR Parameter Ingredients for pNMR Shifts

- Nuclear shieldings (need to be generalized from closed- to open-shell case) \Rightarrow orbital shielding
- Hyperfine couplings (we need both isotropic and anisotropic contributions)
- g-tensor (needed for „dipolar shifts“)
- zero-field splitting (modifies energy levels for $S > \frac{1}{2}$)

Nuclear Shieldings (NMR Chemical Shifts) for Diamagnetic Systems

Application of second-order perturbation theory to nuclear shielding: The nonrelativistic Ramsey equation

$$\sigma_{N,uv} = \frac{\partial^2 E}{\partial \mu_{N,u} \partial \mathbf{B}_v}; u, v = x, y, z$$

$$H(\mathbf{B}, \mu_N) = H^0 + H_u^{10} B_v + \sum_N \mu_{Nu} H_{Nu}^{01} + \sum_N \mu_{Nu} H_{Nuv}^{11} B_v$$

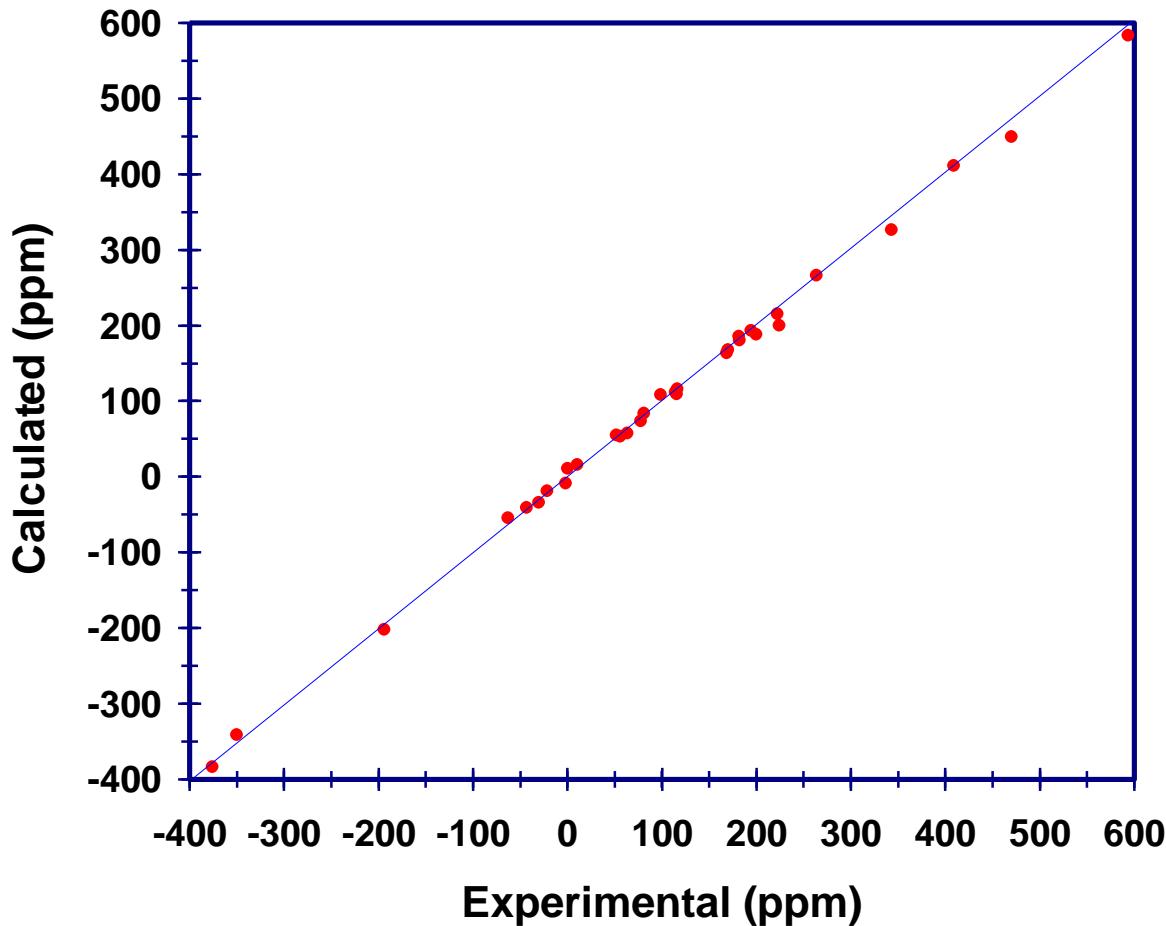
$$\sigma_{N,uv} = \frac{1}{2c^2} \langle 0 | \sum_i \frac{(\mathbf{r}_{iO} \cdot \mathbf{r}_{iN}) \delta_{uv} - r_{iO,v} r_{iN,u}}{r_{iN}^3} | 0 \rangle + \frac{1}{2c^2} \left[\sum_{n \neq 0} \frac{\langle 0 | L_{O,v} | n \rangle \cdot \langle n | L_{N,u} \cdot r_{kN}^{-3} | 0 \rangle}{E_0^{-1} E_n} + c.c. \right]$$

σ^d (diamagn. shielding)

σ^p (paramagn. shielding)

gauge problem for finite basis sets \Rightarrow need for specialized basis sets to
expand the first-order wave function \Rightarrow GIAO, IGLO

Shielding constants calculated with SOS-DFPT versus experimental data

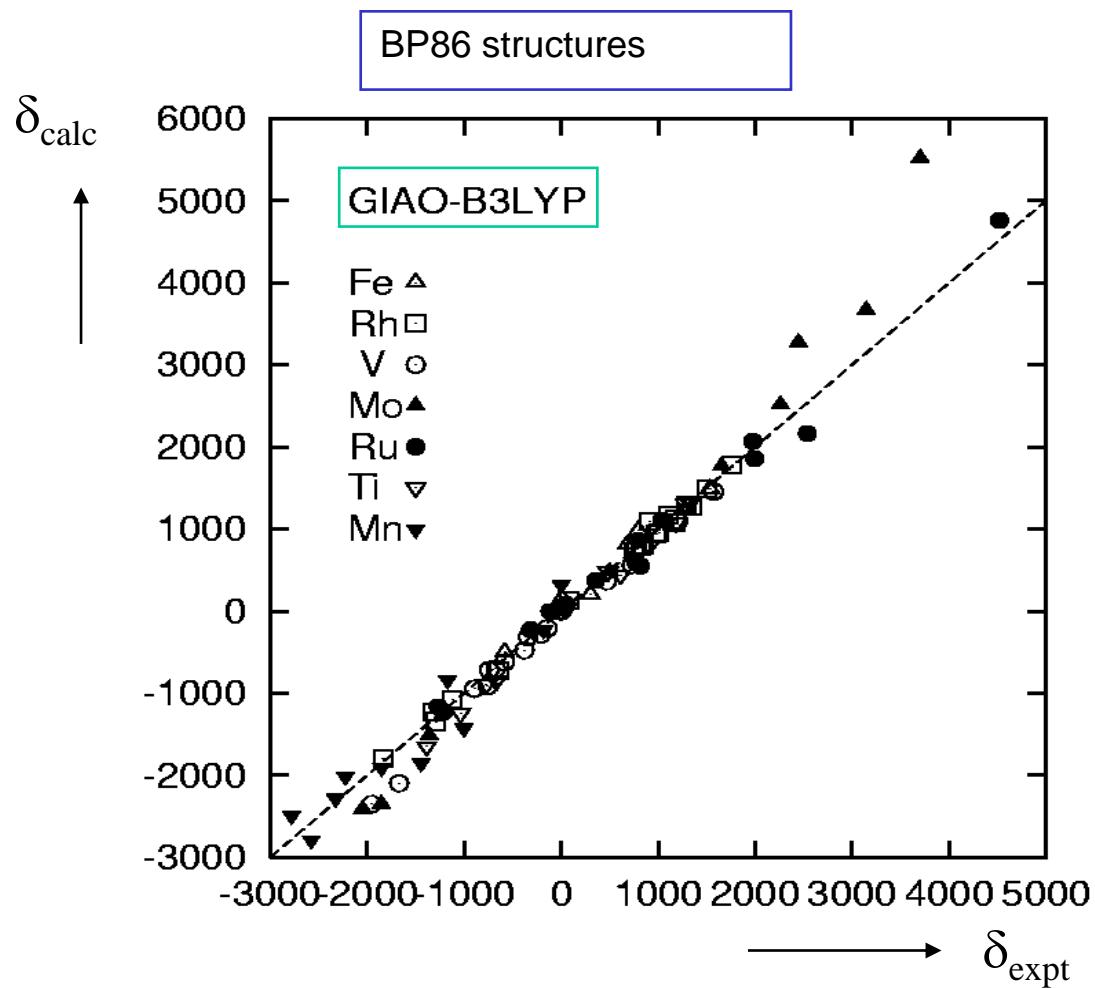


BP86 functional, SOS-DFPT correction

Molecules: CH₄, C₂H₂, C₂H₄, allene, C₃H₈, c-C₃H₆, c-C₃H₄, benzene, CO, H₂CO, H₂O, N₂O, NH₃, N₂, HCN, CH₃F, HF, F₂, PN, PH₃, PF₃.

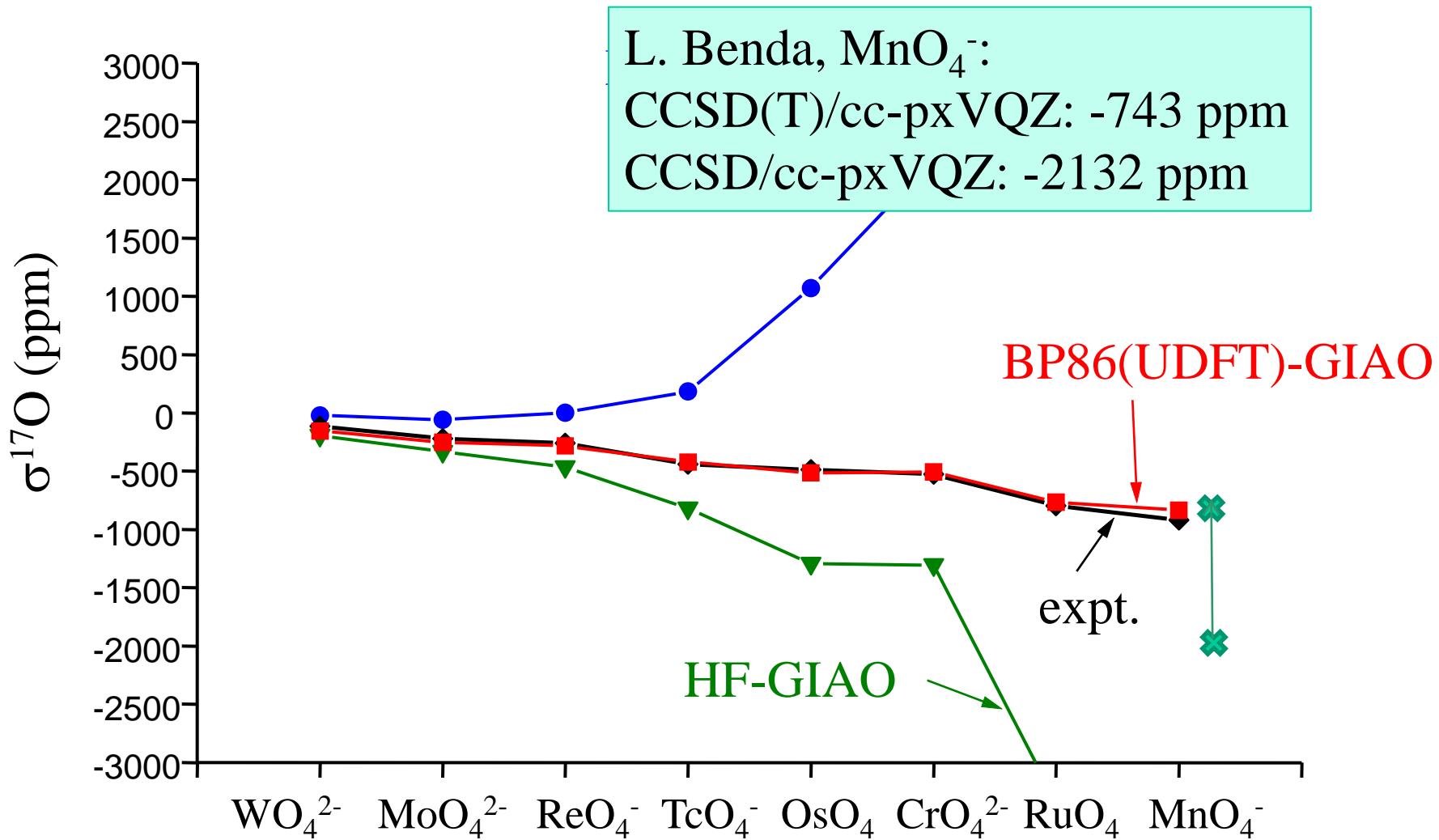
V. G. Malkin, O. L. Malkina, L. A. Eriksson, and D. R. Salahub, in *Modern Density Functional Theory: A Tool for Chemistry; Theoretical and Computational Chemistry*, Vol. 2, edited by J. M. Seminario and P. Politzer (Elsevier, Amsterdam, 1995).

DFT computations of transition metal NMR chemical shifts



Review: M. Bühl, in: M. Kaupp, M. Bühl, V. G. Malkin (Eds.), *Calculation of NMR and EPR Parameters. Theory and Applications*, Wiley-VCH, Weinheim, 2004.

Importance of Nondynamical Correlation for Nuclear Shieldings



M.K., O. L. Malkina, V. G. Malkin *J. Chem. Phys.* **1997**, *106*, 9201.

QR-ECP//exp., IGLO-II on oxygen, exptl. shifts converted, UDFT with BP86 functional

A few useful practical details on NMR parameter calculations

- NMR shifts: use GIAOs (or IGLO or) to deal with gauge problem
- flexible basis sets needed for shifts and particularly for couplings (e.g. IGLO-III, tzp,.....). 6-31G* is definitely not good enough!
- MP2 can be best for „moderate“ correlation cases, CCSD or CCSD(T) are the most powerful (and expensive) ab initio methods
- DFT has the best cost/performance ratio and is often stable even in cases of significant nondynamical correlation
- main-group shifts are less critical (GGA after corrections is OK)
TM shifts and spin-spin couplings are typically better reproduced with hybrid functionals

Analyses of the paramagnetic term

Interaction of electronic orbital angular momentum with external magnetic field
(Orbital Zeeman Term).

Interaction of nuclear magnetic dipole with electronic orbital motion (*PSO Term*).

$$\sigma_{p1} = \sum_{n \neq 0} \left\langle \Psi_n \left| \sum_k L_k \right| \Psi_0 \right\rangle \cdot \left\langle \Psi_0 \left| \sum_k L_{kN} \cdot r_{kN}^{-3} \right| \Psi_n \right\rangle + c.c.$$

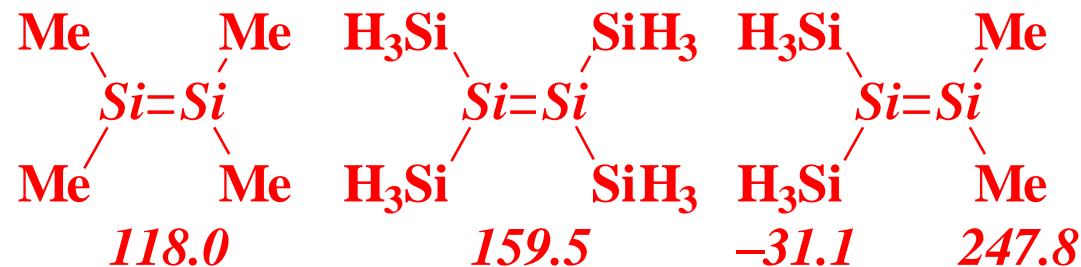
$^1 E_n - E_0$

Sum over all singlet excited states.

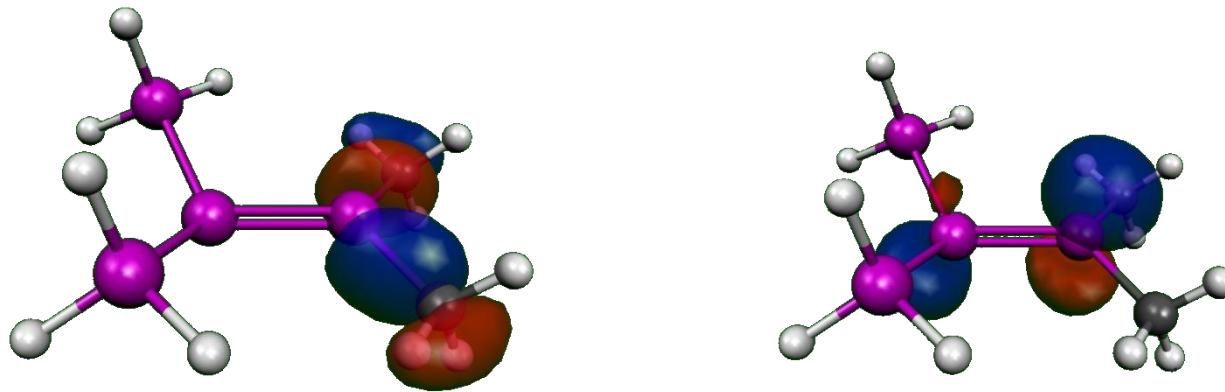
Difference in the energies of excited (n) and ground (0) states.

**Interpretations depend on the choice of gauge and choice of MOs.
Obviously, NMR chemical shifts are not a simple property!**

A Simple Example: Counter-Intuitive ^{29}Si Shifts in Unsymmetrically Substituted Disilenes



- Differences between symmetrical species may be understood from energy denominators.
- But what about the unsymmetrical one?



PSO term couples $\sigma(\text{Si-C})$ and $\pi^*(\text{Si=Si})$ MOs much more strongly for Si2!

„Spin-Orbit Chemical Shifts“

$$\sigma_{N,uv} = \frac{1}{2c^2} \langle 0 | \sum_i \frac{(\mathbf{r}_{iO} \mathbf{r}_{iN}) \delta_{uv} - r_{iO,v} r_{iN,u}}{r_{iN}^3} | 0 \rangle + \frac{1}{2c^2} \left[\sum_{n \neq 0} \frac{\langle 0 | L_{O,v} | n \rangle \cdot \langle n | L_{N,u} \cdot r_{kN}^{-3} | 0 \rangle}{E_0^{-1} E_n} + c.c. \right]$$

σ^d (diamagn. shielding)

σ^p (paramagn. shielding)

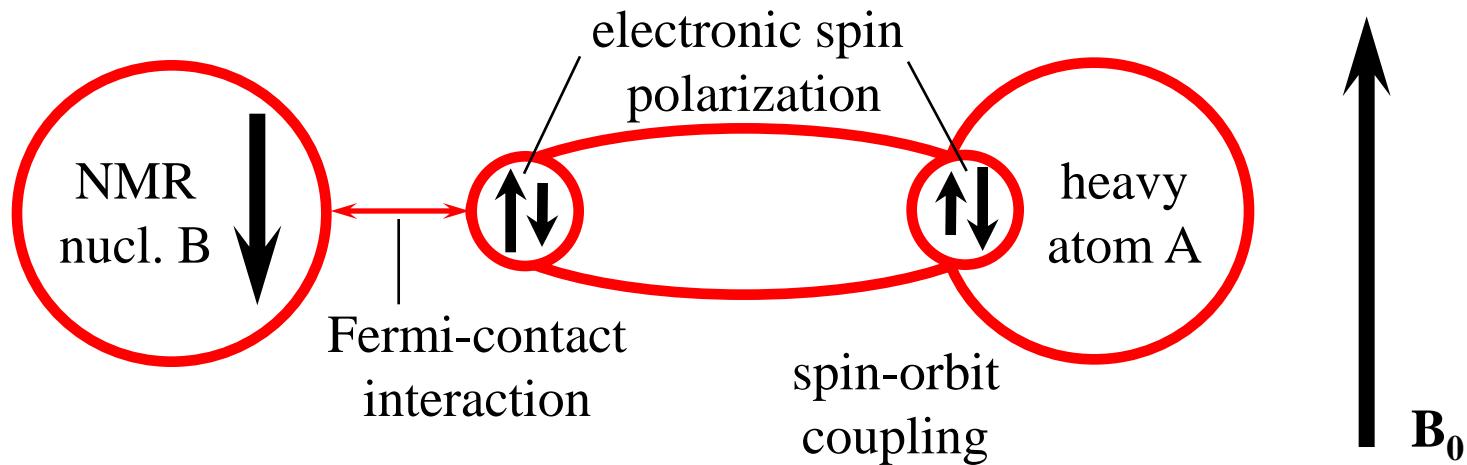
nonrelativistic Ramsey Equation

$$\sigma_{N,uv}^{SO-I} = \frac{\partial^2}{\partial \mu_{N,u} \partial B_{0,v}} \left[\sum_{m,n \neq 0} \frac{\langle 0 | \mathbf{H}^{FC+SD} | \mathbf{m}_T \rangle \langle \mathbf{m}_T | \mathbf{H}^{SO(i)} | \mathbf{n}_s \rangle \langle \mathbf{n}_s | \mathbf{H}^{B_0} | 0 \rangle}{(E_0^{-3} E_m)(E_0^{-1} E_n)} + \text{permutations} \right]$$

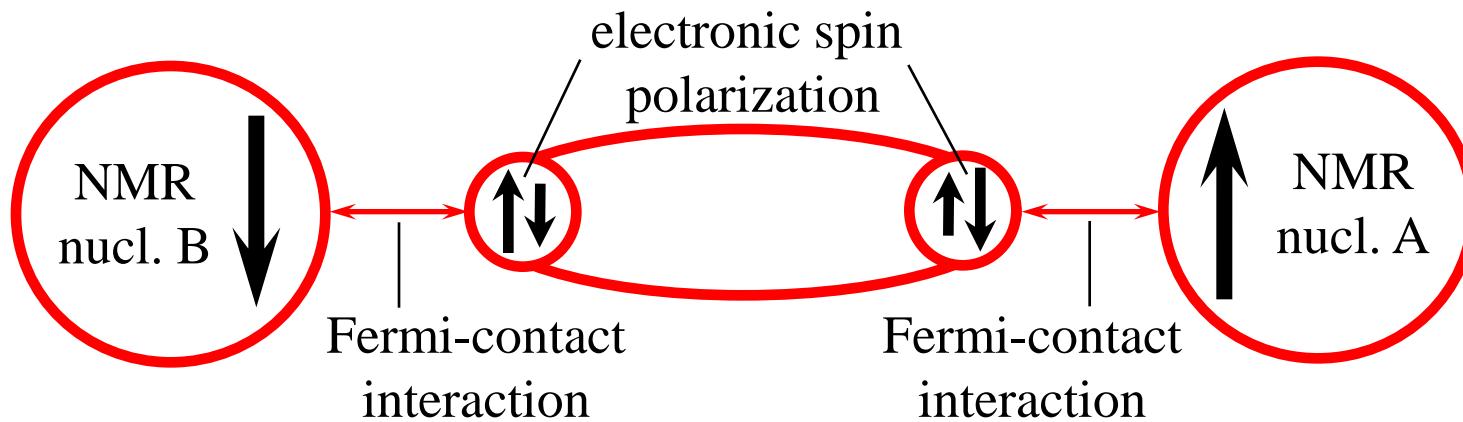
σ^{SO} (third-order spin-orbit corrections)

dominant heavy-atom effect for neighbor atoms

Spin-Orbit Chemical Shifts

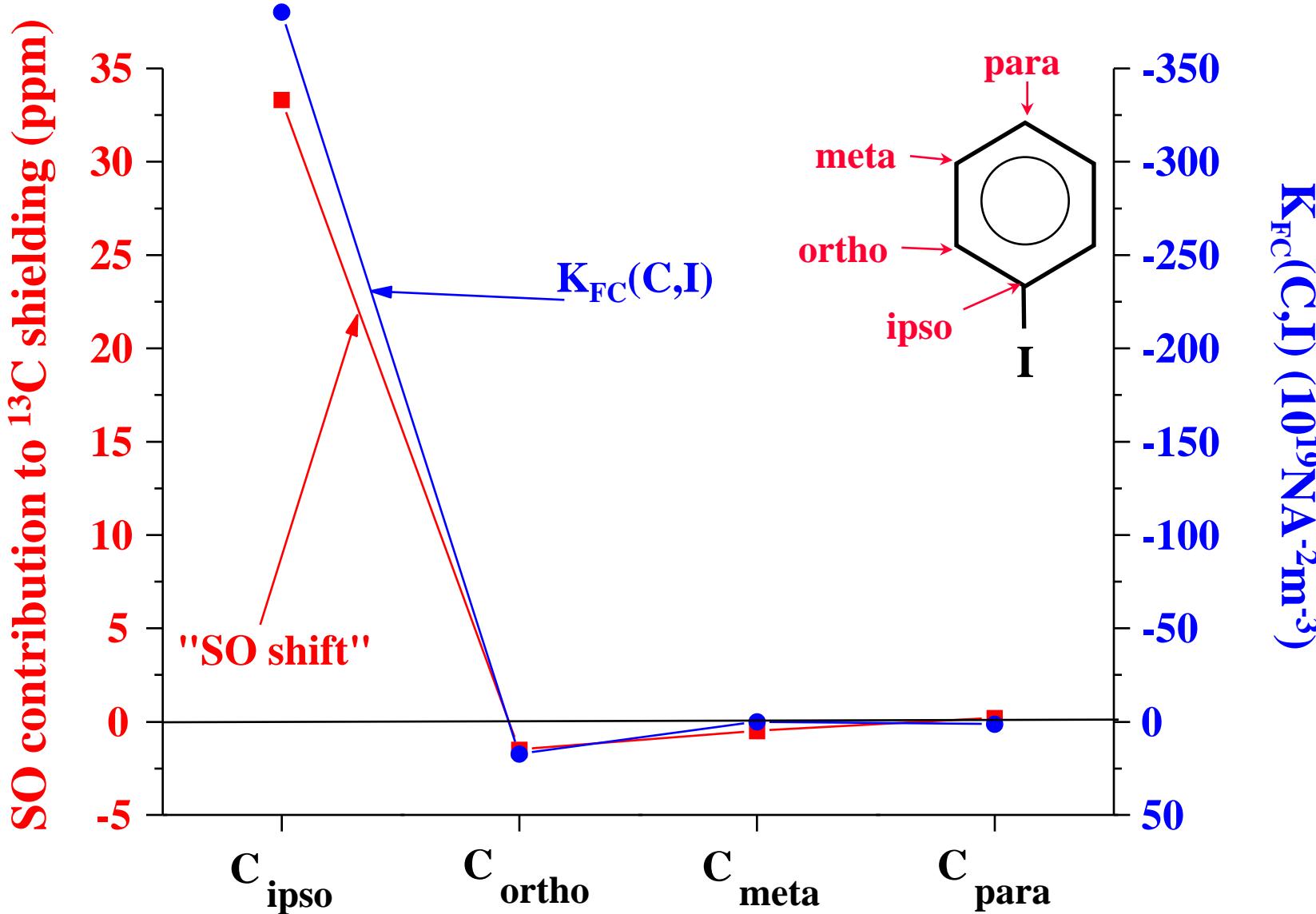


Fermi-Contact Spin-Spin Coupling

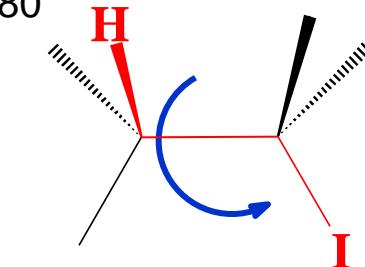
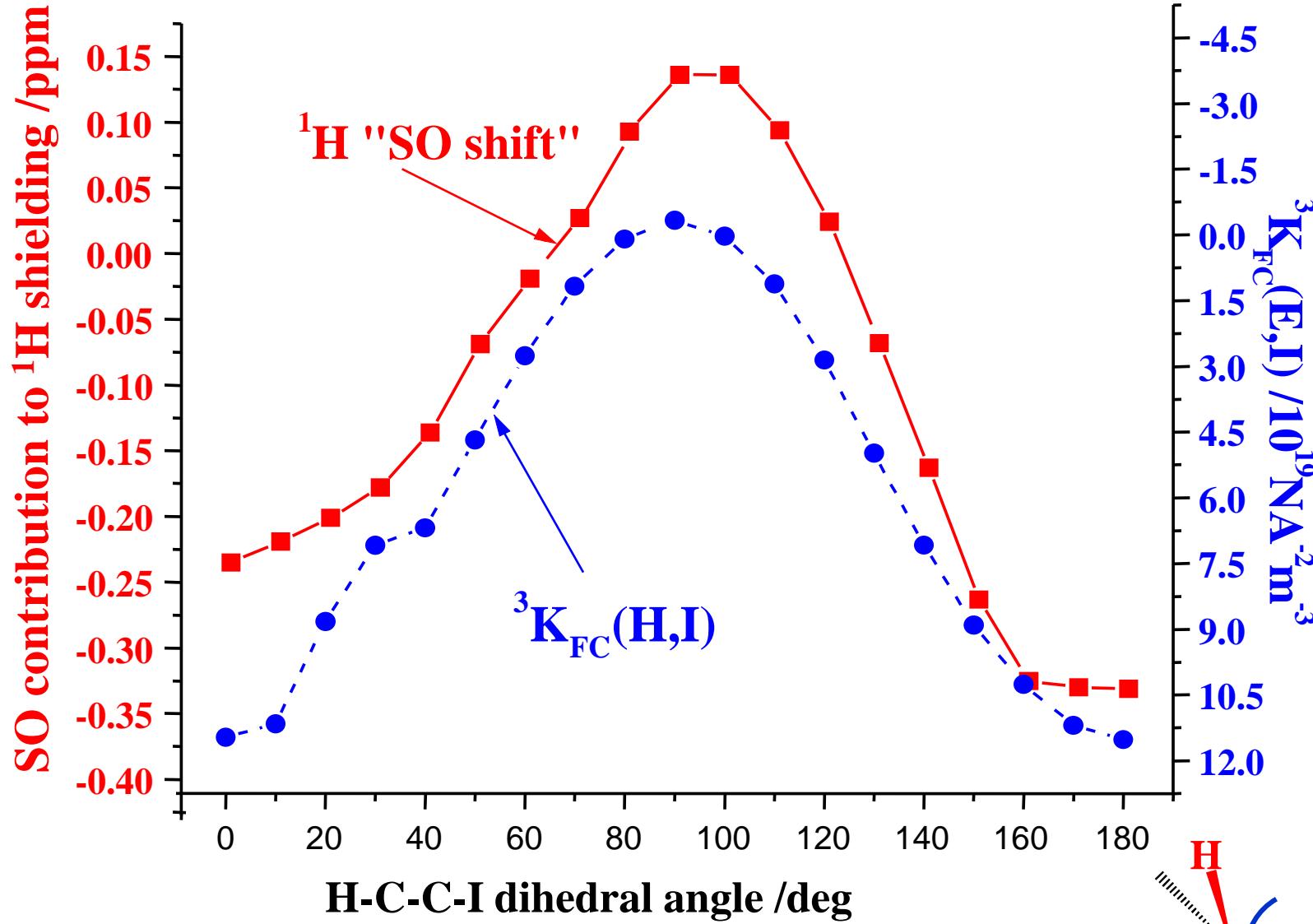


A useful analogy...

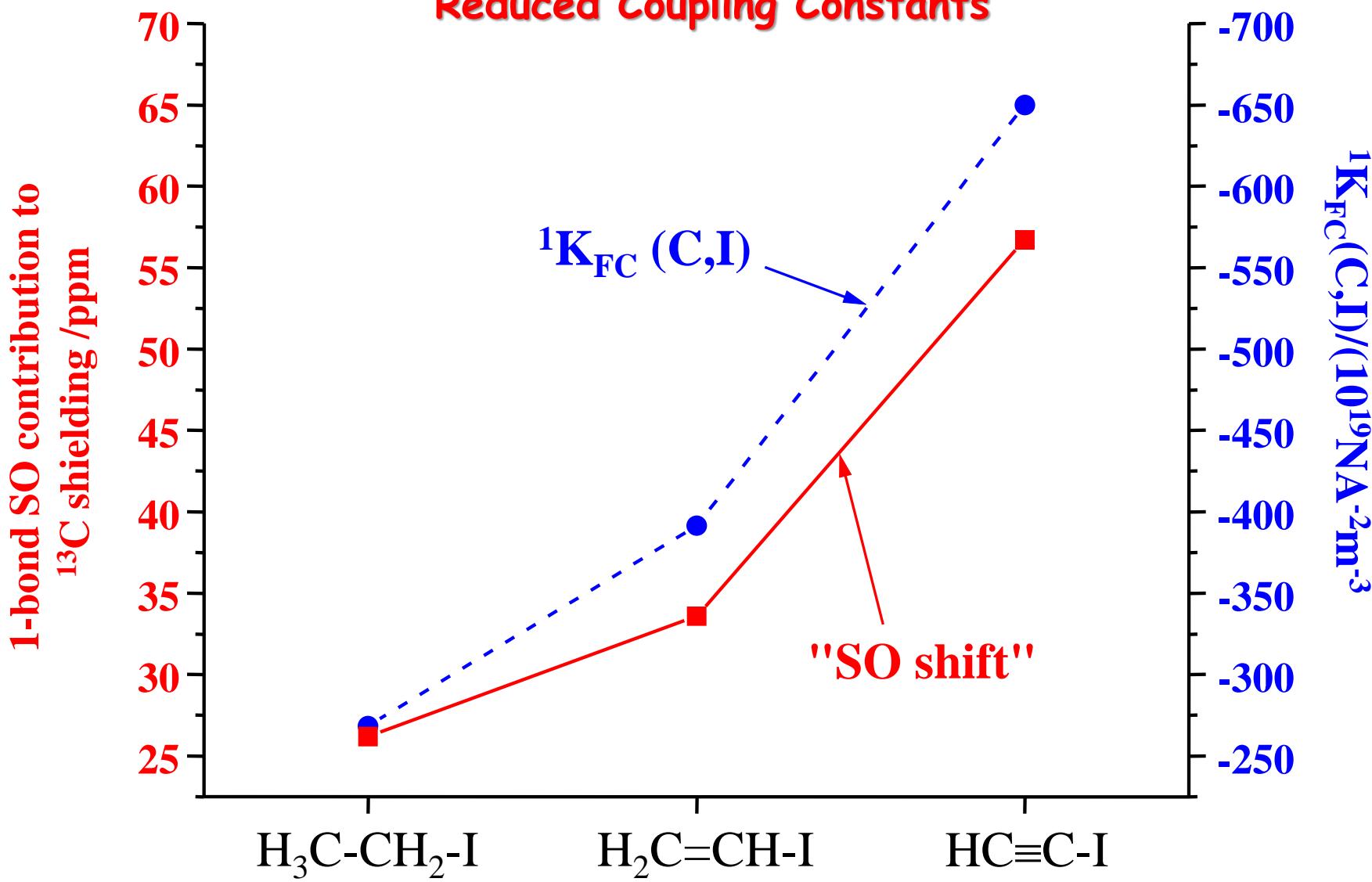
Correlation between ^{13}C "SO Shifts" and Reduced Coupling Constants in $\text{C}_6\text{H}_5\text{I}$



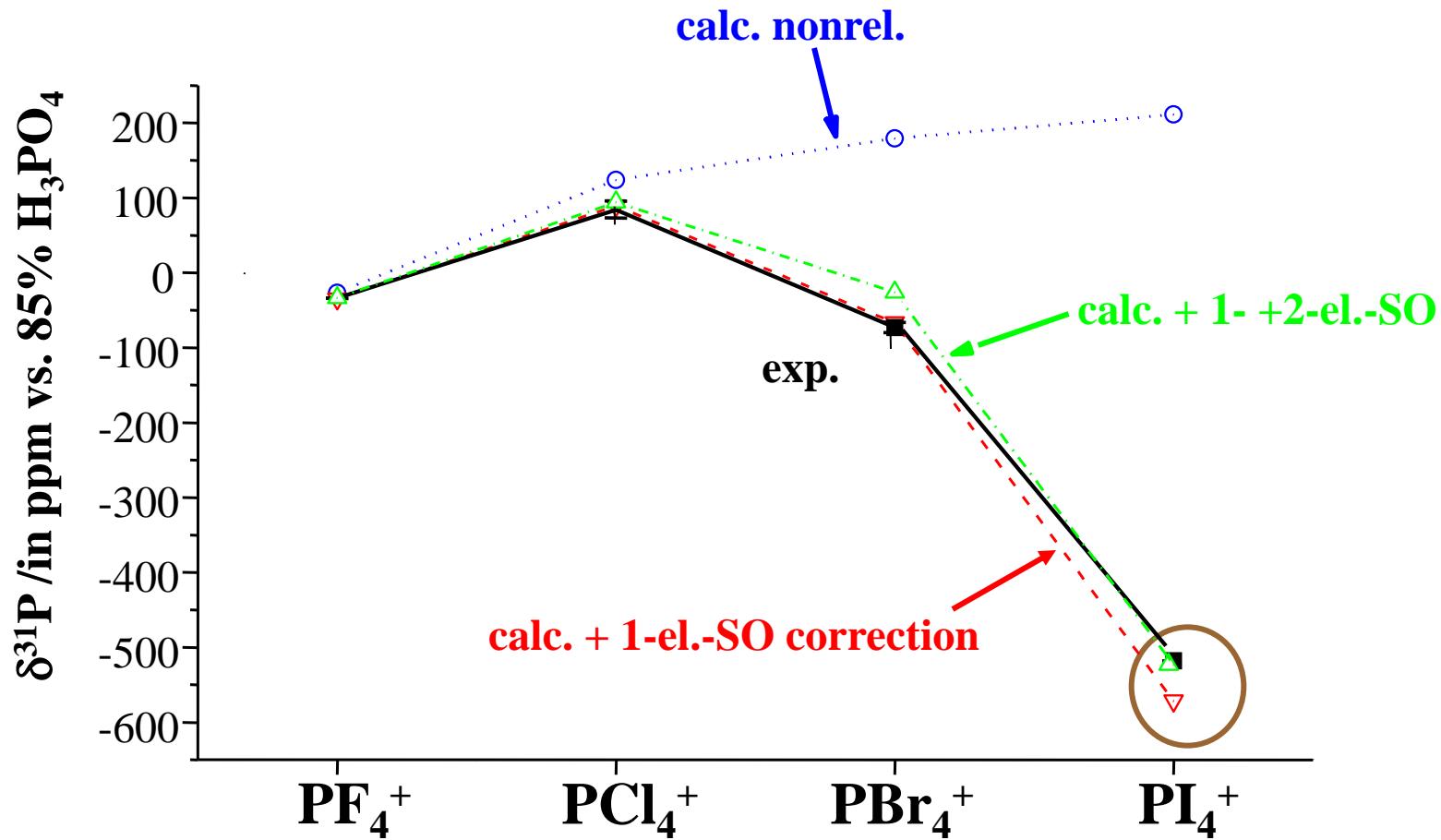
A Karplus-Type Relation for Spin-Orbit Shifts in Iodoethane

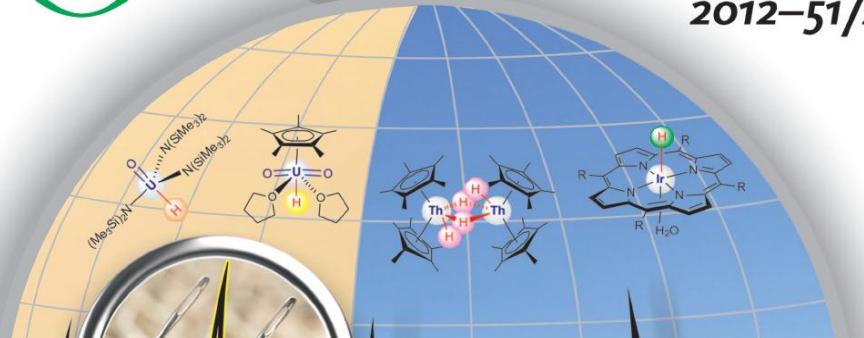


The Role of s-Character for "SO Shifts" and Reduced Coupling Constants



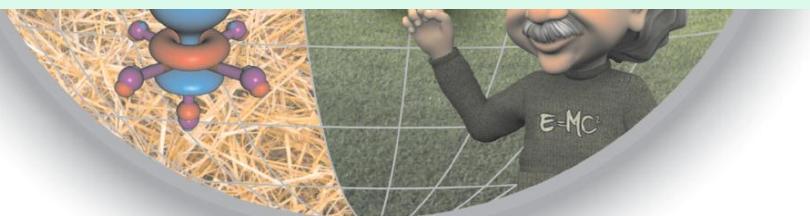
Confirmation of the Extreme High-Field ^{31}P NMR Shift of the PI_4^+ Cation





Possibly, uranium(VI) hydride complexes had been made but were not identified.

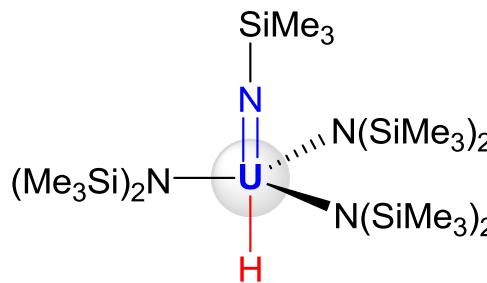
The search is on!



The known ^1H NMR chemical shifts ...

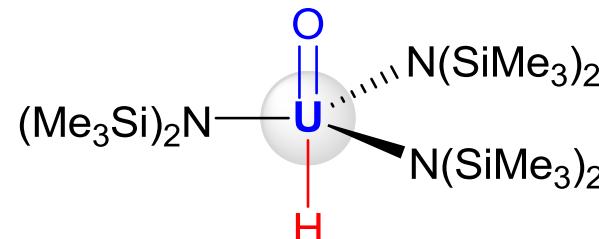
... of diamagnetic compounds so far range from around $\delta = -60$ ppm to about +20 ppm. In their Communication on page 10884 ff., P. Hrobarík, M. Kaupp, et al. predict that, because of giant relativistic spin-orbit effects, the ^1H NMR shifts of the to-date elusive uranium(VI) hydride complexes will be between $\delta = +40$ ppm and more than +150 ppm, a completely unprecedented range. Knowing the correct spectral range to look for should facilitate the characterization of this new compound class.

Predictions of ^1H NMR shifts in valid target hydride complexes



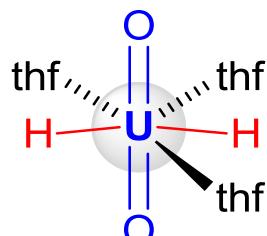
PBEO: 164.8 ppm ($\delta_{\text{so}} 98.0$)

PBEO-40HF: 187.9 ppm ($\delta_{\text{so}} 196.2$)



PBEO: 105.8 ppm ($\delta_{\text{so}} 107.3$)

PBEO-40HF: 125.0 ppm ($\delta_{\text{so}} 155.4$)



PBEO: 100.7 ppm ($\delta_{\text{so}} 90.6$)

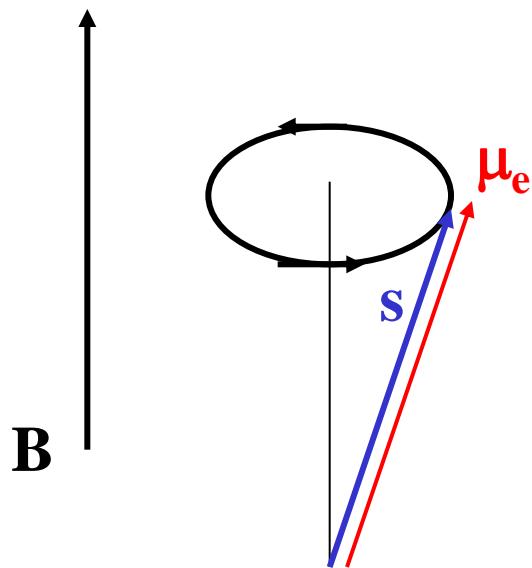
PBEO-40HF: 86.9 ppm ($\delta_{\text{so}} 77.5$)

P. Hrobárik, V. Hrobáriková, A. H. Greif, M. Kaupp
Angew. Chem. Int. Ed. Engl. **2012**, *51*, 10884.

g-Tensors

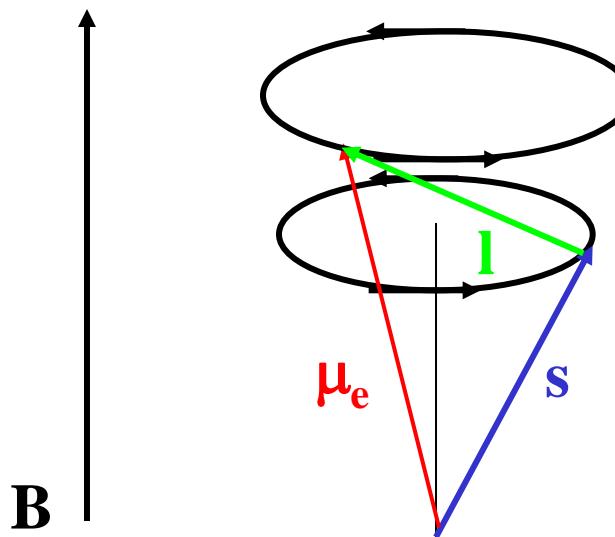
Phenomenological Picture of the g -Tensor: Effective Spin Hamiltonian

free electron:



$$E \sim B g S$$
$$g = 2.002319$$

molecule:



$$E \sim B g S$$

g-matrix

due to
spin-orbit coupling!

experiment:
 $G = g \bullet g'$

g -Tensor: 2nd-Order Perturbation Theory

$$\mathbf{g} = g_e \mathbf{1} + \Delta g$$

$$\Delta g = \Delta g_{SO/OZ} + \Delta g_{GC} + \Delta g_{RMC}$$

$$g_{uv} = \frac{1}{\mu_B} \frac{\partial^2 E}{\partial S_u \partial \mathbf{B}_v} \Big|_{\vec{B}=0, \vec{S}=0}$$

$u, v = x, y, z$

dominant term



$$\Delta g_{SO/OZ,uv} = \frac{g_e \alpha^2}{2S} \left[\sum_n \frac{\langle \Psi_0^{(0)} | H_{SO,v} | \Psi_n^{(0)} \rangle \langle \Psi_n^{(0)} | H_{OZ,u} | \Psi_0^{(0)} \rangle}{E_0^{(0)} - E_n^{(0)}} + c.c \right]$$

spin-orbit operator



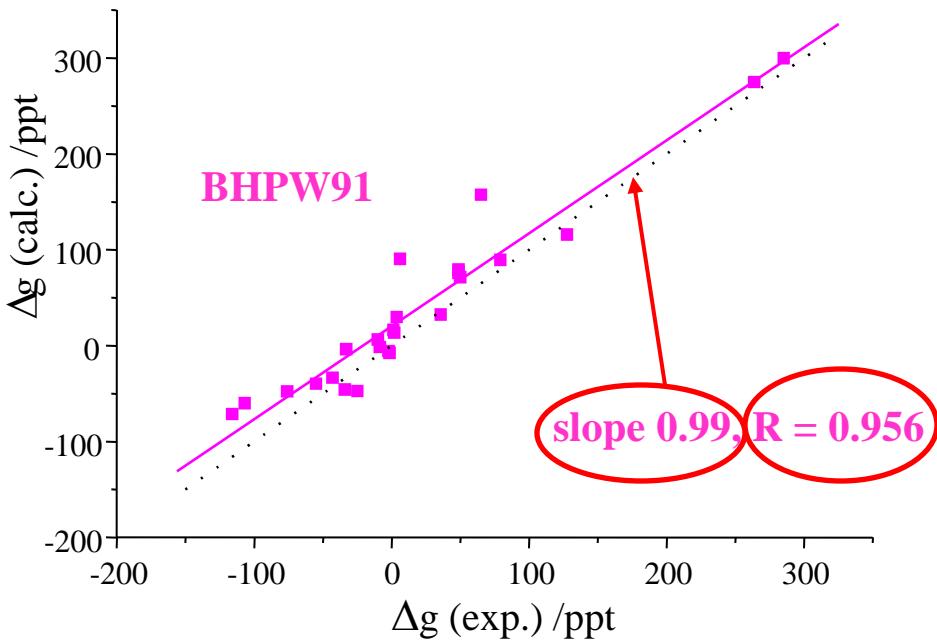
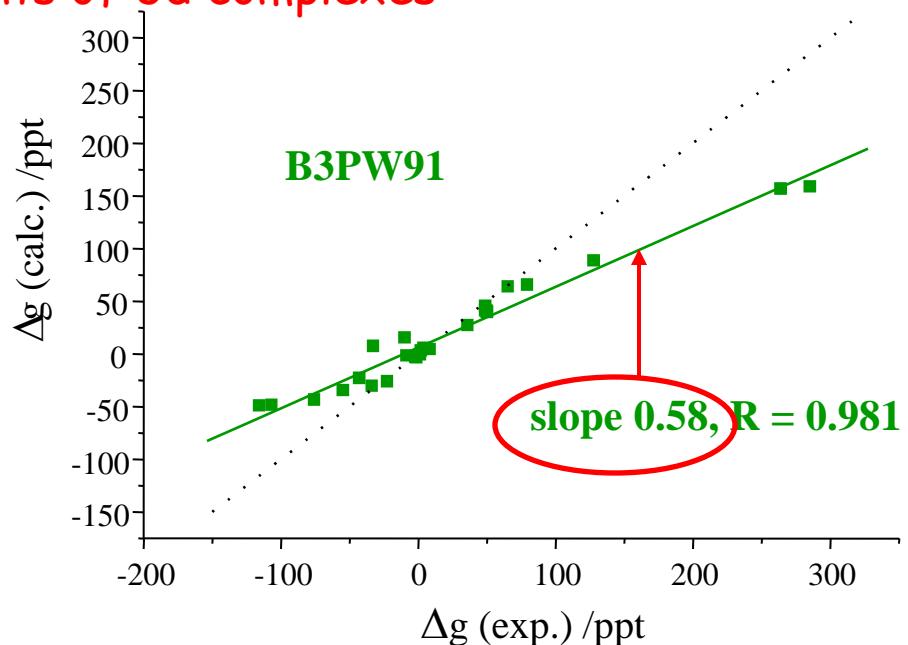
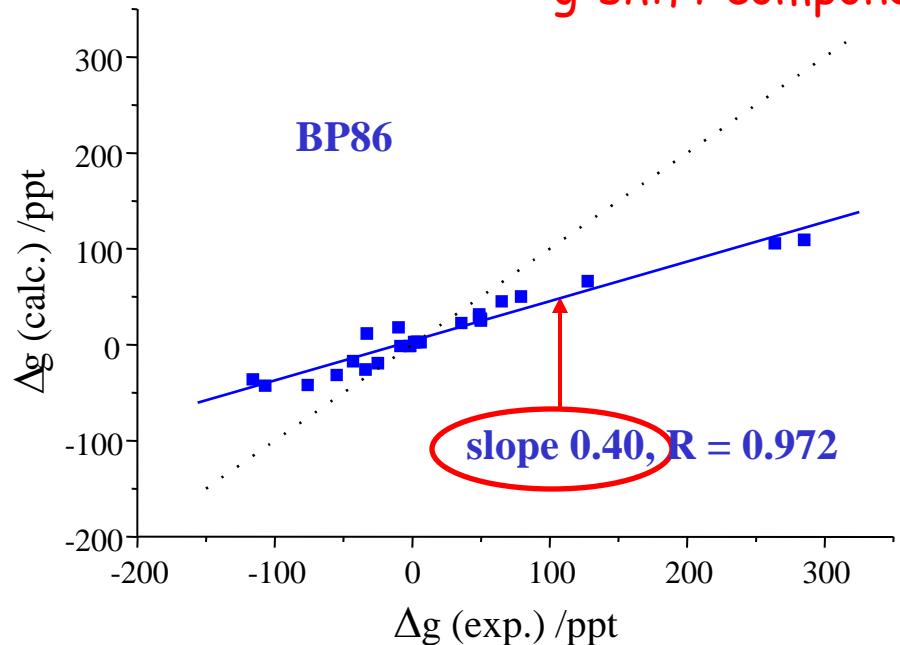
$$\mathbf{H}_{SO,iu} = \frac{\alpha^2}{4} g_e \left(\sum_N \frac{Z_N \mathbf{L}_{iNu}}{\mathbf{r}_{iN}^3} - \sum_{j \neq i} \frac{\mathbf{L}_{ju}^i}{\mathbf{r}_{ij}^3} - 2 \sum_{j \neq i} \frac{\mathbf{L}_{iu}^j}{\mathbf{r}_{ij}^3} \right)$$

$\mathbf{H}_{SO}(1\text{-el.})$

$\mathbf{H}_{SO}(2\text{-el.})$

\mathbf{H}_{SO} (other orbit)

Performance of different functionals in calculating g-shift components of 3d complexes



improved slope by
exact-exchange admixture

but: potential problems
with spin contamination

Hyperfine-Tensors

A-Tensor: The nonrelativistic first-order approximation

isotropic contribution: the Fermi contact term

$$A_{FC}^N = \frac{8\pi}{3} \frac{g_e g_N \beta_e \beta_N}{c^2} \frac{1}{\langle S_z \rangle} \langle 0 | \sum_i [\delta(r_{iN}) s_{iz}] | 0 \rangle$$



difficult: spin density at the nucleus depends frequently on spin polarization

anisotropic contribution: the dipolar term

$$A_{D,uv}^N = \frac{g_e g_N \beta_e \beta_N}{c^2} \frac{1}{\langle S_z \rangle} \langle 0 | \sum_i \frac{\delta_{uv}(r_{iN}) - 3(r_{iN})_u 3(r_{iN})_v}{r_{iN}^5} s_{iz} | 0 \rangle$$

easier: less dependent on spin polarization

A-Tensor: 2nd-Order Spin-Orbit Effects

$$A_{N,uv} = \frac{\partial^2 E}{\partial I_{N,u} \partial S_v} \Big|_{I_N=0, \vec{S}=0} \quad u, v = x, y, z$$

$$A^N = A_{FC}^N + A_D^N + A_{HC-SO}^N + A_{SO/PSO}^N$$

dominant second-order term (SO/PSO cross term):

$$A_{SO/PSO,uv}^N = \frac{2e g_e g_N \beta_e^2 \beta_N}{m k_0^2 c^4 \hbar} \frac{1}{\langle S_z \rangle} \sum_n \left\{ \frac{\langle 0 | \sum_i H_{SO(1+2e)} | n \rangle \langle n | H_{PSO}^N | 0 \rangle}{E_0 - E_n} + c.c. \right\}$$

contributions to:

- A_{iso} (pseudocontact Term)
- A_{dip} (second-order anisotropy)
- A_{anti} (antisymmetric Tensor)

an accurate treatment of
spin-orbit operators is
mandatory!

Hyperfine Coupling Constants in Transition Metal Complexes

-performance of density functionals for metal HFCCs

-analysis of the problems

-mechanisms of spin polarization:
core-shell and valence-shell contributions

-valence-shell spin polarization: spin contamination

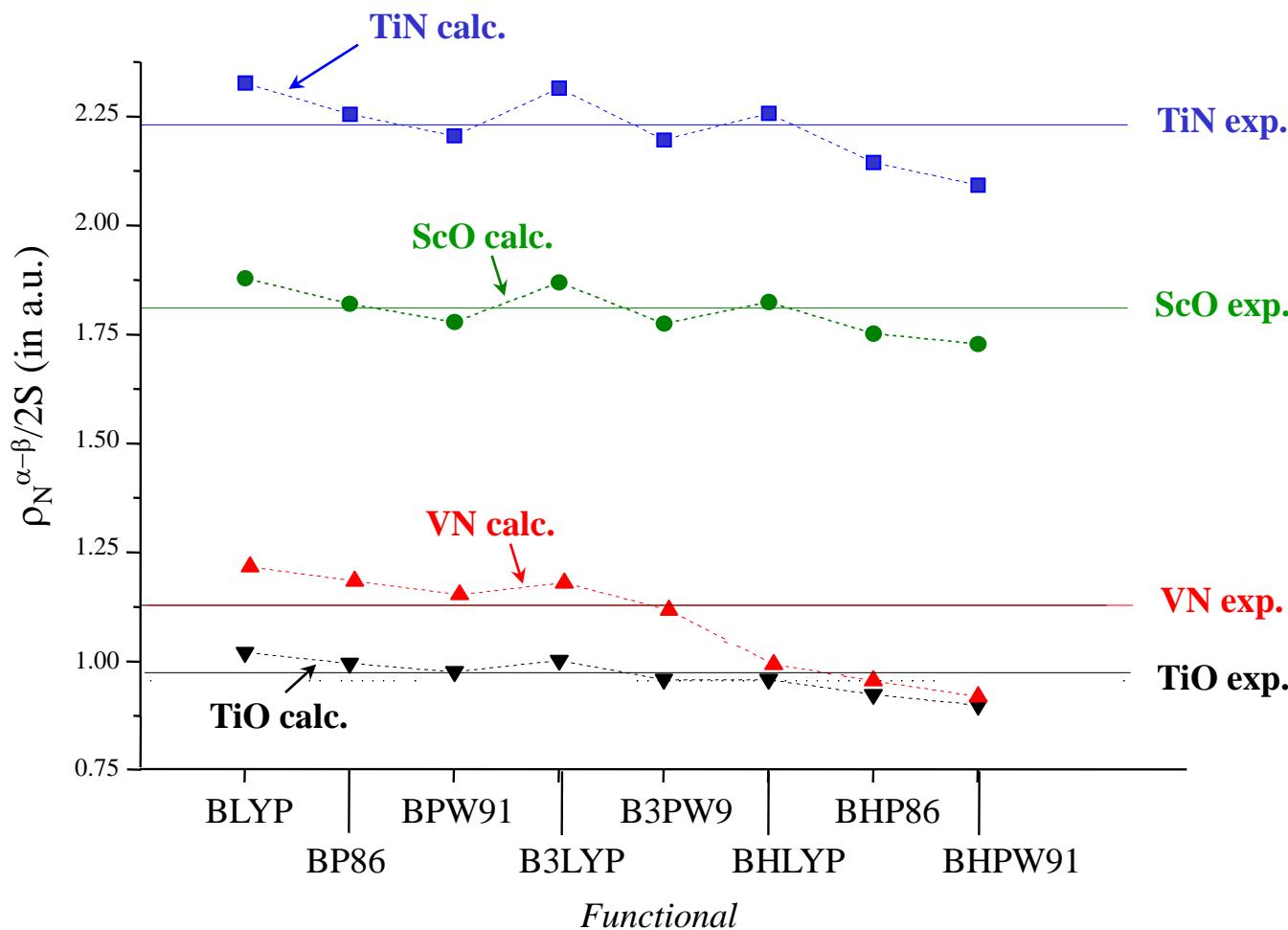
M. Munzarová, M. Kaupp *J. Phys. Chem. A* **1999**, *103*, 9966.

M. Munzarová, Pavel Kubáček, M. Kaupp *J. Am. Chem. Soc.* **2000**, *122*, 11900.

-spin-orbit contributions

C. Remenyi, A. V. Arbuznikov, R. Reviakine, J. Vaara, M. Kaupp *J. Phys. Chem. A* **2004**, *108*, 5026.
A. V. Arbuznikov, J. Vaara, M. Kaupp *J. Chem. Phys.* **2004**, *120*, 2127.

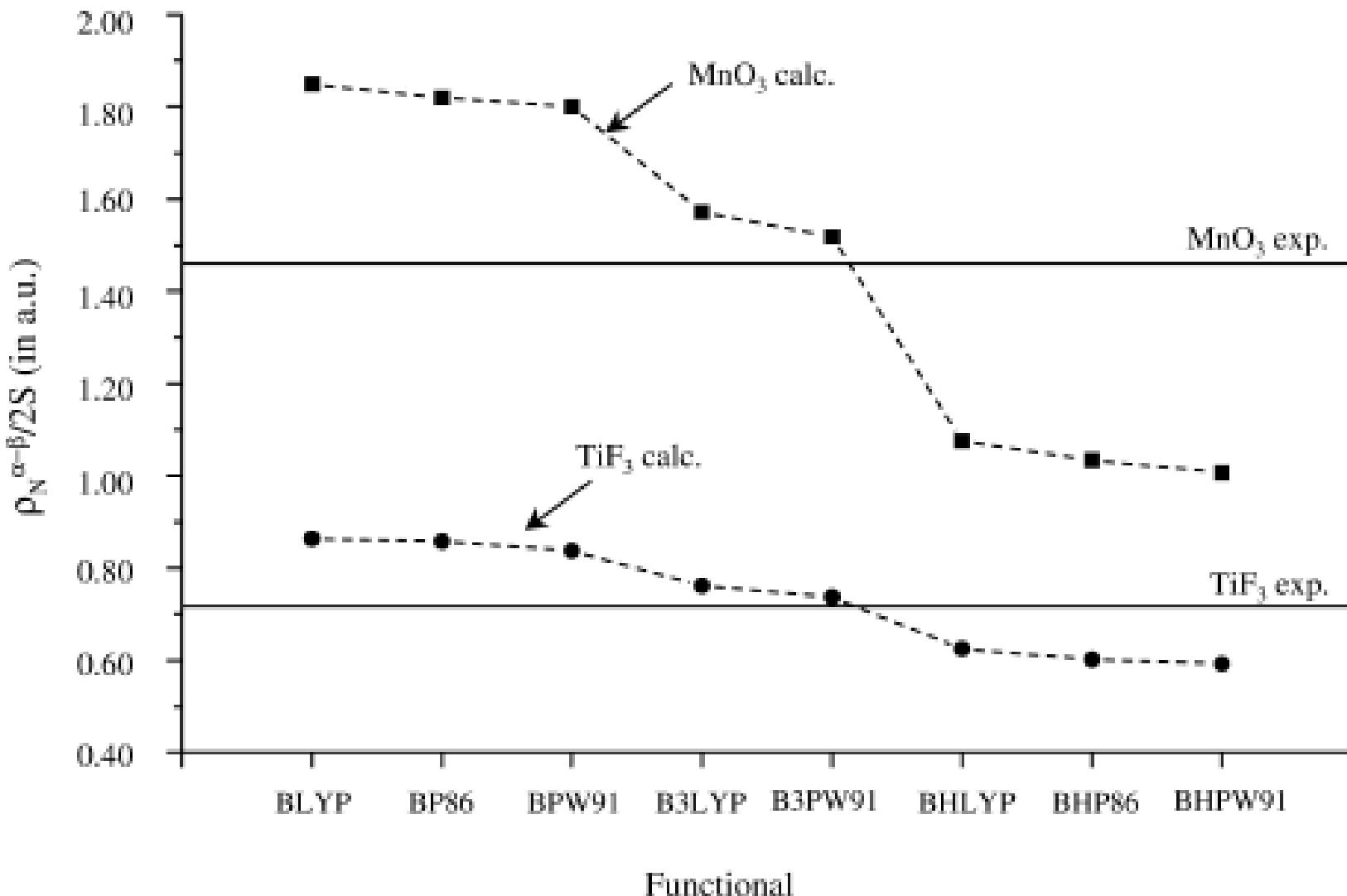
Performance of DFT for the calculation of isotropic hyperfine coupling constants



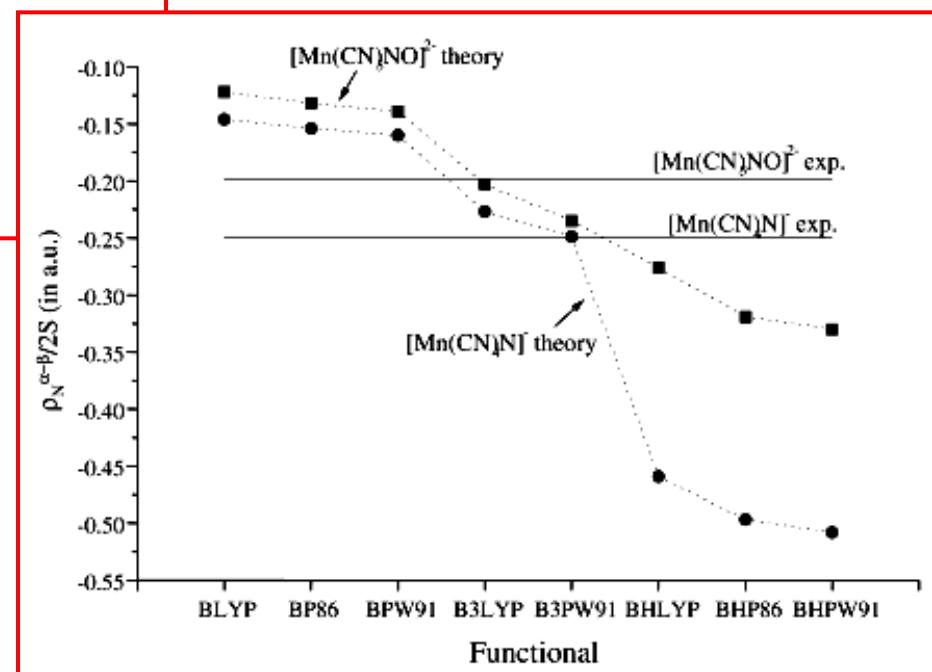
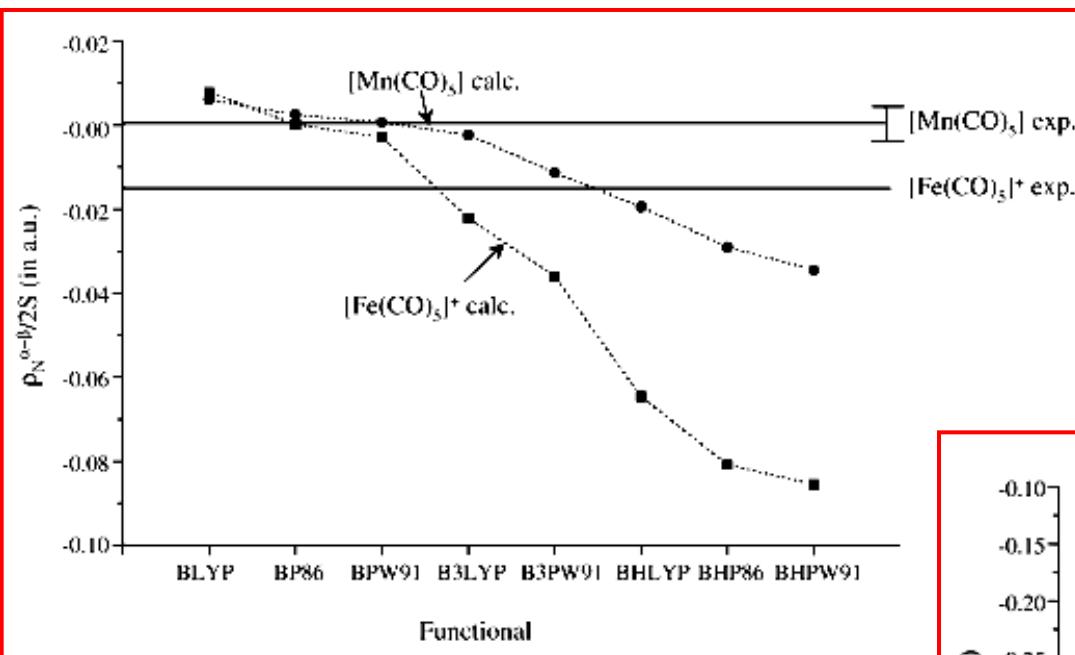
Spin density $\rho_{N}^{\alpha-\beta}$ at the metal nuclei, normalized to the number of unpaired electrons.

M. Munzarová, M. Kaupp *J. Phys. Chem. A* 1999, 103, 9966.

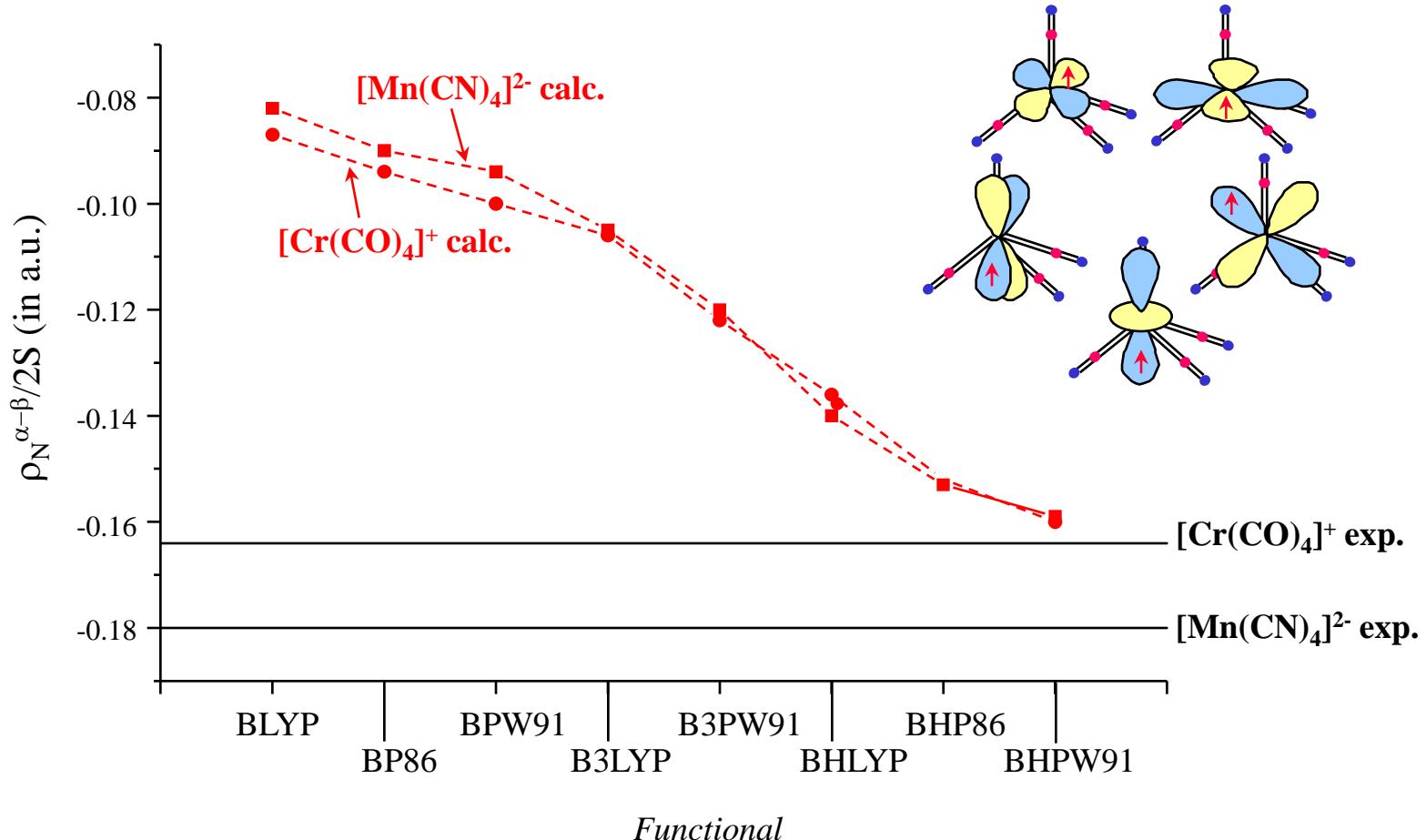
Performance of DFT for the calculation of isotropic hyperfine coupling constants



Performance of DFT for the Calculation of Hyperfine Coupling Constants: Effect of Spin Contamination



Performance of DFT for the calculation of isotropic hyperfine coupling constants



Spin density $\rho_N^{\alpha-\beta}$ at the metal nuclei, normalized to the number of unpaired electrons.

M. Munzarová, M. Kaupp *J. Phys. Chem. A* **1999**, *103*, 9966.

core-shell spin polarization dominates, no problem with spin contamination!

Spin Polarization in Transition Metal Ions

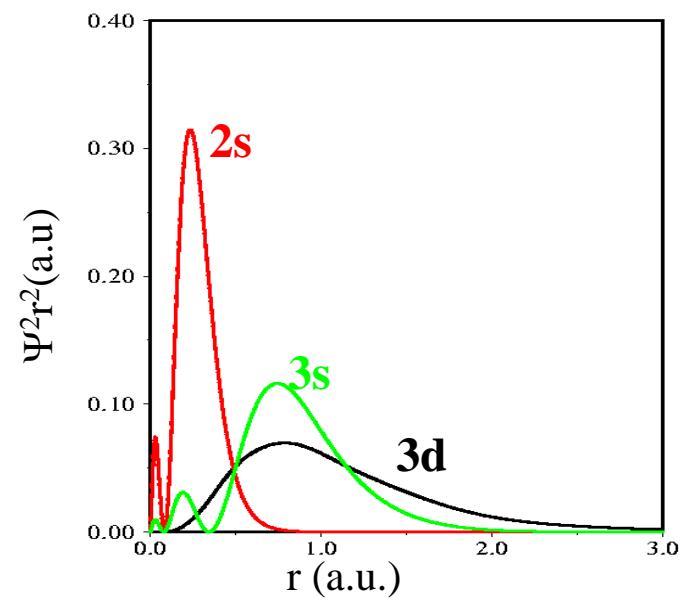
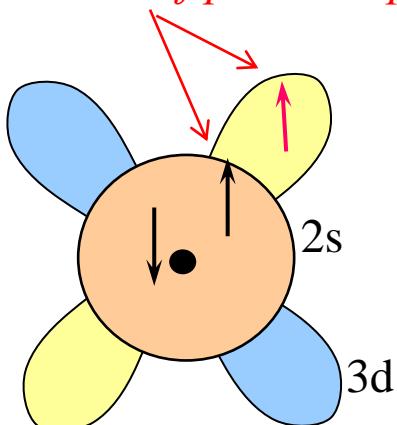
Watson and Freeman 1961:

- negative spin density at the nucleus.
- negative 2s-contribution larger than positive 3s-contribution

Theoretical Contact-Term $\rho^{\alpha-\beta}$ and Individual s-Shell contributions

Ion	Mn ²⁺ (3d ⁵)	Fe ³⁺ (3d ⁵)	Fe ²⁺ (3d ⁶)	Ni ²⁺ (3d ⁸)
$\rho^{\alpha-\beta}$ (a.u.)	-3.34	-3.00	-3.29	-3.94
1s-Shell contribution to $\rho^{\alpha-\beta}$	-0.16	-0.25	-0.21	-0.27
2s-Shell contribution to $\rho^{\alpha-\beta}$	-6.73	-8.51	-7.80	-9.62
3s-Shell contribution to $\rho^{\alpha-\beta}$	+3.55	+5.77	+4.72	5.95

*exchange interaction -
„attraction of parallel spins“*



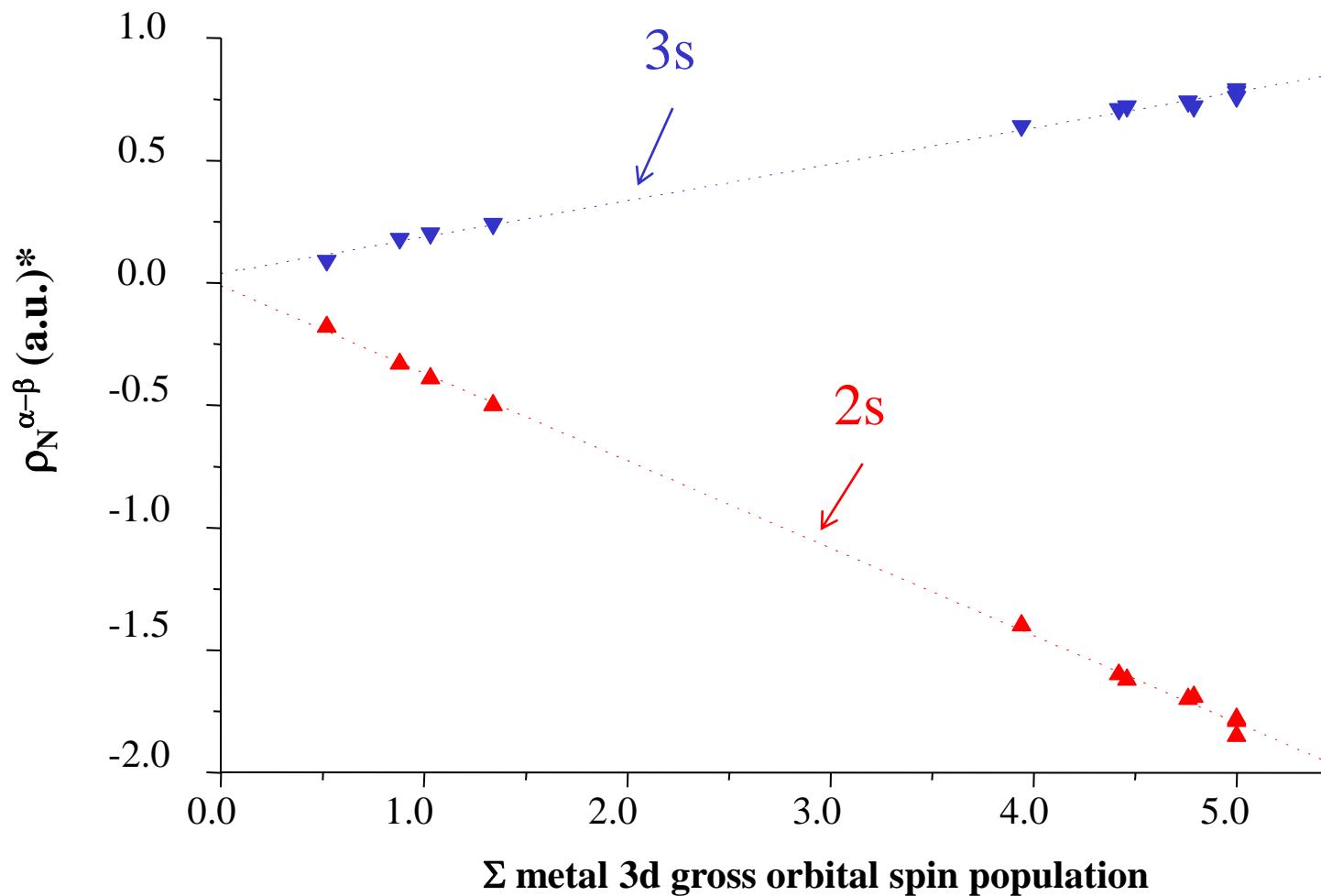
Analysis of Spin Polarization in Manganese Complexes

Contributions to Isotropic hyperfine coupling constants (A_{iso} , in MHz)^a

complex	1σ	2σ	3σ	valence	SOMO(s)	total	Expt.
² [Mn(CO) ₅]	15.5	-262.8	135.8	60.7	61.8	-12.1	-2.8... 5.6
² [Mn(CN) ₄ N] ⁻	0.0	-474.7	247.3	22.1	0.0	-275.0	-276
⁶ MnO	3.0	-362.9	184.5	-141.5	824.9	507.5	479.8
⁶ MnF ₂	0.0	-406.3	194.3	-86.2	512.3	214.1	104... 134
⁶ [Mn(CN) ₄] ²⁻	-9.1	-407.2	187.9	94.7	0.0	-132.0	-199
⁶ Mn ⁰	-6.0	-433.0	196.7	208.0	0.0	-31.4	-72.4
⁶ Mn ²⁺	-6.2	-450.4	197.0	0.0	0.0	-260.0	-273...-168
⁷ MnH	-2.6	-347.8	163.6	-194.9	709.3	329.6	279.4
⁷ MnF	2.4	-347.8	169.1	-44.9	666.1	443.6	442
⁷ Mn ⁺	7.5	-358.4	173.7	0.0	936.2	759.2	757.8

^aB3PW91 results using standard metal 9s7p4d basis.

Core-Shell Spin-Polarization Contributions in Different Manganese Complexes are Proportional to the 3d Spin Population!



*normalized spin density at the metal nucleus

M. Munzarová, Pavel Kubáček, M. Kaupp *J. Am. Chem. Soc.* **2000**, *122*, 11900.

Zero-Field Splitting

Zero-Field Splitting

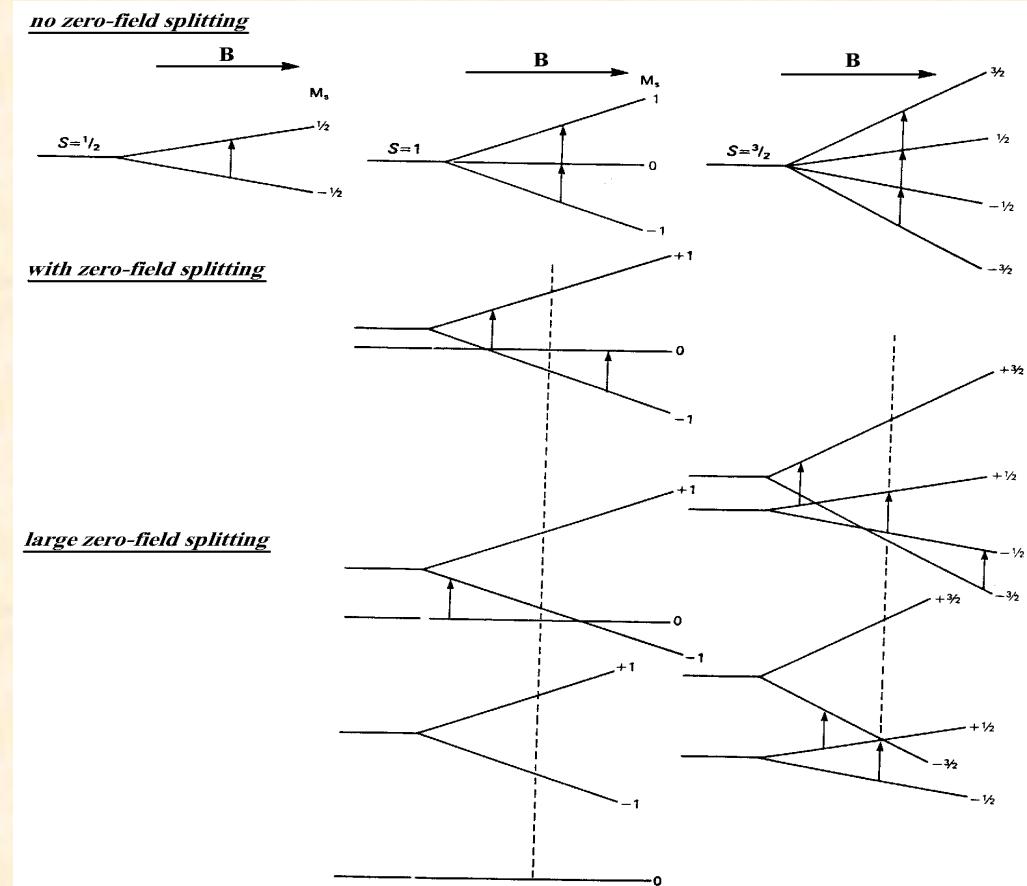
For $S > \frac{1}{2}$, already in the absence of magnetic field, $2S + 1$ energy states split, due to:

- a) spin-orbit coupling (dominant for transition-metal systems)
 - b) spin-spin coupling (dominant for organic radicals)
- ⇒ fine structure in spectra

$$H_{\text{ZFS}} = D \left[S_z^2 - \frac{1}{3} S(S+1) \right] + E \left[S_x^2 - S_y^2 \right]$$

$$D = D_{zz} - \frac{1}{2}(D_{xx} + D_{yy}); \quad E = \frac{1}{2}(D_{xx} - D_{yy})$$

For pNMR this affects the Boltzmann distribution of occupied energy levels.



Thank you!