

Dear Mrs. [REDACTED],

April 20th, 1994

You may already know this, but in case Alex has neglected to tell you, I am assigning him to detention for one hour this Friday, April 22nd. The reason is as follows:

Alex consistently defied me. During class he contradicted me numerous times when I insisted that the length of one kilometer was greater than that of one mile. Every other student in class accepted my lesson without argument, but your son refused to believe what I told him, offering such rebuttals as, "You're lying to the class," and commanding other students to challenge my curriculum.

Although he was correct, Alex's actions show a blatant disregard for authority, and a complete lack of respect for his school. In the future, Alex would be better off simply accepting my teachings without resistance.

Please see to it that your son understands this.

Regards,
Adam Hilliker

"TO DO IS TO BE" – SOCRATES

"TO BE IS TO DO" – SARTRE

"OO BE DO BE DO" – SINATRA

Practical Quantum Chemistry, L9: Magnetic properties, part B

*electromagnetic gauges, gauge-including atomic orbitals,
nuclear quadrupole interaction, J-coupling, g-tensor*

Prof Ilya Kuprov, Weizmann Institute of Science, 2025

For all lecture notes and video records see <https://spindynamics.org>

A closer look at gauge transformations

For non-relativistic electrons in a static external electromagnetic field in atomic units ($m=1$, $e=-1$), the Hamiltonian is:

$$\hat{H} = \frac{1}{2} \sum_k \left[\hat{\mathbf{p}}_k - \frac{1}{c} \mathbf{A}(\mathbf{r}_k) \right]^2 + V(\{\mathbf{r}_k\})$$

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

$$\nabla \times \nabla = 0$$

There is therefore a liberty in the choice of $\mathbf{A}$ here:

$$\mathbf{A}_{\text{G1}}(\mathbf{r}) \xrightarrow{\text{Gauge 1}} \mathbf{A}_{\text{G2}}(\mathbf{r}) = \mathbf{A}_{\text{G1}}(\mathbf{r}) + \nabla \Lambda(\mathbf{r}) \xleftarrow{\text{any well behaved function}}$$

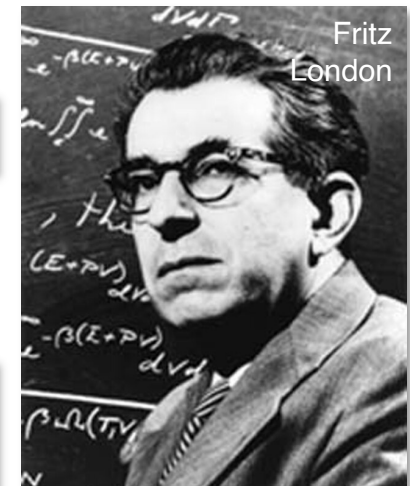
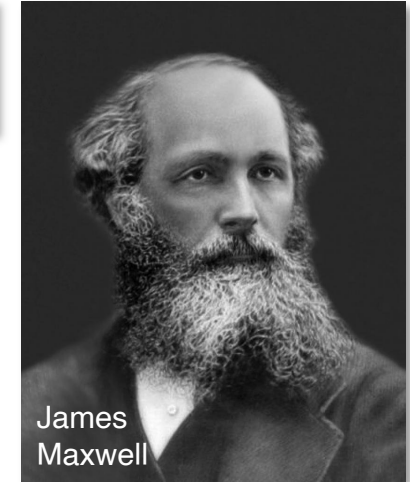
Skipping the voluminous math; it may be demonstrated that:

$$\Psi_{\text{G1}}(\{\mathbf{r}_k\}) \rightarrow \Psi_{\text{G2}}(\{\mathbf{r}_k\}) = \exp \left[-\frac{i}{c} \sum_k \Lambda(\mathbf{r}_k) \right] \Psi_{\text{G1}}(\{\mathbf{r}_k\})$$

Conclusion: *changing the gauge is equivalent to multiplying the wavefunction by a position-dependent phase factor.*

Physics does not change:

$$\langle \psi_{\text{G1}}(\mathbf{r}) | \hat{O} | \psi_{\text{G1}}(\mathbf{r}) \rangle = \langle \psi_{\text{G2}}(\mathbf{r}) | \hat{O} | \psi_{\text{G2}}(\mathbf{r}) \rangle, \quad |\psi_{\text{G1}}(\mathbf{r})|^2 = |\psi_{\text{G2}}(\mathbf{r})|^2$$



► **Unfortunate side effect:** this gauge invariance is broken with incomplete atom-centred basis sets.

Gauge-including atomic orbitals (GIAOs)

When the gauge origin of a uniform field is moved:

$$\mathbf{A}_{\text{G1}}(\mathbf{r}) = \frac{1}{2} \mathbf{B} \times (\mathbf{r} - \mathbf{r}_0^{\text{G1}}), \quad \mathbf{A}_{\text{G2}}(\mathbf{r}) = \frac{1}{2} \mathbf{B} \times (\mathbf{r} - \mathbf{r}_0^{\text{G2}})$$

The gauge term whose gradient is the difference:

$$\Lambda(\mathbf{r}) = \frac{1}{2} \mathbf{B} \times (\mathbf{r}_{\text{G1}} - \mathbf{r}_{\text{G2}}) \cdot \mathbf{r} = \frac{1}{2} \mathbf{B} \cdot [(\mathbf{r}_{\text{G1}} - \mathbf{r}_{\text{G2}}) \times \mathbf{r}]$$

What is wanted is each atomic orbital having no extra phase in its local gauge:

$$\chi_{\mu}(\mathbf{r}) = \varphi_{\mu}(\mathbf{r} - \mathbf{r}_{\mu})$$

where $\mathbf{r}_{\mu}$ is the location of the nucleus.

Therefore, for a one-electron orbital centred at $\mathbf{r}_{\mu}$, the following fits the bill:

$$\chi_{\mu}^{\text{GIAO}}(\mathbf{r}) = \exp\left(-\frac{i}{2c} \mathbf{B} \cdot [\mathbf{r}_{\mu} \times \mathbf{r}]\right) \varphi_{\mu}(\mathbf{r} - \mathbf{r}_{\mu})$$

↑
gauge-including atomic orbitals
(GIAOs, London orbitals)

These phase terms cancel exactly in all expectation values, meaning that *calculations with incomplete basis sets become gauge-invariant*.



Gauge-including atomic orbitals (GIAOs)

GIAOs have had many predecessors trying to solve the same problem:

TABLE 1: Classification of Computational Magnetic Shielding Techniques

	method	technique	performance comments
class I	SGO ^a	gauge origin taken as the molecular origin	relatively poor performance unless Hartree–Fock basis set limit considered
class II	CSGT ^b	gauge continuously transformed back to the reference	superior to SGO methods, although still requires adequate basis set functionality. CSGT and IGAIM perform identically in most cases.
	IGAIM ^c	gauge origin taken as the basin of charge density within bonds	
class III	IGLO ^d	partition shielding into parts related to specific spatial regions of the molecule	significant improvements over class I and II methods, with reasonable computational effort required
	LORG ^e		
	GIAO ^f	complex exponential dependence on the part of the vector potential arising from the external uniform magnetic field	efficient in terms of convergence of chemical shift values as a function of basis set. Allows reliable values with relatively smaller basis sets.

For chemical shielding tensors, all other methods are usually a bad choice:

TABLE 4: Correlation Parameters (Slope, Intercept, and R^2) for Alternative Computational Methods^a

method	intercept (b)		slope (m)		R^2 factor	
	SGO	CSGT	SGO	CSGT	SGO	CSGT
RHF/3-21G	5.17	21.50	−0.1682	−0.6567	0.8113	0.6591
RHF/6-31G	5.03	22.98	−0.1668	−0.7151	0.8069	0.6790
RHF/6-31G(d)	7.52	31.56	−0.2697	−1.025	0.7778	0.8281
RHF/6-311G(d,p)	14.68	32.21	−0.4647	−1.028	0.9229	0.9800
B3PW91/cc-pVDZ	9.97	33.18	−0.3242	−1.100	0.8802	0.9794
B3PW91/aug-cc-pVTZ	16.55	29.31	−0.5368	−0.9240	0.9479	0.9984

Back to Hellmann-Feynman theorem

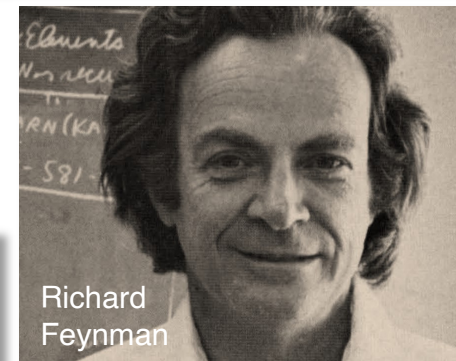
The derivative of the energy with respect to a parameter α is:

$$\begin{aligned}
 \frac{\partial E_n}{\partial \alpha} &= \frac{\partial}{\partial \alpha} \langle \Psi_n | \hat{H} | \Psi_n \rangle = \overbrace{\left\langle \frac{\partial \Psi_n}{\partial \alpha} \middle| \hat{H} | \Psi_n \right\rangle + \left\langle \Psi_n \middle| \frac{\partial \hat{H}}{\partial \alpha} | \Psi_n \right\rangle + \left\langle \Psi_n | \hat{H} \middle| \frac{\partial \Psi_n}{\partial \alpha} \right\rangle}^{\text{product rule}} = \\
 &= \left\langle \Psi_n \middle| \frac{\partial \hat{H}}{\partial \alpha} | \Psi_n \right\rangle + E \underbrace{\left\langle \frac{\partial \Psi_n}{\partial \alpha} \middle| \Psi_n \right\rangle + \left\langle \Psi_n \middle| \frac{\partial \Psi_n}{\partial \alpha} \right\rangle}_{\text{product rule}} = \left\langle \Psi_n \middle| \frac{\partial \hat{H}}{\partial \alpha} | \Psi_n \right\rangle + E \underbrace{\frac{\partial \langle \Psi_n | \Psi_n \rangle}{\partial \alpha}}_{\text{zero}} \\
 \Rightarrow \quad \frac{\partial E_n}{\partial \alpha} &= \left\langle \Psi_n \middle| \frac{\partial \hat{H}}{\partial \alpha} | \Psi_n \right\rangle \quad \leftarrow \text{Hellmann-Feynman theorem}
 \end{aligned}$$

The second derivative version also exists (much longer derivation):

$$\frac{\partial^2 E_n}{\partial \alpha \partial \beta} = \langle \Psi_n | \hat{H}_{\alpha\beta}'' | \Psi_n \rangle + \sum_{k \neq n} \frac{\langle \Psi_n | \hat{H}'_{\alpha} | \Psi_k \rangle \langle \Psi_k | \hat{H}'_{\beta} | \Psi_n \rangle}{E_n - E_k} + c.c.$$

N.B. Although it looks similar, this is not perturbation theory; both expressions are exact.



Richard Feynman

J-couplings and K-couplings

J-coupling is actually a *tensor* (but its anisotropy is usually inconsequential):

$$E = \vec{\mu}^{(A)} \cdot \mathbf{J} \cdot \vec{\mu}^{(B)}, \quad J_{nk}^{(AB)} = \frac{\partial^2 E}{\partial \mu_n^{(A)} \partial \mu_k^{(B)}}, \quad J_{nk}^{(AB)} = h \left(\frac{\gamma_A}{2\pi} \right) \left(\frac{\gamma_B}{2\pi} \right) K_{nk}^{(AB)}$$

K-couplings are isotope-independent (nuclear mass does not influence energy). The units are conventionally Hz; the terms in the Hellmann-Feynman theorem are:

$$h\mathbf{J}^{(AB)} = \langle \Psi_0 | \hat{H}_{AB}^{NSS} | \Psi_0 \rangle + \sum_{m>0} \frac{\langle \Psi_0 | \hat{H}_A^{NSO} + \hat{H}_A^{NEC} + \hat{H}_A^{NED} | \Psi_m \rangle \langle \Psi_m | \hat{H}_B^{NSO} + \hat{H}_B^{NEC} + \hat{H}_B^{NED} | \Psi_0 \rangle}{E_0 - E_m}$$

Diagram labels with arrows pointing to terms in the equation:

- nuclear spin with electron orbit (points to $\hat{H}_A^{NSO}$)
- nuclear-electron contact (points to $\hat{H}_A^{NEC}$)
- electron-mediated nuclear spin-spin interaction (points to $\hat{H}_{AB}^{NSS}$)
- nuclear-electron dipolar (points to $\hat{H}_B^{NED}$)

Fermi contact term dominates in one-bond *J*-couplings in CHNO molecules.

NED and NSO terms dominate in multiple-bond *J*-couplings and those involving heavy elements and conjugated double bond systems.

NSS term is usually negligible.

Contributions to the J -coupling

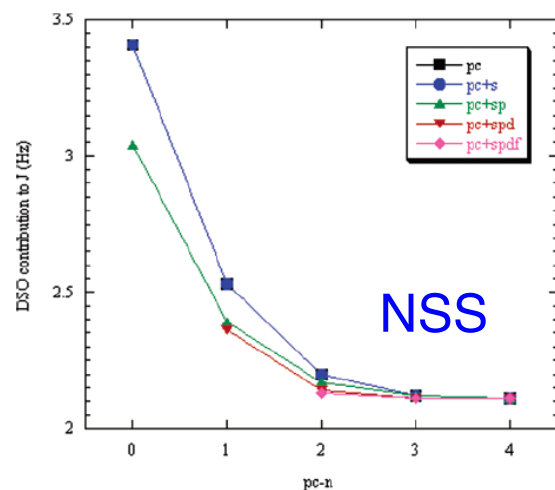


Figure 2. DSO contribution to the coupling constant for F_2 calculated by the $pc-n$ basis sets augmented with tight functions.

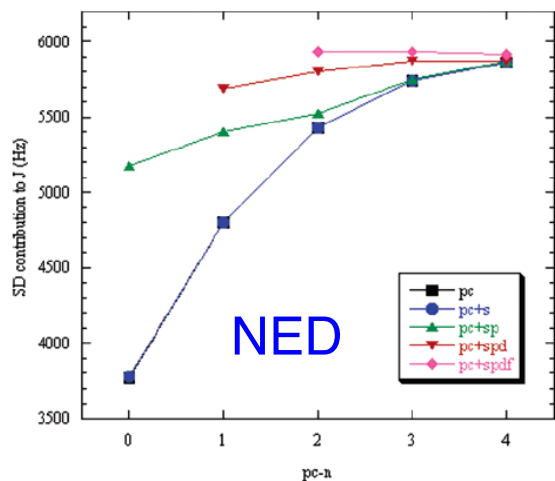


Figure 4. SD contribution to the coupling constant for F_2 calculated by the $pc-n$ basis sets augmented with tight functions.

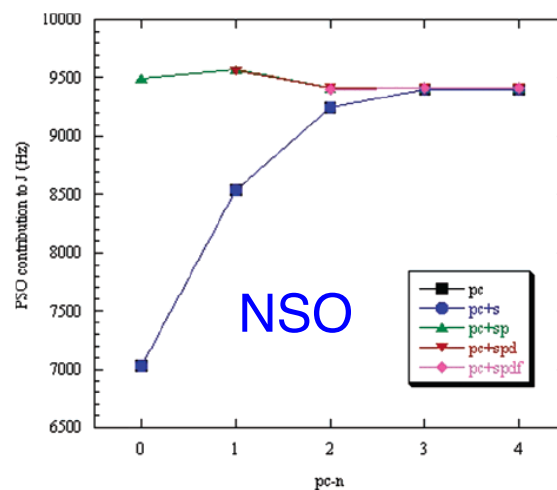


Figure 3. PSO contribution to the coupling constant for F_2 calculated by the $pc-n$ basis sets augmented with tight functions.

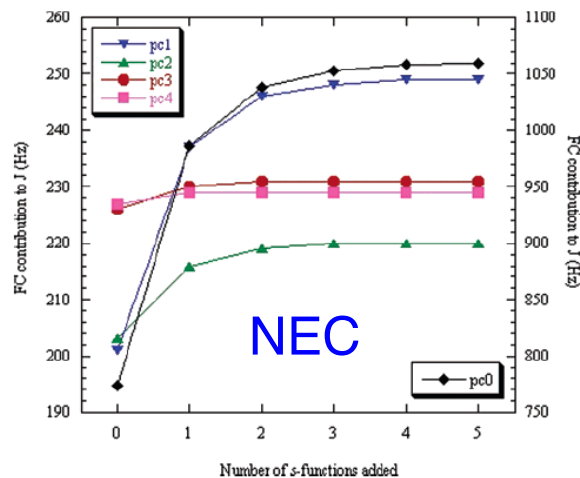


Figure 5. FC contribution to the coupling constant for F_2 as a function of added s functions with large exponents.

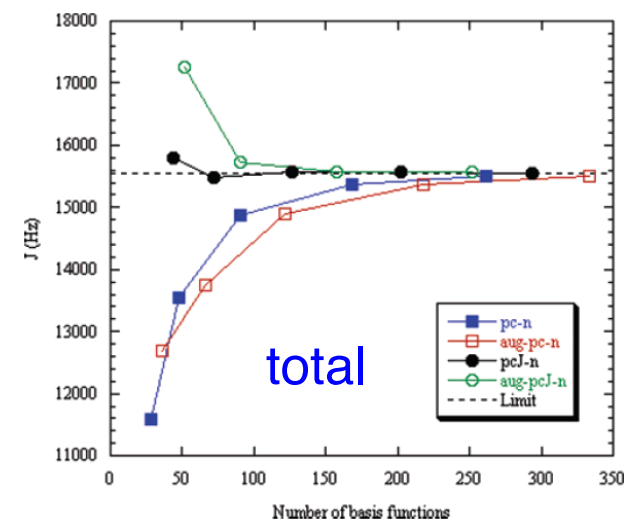


Figure 7. Coupling constant for F_2 calculated by the (uncontracted) $pc-n$, $aug-pc-n$, $pcJ-n$, and $aug-pcJ-n$ basis sets.

Polarised core basis sets ($aug-cc-pCVnZ$) with large zeta numbers are essential – basis set convergence for J -couplings is very slow.

Non-contact terms become more prominent for longer range J -couplings.

Contributions to the J -coupling

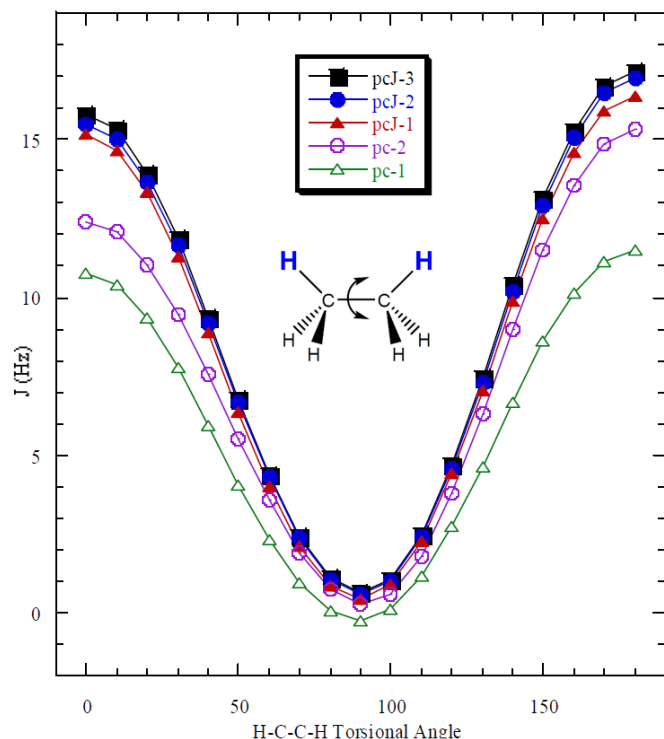
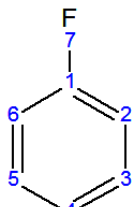


Table 9. Spin-Spin Coupling Constants in CH_3CN (in Hz)^a

	SCF	CASSCF ^b	RASSCF ^b	EOM-CCSD	exp
$^1J(\text{CC})$	128.10	91.96	71.79	<i>c</i>	58.0
$^1J(\text{CN})$	-99.50	-30.94	-21.55	-17.20	-17.8
$^1J(\text{CH})$	168.25	156.94	142.43	125.69	135.73
$^2J(\text{CN})$	15.90	2.41	2.82	3.08	2.9
$^2J(\text{CH})$	-59.13	-21.26	-15.46	-10.44	-9.94
$^3J(\text{NH})$	-16.76	-2.64	-2.03	-1.33	-1.63
$^2J(\text{HH})$	-38.67	-27.82	-22.91	-16.63	-16.9

TABLE X. The NMR spin-spin coupling constants of CH_3CN (in Hz).^a

		FC	SD	PSO	DSO	Total	Expt.
$^1J(^{13}\text{C}^{15}\text{N})$	CPHF	-64.48	-16.24	-4.95	0.01	-85.66	
	EOM-CCSD	-13.15	-4.39	0.33	0.00	-16.99(-17.20)	$\pm 17.5 \pm 0.4^b$
$^1J(^{13}\text{C}^1\text{H})$	CPHF	171.32	-0.22	1.06	0.49	172.65	
	EOM-CCSD	123.29	0.03	1.07	0.52	124.91(125.69)	$\pm 136.0 \pm 0.2^b$
$^2J(^{13}\text{C}^{15}\text{N})$	EOM-CCSD	2.46	-0.10	0.40	0.08	3.01(3.08)	$\pm 3.0 \pm 0.4^b$
	CPHF	-50.27	0.57	-0.02	-0.17	-49.89	
$^2J(^{13}\text{C}^1\text{H})$	EOM-CCSD	-9.91	0.13	0.16	-0.17	-10.00(-10.44)	$\pm 10.0 \pm 0.2^b$
	CPHF	-12.91	0.31	-0.50	0.23	-12.87	
$^3J(^{15}\text{N}^1\text{H})$	EOM-CCSD	-1.16	0.03	-0.36	0.23	-1.23(-1.33)	$\pm 1.80 \pm 0.1^b$
	CPHF	-37.56	0.40	2.88	-3.11	-37.39	
$^2J(^1\text{H}^1\text{H})$	EOM-CCSD	-15.99	0.31	2.81	-3.06	-16.29(-16.63)	

Compound	Coupling	Method	J_{OD}	J_{OP}	J_{SD}	J_{FC}	J
	$^1J(^{13}\text{C}_1\text{-}^{19}\text{F})$	DFT/B3LYP, <i>a</i>	0.88	-6.19	6.12	-321.09	-320.2
		SOPPA, <i>b</i>	0.87	4.76	6.81	-266.88	-254.43
		SOPPA, <i>c</i>	0.93	4.21	6.31	-259.29	-247.84
	$^2J(^{13}\text{C}_2\text{-}^{19}\text{F})$	Experimental					245.40
		DFT/B3LYP, <i>a</i>	-0.13	-15.01	3.53	31.20	19.59
		SOPPA, <i>b</i>	-0.13	-13.53	2.95	31.56	20.85
	$^2J(^{13}\text{C}_2\text{-}^{19}\text{F})$	SOPPA, <i>c</i>	-0.13	-12.60	2.83	29.73	19.83
		Experimental					20.76

Highly correlated response methods (EOM-CCSD, SOPPA/CCSD) are often required.

Electron g -tensor

The g -tensor is defined similarly to chemical shielding – as a second derivative of the energy with respect to the magnetic field and the electron magnetic moment:

$$E = \mu^{(e)} \cdot \mathbf{g} \cdot \mathbf{B}, \quad g_{nk} = \frac{\partial^2 E}{\partial \mu_n^{(e)} \partial B_k}$$

The following terms appear in the Hellmann-Feynman second derivative:

$$\mathbf{g} = \langle \Psi_0 | \hat{H}^{\text{EZ}} + \hat{H}^{\text{ES}} | \Psi_0 \rangle + 2 \text{Re} \sum_{m>0} \frac{\langle \Psi_0 | \hat{H}^{\text{ESO}} | \Psi_m \rangle \langle \Psi_m | \hat{H}^{\text{OZ}} | \Psi_0 \rangle}{E_0 - E_m}$$

electron Zeeman electron shielding electron spin-orbit orbital Zeeman

Table 1

Calculated Δg -values (deviation from the free-electron g -value in ppt) for $[\text{MoOCl}_5]^{2-}$ complex in comparison with experimental data.

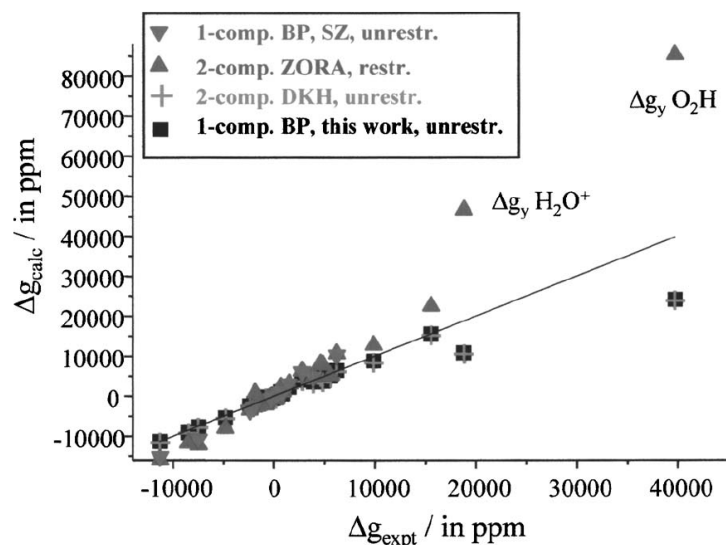
Method	Functional	$\Delta g_{\parallel}$	$\Delta g_{\perp}$
1-Comp. ^a	BP86	−0.4	−61.5
	B3PW91	−11.8	−65.1
2-Comp. ^a	BP86	−7.1	−64.2
	B3PW91	−19.5	−67.8
4-Comp. ^b	BP86	−7.1	−69.5
Exp. ^a		−32.3	−64.3

Table 3

Calculated Δg -values (deviation from the free-electron g -value in ppt) for $[\text{MoO}(\text{bdt})_2]^-$ (bdt = benzene-1,2-dithiolate) complex in comparison with experimental data.

Method	Functional	Δg_{11}	Δg_{22}	Δg_{33}	Δg_{iso}
1-Comp. ^a	BP86	23	−7	−16	0
	B3PW91	21	−13	−22	−5
2-Comp. ^a	BP86	22	−9	−18	−2
	B3PW91	20	−15	−23	−6
4-Comp. ^b	BP86	22	−10	−20	−3
Exp. ^a		20	−18	−26	−8

Electron g -tensor



The derivative approach is not applicable to systems with g -shifts in excess of 20,000 ppm because higher order effects appear.

For heavy atoms, relativistic effect must be included into the reference Hamiltonian.

High level treatment of electron correlation is essential (there is a sum over excited states in the Hellmann-Feynman denominators).

Table 4. Calculated and experimental isotropic g -shifts Δg for a few radicals (ppm). All numbers cited from Ref. [132]. Note that experimental numbers are generally given with two significant digits less

Molecule/ Component	Pauli operator		ZORA operator (spin-restricted)	Experiment		
	spin-unrestricted	spin-restricted				
NO ₂	Δ_{xx}	4200	5000			3900
	Δ_{yy}	-13800	-16400			-11300
	Δ_{zz}	-800	-600			-300
HCO	Δ_{xx}	2700	3200			1400
	Δ_{yy}	-300	-100			0
	Δ_{zz}	-9700	-12400			-7500
TiF ₃	$\Delta_{xx} = \Delta_{yy}$	-42800	-73300	-111300	-121500	-123700
	Δ_{zz}	-1700	100	-11100	-11100	-3700

► Lanthanide, actinide, and d -element g -tensors should not be computed in this way.

Nuclear quadrupolar interaction

Nuclei with spin $> 1/2$ have non-spherical charge density distribution. The resulting electric quadrupole moment:

$$Q_{nk} = \int \rho(\mathbf{r}) (3r_n r_k - r^2 \delta_{nk}) d^3\mathbf{r}$$

interacts with the electric field gradient at the nucleus point:

$$U = \frac{1}{6} \sum_{nk} Q_{nk} V_{nk} \quad V_{nk} = \left. \frac{\partial E_n}{\partial r_k} \right|_{\text{nucleus}} = \left. \frac{\partial^2 \varphi}{\partial r_n \partial r_k} \right|_{\text{nucleus}}$$

The direction of the electric quadrupole moment of the nucleus is rigidly linked to the direction of its spin. As a result, an electrostatic interaction becomes also a spin interaction with the following Hamiltonian:

$$\hat{H} = \frac{1}{6} \sum_{nk} \hat{Q}_{nk} V_{nk} \quad \hat{Q}_{nk} = \frac{eQ}{S(2S+1)} \left[\frac{3}{2} (\hat{S}_n \hat{S}_k + \hat{S}_k \hat{S}_n) - \delta_{nk} \hat{S}^2 \right]$$

where eQ is the *nuclear quadrupole moment*. It is a property of the ground state of the nucleus that may be measured. A method for computing NQI need therefore only calculate the derivatives of the electrostatic potential.

Nuclear quadrupolar interaction

Table 3

Calibration of the B3PW91/6-311G model augmented with different combinations of diffuse and polarization functions. RSD (residual standard deviation) is in kHz, eQ/h (slope) is in MHz/a.u.

Basis	RSD	eQ/h
6-311 + +G(3df,3pd)	33	4.546
+ +G(2df,3pd)	69	4.492
+ +G(df,3pd)	31	4.562
+ +G(3d,3pd)	64	4.581
+ +G(2d,3pd)	52	4.542
+ +G(d,3pd)	126	4.632
6-311G(3df,3pd)	49	4.492
6-311 + G(3df,3pd)	33	4.546
+ G(3df,2pd)	34	4.548
+ G(3df,pd)	33	4.545
+ G(3df,3p)	34	4.548
+ G(3df,2p)	33	4.547
+ G(3df,p)	33	4.546
6-311 + G(df,3pd)	31	4.562
+ G(df,2pd)	31	4.562
+ G(df,pd)	29 ₉	4.558
+ G(df,3p)	32	4.563
+ G(df,2p)	32	4.562
+ G(df,p)	30 ₄	4.559

Table 4

Calibration of the B3PW91 method in conjunction with cc-pVTZ Dunning type bases. RSD (residual standard deviation) is in kHz, eQ/h (slope) is in MHz/a.u.

Nitrogen	Other atoms	RSD	eQ/h
aug-cc-pVTZ	aug-cc-pVTZ	64	4.539
aug-cc-pCVTZ	aug-cc-pVTZ	37	4.569
cc-pCVTZ	cc-pVTZ	50	4.516

Electron density distribution must be reproduced precisely, so a large and flexible basis set is needed: at least triple-zeta, with multiple sets of diffuse and polarisation functions, as well as core polarisation functions (e.g. in aug-cc-pCVTZ basis).

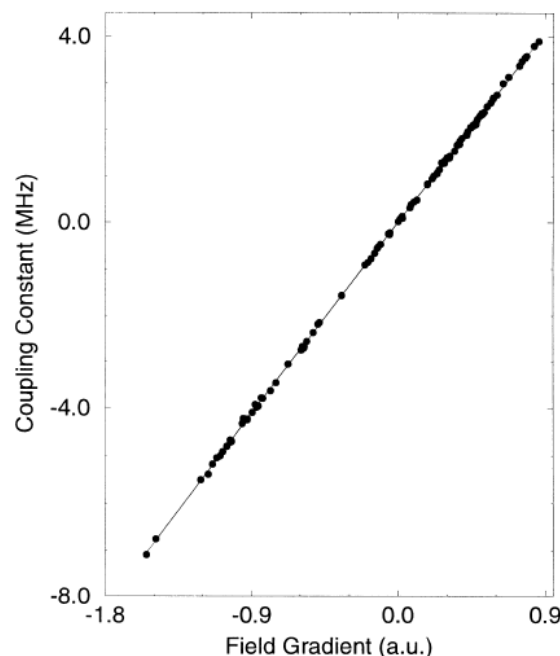


Fig. 1. B3PW91/6-311 + G(df,pd) calibration curve. Calculated efg's (a.u.) vs. experimental nqcc's (MHz). The residual standard deviation is 30 kHz, the correlation coefficient is 0.99994, and the slope (eQ/H) is 4.5617 MHz/a.u.

Table 2

Calibration of the HF, DFT, and HF-DFT methods using 6-311 + +G(3df,3pd) and aug-cc-pVTZ bases. RSD (residual standard deviation) is in kHz, eQ/h (slope) is in MHz/a.u.

Theory	6-311 + +G(3df,3pd)		aug-cc-pVTZ	
	RSD	eQ/h	RSD	eQ/h
HF	347	3.849	364	3.863
BLYP	103	4.652	115	4.643
BP86	108	4.768	111	4.753
BPW91	119	4.773	104	4.763
VWN5	114	4.622	96	4.619
B3LYP	45	4.449	94	4.443
B3P86	34	4.532	75	4.525
B3PW91	33	4.546	64	4.539

The calibration is not a perfect 45° line, but the fit is precise (same story as for vibration frequencies).

Nuclear quadrupolar interaction

All factors affecting the electrostatics (lattice, solvent, *etc.*) must be accounted for.

Table 5 QCT of 5-anthracene cluster obtained from crystal anthracene at T=220K

Geometry	vac		PCM	
deuterium	$q_{CD}(KHz)$	η	$q_{CD}(KHz)$	η
1	186.177	0.0752	185.078	0.0755
2	182.382	0.0741	181.277	0.0744
3	183.857	0.0882	182.755	0.0886
4	186.264	0.0800	185.165	0.0804
5	187.437	0.0750	186.337	0.0753
<exp>	$q_{CD}=181 \pm 3$		$\eta=0.064 \pm 0.013$	

The calculated values have been obtained using a mixed basis set: 6-311+G(d,3p2d) for the inner fragment and 6-31+G(d) for the other four fragments. The two sets of data refer to two different CH bond lengths, namely $R_{CH}=1.0875$ (vac), and $R_{CH}=1.0885$ (PCM)

Table 6 B3LYP/6-311+G(d,3p2d) QCT of the embedded dimer of anthracene

Deuterium	$q_{CD}(KHz)$	η
1	184.558	0.0782
2	181.388	0.0765
3	182.456	0.0902
4	184.700	0.0816
5	185.302	0.0801

Explicit first solvation shell is in most cases required for PCM calculations.

Table 5

The ^{14}N NQCCs (in MHz) for the 1-methyltriazoles based on the DFT/MM calculations using the KT3 xc-functional and 6-311++G(3df,3pd) basis

Molecule	Model	Atom	Vacuum	Exp.	Solution	Exp.
<123>	QM/MM	N_1	-2.790	–	-2.426 ± 0.002	–
		N_2	-4.246	–	-3.926 ± 0.002	–
		N_3	-4.705	–	-4.312 ± 0.003	–
		$\Delta v_{\frac{1}{2}}^{N_2} / \Delta v_{\frac{1}{2}}^{N_1}$	2.74	2.47	3.10	4.98
		$\Delta v_{\frac{1}{2}}^{N_3} / \Delta v_{\frac{1}{2}}^{N_1}$	2.76	2.33	2.92	4.42
		$\Delta v_{\frac{1}{2}}^{N_2} / \Delta v_{\frac{1}{2}}^{N_3}$	0.99	1.06	1.06	1.13
<124>	QM/MM	N_1	-3.137	–	-3.007 ± 0.002	–
		N_2	-4.471	–	-4.100 ± 0.003	–
		N_4	-4.033	–	-3.532 ± 0.003	–
		$\Delta v_{\frac{1}{2}}^{N_2} / \Delta v_{\frac{1}{2}}^{N_1}$	2.28	2.04	2.13	3.94
		$\Delta v_{\frac{1}{2}}^{N_3} / \Delta v_{\frac{1}{2}}^{N_1}$	1.55	1.61	1.25	2.50
		$\Delta v_{\frac{1}{2}}^{N_2} / \Delta v_{\frac{1}{2}}^{N_3}$	1.47	1.27	1.70	1.58
<125>	QM/MM	N_1	-3.472	–	-3.401 ± 0.002	–
		N_2	-4.604	–	-4.417 ± 0.003	–
		$\Delta v_{\frac{1}{2}}^{N_2} / \Delta v_{\frac{1}{2}}^{N_1}$	1.77	1.74	1.68	2.84
		PCM	N_1	–	-3.423 ± 0.002	–
<134>	QM/MM	N_2	-4.604	–	-4.428 ± 0.003	–
		$\Delta v_{\frac{1}{2}}^{N_2} / \Delta v_{\frac{1}{2}}^{N_1}$	1.77	1.74	1.68	2.84
		N_1	-2.789	–	-2.315 ± 0.002	–
		N_3	-4.676	–	-4.210 ± 0.003	–
		$\Delta v_{\frac{1}{2}}^{N_3} / \Delta v_{\frac{1}{2}}^{N_1}$	2.79	2.73	3.57	5.97

The two water molecules closest to the pyridine-type nitrogen atoms have been included in the QM region. Relative half-height widths have also been included. The experimental results are obtained from Ref. [44]. The experimental results for vacuum refer to cyclohexane solution.