Electric field gradient calculations by quantum chemical methods

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The electric field at the given nucleus *X,* produced by all electrons and other nuclei of the molecule, is not uniform and has a non-vanishing gradient. EFG, which from the point of view of the given nucleus is a measure of the inhomogeneity of the external electric field, is a molecular property of the first order and can be **determined from the knowledge of the electronic wave function and positions of other nuclei**.

Accurate *ab initio* calculations

Electron correlation effects:

> ➢ CCSD(T)

Relativistic effects:

> ➢ DKH2, sfIOTC

Saturated basis set of atomic functions

> ➢ Large uncontracted (mostly) bases

Computer program:

> ➢ MOLCAS (University of Lund, Sweden)

All properties other than energy can be considered as resulting from the action of some perturbation operator. Derivatives of energy with respect to the perturbation strength parameter define atomic and molecular properties of the given order e.g.

- 1st order: electric moments, electric field gradient,
              the Hellman-Fyenman force, …

- 2nd order: electric polarizabilities, force constants, geometry
              derivatives of the 1st order properties,…

2-component methods

*L.L.Foldy, S.A.Wouthuysen; Phys.Rev. **78**, 29 (1950)*

$$4 \Rightarrow 2 + 2 \Rightarrow 2$$

- *M.Douglas, N.M.Kroll; Ann.Phys. (N.Y.) **82**, 89 (1974)*

- *J.Sucher; Phys.Rev. A **22**, 348 (1980)*

- *G.Hardekopf, J.Sucher; Phys.Rev. A **30**, 703 (1984)*

- *J.Almlöf, K.Faegri, H.H.Grelland; Chem.Phys.Letters **114**, 53 (1985)*

- *B.A.Hess; Phys.Rev. A **33**, 3742 (1986)*

- *G.Jansen, B.A.Hess; Phys.Rev. A **39**, 6016 (1989)*

In 2-component relativistic calculations

- Should the perturbation be added at the level of the 4-component theory and then reduced to the 2-component approximation?

- Can the perturbation be added *a posteriori* to the given 2-component Hamiltonian?

The difference between the two ways of handling the perturbation makes what is known as the **change of picture** contribution.

A.Messiah, Quantum Mechanics, North-Holland, Amsterdam, 1969, Vol.II p.943

The transformation of the 4-component Hamiltonian to some 2-component form requires that all other operators should be transformed in the same way.

The first consideration of this problem in the framework of the DKH method was done for dipole moments of CuH, AgH, and AuH.

V.Kellö, A.J.Sadlej, B.A.Hess; J.Chem.Phys. **105**, *1995 (1996)*

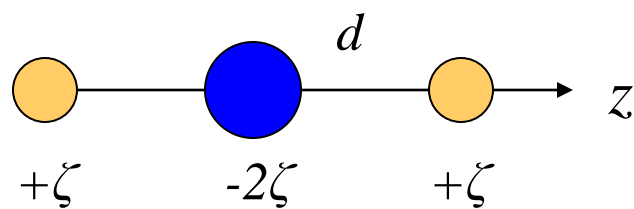- The change of picture effect for the dipole moment operator is negligible

Should the change of picture be taken into account?

- **YES:** The change of picture is the α^2 effect
  *M.Barysz, A.J.Sadlej; Theor.Chim.Acc. **97**, 260 (1997)*
  *M.Barysz; Pol.J.Chem. **74**, 1329 (2000)*
  *K.G.Dyall; Int.J.Quantum Chem. **78**, 412 (2000)*

- **NO:** In spite of being of the order of α^2, the change of picture negligibly affects the valence-determined properties
  *V.Kellö, A.J.Sadlej, B.A.Hess; J.Chem.Phys. **105**, 1995 (1996)*

- **YES:** Important for operators which assume large values in the vicinity of nuclei, e.g. electric field gradient
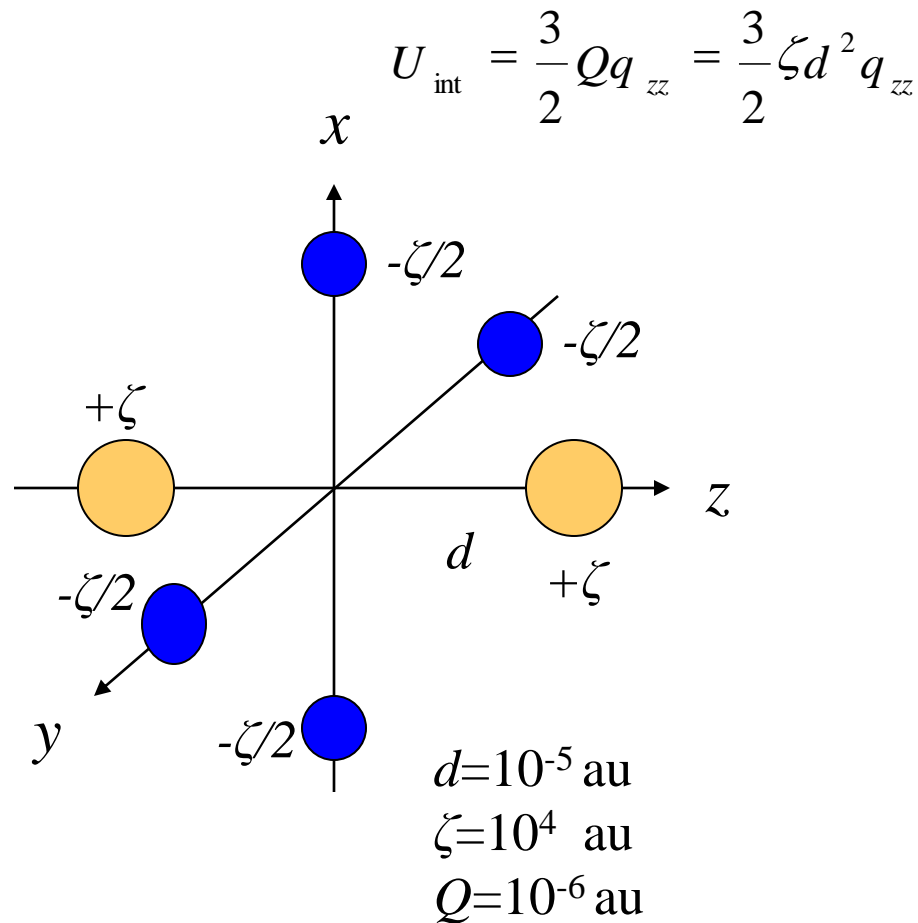 *V.Kellö, A.J.Sadlej; Int.J.Quantum Chem. **68**, 159 (1998)*

Electric field gradient (EFG)

Point charge nuclear quadrupole moment (PCNQM) model

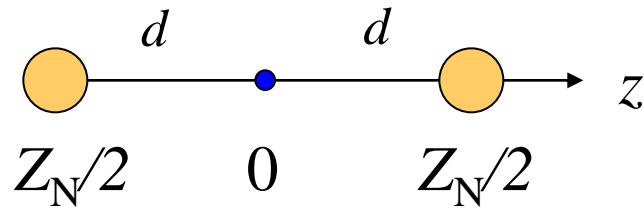*M.Pernpointer, M.Seth, P.Schwerdtfeger; J.Chem.Phys **108**, 6722 (1998)*

$$U_{int} = \frac{3}{2}Qq_{zz} = \frac{3}{2}\zeta d^2 q_{zz}$$

$$U_{int} = Qq_{zz} = \zeta d^2 q_{zz}$$

$d=10^{-5}$ au
$\zeta=10^4$ au
$Q=10^{-6}$ au

Shifted nucleus model (SNM)

*V.Kellö, A.J.Sadlej; J.Chem.Phys **120**, 9424 (2004)*

$$d = 0.0001 - 0.001 \text{ a.u.}$$

$Z_N/2$ 0 $Z_N/2$ z

$$q_{zz}(\mathrm{N}) = -\frac{4}{3Z_N}\left(\frac{\partial \Delta(d^2)}{\partial(d^2)}\right)_{d=0}$$

$$\Delta(d^2) = E_z(d^2) - \frac{1}{2}\left[E_x(d^2) + E_y(d^2)\right] = E_{\mathrm{II}}(d^2) - E_{\perp}(d^2)$$

$$= a_1 d^2 + a_2 d^4 + ...$$

$$\left(\frac{\partial \Delta(d^2)}{\partial(d^2)}\right)_{d=0} = -\frac{\Delta(4d^2) + 320\,\Delta(2d^2) - 5376\,\Delta(d^2)}{4080\,d^2}$$

The important difference between the SN approach and the PCNQM model is that the value Z_N is *a priori* known. Thus the SN approach is a one-parameter method and its performance can be easily tested.

The explicit transformation of EFG operator within the DKH approach taking picture-change effects analytically into account

*R. Mastalerz, G. Barone, R. Lindh, M. Reiher; J. Chem. Phys. **127**, 074105 (2007)*

Testing the accuracy of the shifted nucleus model in calculation of EFG (nonrelativistic SCF electronic contribution) at As in AsP (a.u.).

d	q_{zz}
0.0012	–4.575 5499
0.0006	–4.578 3165
0.0003	–4.578 9899
0.00015	–4.579 1246
0.00015, 0.0003, 0.0006	–4.579 1700
0.0003, 0.0006, 0.0012	–4.579 2147
expectation value	–4.579 2408

Change of picture effect on the electric field gradients in one-electron ions as calculated in DKH-SCF approximation [a.u.].

Ion	Term	no-CP $\langle q_{zz} \rangle$	CP $\langle q_{zz} \rangle$	
Ne^{+9}	$2p^1, {}^2P$	-33.614	-33.449	(0.5%)
Ar^{+17}	$2p^1, {}^2P$	-199.73	-196.58	(1.6%)
Kr^{+35}	$2p^1, {}^2P$	-1735.05	-1624.69	(6.8%)
Xe^{+53}	$2p^1, {}^2P$	-6777.89	-5760.44	(17.7%)
Rn^{+85}	$2p^1, {}^2P$	-44728.2	-25171.8	(77.7%)

Change of picture effect on the electronic contribution to electric field gradients at the halogen nucleus in hydrogen halides as calculated in DKH-SCF approximation [a.u.].

Molecule	no-CP $\langle q_{zz} \rangle$	CP $\langle q_{zz} \rangle$	
HCl	3.540	3.511	(0.8%)
HBr	7.806	7.520	(3.8%)
HI	12.657	11.683	(8.3%)
HAt	34.621	26.656	(29.9%)

Electronic contribution to electric field gradients at the halogen nucleus in hydrogen halides calculated as expectation value and using the PCNQM model in non-relativistic SCF approximation [a.u.].

Molecule	EV_$\langle q_{zz} \rangle$	PCNQM_$\langle q_{zz} \rangle$
HCl	3.464	3.464
HBr	6.998	7.000
HI	9.726	9.734
HAt	15.443	15.433

For a quadrupolar nucleus there is an interaction between nuclear quadrupole moment $Q(\mathbf{X})$ of the nucleus $\mathbf{X}$ and electric field gradient $q^{\mathbf{X}}$ resulting from the distribution of other charges.

The effect of the Q-q interaction can be seen as:
- *splittings of lines in atomic spectra*
- *splittings in rotational spectra of molecules*
- *affecting NQR and Mössbauer spectra of solids*

and is measured with a high accuracy. It is often called nuclear quadrupole coupling constant (NQCC)

Hence, by combining the experimental and theoretical results one can obtain NQM values, which, according to the source of the experimental data, are referred to as:

- *Atomic*
- *Molecular*
- *Solid-state*

It does not happen frequently that molecular spectroscopic data combined with accurate quantum chemical calculations can be of great help in as remote an area as nuclear physics. The determination of nuclear quadrupole moments (NQM) from molecular spectroscopic data gives one such rare example and its high accuracy surpass that of other methods.

➢ The main competitor of this method was the mesonic way, based on measuring the hyper-structure of essentially Coulombic energy levels of μ or π mesons near the nucleus studied. No such experiments have been published for almost three decades, however, these mesonic NQM values still stand as the benchmark ones for heavier elements.

➢ Low-precision determinations of NQM are available from:
  • nuclear Coulomb scattering
  • nuclear rotational energy levels
  • nuclear theory

The knowledge of reliable NQM is of considerable interest in:

➢ chemical and solid state spectroscopy; NQR, NMR, Mössbauer

➢ nuclear physics for testing nuclear models for stable isotopes.

1992   P. Pyykkö, Z. Naturforsch. **47a**, 189 (1992)

2001   P. Pyykkö, Mol. Phys. **99**, 1617 (2001)

2008   P. Pyykkö, Mol. Phys. **106**, 1965 (2008)

Molecular (diatomic) calculations of NQM

$$Q(X) = \frac{v_Q^X(v)}{234.96473 \, q^X(v)}$$

$v_Q{}^X(v)$ - nuclear quadrupole coupling constant (NQCC) for the nucleus X and the vibration state v; MHz

$q^X(v)$ - axial (zz) component of the electric field gradient tensor (EFG) at X and the vibration state v; a.u.

$Q(X)$ - nuclear quadrupole moment of the nucleus X; barns ($1b = 10^{-28}$ m^2)

Vibrational contributions to $q^X(v)$ estimated usually by using Buckingham formula. *A.D.Buckingham J.Chem.Phys.* **36**, 3096 (1962)

$$q^X(v) = q_e^X + q_{vib}^X \approx q_e^X + q_1^X\left(v + \frac{1}{2}\right)$$

$$q_1^X = \frac{B_e}{\omega_e}\left[3\left(1 + \frac{\alpha_e \omega_e}{6B_e^2}\right)\left(\frac{\partial q^X}{\partial \xi}\right)_{\xi=0} + \left(\frac{\partial^2 q^X}{\partial \xi^2}\right)_{\xi=0}\right] \quad ; \quad \xi = (R - R_e) / R_e$$

Values for the nuclear quadrupole moments of ^{79}Br and ^{127}I nuclei

System	q/a.u.	Q/mb
$^1H^{79}Br$, ($v=0$)		
no-CP CCSD(T)_8el.	7.579	299
CP CCSD(T)_8el.	7.308 (3.7%)	310
CP CCSD(T)_18el.	7.313	310
Recommended value this work (considering atomic value of 314)		313(3)
$^1H^{127}I$, ($v=0$)		
no-CP CCSD(T)_8el.	11.935	-651
CP CCSD(T)_8el.	11.013 (8.5%)	-707
CP CCSD(T)_18el.	11.038	-705
Recommended value based on 4-component CCSD(T)[a]		-696(12)

[a] J. N. P. Van Stralen, L.Visscher, Mol. Phys. **101**, 2115 (2003)

'Molecular' values for the nuclear quadrupole moment of ^{73}Ge[a]

System Q(^{73}Ge)/mb	υ_Q/MHz	electronic contributions to q/a.u.			
		DKH-SCF	DKH-CCSD	DKH(T)[b]	
^{73}Ge^{16}O, (v=0)	208.33	-6.332	0.947	0.235	-195.2
			(15.0%)	(3.7%)	
^{73}Ge^{32}S, (v=0)	187.76	-5.160	0.861	0.289	-196.6
			(16.7%)	(5.6%)	
Reference 'atomic' value[c]					-173(26)
Recommended value this work					-196(3)

[a] Calculated at experimental bond distance, 20 electron correlated
basis sets: O - [14s11p4d/7s7p2d], S - [18s14p6d/10s8p3d], Ge - 21s15p9d4f/21s15p6d4f]
[b] Contribution of noniterative triples CCSD(T) - CCSD
[c] P.Pyykkö, J.Li, 1992 Nuclear quadrupole moments. Report HUKI 1-92

'Atomic' and 'molecular' values for the NQM of ^{27}Al

System	υ_Q/MHz	q^{Al}/a.u.	$Q(^{27}Al)$/mb
'Molecular' values this work			
$^{27}Al^{19}F$, R_e	-37.75 ± 0.08	-1.099[a]	146.2[b]
$^{27}Al^{19}F$, ($v=0$)	-37.53 ± 0.12	-1.091[a]	146.4[b]
$^{27}Al^{35}Cl$, ($v=0$)	-30.4081 ± 0.0027	-0.879[a]	147.2[c]
$^{27}Al^{37}Cl$, ($v=0$)	-30.4112 ± 0.0028	-0.879[a]	147.2[c]
'Atomic' value this work			
$^{27}Al(^2P_{3/2})$	18.91526 ± 0.0007	-0.5493	146.6[c]
Reference 'atomic' value[d]			140.3 ± 1.0
Reference 'muonic' value[e]			$150.\pm6.$
Recommended value this work			146.6 ± 1.0

[a] The DKH CCSD(T) value
[b] The experimental uncertainties of υ_Q correspond to ΔQ values of 0.3 -0.5 mb
[c] The experimental uncertainties of υ_Q do not affect the error bars of the obtained $Q(^{27}Al)$
[d] D.Sundholm, P.Pyykkö, L.Laaksonen, A.J.Sadlej, Chem.Phys.Letters **112**, 1 (1984)
[e] R.Weber et al., Nucl.Phys. A**377**, 361 (1982)

'Molecular' values for the nuclear quadrupole moment of ^{91}Zr nucleus

System	υ_Q/MHz[a]	q^{Zr}/a.u.	$Q(^{91}$Zr)/mb
^{91}Zr^{16}O, (v=0)	130.5499(46)	-3.11[b]	179
		-3.16[c] ($\varDelta_{SO}$=-0.0056)	176
^{91}Zr^{32}S, (v=0)	116.4609(47)	-2.86[b]	173
Reference 'atomic' values			206(10)[d]
			257[e]
			230(20)[f]
Recommended value this work			176(3)

[a] S.A.Beaton, M.C.L.Gerry, J.Chem.Phys. **110**, 10715 (1999).
[b] The DKH CCSD(T) values, 28 respectively 34 electrons correlated.
[c] The 4-component CCSD(T) values.
[d] S.Büttgenbach, Hyperfine structure in 4d- and 5d-shell atoms. Springer, Berlin 1992, p.83 ('blue card value').
[e] L.Young, C.A.Kurtz, D.R.Beck, D.Datta, Phys.Rev. A **48**, 173 (1993)
[f] S.Bouazza, J.Dembczyski, E.Stachowska, G.Szawiola, J.Ruczkowski, Eur.Phys.D**4**, 39 (1998)

'Molecular' values for NQM of ^{121}Sb nucleus

System	υ_Q/MHz[a]	q^{Sb}/a.u.	$Q(^{121}Sb)$/mb
SbN	649.669	-5.199	-532
SbP	620.350	-4.931	-535
SbF	-586.802	4.407	-567
SbCl	-515.124	3.788	-579
1955 atomic value[b]		-530 100	
2001"recommended" value[c]		-360±40	
2003 solid state value[d]		-669 15	
2006 IOTC-CCSD(T) value, this work		-556±24	
2006 DC-CCSD-T value[e]		-543 11	

[a] S.A.Cooke, M.C.L.Gerry, PCCP **6**, 4579 (2004); J.Mol.Spectr. **234**, 195 (2005)
[b] K.Murakawa, Phys. Rev. **100** 1369 (1955); [c] P.Pyykkö, Mol.Phys. **99**, 1617 (2001);
[d] A.Svane, Phys.Rev. B **68**, 064422 (2003);
[e] R.L.A.Haiduke, A.B.F. da Silva, L.Visscher, J. Chem. Phys. **125**, 064301 (2006)

Contributions to electric field gradient at As in AsP (a.u.)

Method	NR	IOTC
contributions to q(As)		
SCF	-4.5825	-4.7675
CCSD	0.5752	0.6139
T_3	0.1724	0.1824
Δ(core)MP2	0.0058	0.0021
CCSD(T)+Δ(core)MP2	0.7533	0.7984
q_{el}(As)	-3.8291	-3.9691
q_{nuc}(As)	0.5557	
q (As)	-3.2735	-3.4134

Basis set As (21s18p15d8f7g3h3i), P (19s14p9d8f)

Molecular value of $Q(^{75}\text{As})$ and comparison with other data.

	Q/mb
Present value	311±2
Reference 'atomic' value [a]	300±50
Reference 'muonic' value [b]	314±6

[a] B. Effenberger, W. Kunold, W. Oesterle, M. Schneider, L.M. Simons, R. Abela, J. Wüest, Z. Phys. A **309**, 77 (1982).

[b] M. Voss, W. Weiss, R. Winkler, Physica B+C **123**, 21(1983).

Testing the saturation of the basis set in calculation of EFG (electronic contribution) at As in AsP (a.u.).

Basis As	$q_{IOTC\ CCSD(T)}$
21s16p13d8f5g	−3.9558
21s17p13d8f5g	−3.9581
21s18p13d8f5g	−3.9603
21s18p15d8f5g	−3.9696
21s18p15d8f6g	−3.9610
21s18p15d8f7g	−3.9612
21s18p15d8f7g2h	−3.9638
21s18p15d8f7g3h	−3.9666
21s18p15d8f7g3h2i	−3.9689
21s18p15d8f7g3h3i	−3.9707

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Basis set dependence of EFG (q a.u.) calculated at N in the NP molecule. Study of the 'spectator' atom basis set.

Basis N *actor*	Basis P *spectator*	q_{HF}	$q_{corr/CCSD(T)}$	q^a
A-16s11p5d	**A**-19s14p7d	−2.7312	0.3103	−1.0793
C-16s12p7d6f	**A**-19s14p7d	−2.7385	0.3104	−1.0865
C-16s12p7d6f	**B**-19s14p9d8f	−2.7415	0.2973	−1.1026
C-16s12p7d6f	**C**-19s15p10d9f	−2.7416	0.2973	−1.1027
E-16s14p9d8f	**B**-19s14p9d8f	−2.7114	0.2885	−1.0813
E-16s14p9d8f	**C**-19s15p10d9f	−2.7115	0.2885	−1.0814
E-16s14p9d8f	**E**-19s17p12d11f	−2.7115	0.2885	−1.0814

[a] The total value of q which includes the nuclear contribution 1.3416 a.u.

Basis set dependence of EFG (q a.u.) calculated at N in the NP molecule. Study of the 'actor' atom basis set.

Basis N *'actor'*	Basis P *'spectator'*	q_{HF}	$q_{corr/CCSD(T)}$	q^a
B-16s12p7d6f	**B**-19s14p9d8f	−2.7524	0.3037	−1.1072
C-16s12p7d6f	**B**-19s14p9d8f	−2.7415	0.2973	−1.1026
E-16s14p9d8f	**B**-19s14p9d8f	−2.7114	0.2885	−1.0813
H-16s15p12d11f	**B**-19s14p9d8f	−2.7079	0.2876	−1.0787
C-16s12p7d6f	**C**-19s15p10d9f	−2.7416	0.2973	−1.1027
E-16s14p9d8f	**C**-19s15p10d9f	−2.7115	0.2885	−1.0814
H-16s15p12d11f	**C**-19s15p10d9f	−2.7079	0.2876	−1.0787

[a] The total value of q which includes the nuclear contribution 1.3416 a.u.

The most accurate value of q obtained in this paper –1.0762 a.u., combined with the experimental NQCC value of ^{14}N –5.1728±0.0005 MHz [a], leads to the 'molecular' result Q(^{14}N) 20.46 mb which is perfectly within the error bars of the very accurate 'atomic' value 20.44±0.03 mb [b].

[a] *J. Raymonda, W. Klemperer; J. Chem. Phys.* **55,** *232 (1971)*
[b] *M.Tokman, D.Sundholm, P.Pyykkö, J.Olsen; Chem. Phys. Lett.* **265,** *60 (1997).*

The gold challenge

Source	Q(^{197}Au)/barn	year	Ref.
muonic spectroscopy	0.547(16)	1974	1
solid state DFT & Mössbauer	0.600-0.640	2005	2
DC CCSD(T)	0.519(19)	2007	3
4-component DFT	0.526	2007	4
IOTC/DC CCSD(T)	0.480	2008	5

1. *R.J. Powers, P.Martin, G.H.Miller, R.E.Welsh, D. A.Jenkins; Nucl.Phys. A**230,** 413 (1974)*
2. *P.Schwerdtfeger, R.Bast, M.C.L.Gerry, C.R.Jacob, M.Jansen, V.Kellö, A.V.Mudring, A.J. Sadlej, T.Saue, T.Sohnel, F.E.Wagner; J.Chem.Phys. **122,** 124317 (2005)*
3. *L. Belpassi, F. Tarantelli, A. Sgamellotti, H. M. Quiney, J. N. P. van Stralen, L. Visscher; J. Chem. Phys. **126**, 064314 (2007).*
4. *C.Thierfelder, P.Schwerdtfeger, T. Saue; Phys. Rev. A **76**, 034502 (2007)*
5. *C.Clavaguéra, J-P.Dognon, V.Kellö, P.Pyykkö, A.J.Sadlej, P.Schwerdtfeger; to be published*

Conclusions

The presented results clearly proved that accurate *ab initio* calculations of electric filed gradients at nuclei in combination with nuclear quadrupole coupling constants obtained from microwave spectra are reliable source of nuclear quadrupole moments. This is a nice example of the synergy effect of experiment and theory.

Review; M. Iliaš, V. Kellö, M. Urban; Acta Phys. Slovaca **60***, 259-391 (2010)*

My thanks to:

Andrzej Sadlej
Pekka Pyykkö, Helsinki
Steve Cooke, Denton
Peter Schwerdtfeger, Auckland
Miroslav Urban, Bratislava
Lukáš Demovič, Bratislava

Thank you for your attention