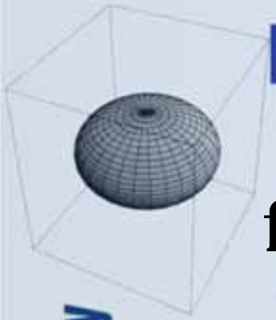
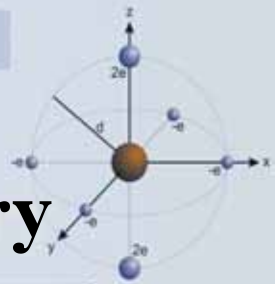
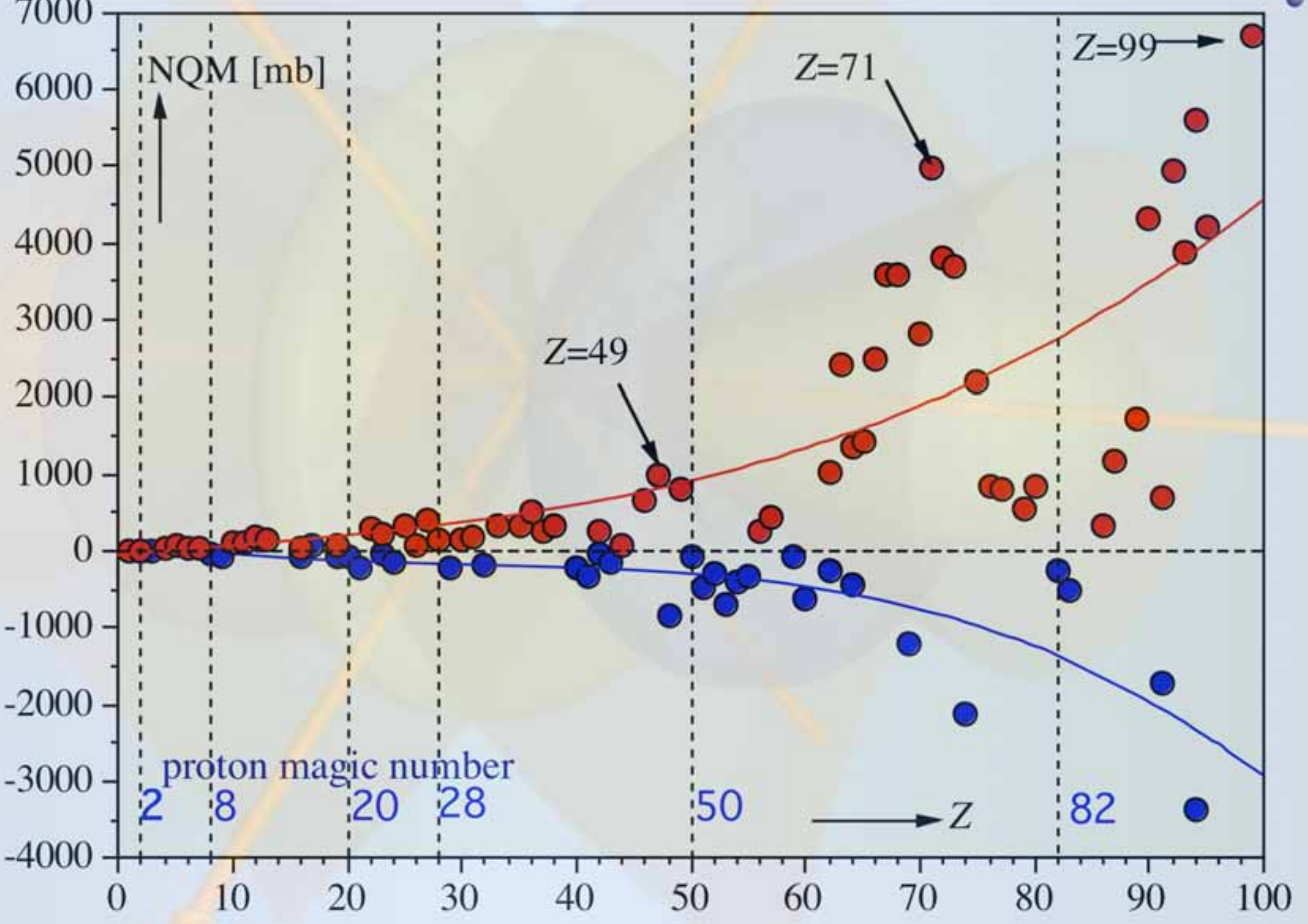


Nuclear Multipole Moments from Relativistic Electronic Structure Theory



Massey University

New Zealand INSTITUTE for Advanced Study



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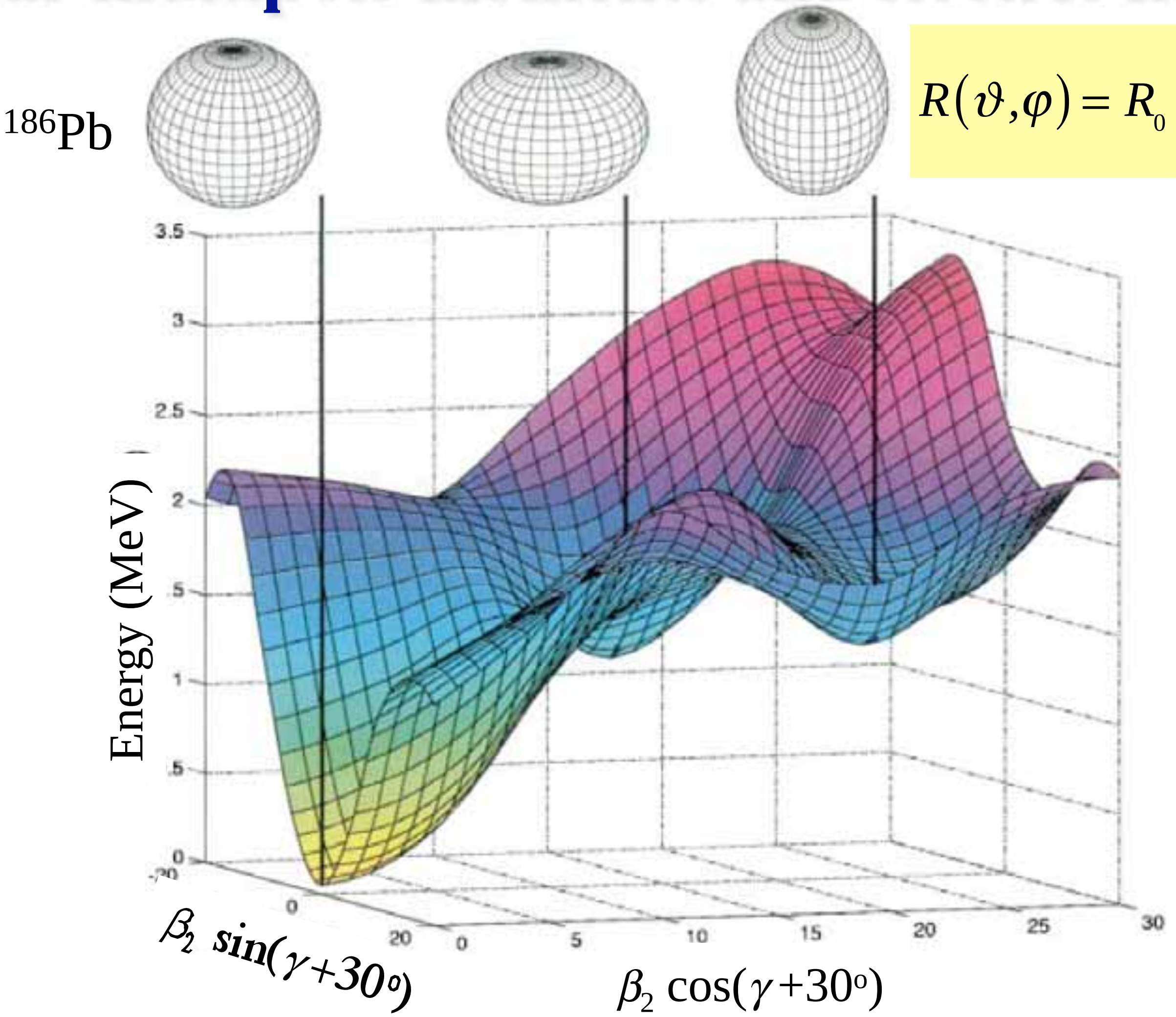
1. Nuclear multipole moments and electric field derivatives



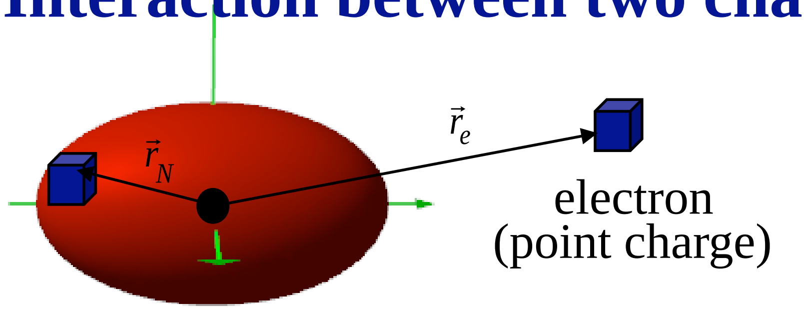
$$R(\vartheta,\varphi)=R_0\left[1+\sum_{\lambda,\mu}a_{\lambda,\mu}Y^*_{\lambda\mu}(\vartheta,\varphi)\right]$$

$$a_{20}=\beta_2\cos\gamma$$

$$a_{22}=\frac{1}{\sqrt{2}}\beta_2\sin\gamma$$

Calculated potential energy surface of ^{186}Pb. The β_2 parameter expresses the elongation of the nucleus along the symmetry axis, while the γ parameter relates to the degree of triaxiality in the deformation. γ=0° corresponds to a prolate and γ=60° to an oblate (disk-like) shape.
A. N. Andreyev et al., *Nature* 405, 430 (2000).

Probing the nuclear deformation with external charges: The Coulomb Interaction between two charge distributions



Charge distribution of
nucleus or molecule

$$E = \int\int d\vec{r}_N d\vec{r}_e \frac{n_N(\vec{r}_N) n_e(\vec{r}_e)}{\left|\vec{r}_N - \vec{r}_e\right|} = \int d\vec{r}_N \left[n_N(\vec{r}_N) \int d\vec{r}_e \frac{n_e(\vec{r}_e)}{\left|\vec{r}_N - \vec{r}_e\right|} \right]$$

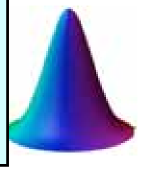
electronic structure
calculations

NMC, decomposition in
nuclear multipole moments

$$E_{eN} = \int V_N(\vec{r}_e) n_e(\vec{r}_e) d\vec{r}_e$$

$$V_N^{PC}(\vec{r}) = -\frac{Z}{\left|\vec{r} - \vec{R}_N\right|}$$

$$V_N^{SGCD}(\vec{r}) = -\frac{Z}{\left|\vec{r} - \vec{R}_N\right|} erf\left(\sqrt{3}\left|\vec{r} - \vec{R}_N\right| / \sqrt{2} R_{rms}\right)$$



$$E_{eN} = \int V_e(\vec{r}_N) n_N(\vec{r}_N) d\vec{r}_N$$

$$V_e(\vec{R}) = V_e(\vec{R}_N) + \vec{E}_e(\vec{R}_N) \cdot \vec{R} + \tfrac{1}{2} \vec{R}^T \cdot \boldsymbol{F}_e(\vec{R}_N) \cdot \vec{R} + \ldots$$

The Spherical Multipole Expansion of the Interaction Energy

J.Thyssen, P.Schwerdtfeger, M. Bender, W. Nazarewicz, P. B. Semmes, *Phys. Rev. A* 63, 022505 (2001).
M.A. Eptonand B. Dembart, Multipole translation theory for the three-dimensional Laplace and Helmholtz equations, *SIAM J. Sci. Comput.* 16, 865 (1995).

Nuclear radii: Lighter elements: $R_{\text{rms}} = 1.2\ A^{1/3}$ [fm] (Rutherford)
Heavier elements: $R_{\text{rms}} = 1.12\ A^{1/3} + 2.15\ A^{-1/3} - 1.74\ A^{-1}$ [fm]

This gives: 1 fm for H and 7 fm for ^{300}120

In comparison the electronic 1s $\langle r \rangle$ is for H =79376 fm, for E120 = 450 fm ⇨ $R_{\text{rms}} \ll \langle r \rangle$

Laplace (multipole) expansion:

$$\frac{1}{\left|\vec{r}_e - \vec{r}_N\right|} = \sum_{\lambda=0}^{\infty}\sum_{\mu=-\lambda}^{\lambda}\frac{4\pi}{2\lambda+1}\frac{r_N^{\lambda}}{r_e^{\lambda+1}}Y^{*}_{\lambda\mu}\left(\hat{r}_e\right)Y_{\lambda\mu}\left(\hat{r}_N\right)$$

$$^{S}E = \sum_{\lambda=0}^{\infty}\frac{4\pi}{2\lambda+1}\sum_{\mu=-\lambda}^{\lambda}\left[\int d\vec{r}_N\; n_N\left(\vec{r}_N\right)Y^{*}_{\lambda\mu}\left(\hat{r}_N\right)r_N^{\lambda}\right]\left[\int d\vec{r}_e\; n_e\left(\vec{r}_e\right)Y_{\lambda\mu}\left(\hat{r}_e\right)r_e^{-\lambda-1}\right]$$

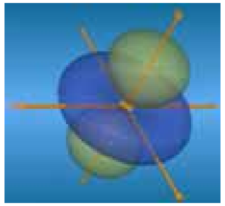
nuclear multipole moments $Q_{\lambda\mu}$ ***electric field moments $V_{\lambda\mu}$***

in order of λ
transformation in Cartesian coordinates

$$^{S}E = qV_0 - \mu_\alpha V_\alpha - \underbrace{\frac{1}{3}\Theta_{\alpha\beta}V_{\alpha\beta}}_{\textbf{NQC}} - \frac{1}{15}\Omega_{\alpha\beta\gamma}V_{\alpha\beta\gamma} - \underbrace{\frac{1}{105}\Phi_{\alpha\beta\gamma\delta}V_{\alpha\beta\gamma\delta}}_{\textbf{NHC}} + \ldots$$

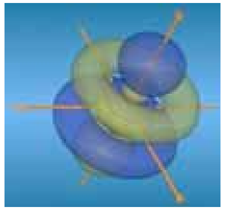
The nuclear multipole moments and fields:

$$\Theta_{zz} = \int d\vec{r}\; n_N(\vec{r})\, r^2 P_2(\hat{z})$$



$$\Theta_{xy} = \frac{3}{2}\int d\vec{r}\; n_N(\vec{r})\; xy$$

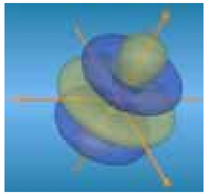
$$\Omega_{zzz} = \int d\vec{r}\; n_N(\vec{r})\, r^3 P_3(\hat{z})$$



$$\Omega_{xxy} = \frac{1}{2}\int d\vec{r}\; n_N(\vec{r})\; \left(5x^2y - xr^2\right)$$

$$\Omega_{xyz} = \frac{5}{2}\int d\vec{r}\; n_N(\vec{r})\; xyz$$

$$\Phi_{zzzz} = \int d\vec{r}\; n_N(\vec{r})\, r^4 P_4(\hat{z})$$



$$\Phi_{xxxy} = \frac{5}{8}\int d\vec{r}\; n_N(\vec{r})\; \left(4x^3y - 3xy^3 - 3xyz^2\right)$$

$$\Phi_{xxyy} = \frac{1}{2}\int d\vec{r}\; n_N(\vec{r})\, r^4\left[P_4(\hat{z}) - P_4(\hat{x}) - P_4(\hat{y})\right]$$

$$\Phi_{xxyz} = \frac{5}{8}\int d\vec{r}\; n_N(\vec{r})\; \left(6x^2yz - y^3z - yz^3\right)$$

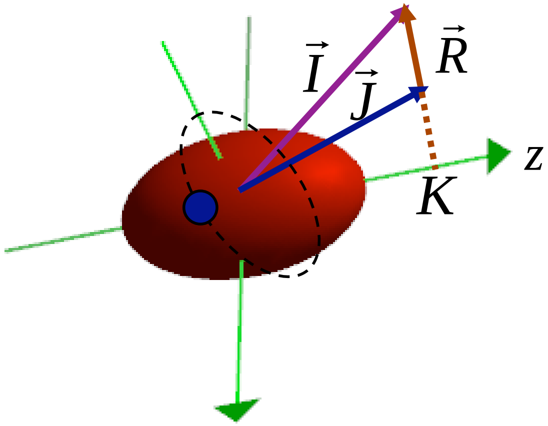
In the spherical multipole expansion the electric field gradient tensor is traceless:

The Laplace equation is fulfilled: $\boxed{V_{\alpha\alpha} = -4\pi n(0) = 0}$ (<u>but:</u> not fulfilled for *s*-orbitals)

All derivatives of the electronic density $n(\vec{r})$ vanish at the origin: $\left(\frac{\partial^k n(\vec{r})}{\partial \vec{r}_{\alpha_1}\partial \vec{r}_{\alpha_2}\cdots\partial \vec{r}_{\alpha_k}}\right)_0 = 0$

⇨ $V_{\alpha\alpha} = 0 \quad \wedge \quad V_{\alpha\beta\beta} = 0 \quad \wedge \quad V_{\alpha\beta\gamma\gamma} = 0 \;\ldots$

Intrinsic vs. spectroscopic nuclear quadrupole moments



Rotating deformed nucleus: $\underset{\text{total}}{\vec{I}} = \underset{\text{core}}{\vec{R}} + \underset{\text{particle AM}}{\vec{J}}$

$$H = H_0 + \frac{1}{2\theta}\left(\vec{I}^2 - I_z^2\right) - \frac{1}{\theta}\left(I_x J_x + I_y J_y\right)$$

Neglecting the last (Coriolis) term:

$$E = \frac{1}{2\theta}\left[I(I+1) - K^2\right]$$

strong coupling limit
(δ large)

In this approximation we get

$$\boxed{Q_s = \frac{3K^2 - I(I+1)}{(I+1)(2I+3)} Q_{int}}$$

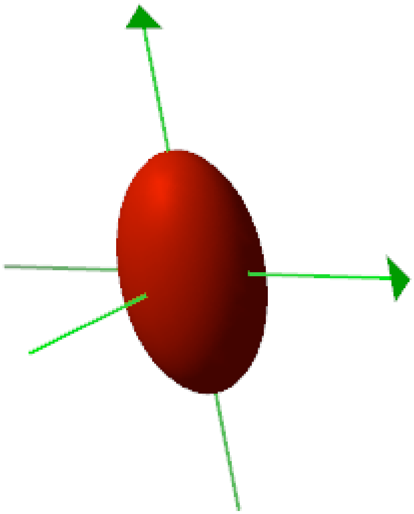
(Q_s=0 for I=0 and I=1/2)
Bohr and Mottelson (1953)

$$Q_{int} \approx \frac{4}{5} Z R_{rms}^2 \delta\left(1 + a\delta + \ldots\right)$$

available from P.Moller, 1997

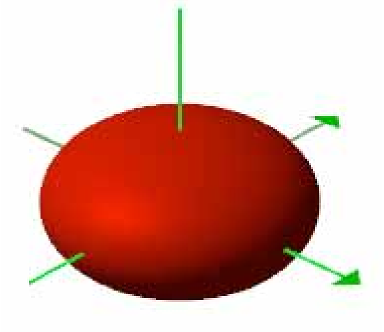
“We therefore call the agreement between calculated and experimental results good if the deviation is less than about three orders of magnitude.”
Moller and Nix 1994

The Determination of NQCCs and NQMs



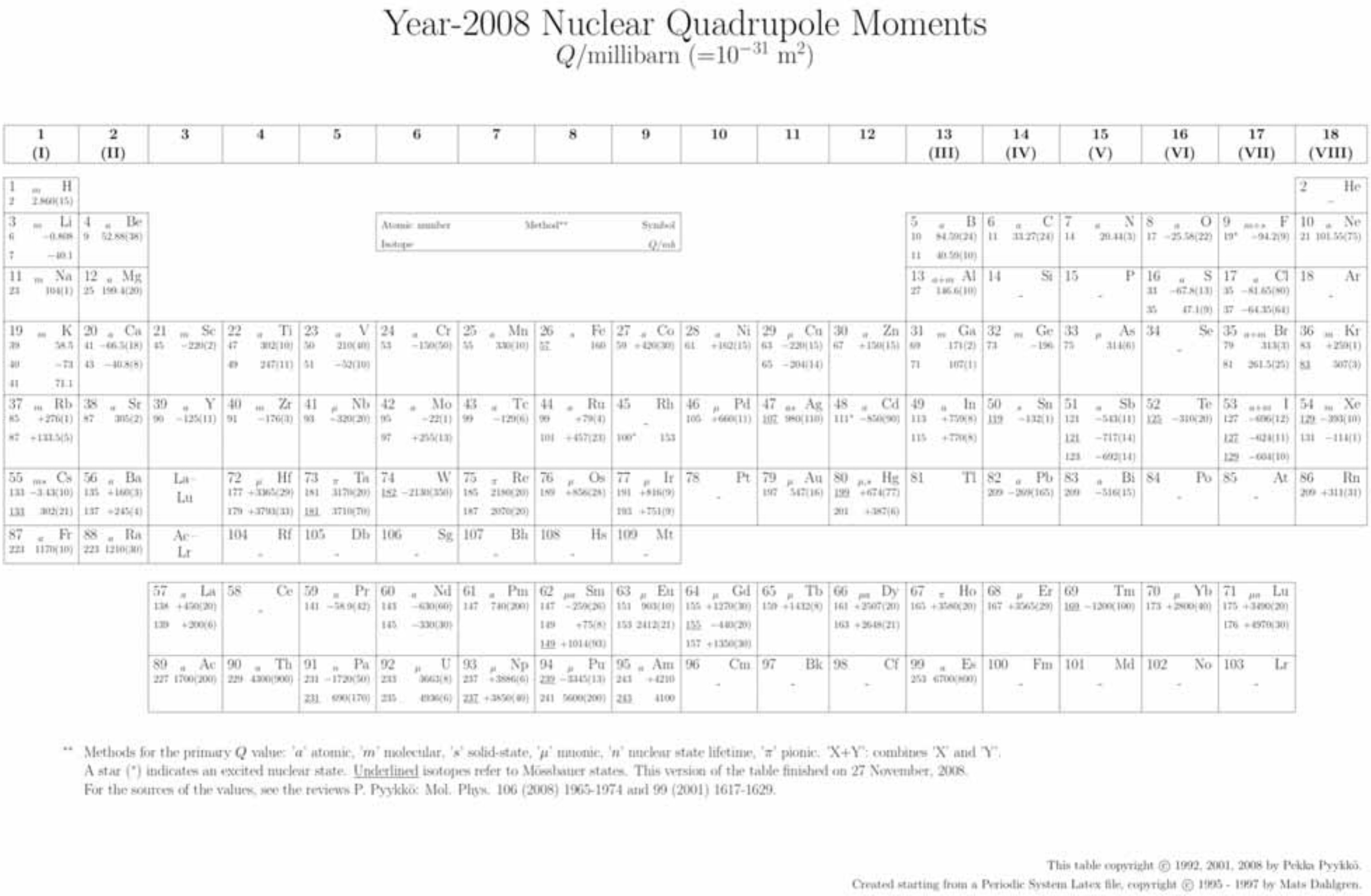
(NQM)s are obtained from:

- First principles nuclear structure calculations (Q_{int} or Q_s)
- Scattering experiments
- From NQCCs if the electric field gradient (EFG) q is known (*most precise method*) $C_{NQCC} = eQ_s$ ($q=V_{zz}$)



NQCCs are obtained from:

- Atomic emission spectroscopy (HFS, mesonic X-rays)
- Atomic Beam Resonance Spectroscopy
- Molecular Beam Resonance Spectroscopy
- Microwave Spectroscopy (*for linear molecules most precise method*)
- Nuclear Quadrupole Resonance
- Nuclear Magnetic Resonance
- Electron Spin Resonance
- Mössbauer Spectroscopy
- Muonic transitions



Year-2008 Nuclear Quadrupole Moments

Q/millibarn (=10^{-31} m^2)

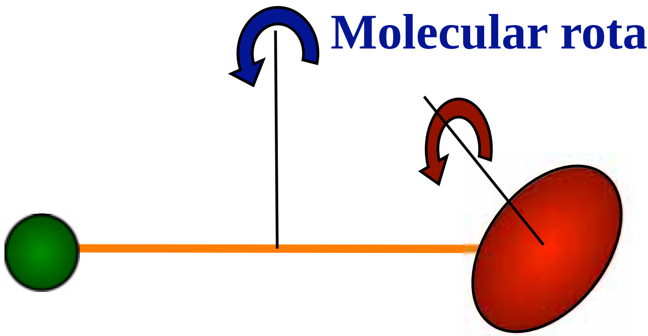
** Methods for the primary Q value: 'a' atomic, 'm' molecular, 's' solid-state, 'μ' muonic, 'n' nuclear state lifetime, 'π' pionic. 'X+Y': combines 'X' and 'Y'.
A star (*) indicates an excited nuclear state. Underlined isotopes refer to Mössbauer states. This version of the table finished on 27 November, 2008.
For the sources of the values, see the reviews P. Pyykkö: Mol. Phys. 106 (2008) 1965-1974 and 99 (2001) 1617-1629.

Tables of NQMs: P. Pyykkö, *Mol. Phys.* <u>106</u>, 1965 (2008).

NQMs from rotational spectroscopy

Rotational spectra of small molecules

The coupling between the nuclear quadrupole moment Q_s and the electric field gradient (EFG) $q(=V_{zz})$ at a specific nucleus gives rise to an energy splitting ΔE_Q that depends on the orientation of the nuclear spin $\vec{I}$. This can be observed with high precision in microwave (rotational) spectroscopy on small molecules.



Molecular rotation (*J*,*K*)

diatomic molecule

Nuclear spin (*I*)

$$\boxed{\Delta E_Q = -Y(JIF)C_{NQCC}\left[\frac{3K^2}{J(J+1)}-1\right]}$$

symmetric top

Casimir's function

$$C_{NQCC} \equiv eQ_s q[\mathrm{MHz}] = 234.9647\,Q_s[\mathrm{mb}]\,q[\mathrm{a.u.}]$$

$$Y(JIF) = -\frac{\frac{3}{4}C(C+1) - I(I+1)J(J+1)}{2I(2I-1)(2J-1)(2J+3)}$$

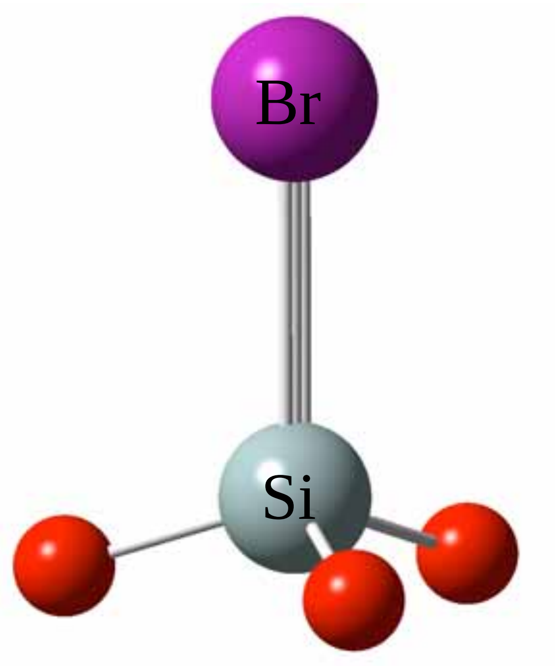
$$C = F(F+1) - I(I+1) - J(J+1)$$

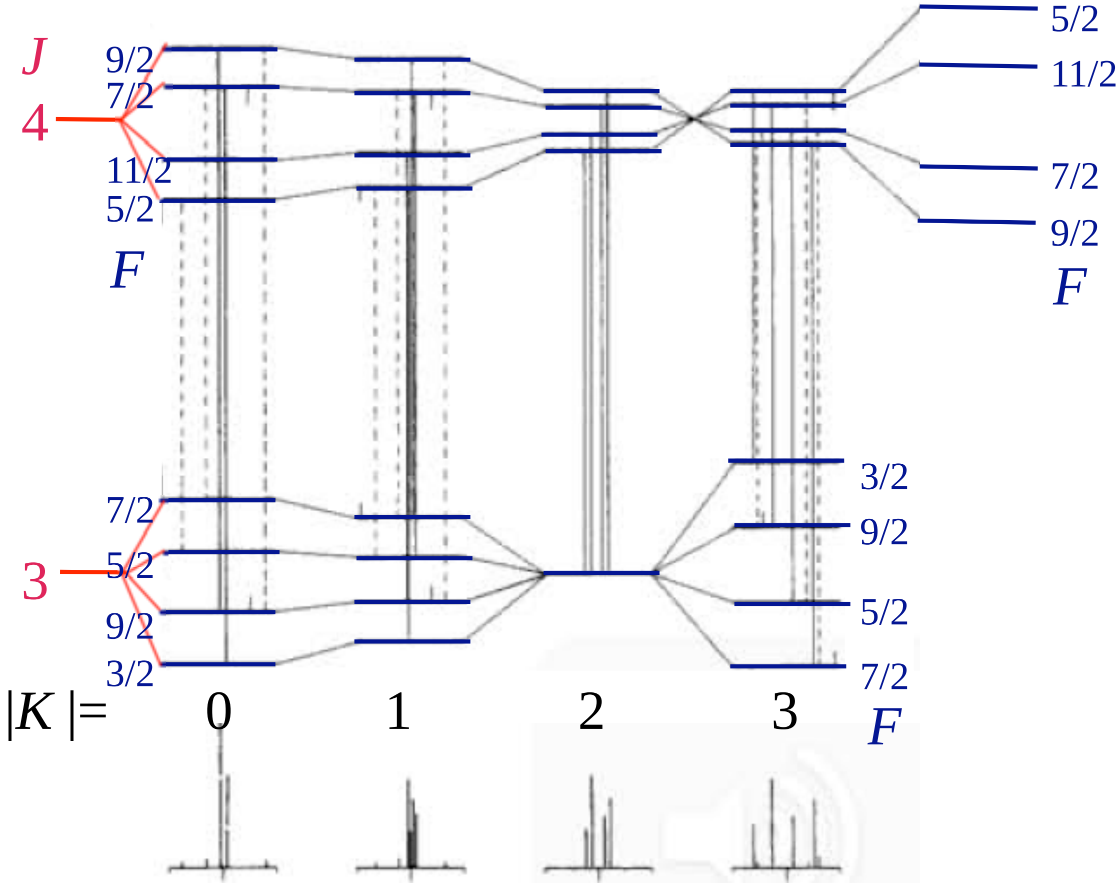
$$\vec{F} = \vec{I} + \vec{J}$$

H.W.Kroto, *Molecular Rotation Spectra*, Wiley (1975)

Energy level and transition diagram for rotational spectrum of $SiH_3{}^{79}Br$

I=3/2 for ^{79}Br and eQq = 336 MHz.





$$\frac{3K^2}{J(J+1)} - 1 = 0$$ for K=2 and J=3.

H.W.Kroto, *Molecular Rotation Spectra*, Wiley (1975)

The Accurate Determination of NQMs

Accurate NQMs are very useful for testing nuclear models!

Problem 1:

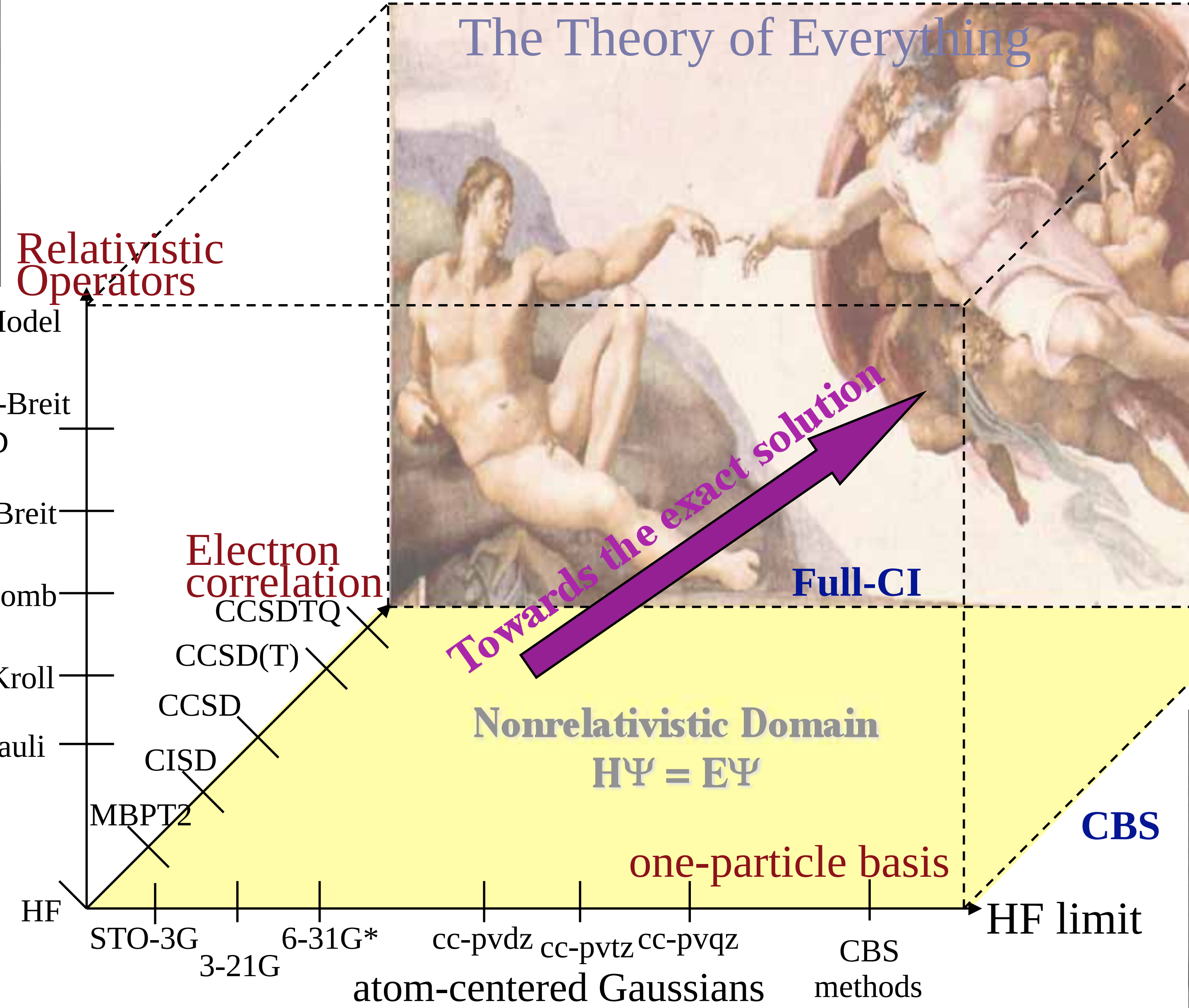
- First principle calculations of the nuclear structure is difficult and currently very time consuming and often “inaccurate” (at least for the heavier elements).
- NQMs directly from scattering experiments with charged particles is currently not very accurate either.

⇨ The most accurate method for the determination of NQMs is via the NQCC. The EFG is obtained from accurate *wavefunction* based calculations.

Problem 2:

- Numerical calculations for EFGs are only feasible for the lighter atoms.
- Finite basis set calculations require **very** large *basis sets*, especially in the *p*-part.
- Since the EFG is a typical core-property, *relativistic effects* become important even for the lighter elements. Problem: *picture change errors*.
- EFGs are very sensitive to *electron correlation*.
- *Density functional theory* may currently not be very accurate.

2. Treating the electronic Dirac equation: Relativistic and QED effects in electric field gradients and the PCNQM model.



The Relativistic Formalism (The Dirac Picture)

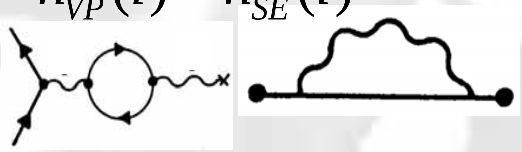
$$\boxed{H_D = \sum_i \left\{ h_D(i) + h_{QED}(i) \right\} + \sum_{i<j} g_{CB}(i,j) + \ldots}$$

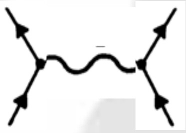
one-particle Dirac: $h_D(i) = c\vec{\alpha}_i \vec{p}_i + mc^2(\beta_i - 1) + V_{ext}(i) + \;\ldots, \quad \vec{p}_i = -i\hbar\vec{\nabla}_i$

$$\vec{\alpha} = \begin{pmatrix} 0 & \vec{\sigma} \\ \vec{\sigma} & 0 \end{pmatrix}, \quad \beta = \begin{pmatrix} \mathrm{I} & 0 \\ 0 & \text{-}\mathrm{I} \end{pmatrix}, \quad \sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad \sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \quad \sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & \text{-}1 \end{pmatrix}$$

Coulomb+Breit $O(c^{-2})$: $g_{CB}(i, j, \frac{\omega_{ij}}{c} \to 0) \cong r_{ij}^{-1} - \frac{1}{2} r_{ij}^{-1} \left[\vec{\alpha}_i \vec{\alpha}_j + (\vec{\alpha}_i \vec{r}_{ij})(\vec{\alpha}_j \vec{r}_{ij}) r_{ij}^{-2} \right]$

Vaccum polarization + electron self energy $O(c^{-2+})$: $h_{QED}(i) = h_{VP}(i) + h_{SE}(i)$





The stationary Dirac-equation

$$\boxed{\begin{pmatrix} V - E & c\vec{\sigma}\vec{p} \\ c\vec{\sigma}\vec{p} & -2mc^2 + V - E \end{pmatrix} \begin{pmatrix} \varphi_L \\ \varphi_S \end{pmatrix} = 0}$$

Programs: For atoms: GRASP; for molecules: DIRAC, UTCHEM, BERTHA

The Nonrelativistic Formalism (Schrödinger Picture)

Problem: H_D in the Dirac picture is unbound and the small component φ_S of the Dirac bi-spinor only accounts for less than 1% of the total wavefunction

Goal: Find semi-bound H_S in the Schrödinger picture. The unitary (Foldy-Wouthuysen, FW) transformation from the Dirac- to the Schrödinger picture (in au):

$$\begin{pmatrix} V & c\vec{\sigma}\vec{p} \\ c\vec{\sigma}\vec{p} & V-2mc^2 \end{pmatrix}\begin{pmatrix} \varphi_L \\ \varphi_S \end{pmatrix} = \begin{pmatrix} h_{11} & h_{12} \\ h_{21} & h_{22} \end{pmatrix}\begin{pmatrix} \varphi_L \\ \varphi_S \end{pmatrix} = H_D\begin{pmatrix} \varphi_L \\ \varphi_S \end{pmatrix} E\begin{pmatrix} \varphi_L \\ \varphi_S \end{pmatrix}$$

$$H_S = UH_DU^\dagger = \begin{pmatrix} H_+ & 0 \\ 0 & H_- \end{pmatrix} \quad , \quad \boxed{U = \begin{pmatrix} (1+X^\dagger X)^{-1/2} & (1+X^\dagger X)^{-1/2}X^\dagger \\ -e^{i\varphi}(1+X^\dagger X)^{-1/2}X & e^{i\varphi}(1+X^\dagger X)^{-1/2} \end{pmatrix}}$$

$$\varphi_S = X\varphi_L \,, \quad \psi^{FW} = U\varphi_L \,, \quad (\psi^{FW}, \psi^{FW}) = 1 \quad \text{and} \quad \boxed{X = \left(2mc^2 + E - V\right)^{-1} c\vec{\sigma}\vec{p}}$$

$$\Longrightarrow \quad \boxed{h_+ = \frac{1}{\sqrt{1+X^\dagger X}}\left[h_{11} + h_{12}X + X^\dagger\left(h_{21} + h_{22}X\right)\right]\frac{1}{\sqrt{1+X^\dagger X}}}$$

We need only h_+. **Problem**: X does not commute with either $X^\dagger$ or V. Even if we take the nonrelativistic limit $X = c\vec{\sigma}\vec{p}$, an iterative procedure will generate singular operators.

But: The picture change error (PCE) in two-component theory

The unitary transformation from the Dirac- to the Schrödinger picture also requires perturbation operators (electric and magnetic fields) to be transformed:

1) Diagonal perturbation operators f:
(e.g. *the nuclear quadrupole coupling operator*)

$$\begin{pmatrix} V-E+f & c\sigma p \\ c\sigma p & -2mc^2+V-E+f \end{pmatrix}\begin{pmatrix} \varphi_L \\ \varphi_S \end{pmatrix} = 0$$

Substitution of *V* by *V+f* in the power series leads to the following expression for the Pauli-series:

$$\tilde{H}_+ = V + f + \frac{1}{2c^2}(c\boldsymbol{\sigma}\mathbf{p})^2 - \frac{1}{8c^4}[c\boldsymbol{\sigma}\mathbf{p},[c\boldsymbol{\sigma}\mathbf{p},V+f]] - \frac{1}{8c^6}(c\boldsymbol{\sigma}\mathbf{p})^4 + \dots$$

$$\boxed{f^S = f + \frac{1}{8c^2}\Delta f + \dots}$$

Neglect of these higher order terms leads to the so-called picture change error which becomes important for heavy elements.

2) Off-diagonal perturbation operators f:

$$\begin{pmatrix} V-E & c\sigma p+f \\ c\sigma p+f & -2mc^2+V-E \end{pmatrix}\begin{pmatrix} \varphi_L \\ \varphi_S \end{pmatrix} = 0 \qquad \gamma^5 = \begin{pmatrix} 0 & I \\ I & 0 \end{pmatrix}$$

Substitution of $c\vec{\sigma}\vec{p}$ by $c\vec{\sigma}\vec{p}+f$:

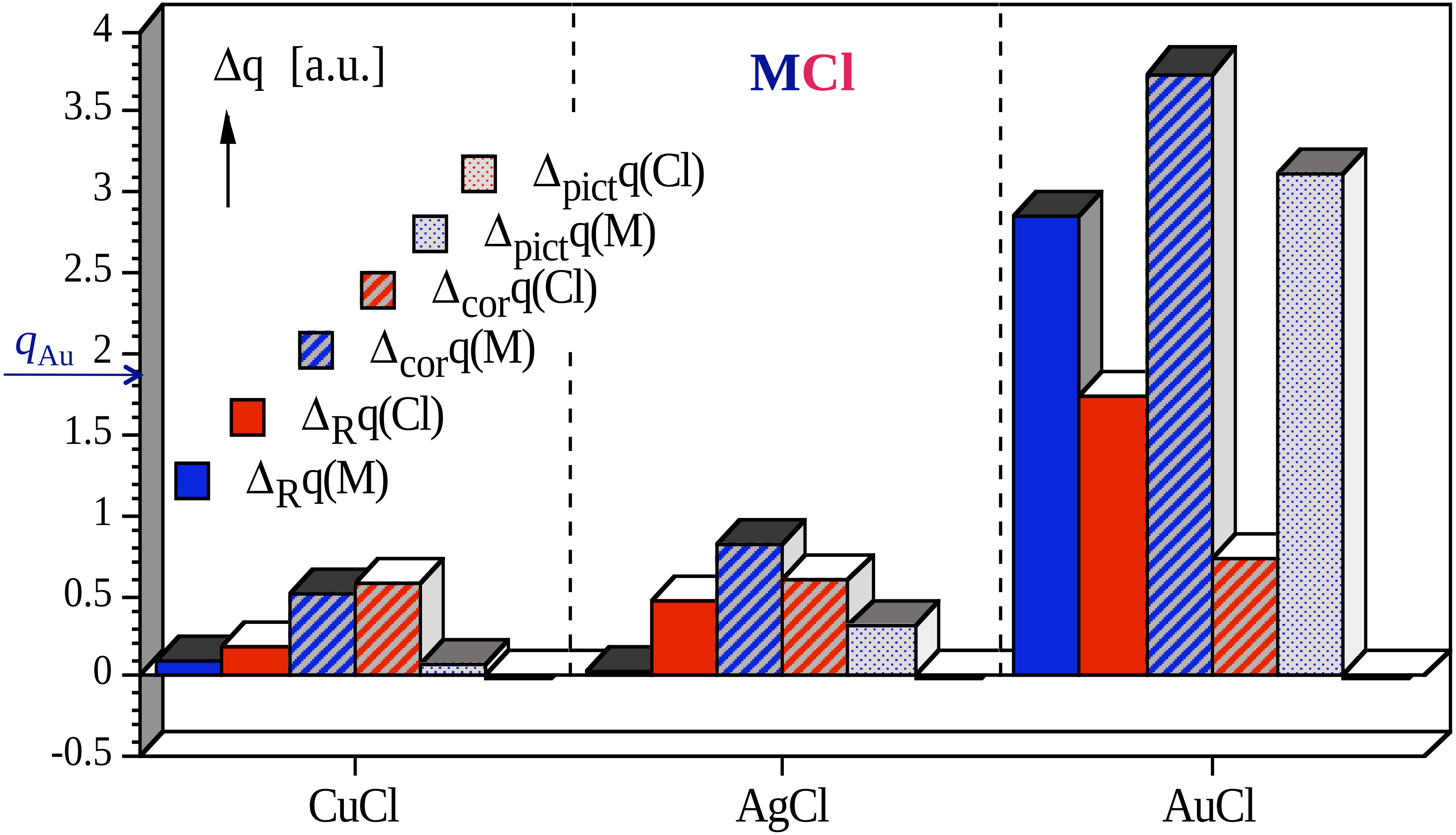
$$\tilde{H}_+ = V + \frac{1}{2c^2}(c\boldsymbol{\sigma}\mathbf{p}+f)^2 - \frac{1}{8c^4}[c\boldsymbol{\sigma}\mathbf{p}+f,[c\boldsymbol{\sigma\pi}+f,V]] - \frac{1}{8c^6}(c\boldsymbol{\sigma}\mathbf{p}+f)^4 + \dots$$

$$\boxed{f^S = \frac{1}{2mc}[\boldsymbol{\sigma\pi}, f]_+ + \dots}$$

$$\longrightarrow \boxed{H_{eN}^{PNC} = \frac{G_F}{4\sqrt{2}mc}\sum_{i,n} Q_{W,n}\left\{\vec{\sigma}_i\vec{p}_i,\rho_n(\vec{r}_{in})\right\}_+}$$

Bouchiat-Hamiltonian

The Picture-Change Effect for Electric Field Gradients



E. J. Baerends, W. H. E. Schwarz, P. Schwerdtfeger, J. G. Snijders, *J. Phys. B: At. Mol. Phys.* 23, 3225 (1990); M.Pernpointner, B.A.Heß, P.Schwerdtfeger, *Int. J. Quantum Chem.* 76, 371 (2000).

Methods for the determination of electric field gradients

DC TC/SR NR

1) Through the expectation value (HF, KS, …) ✓ ✗ ✓

$$q_{\alpha\beta} = \left\langle V^{el}_{\alpha\beta}(\vec{R}_N)\right\rangle + V^{nuc}_{\alpha\beta}(\vec{R}_N) \qquad \left\langle V^{el}_{\alpha\beta}(\vec{R}_N)\right\rangle = \left\langle \Psi \middle| \sum_i^n \frac{3(r_{i\alpha}-R_{N\alpha})(r_{i\beta}-R_{N\beta})-\delta_{\alpha\beta}\left|\vec{r}_i-\vec{R}_N\right|^2}{\left|\vec{r}_i-\vec{R}_N\right|^5} \middle| \Psi \right\rangle$$

e.g DK wavefunction

untransformed EFG operator

For correlated methods like CCSD(T) reduced density matrix is obtained by the *Z*-vector method (Handy, Schaefer). **Solution:** Transform the EFG tensor (F.Neese, A. Wolf, T. Fleig, M. Reiher, B.A. Hess, *J. Chem. Phys.* 122, 204107 (2005))

2) Finite Field Method ✓ ✗ ✓ (good for MRCI, CC)

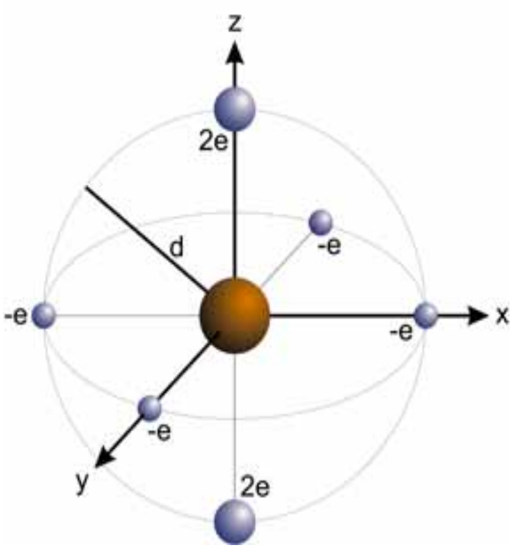
P.L.Cummins, G.B.Bacskay, N.S.Hush, *J. Chem. Phys.* 86, 6908 (1987);
ibid. 87, 416 (1987).

Perturbation by $V^{el}_{\alpha\beta}(\vec{R}_X)$ $\Longrightarrow$ $H = H_0 + \lambda V^{el}_{\alpha\beta}(\vec{R}_N)$ $\Longrightarrow$ $\left\langle V^{el}_{\alpha\beta}(\vec{R}_X)\right\rangle = \frac{dE(\lambda)}{d\lambda}$

untransformed EFG operator

3) The Point-Charge Nuclear Quadrupole Model ✓ ✓ ✓

(good for MRCI, CC)



$$U_{int} = \left\langle \frac{1}{2}(2\varsigma d^2 V_{zz} - \varsigma d^2 V_{xx} - \varsigma d^2 V_{yy}) \right\rangle = \frac{3}{2}\varsigma d^2 q_{zz} = \frac{3}{2} Q q_{zz}$$

⇨ $$q_{zz} = \frac{2}{3}\frac{dU_{int}}{Q}$$

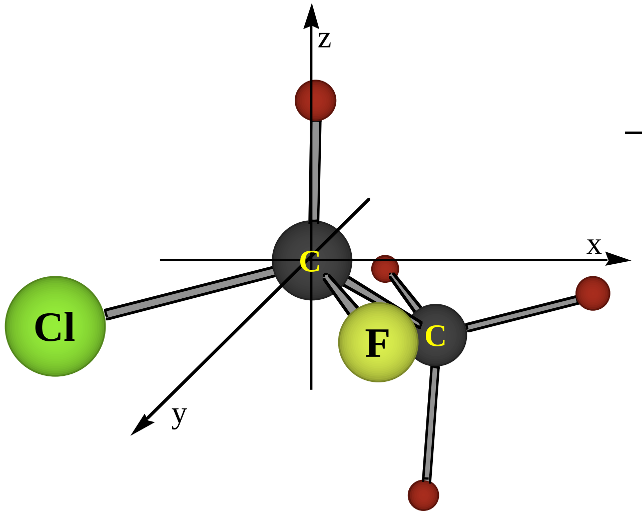
off-diagonal elements:

$$V_{xy} = \frac{2}{3}\left(\frac{dU^{xy}_{int}(Q)}{dQ}\right)_0 + \frac{1}{2}V_{zz}$$

$$V_{xz} = \frac{2}{3}\left(\frac{dU^{xz}_{int}(Q)}{dQ}\right)_0 + \frac{1}{2}V_{yy}$$

$$V_{yz} = \frac{2}{3}\left(\frac{dU^{yz}_{int}(Q)}{dQ}\right)_0 + \frac{1}{2}V_{xx}$$

Accuracy of the PCNQM Model:



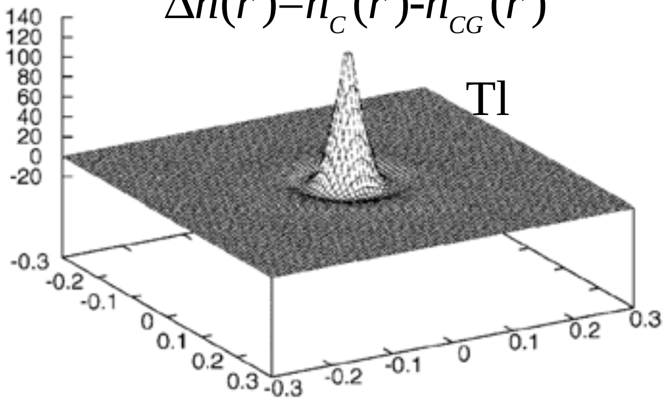
Method	V_{xx}	V_{yy}	V_{zz}	V_{xy}	V_{xz}	V_{yz}
PCNQM(HF)	-0.0651	-0.2147	+0.2799	+0.0739	+0.1461	-0.0653
$\langle V_{\alpha\beta}\rangle$(HF)	-0.0651	-0.2148	+0.2799	+0.0739	+0.1460	-0.0653
PCNQM(MP2)	-0.0231	+0.0122	+0.0109	-0.0340	-0.0236	+0.0265
$\langle V_{\alpha\beta}\rangle$(MP2)	-0.0231	+0.0122	+0.0109	-0.0340	-0.0236	+0.0265

How important are Breit and other QED contributions for EFGs?

- Pernpointner studied the Gaunt interaction in TlH (*J. Phys. B: At. Mol. Phys.* 35, 383 (2002))

Method	C	CG
$q^{\mathrm{Tl}}_{\mathrm{DHF}}$	–1.7953	–1.7945
$\Delta q^{\mathrm{Tl}}_{\mathrm{MP2}}$	0.06533	0.06529
$\Delta q^{\mathrm{Tl}}_{\mathrm{CCSD}}$	0.08642	0.08632
$\Delta q^{\mathrm{Tl}}_{\mathrm{(T)}}$	0.02041	0.02040

$\Delta n(\vec{r}) = n_C(\vec{r}) - n_{CG}(\vec{r})$



$$g_{CG}\left(i, j, \frac{\omega_{ij}}{c} \to 0\right) \cong r_{ij}^{-1}\left(1 - \vec{\alpha}_i \vec{\alpha}_j\right)$$

- Pyykkö *et al*. studied VP+SE for AuH

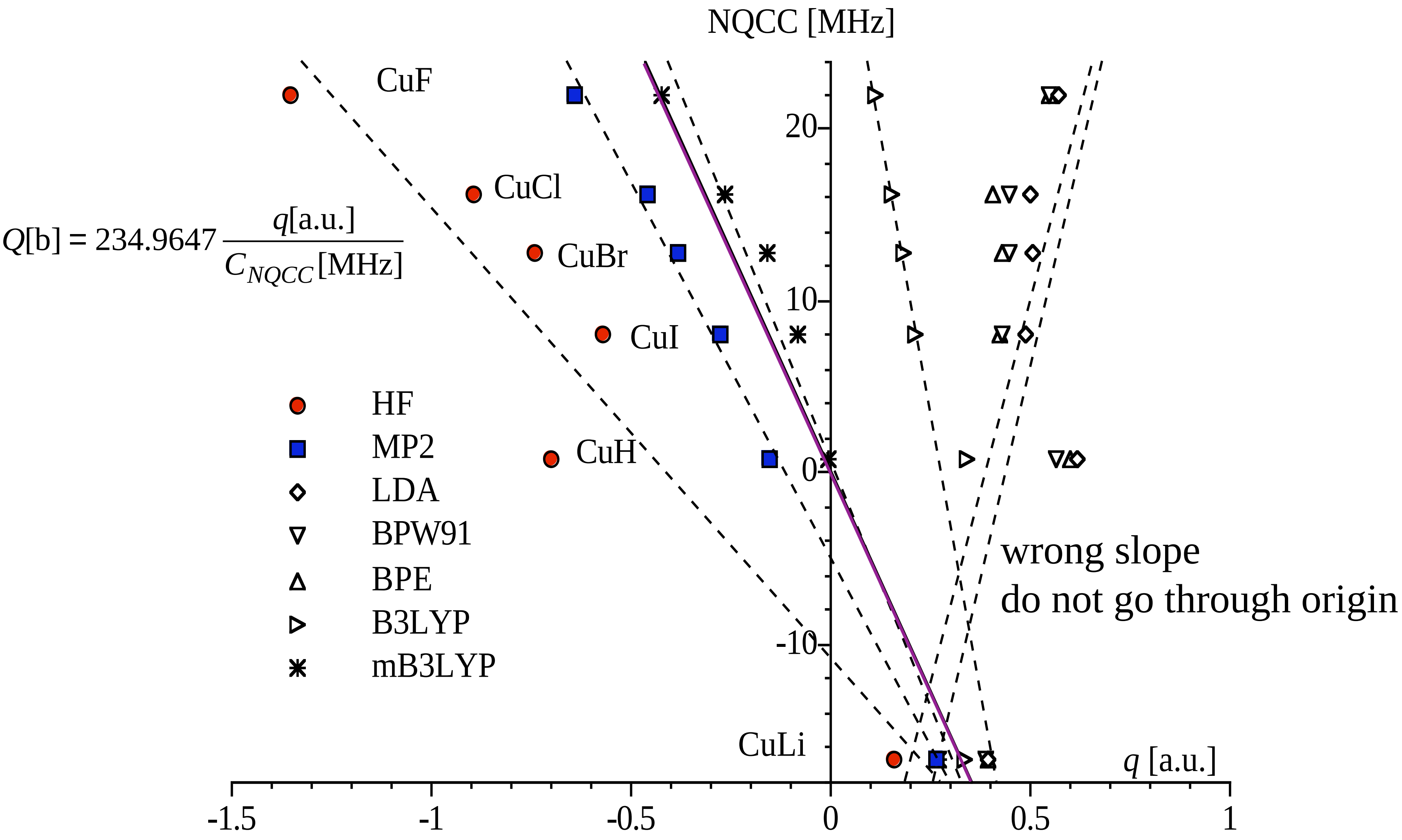
Method	at Au
q_{DHF}	–2.3340
$\Delta q_{\mathrm{CCSD(T)}}$	3.9721
Δq_{G}	–0.0226
$\Delta q_{\mathrm{VP+SE/DHF}}$	–0.0460

?

Kramers restricted relativistic coupled cluster theory for EFGs.

(or why density functionals are bad news for EFGs)

Late Transition Element: Copper Halides (^{63}Cu)



$$Q[\mathrm{b}] = 234.9647 \frac{q[\mathrm{a.u.}]}{C_{NQCC}[\mathrm{MHz}]}$$

wrong slope
do not go through origin

Kramers restricted coupled cluster (KRCC)

- The CC expression is derived by applying the wave operator to the *N*-particle wavefunction,

$$\boxed{\psi = e^{\hat{T}}\phi_0}$$

with $\hat{T} = \sum_{i=1} \hat{T}_i = \sum_i \sum_a t_i^a \hat{E}_i^a + \sum_{ij} \sum_{ab} t_{ij}^{ab} \hat{E}_{ij}^{ab} + \sum_{ijk} \sum_{abc} t_{ijk}^{abc} \hat{E}_{ijk}^{abc} + \ldots$

- Up to $\hat{T}_2$: CCSD, up to $\hat{T}_3$: CCSDT etc. The CC *amplitudes* $t_{ij\ldots}^{ab\ldots}$ are antisymmetric in the occupied spinor space and the virtual spinor space. The *excitation* $\hat{E}_{ij\ldots}^{ab\ldots}$ *operators* are

$$\hat{E}_{ij\ldots}^{ab\ldots} = a_a^\dagger a_b^\dagger \ldots a_i a_j \ldots$$

- Closed shell KR-CCSD including perturbative triples, CCSD(T), utilizing
- Kramers symmetry for the closed-shell case:

$$\left[\hat{K}, e^{\hat{T}}\right] = 0$$

Kramers restricted CC calculations

Dirac relativistic SCF calculations are far more computer time expensive compared to nonrelativistic/scalar relativistic calculations as

- The spin cannot be factored out anymore (factor 2 for each basis function

  → $2^4=16$ increase in computer time

- This can be reduced to a factor of 4 if Kramers (time-reversal) symmetry $\hat{K}$ is considered.

- In nonrelativistic time reversal symmetry leaves positions invariant, but changes sign of all velocities. In QM it also changes sign of spin and orbital angular momentum. This results in $\hat{K}$ being anti-unitary and $\boxed{\hat{K} = -i\Sigma_y \hat{C}}$

  with $\Sigma_y = \begin{pmatrix} \sigma_y & 0 \\ 0 & \sigma_y \end{pmatrix}$, $\hat{K}\left(\lambda_1\psi_1 + \lambda_2\psi_2\right) = \lambda_1^*\hat{K}\psi_1 + \lambda_2^*\hat{K}\psi_2$, $\hat{K}\hat{H}_D\hat{K}^\dagger = \hat{H}_D$

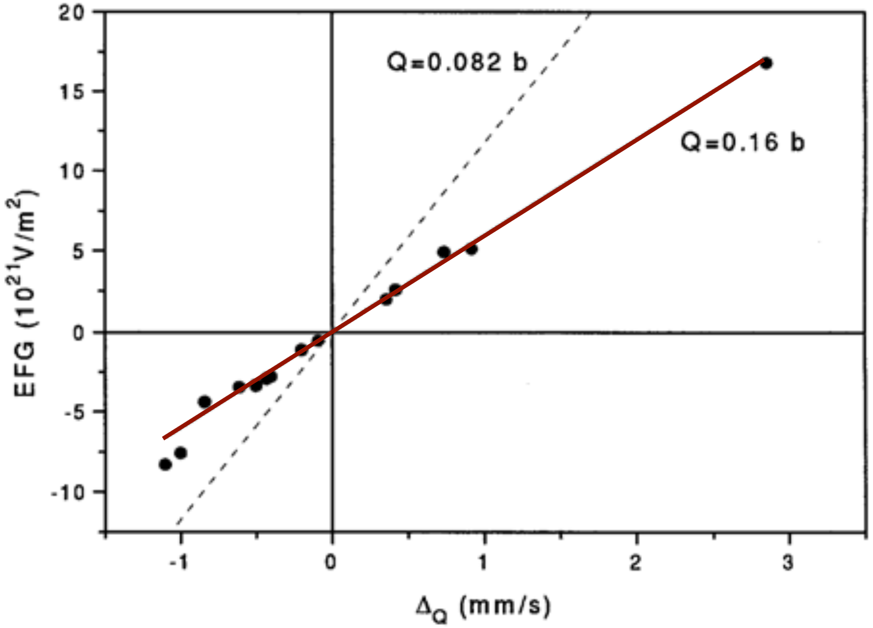
  and ψ and $\hat{K}\psi$ are energy degenerate (in covariant form: $\hat{K} = i\gamma_1\gamma_3\gamma_0$).

3. The nuclear quadrupole moment of ^{57}Fe (I=3/2) and ^{197}Au, and the nuclear hexadecapole moment of ^{127}I.

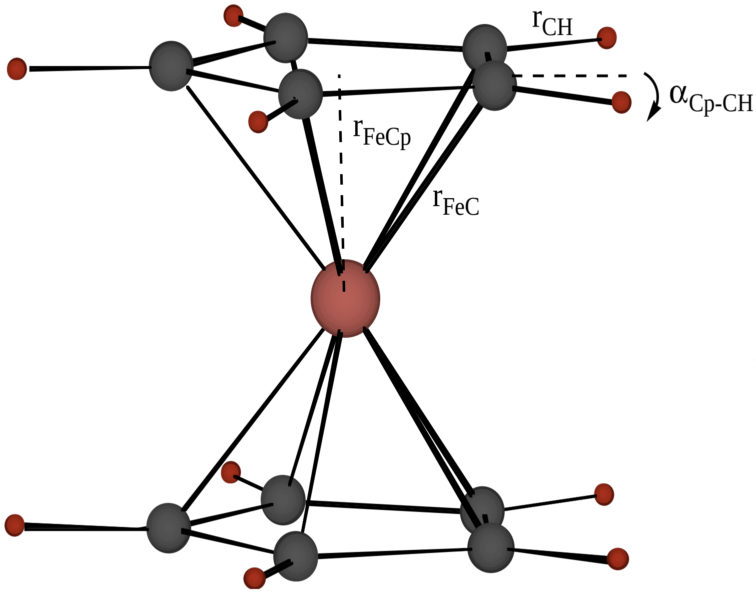
- The ^{57}Fe (I=3/2$^-$ excited state) nuclear quadrupole moment

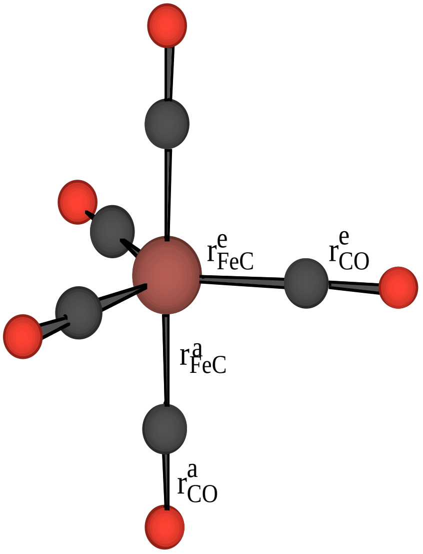
- Needed in Mössbauer spectroscopy (ground state: I=1/2$^-$)
- Accepted NQM for ^{57}Fe before 1998: 82 mbarn (Mishra, Das 1981) using Mössbauer data with calculated HF field gradients, supported by Vajda et al from nuclear shell structure calculations
- Reset of this value from LAPW-DFT using Perdew's GGA functional calc. for a variety of solid state compounds: 160 mbarn

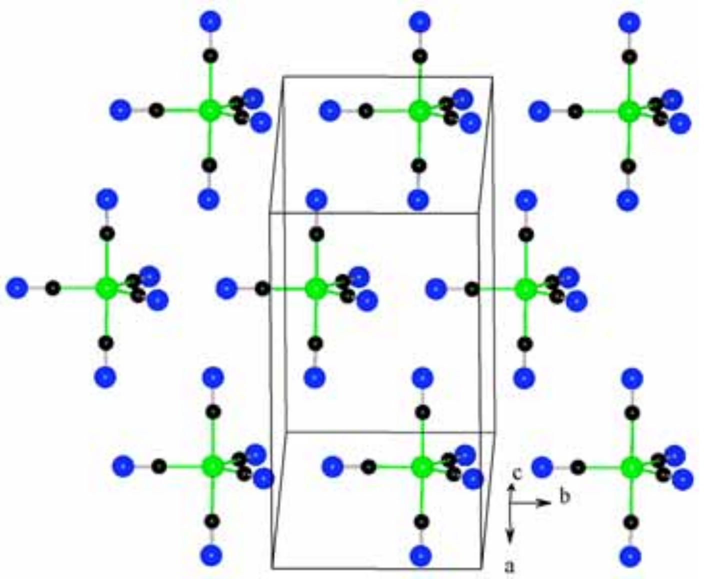
(P.Dufek, P.Blaha, K.Schwarz, *Phys. Rev. Lett.* 75, 3545 (1995))



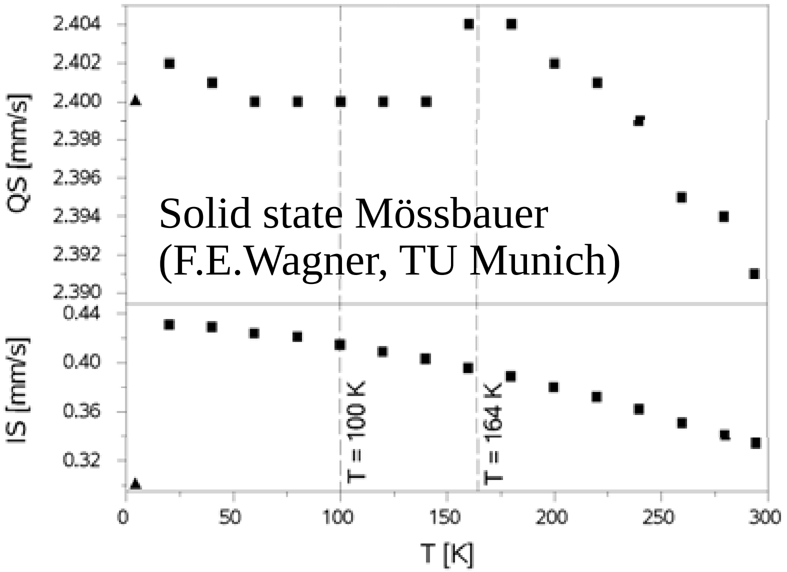
Molecular Douglas-Kroll PCNQM calculations for $Fe(CO)_5$, $Fe(C_5H_5)_2$







Solid state structure $Fe(CO)_5$



Solid state Mössbauer
(F.E.Wagner, TU Munich)

$Fe(CO)_5$:

$$q_T = q_{CCSD(T)} + \Delta q_{rest.space} + \Delta q_{Basis}$$

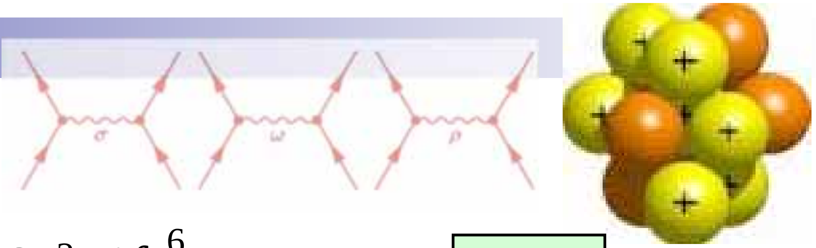
$$1.439 + 0.082 + 0.476(?)$$

$$+ \Delta q_{Solid\text{-}State} + \Delta q_{Struct} + \Delta q_{relativistic}$$

$$-0.036 + 0.074 + 0.065$$

$$= \underline{2.1\ \text{a.u.}}$$

⇨ $$Q_s[\text{mb}] = 98.93 \frac{\Delta[\text{mm/s}]}{q[\text{a.u.}]} = 0.12\ \text{b}$$



Nuclear shell-structure calculations

- ^{57}Fe: 26p$^+$, proton shell: $1s^2, 1p^6, 1d^{10}, 2s^2, 1f_{7/2}^6$
  31n, neutron shell: $1s^2, 1p^6, 1d^{10}, 2s^2, 1f_{7/2}^8, 2p_{3/2}^3$

$\Rightarrow$ $\boxed{3/2^-}$

pf-shell

↑

25.7×10^6 states

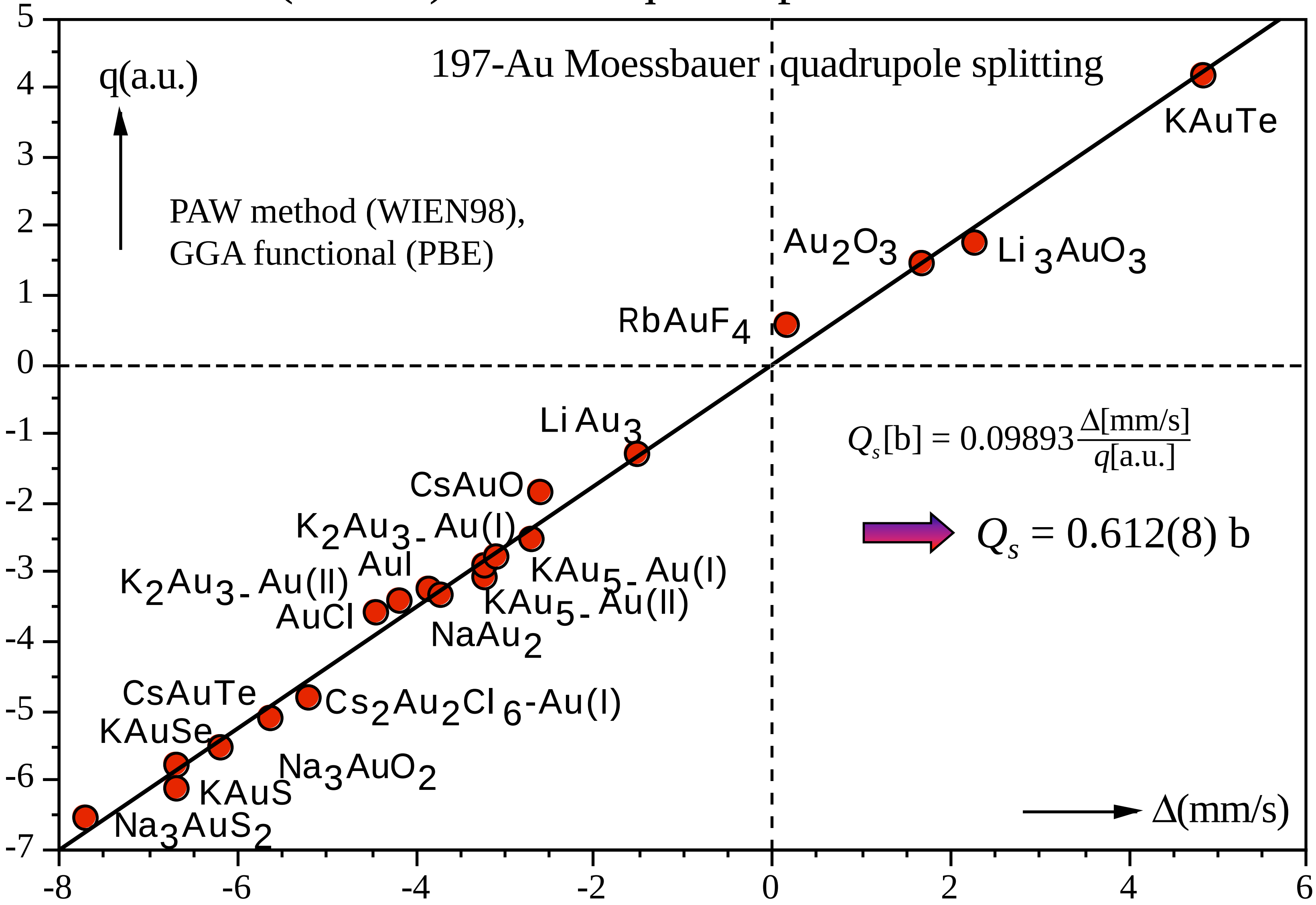
- The $Q_s(^{54}\mathrm{Fe}\ 10^+)/Q_s(^{57}\mathrm{Fe}\ 3/2_1^-) = 3.63\pm0.22$ is known (M. Hass *et al.*, *Nucl. Phys. A* 414, 316 (1984)).

		KB3F	KB3G	FPD6
Q_s[b]	$3/2_1^-$	0.16	0.06	−0.17
(+353keV)	$3/2_2^-$	−0.16	−0.07	0.17
^{54}Fe	10^+	0.51	0.50	0.56
$Q_s(^{54}\mathrm{Fe})/Q(^{57}\mathrm{Fe})$		3.19	8.33	−3.29
$\mu[\mu_N]$	$3/2_1^-$	−0.32	−0.49	−0.51
	$3/2_2^-$	0.26	0.23	0.49

Results of the shell-model calculations for the quadrupole *Q* and magnetic moments *μ* of the two lowest $3/2^-$ states in ^{57}Fe using effective interactions KB3F, KB3G, and FPD6. Experimental $\mu(3/2_1^-) = -0.1549(2)\ \mu_N$

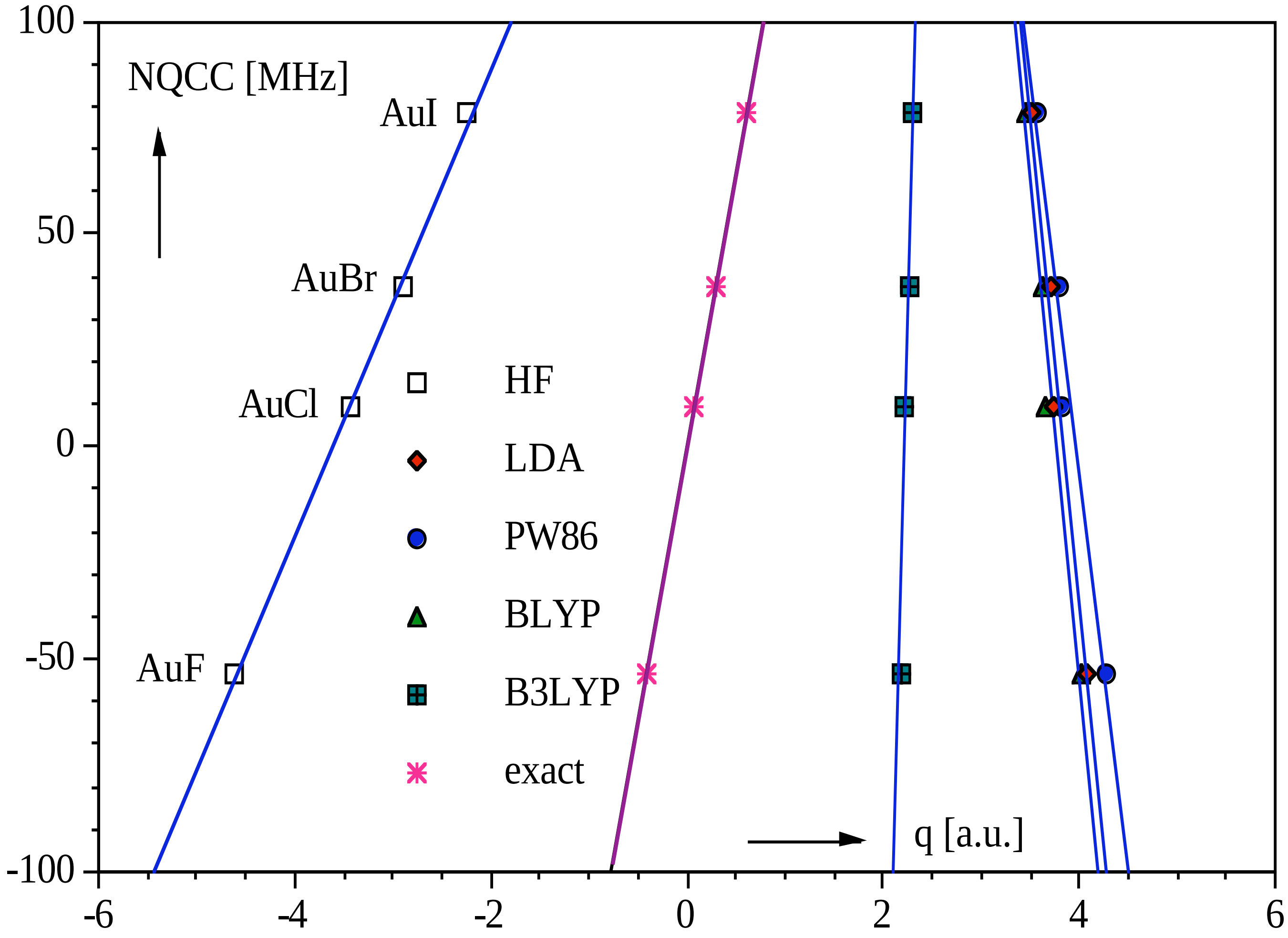
G. Martínez-Pinedo, P. Schwerdtfeger, E. Caurier, K. Langanke, W. Nazarewicz, T. Söhnel, *Phys. Rev. Lett.* 87, 062701 (2001).

The ^{197}Au (I=3/2^{+}) nuclear quadrupole moment



P. Schwerdtfeger, R. Bast, M. C. L. Gerry, C. R. Jacob, M. Jansen, V. Kellö, A. V. Mudring, A. J. Sadlej, T. Saue, T. Söhnel, F. E. Wagner, *J. Chem. Phys.* 122, 124317 (2005).

But: Is DFT reliable for Au EFGs?
Dirac-Coulomb DFT Calculations



Q_s[b]= 3.76 (B3LYP), 0.23 (DHF), -0.44 (LDA), -0.79 (PW86), -0.99 (BLYP)
compare to best estimate from muonic experiments: +0.55 b

Can we achieve better results?
DC-HF calculations for q(Au) for Au, AuH, AuF and AuCl

- The Auckland attempt (compare to muonic value of **+0.547(16) b**)
R.J. Powers et al., *Nucl. Phys.* A230, 413 (1974)

NQCC from C.J. Evans and M.C.L. Gerry, *J. Am. Chem. Soc.* 122, 1560, 2000).

Molecule	q_{nuc}	q_{NRHF}	Δq_{DHF}	$\Delta q_{\mathrm{corr}}^{\mathrm{CCSD(T)}}$	Δq_{zpv}	q_{total}	Q_s(b)
AuF	0.378	−5.636	+0.643	+4.765	−0.019	+ 0.131	−1.729
AuCl	0.474	−4.544	+0.634	+3.062	–	−0.374	−0.110

Problem: EFGs should be around −0.42 a.u for AuF and +0.08 a.u. for AuCl

Solution: look for molecule with larger EFG

Molecule	q_{nuc}	q_{NRHF}	Δq_{DK}	$\Delta q_{\mathrm{corr}}^{\mathrm{CCSD}}$	$\Delta q_{\mathrm{corr}}^{\mathrm{+T(CCSD)}}$	q_{total}	Q_s(b)
FAuCO	0.755	−10.145	−1.845	+3.852	+0.605	−6.777	+0.632

➡ To improve the current muonic value (which neglects the interaction with all the other electrons for the determination of the EFG) is difficult (muonic value is used for the determination of NQMs for a number of different isotopes (G. Passler, *Nucl. Phys.* A580, 173 (1994))

P. Schwerdtfeger, R. Bast, M. C. L. Gerry, C. R. Jacob, M. Jansen, V. Kellö, A. V. Mudring, A. J. Sadlej, T. Saue, T. Söhnel, F. E. Wagner, *J. Chem. Phys.* 122, 124317 (2005).

muonic **+0.547(16) b**

- ## The Colorado attempt

W. M. Itano, *Phys. Rev. A* 73, 022510 (2006).

Atomic beam magnetic resonance value for the $^2D_{5/2}$ state of Au and estimated $\langle r^{-3}\rangle_{5d\ j}$ values gave 0.59(12) b (W.J.Childs, L.S.Goodman, *Phys. Rev.* 141, 176 (1966))

Multireference Dirac-Fock calculations: Q_s= +0.5918 b from $^2D_{5/2}$ and +0.5816 b from $^2D_{3/2}$ hyperfine constants

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- ## The Tel-Aviv attempt

H. Yakobi, E. Eliav, U. Kaldor, *J. Chem. Phys.* 126, 184305 (2007).

Finite Field Method, Dirac-Fock, Fock-space coupled cluster, Gaunt at DHF:
Q_s= +0.521(7) b from $^2D_{5/2}$ and $^2D_{3/2}$ hyperfine constants

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- ## The Amsterdam attempt

L. Belpassi, F. Tarantelli, A. Sgamellotti, H. M. Quiney, J. N.P. van Stralen,
L. Visscher, *J. Chem. Phys.* 126, 064314 (2007)

KR-CCSD(T) for AuF, XeAuF, KrAuF, ArAuF, OCAuF, and AuH

Q_s= +0.510(13) b

- The Helsinki-Bratislava-Auckland response

L. Belpassi, F. Tarantelli, A. Sgamellotti, H. M. Quiney, J. N.P. van Stralen, L. Visscher, *J. Chem. Phys.* 126, 064314 (2007)

Experimental NQCCs for AuH (C_{NQCC} =187.116(99) MHz)
and AuD (C_{NQCC} =188.119(33) MHz)

T. Okabayashi, E. Y. Okabayashi, M. Tanimoto, T. Furuya, S. Saito, *Chem. Phys. Lett.* 422, 58 (2006)

Finite Field Method, Dirac-Fock, Kramers restricted coupled cluster, Gaunt QED:

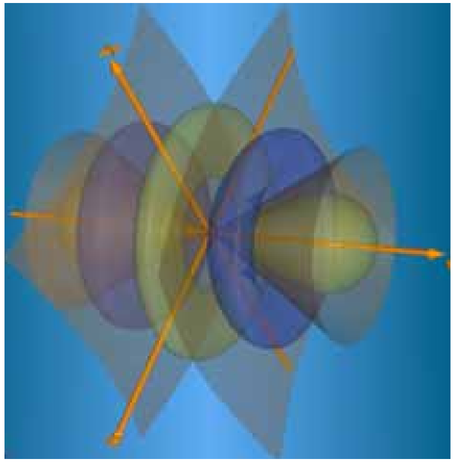
Molecule	q_{nuc}	q_{MP2}	q_{CCSD}	$q_{\text{CCSD(T)}}$	Δq_{Gaunt}	Δq_{vib}	Δq_{QED}	q_{total}
AuH	-2.241	2.526	1.236	1.744	-0.023	0.053	-0.045	1.510

➡ Q_s= +0.509 b

Problem: Uncertainty in QED, Large triples contribution in CCSD, one may have
to do CCSDTQ

The nuclear hexadecapole moment of ^{127}I (I=5/2$^+$)

Situation: A number of claims since 1954 for the successful measurement of the coupling between the electric field third derivative and the nuclear hexadecapole (NHD) moment ranging from 100 kHz down to 10 Hz:



- Wang (1955) 24 ± 5 kHz for ^{123}Sb ($SbBr_3$)
- Hewitt and William (1963) 13 ± 30 kHz for ^{123}Sb (Sb)
- Goutou (1983) 110 ± 61 kHz ($SbCl_3$)
- Ni and Sears (1991) 2.8 Hz ^{127}I (KI)
- Cederberg *et al* (1999) 15.1±3.0 Hz for ^{127}I (LiI)

(J.Cederberg et al, *J. Chem. Phys*. 110, 2431 (1999).

However:

Negative results and criticism by Zorn et al (1970), Hammerle and Zorn (1973), Segel (1978), Doering and Waugh (1986), Liao and Harbison (1994)

Difficulties:

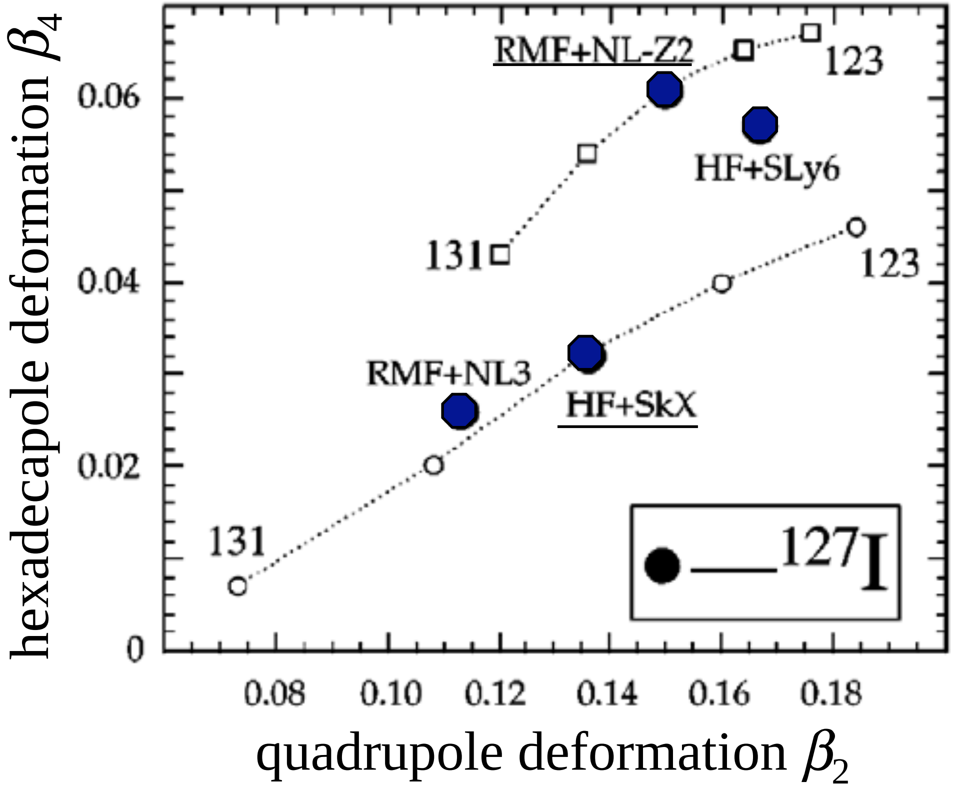
1) Point charge NHD model is numerically unstable. One has to perform fully 4-component relativistic calculations.
2) In order to verify the experimentally measured NHD coupling constant (NHCC) one needs the NHD moment from first principle nuclear calculations.

The electric field third derivative

Implementation of up to fourth rank tensors of the potential derivatives into the four-component program package DIRAC.

→ $V_{zzzz}(^{127}\mathrm{I}) = 7.274$ a.u. in LiI

Nuclear structure calculations:



Surface of a deformed nucleus:

$$R(\vartheta,\varphi) = R_0\left[1 + \sum_{\lambda,\mu} a_{\lambda,\mu} Y^*_{\lambda\mu}(\vartheta,\varphi)\right]$$

$$a_{20} = \beta_2 \cos\gamma \qquad a_{22} = \frac{1}{\sqrt{2}}\beta_2 \sin\gamma$$

Axial deformation parameters:

$$\beta_\lambda = \frac{\sqrt{2\lambda+1}\,\pi}{3ZeR_0^\lambda} M_0(\lambda)$$

$$M_0(2) = Q_0 \qquad M_0(4) = H_0$$

$$M_0(\lambda) = \left(\frac{16\pi}{2(\lambda+1)}\right)^{1/2} \int d\vec{r}\; n_N(\vec{r})\, r^\lambda Y_{\lambda 0}(\vartheta,\varphi)$$

J.Thyssen, P.Schwerdtfeger, M. Bender, W. Nazarewicz, P. B. Semmes, *Phys. Rev. A* 63, 022505 (2001).

Final results:

	Experimental	Calculated	Used NQM(NHM)
NQCC [MHz]	−194.351212(17)	−172	−0.70 b
NHCC [Hz]	−15.1(30)	+0.060	+0.006 b^2
		+0.020	+0.002 b^2

Q_s=0.696(12) b taken from
J. N. P. van Stralen, L. Visscher, *Mol. Phys.* 101, 2115 (2003)

- Total NHCC: 30 - 60 mHz
- contradicts experimental analysis of Cederberg (second-order quadrupole term?).
- NHC in the range of electroweak interactions
- NHC possibly never observed

Conclusions

- DFT seems to work o.k. for most main group elements, but performs particularly bad for late-transition elements like Cu or Au: polarization of the *d*-core not well described. The bad performance is related to the wrong charge distribution around the nucleus which is not well described by the exchange part of the functional (Known in solid-state physics, LDA+U).

- KR-CC is the method of choice, but needs further development to go up to CCSDTQ. Analytical DC-CCSD for properties would be desirable.

- The full Breit term up to order c^{-2} needs to be explored. Vacuum polarization and self-energy need to be parametrized as semi-local potentials for molecular applications.

- The PCNQM model is a useful application to avoid picture change errors in molecular calculations. Otherwise transor the EFG operator.

- We believe that nuclear hexadecapole coupling to the electronic field has never been observed experimentally.

- We have also done ^{133}Cs, ^{99,101}Ru, ^{191,193}Ir and ^{139}La