Relativistic Coupled Cluster Theory for Nuclear Multipole Moments
Acknowledgment
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1. Nuclear multipole moments and electric field derivatives.

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

3. Kramers restricted relativistic coupled cluster theory for electric field gradients (or why density functionals are bad news).

4. The nuclear quadrupole moment of $^{57}\text{Fe}$ ($I=3/2^-$) and $^{197}\text{Au}$ ($I=3/2^+$), and the nuclear hexadecapole moment of $^{127}\text{I}$ ($I=5/2^+$).
1. Nuclear multipole moments and electric field derivatives

Calculated potential energy surface of $^{186}\text{Pb}$. The $\beta_2$ parameter expresses the elongation of the nucleus along the symmetry axis, while the $\gamma$ parameter relates to the degree of triaxiality in the deformation, i.e. $\gamma=0^\circ$ corresponds to a prolate and $\gamma=60^\circ$ 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

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

Electronic structure calculations

NMC, decomposition in nuclear multipole moments

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

\[ V_N^{PC}(\vec{r}) = -\frac{Z}{|\vec{r} - \vec{R}_N|} \]

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

\[ V_e(\vec{R}) = V_e(\vec{R}_N) + \tilde{E}_e(\vec{R}_N) \cdot \vec{R} + \frac{1}{2} \vec{R}^T \cdot \vec{F}_e(\vec{R}_N) \cdot \vec{R} + \ldots \]
Finite nucleus influence on the Coulomb potential

\[ n_N(r) = n_0 \left( 1 + \exp \left( \frac{r}{bR} \right) - \frac{1}{b^n} \right) \]

\[ n_N(r) = n_0 e^{-r/R^2} \]

\[ n_N(r) = n_0 e^{-r/R} \]

A) The Spherical Multipole Expansion of the Interaction Energy


**Nuclear radii:** Lighter elements: \( R_{\text{rms}} = 1.2 \ A^{1/3} \ [\text{fm}] \) (Rutherford)

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

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

In comparison the electronic 1s \(<r>\) is for H = 79376 fm, for E120 = 450 fm \( \rightarrow R_{\text{rms}} \ll <r> \)

Laplace (multipole) expansion:

\[
\frac{1}{|\hat{r}_e - \hat{r}_N|} = \sum_{\lambda=0}^{\infty} \sum_{\mu=-\lambda}^{\lambda} \frac{4\pi}{2\lambda + 1} \frac{r^\lambda_N}{r^\lambda_e + 1} Y^*_\lambda\mu(\hat{r}_e) Y_{\lambda\mu}(\hat{r}_N)
\]

\[sE = \sum_{\lambda=0}^{\infty} \frac{4\pi}{2\lambda + 1} \sum_{\mu=-\lambda}^{\lambda} \left[ \int d\hat{r}_N \ n_N(\hat{r}_N) Y^*_\lambda\mu(\hat{r}_N) r^\lambda_N \right] \left[ \int d\hat{r}_e \ n_e(\hat{r}_e) Y_{\lambda\mu}(\hat{r}_e) r^{-\lambda-1} \right]
\]

**nuclear multipole moments** \( Q_{\lambda\mu} \)

**electric field moments** \( V_{\lambda\mu} \)

in order of \( \lambda \) transformation in Cartesian coordinates

\[sE = qV_0 - \mu_\alpha V_\alpha - \frac{1}{3} \Theta_{\alpha\beta} V_{\alpha\beta} - \frac{1}{15} \Omega_{\alpha\beta\gamma} V_{\alpha\beta\gamma} - \frac{1}{105} \Phi_{\alpha\beta\gamma\delta} V_{\alpha\beta\gamma\delta} + \ldots\]
The nuclear multipole moments and fields:

\[
\Theta_{zz} = \int d\vec{r} \ n_N(\vec{r}) r^2 P_2(\hat{z})
\]
\[
\Theta_{xy} = \frac{3}{2} \int d\vec{r} \ n_N(\vec{r}) \ xy
\]
\[
\Omega_{zzz} = \int d\vec{r} \ n_N(\vec{r}) r^3 P_3(\hat{z})
\]
\[
\Omega_{xxxy} = \frac{1}{2} \int d\vec{r} \ n_N(\vec{r}) (5x^2y - xr^2)
\]
\[
\Omega_{xyz} = \frac{5}{2} \int d\vec{r} \ n_N(\vec{r}) \ xyz
\]
\[
\Phi_{zzzz} = \int d\vec{r} \ n_N(\vec{r}) r^4 P_4(\hat{z})
\]
\[
\Phi_{xxxy} = \frac{5}{8} \int d\vec{r} \ n_N(\vec{r}) (4x^3y - 3xy^3 - 3xyz^2)
\]
\[
\Phi_{xxyy} = \frac{1}{2} \int d\vec{r} \ n_N(\vec{r}) r^4 \left[ P_4(\hat{z}) - P_4(\hat{x}) - P_4(\hat{y}) \right]
\]
\[
\Phi_{xxyz} = \frac{5}{8} \int d\vec{r} \ n_N(\vec{r}) (6x^2yz - y^3z - yz^3)
\]

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

The Laplace equation is fulfilled: \( V_{\alpha\alpha} = -4\pi n(0) = 0 \) (but: not fulfilled for \( s \)-orbitals)

All derivatives of the electronic density \( n(\vec{r}) \) vanish at the origin:

\[
\left. \frac{\partial^k n(\vec{r})}{\partial \vec{r}_{\alpha_1} \partial \vec{r}_{\alpha_2} \cdots \partial \vec{r}_{\alpha_k}} \right|_0 = 0
\]

\[\rightarrow\ V_{\alpha\alpha} = 0 \quad \land \quad V_{\alpha\beta\beta} = 0 \quad \land \quad V_{\alpha\beta\gamma\gamma} = 0 \quad \ldots\]
B) The Taylor Expansion of the Interaction Energy

\[ V(\vec{r}) = V_0 + \left( \frac{\partial V}{\partial r_\alpha} \right)_0 \vec{r}_\alpha + \frac{1}{2} \left( \frac{\partial^2 V}{\partial r_\alpha \partial r_\beta} \right)_0 \vec{r}_\alpha \vec{r}_\beta + \frac{1}{6} \left( \frac{\partial^3 V}{\partial r_\alpha \partial r_\beta \partial r_\gamma} \right)_0 \vec{r}_\alpha \vec{r}_\beta \vec{r}_\gamma \]

\[ + \frac{1}{24} \left( \frac{\partial^4 V}{\partial r_\alpha \partial r_\beta \partial r_\gamma \partial r_\delta} \right)_0 \vec{r}_\alpha \vec{r}_\beta \vec{r}_\gamma \vec{r}_\delta + \ldots \]

\[ cE = qV_0 - \mu_\alpha V_\alpha - \frac{1}{2} Q_{\alpha\beta} V_{\alpha\beta} - \frac{1}{6} R_{\alpha\beta\gamma} V_{\alpha\beta\gamma} - \frac{1}{24} H_{\alpha\beta\gamma\delta} V_{\alpha\beta\gamma\delta} + \ldots \]

\[ q = \int d\vec{r} \ n_N(\vec{r}) \]

\[ \mu_\alpha = \int d\vec{r} \ n_N(\vec{r}) \vec{r}_\alpha \]

\[ Q_{\alpha\beta} = \int d\vec{r} \ n_N(\vec{r}) \vec{r}_\alpha \vec{r}_\beta \]

\[ R_{\alpha\beta\gamma} = \int d\vec{r} \ n_N(\vec{r}) \vec{r}_\alpha \vec{r}_\beta \vec{r}_\gamma \]

\[ H_{\alpha\beta\gamma\delta} = \int d\vec{r} \ n_N(\vec{r}) \vec{r}_\alpha \vec{r}_\beta \vec{r}_\gamma \vec{r}_\delta \]

\[ V_\alpha = -\left( \frac{\partial V}{\partial \vec{r}_\alpha} \right)_0 \]

\[ V_{\alpha\beta} = -\left( \frac{\partial^2 V}{\partial \vec{r}_\alpha \partial \vec{r}_\beta} \right)_0 \]

\[ V_{\alpha\beta\gamma} = -\left( \frac{\partial^3 V}{\partial \vec{r}_\alpha \partial \vec{r}_\beta \partial \vec{r}_\gamma} \right)_0 \]

\[ V_{\alpha\beta\gamma\delta} = -\left( \frac{\partial^4 V}{\partial \vec{r}_\alpha \partial \vec{r}_\beta \partial \vec{r}_\gamma \partial \vec{r}_\delta} \right)_0 \]
In the Taylor expansion the electric field gradient tensor is not traceless as s-orbitals have a finite density at the nucleus:

\[
\mathbf{C} \mathbf{E} = S \mathbf{E}_{\text{anisotropic}} + \sum_{\lambda=2}^{\infty} \Delta \mathbf{E}^{\lambda, \text{isotropic}}
\]

**Isotropic (spherical) contributions:**

**Quadrupole term**

\[
\Delta \mathbf{E}^{(2)}_{\text{iso}} = -\frac{1}{6} \mathbf{V} \alpha \alpha \int d\mathbf{\bar{r}} \ n_N(\mathbf{\bar{r}}) \mathbf{r}^2
\]

**Octupole term**

\[
\Delta \mathbf{E}^{(3)}_{\text{iso}} = -\frac{1}{10} \mathbf{V} \beta \alpha \alpha \int d\mathbf{\bar{r}} \ n_N(\mathbf{\bar{r}}) \mathbf{r}^2 \mathbf{r}_\beta \mathbf{r}^2
\]

**Hexadecapole term**

\[
\Delta \mathbf{E}^{(4)}_{\text{iso}} = -\frac{1}{28} \mathbf{V} \alpha \beta \gamma \int d\mathbf{\bar{r}} \ n_N(\mathbf{\bar{r}}) \mathbf{r}^2 \left( \mathbf{r}_\alpha \mathbf{r}_\beta - \frac{1}{10} \mathbf{r}^2 \delta_{\alpha\beta} \right)
\]

The isotropic components \(\Delta \mathbf{E}^{(\lambda)}\) only shift the total energy, and do not contribute (in first order) to the splitting of the energy levels due to nuclear multipole coupling.
The Determination of NQCCs and NQMs

**NQCCs are obtained from:** \( C_{NQCC} = e q Q_s \)
- 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

**(NQM)s are obtained from:**
- First principles nuclear structure calculations (*Q\text{int} or Q_s*)
- Scattering experiments
- From NQCCs if the electric field gradient (EFG) \( q \) is known
  *most precise method*

Intrinsic vs. spectroscopic nuclear quadrupole moments

Rotating deformed nucleus: \( \vec{I} = \vec{R} + \vec{J} \)

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

Neglecting the last (Coriolis) term:

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

strong coupling limit (\( \delta \) large)

In this approximation we get

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

\( Q_s = 0 \) for \( I=0 \) and \( I=1/2 \)

Bohr and Mottelson (1953)

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

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
**NQMs from rotational spectroscopy**

Rotational spectra of small molecules

The coupling between the nuclear quadrupole moment $Q_s$ and the electric field gradient (EFG) $q$ at a specific nucleus gives rise to an energy splitting $\Delta E_Q$ 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.

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

**diatomic molecule**

**Molecular rotation ($J,K$)**

**Nuclear spin ($I$)**

Casimir’s function

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

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

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

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

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 $J=3$.

For linear molecules the Taylor expansion simplifies:

\[ cE = qV_0 - \frac{1}{2} \Theta_{zz} V_{zz} - \frac{1}{24} \Phi_{zzzz} V_{zzzz} + \ldots + \Delta E^{(2)} + \Delta E^{(4)} + \ldots \]

\[
\begin{align*}
V_{xx} &= V_{yy} & Q_{xx} &= Q_{yy} & \mu_\alpha &= 0 \\
V_{xxxx} &= V_{yyyy} & H_{xxxx} &= H_{yyyy} & R_{\alpha\beta\gamma} &= 0 \\
V_{xxzz} &= V_{yyzz} & H_{xxzz} &= H_{yyzz} & Q_{xy} &= Q_{xz} = Q_{yz} = 0 \\
V_{xxxx} &= 3V_{xxyy} & H_{xxxx} &= 3H_{xxyy} & H_{xxxy} &= H_{xxxx} = H_{xxyy} = H_{xxyz} = H_{yyyy} = H_{xyyz} = 0 \\
\end{align*}
\]

\[
\Delta E^{(2)}_{iso} = -\frac{1}{6} V_{\alpha\alpha} \int d\vec{r} \ n_N(\vec{r}) r^2
\]

\[
\Delta E^{(4)}_{iso} = -\frac{1}{420} \left(2V_{zz\alpha\alpha} + V_{xx\alpha\alpha}\right) \int d\vec{r} \ n_N(\vec{r}) r^4
\]

\[
-\frac{1}{84} \left(V_{zz\alpha\alpha} - V_{xx\alpha\alpha}\right) \int d\vec{r} \ n_N(\vec{r})(3z^2 - r^2) r^2
\]

The first important term is the quadrupole term \((Y_{20})\), the second the hexadecapole term \((Y_{40})\). The second term in \(\Delta E^{(4)}\) leads to a renormalization of the quadrupole interaction.
The Accurate Determination of NQMs

Accurate NQMs are very useful for the testing of 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).
- Scattering experiments with charged particles give the proton distribution in a nucleus, 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.

Nonrelativistic Nonrelativistic Domain

Electron correlation

Relativistic Operators

Towards the exact solution

The Theory of Everything

Full-CI

Nonrelativistic Domain

\[ H\Psi = E\Psi \]

one-particle basis

atom-centered Gaussians

CBS methods

HF limit

CBS

HF

STO-3G

3-21G

6-31G*

cc-pvdz

cc-pvtz

cc-pvqz

Pauli

Douglas-Kroll

Dirac-Coulomb

Dirac-Breit

+QED

Standard Model

Relativistic Operators

HF limit

The Theory of Everything

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Dirac-Breit

+QED

Standard Model
The Relativistic Formalism (The Dirac Picture)

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

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

\[
\vec{\alpha} = \begin{pmatrix} 0 & \vec{\sigma} \\ \vec{\sigma} & 0 \end{pmatrix}, \quad \beta = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}, \quad \sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad \sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \quad \sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}
\]

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

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

The stationary Dirac-equation

\[
\begin{pmatrix} V - E & c\vec{\sigma}\vec{p} \\ c\vec{\sigma}\vec{p} & -2mc^2 + V - E \end{pmatrix} \begin{pmatrix} \phi_L \\ \phi_S \end{pmatrix} = 0
\]

Programs: For atoms: GRASP; for molecules: DIRAC, UTCHEM, BERTHA
Spectrum of $H_D (+mc^2)$:

Problem: Dirac-operator is unbound. Unconditional Ritz-Rayleigh variational procedure not valid anymore. Minimax procedure to obtain stationary states:

Minimum with respect to PE-PE energy rotations

Maximum with respect to PE-NE energy rotations

Invariant with respect to NE-NE energy rotations

\[ \min_{\tilde{\Psi} \in \text{Def}^+(H_D)} \frac{\langle \tilde{\Psi} | H_D | \tilde{\Psi} \rangle}{\langle \tilde{\Psi} | \tilde{\Psi} \rangle} = \tilde{E} = E_0 \]
How to avoid a variational collapse (prolapse)?

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For comparison: $-2mc^2 = -37557.7$ a.u.
**Solution 1: The Nonrelativistic Formalism (Schrödinger Picture)**

Problem: $H_D$ in the Dirac picture is unbound and the small component $\phi_S$ 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):

$$
S = \chi_L, \quad FW = U_L, \quad (FW, FW) = 1
$$

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

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

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

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.
The free-particle FW transformation: The Breit-Pauli Operator

\[ U_{FPFW} = e^{iS} = \sqrt{\frac{\hat{E}_p + mc^2}{2\hat{E}_p}} \left( I_4 + \frac{c\beta\vec{\alpha}\vec{p}}{\hat{E}_p + mc^2} \right) = \hat{\Lambda}(I + \beta\hat{R}) \]

\[ \hat{E}_p = \sqrt{c^2p^2 + m^2c^4} \]

\[ S = -\frac{i\beta\vec{\alpha}\vec{p}}{2p} \arctan \frac{\vec{p}}{mc} \]

\[ H^{BP}_S = H_{NR} + H_{Breit-Pauli} = H_{NR} - \sum_i \frac{1}{8m^3c^2} \vec{p}_i^4 - \sum_i \frac{\hbar}{4mc^2} \vec{\sigma}_i (\vec{\nabla} V(\vec{r}_i) \times \vec{p}_i) - \sum_i \frac{\hbar^2}{8m^2c^2} \Delta V(\vec{r}_i) \]

- mass-velocity
- spin-orbit
- Darwin

\[ + \sum_{i<j} \frac{\hbar}{2m^2c^2 r_{ij}^3} \left[ \vec{\sigma}_i ((\vec{r}_i - \vec{r}_j) \times \vec{p}_i) + \vec{\sigma}_j ((\vec{r}_j - \vec{r}_i) \times \vec{p}_i) \right] - \sum_{i<j} \frac{\hbar^2 \pi}{m^2c^2} \delta(\vec{r}_i - \vec{r}_j) \]

- spin-other orbit
- spin-orbit (2)
- 2e-Darwin

\[ - \sum_{i<j} \frac{1}{2m^2c^2} \vec{p}_i \left[ \frac{\vec{r}_i - \vec{r}_j}{r_{ij}^5} \right] + \frac{1}{r_{ij}^3} \vec{p}_j - \sum_{i<j} \frac{\hbar^2}{4m^2c^2} \vec{\sigma}_i \left[ \frac{3(\vec{r}_i - \vec{r}_j)(\vec{r}_i - \vec{r}_j)}{r_{ij}^5} - \frac{1}{r_{ij}^3} \right] \vec{\sigma}_j \]

- orbit-other orbit
- spin-other spin

\[ - \sum_{i<j} \frac{2\hbar^2 \pi}{3m^2c^2} \delta(\vec{r}_i - \vec{r}_j) \vec{\sigma}_i \vec{\sigma}_j + \ldots \]

- spin-other spin (2)

Useful for interpretation purposes (historical reasons: derived via perturbation expansion to order \( c^{-2} \)), in use as a perturbation operator (correct to first order), two-electron terms are difficult to treat

Unbound (due to mass-velocity, variationally unstable), is essentially singular
Infinite Order Two-Component (IOTC)

\[
\begin{align*}
    h_+ &= \frac{1}{\sqrt{1 + X^\dagger X}} \left[ h_{11} + h_{12} X + X^\dagger (h_{21} + h_{22} X) \right] \frac{1}{\sqrt{1 + X^\dagger X}} \\
    X &= \frac{1}{2mc} \left( 1 + \frac{E - V}{2mc^2} \right)^{-1} \vec{\sigma} \vec{p}
\end{align*}
\]

**NB**: Two-component Hamiltonians are derived at the operator level, only at a later stage are matrix elements over the final operator expressions programmed. Approximate Hamiltonians can be obtained in a much simpler manner by matrix manipulations starting directly from the Dirac operator in the finite basis approximation.

Iterative (Barysz, Sadlej) or 1-step procedures (Ilias, Saue)


→ Construct \( X \) in matrix form from Dirac eigenvectors \( C^S \) and \( C^L \) in MO basis → \( U \) → \( h_+(MO) \) → \( h_+(AO) \) → SCF for \( h_+(AO) \)
The Douglas-Kroll-Hess Operator


\[ H_n = U_{n-1} U_1 U_0 H_D U_0^\dagger U_1^\dagger ... U_{n-1}^\dagger \]

DK: \( U_0 = U_{FPFW} \) and \( U_i = U_{i,DK} \)

\[ H_{S_{DK}} = H_{NR} + H_{DK} = \sum_i h_{DK}(i) + \sum_{i<j} g_{DK}(i,j) \]

for \( U_1 = \sqrt{1+W_1^2} + W_1 \) we get

\[ h_{DK2}^{SR}(i) = E_i + A_i[V(i) + \tilde{R}_i V(i) \tilde{R}_i]A_i - W(i) E_i W(i) - \frac{1}{2} \{ W(i)^2, E_i \} \]

\[ E_i \equiv \hat{E}_p = c\sqrt{\hat{p}_i^2 + m^2c^2}, \quad A_i \equiv A_p = \sqrt{\frac{E_i + mc^2}{2E_i}}, \quad \tilde{R}_i \equiv R_p = \frac{c\tilde{p}_i}{E_i + mc^2} \]

\[ g_{DK}(i,j) = A_i A_j [r_i^{-1} + \tilde{R}_i r_i^{-1} \tilde{R}_i + \tilde{R}_j r_j^{-1} \tilde{R}_j + \tilde{R}_i \tilde{R}_j r_j^{-1} \tilde{R}_i \tilde{R}_j]A_i A_j \]

\[ W(\vec{p}, \vec{p}') = A_p (R_{\vec{p}} - R_{\vec{p}'}) A_{p'} \frac{V(\vec{p}, \vec{p}')}{E_p + E_{p'}} \]

Other two-component operators in use: ZORA, ESC, DPT, ....
**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)
   
   \[
   \begin{pmatrix}
   V - E + f & c\mathbf{p} \\
   c\mathbf{p} & -2mc^2 + V - E + f
   \end{pmatrix}
   \begin{pmatrix}
   \varphi_L \\
   \varphi_S
   \end{pmatrix} = 0
   \]

   Substitution of $V$ by $V + f$ in the power series leads to the following expression for the Pauli-series:
   
   \[
   \hat{H}_+ = V + f + \frac{1}{2c^2}(c\mathbf{p})^2 - \frac{1}{8c^4}[c\mathbf{p},[c\mathbf{p},V + f]] - \frac{1}{8c^6}(c\mathbf{p})^4 + ...
   \]
   
   \[
   f^S = f + \frac{1}{8c^2} \Delta f + ...
   \]

   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** $f$:
   
   Substitution of $c\vec{\sigma} \vec{p}$ by $c\vec{\sigma} \vec{p} + f$:
   
   \[
   \hat{H}_+ = V + \frac{1}{2c^2}(c\sigma_p + f)^2 - \frac{1}{8c^4}[c\sigma_p + f,[c\sigma_p + f,V]] - \frac{1}{8c^6}(c\sigma_p + f)^4 + ...
   \]
   
   \[
   f^S = \frac{1}{2mc}[\sigma_n, f]_+ + ...
   \]

\[H^{\text{PNC}}_{en} = \frac{G_F}{4\sqrt{2}mc} \sum_{i,n} Q_{Wn} \left\{ \vec{\sigma}_i \vec{p}_i, \rho_n(\vec{r}_i) \right\}_+ \quad \text{Bouchiat-Hamiltonian} \]
The Picture-Change Effect for Electric Field Gradients

Methods for the determination of electric field gradients

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

\[ q_{\alpha\beta} = \langle V_{\alpha\beta}^{el}(\vec{R}_N) \rangle + V_{\alpha\beta}^{nuc}(\vec{R}_N) \]

\[ \langle V_{\alpha\beta}^{el}(\vec{R}_N) \rangle = \left\langle \Psi \left| \sum_{i} \frac{3(r_{i\alpha} - R_{N\alpha})(r_{i\beta} - R_{N\beta}) - \delta_{\alpha\beta}}{|\vec{r}_i - \vec{R}_N|^5} \right| \Psi \right\rangle \]

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


Perturbation by \( V_{\alpha\beta}^{el}(\vec{R}_X) \)

\[ H = H_0 + \lambda V_{\alpha\beta}^{el}(\vec{R}_N) \]

\[ \langle V_{\alpha\beta}^{el}(\vec{R}_X) \rangle = \frac{dE(\lambda)}{d\lambda} \]

untransformed EFG operator
3) The Point-Charge Nuclear Quadrupole Model  ✔ ✔ ✔

(good for MRCI, CC)

\[ U_{\text{int}} = \left\langle \frac{1}{2}(2\xi d^2 V_{zz} - \zeta d^2 V_{xx} - \zeta d^2 V_{yy}) \right\rangle = \frac{3}{2} \xi d^2 q_{zz} = \frac{3}{2} Q q_{zz} \]

\[ q_{zz} = \frac{2}{3} \frac{dU_{\text{int}}}{Q} \]

\[ V_{xy} = \frac{2}{3} \left( \frac{dU_{\text{int}}^{xy}(Q)}{dQ} \right)_0 + \frac{1}{2} V_{zz} \]

\[ V_{xz} = \frac{2}{3} \left( \frac{dU_{\text{int}}^{xz}(Q)}{dQ} \right)_0 + \frac{1}{2} V_{yy} \]

\[ V_{yz} = \frac{2}{3} \left( \frac{dU_{\text{int}}^{yz}(Q)}{dQ} \right)_0 + \frac{1}{2} V_{xx} \]

Accuracy of the PCNQM Model:

<table>
<thead>
<tr>
<th>Method</th>
<th>( V_{xx} )</th>
<th>( V_{yy} )</th>
<th>( V_{zz} )</th>
<th>( V_{xy} )</th>
<th>( V_{xz} )</th>
<th>( V_{yz} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>PCNQM(HF)</td>
<td>-0.0651</td>
<td>-0.2147</td>
<td>+0.2799</td>
<td>+0.0739</td>
<td>+0.1461</td>
<td>-0.0653</td>
</tr>
<tr>
<td>( &lt;V_{\text{off}} &gt; )(HF)</td>
<td>-0.0651</td>
<td>-0.2148</td>
<td>+0.2799</td>
<td>+0.0739</td>
<td>+0.1460</td>
<td>-0.0653</td>
</tr>
<tr>
<td>PCNQM(MP2)</td>
<td>-0.0231</td>
<td>+0.0122</td>
<td>+0.0109</td>
<td>-0.0340</td>
<td>-0.0236</td>
<td>+0.0265</td>
</tr>
<tr>
<td>( &lt;V_{\text{off}} &gt; )(MP2)</td>
<td>-0.0231</td>
<td>+0.0122</td>
<td>+0.0109</td>
<td>-0.0340</td>
<td>-0.0236</td>
<td>+0.0265</td>
</tr>
</tbody>
</table>
- The PCNQM model can be used in any program just by placing charges near the nucleus. This leads to a very large nuclear-nuclear repulsion term because $d$ is small, hence this term should be switched off in a SCF calculation.
- For the variation of $Q$ it is better to vary the charge $\zeta$ rather than the distance $d$. This gives numerically more stable results.
- The point charges set along one axis only yield includes the isotropic contribution which becomes very large for large $Z$. It is therefore convenient to find a charge distribution which cancels out these spherical contributions.
- The PCNQM model is not very different from other point charge models for calculating electric properties (dipole moments, polarizabilities, electric quadrupole moment, etc.).
- The PC arrangement is free of $2^{2n+1}$-pole ($n \geq 0$) contributions, but it contains $2^{2n}$-pole ($n > 1$) contaminations. For small $d$ these contributions can be neglected.
- Since the perturbation in the total electronic energy is relatively small ($<10^{-5}$ a.u.), the SCF convergence should be chosen as very tight. For lighter elements this is usually not a problem.
Solution 2: The Right Boundary Conditions

- The four-component relativistic calculations the negative energy states are a “nuisance” and techniques have to be developed to avoid variational collapse. These negative energy states have of course their importance in QED.

- If the right care is taken with basis sets describing accurately positive energy states, a variational collapse (prolapse) is avoided. The negative energy states are sufficiently far away (about \(-2mc^2\)) to cause any trouble in a variational calculation. One of the necessary (but not sufficient) conditions is the kinetic balance between the small and large Dirac spinor:

\[
\phi_s \sim \bar{\sigma} \bar{p} \phi_L
\]

which leads to the matrix elements

\[
\Pi_{\mu \nu}^{SL} = S_{\nu \mu}^{SS} \Rightarrow \Pi_{\nu \mu}^{LS} = 2mT_{LL}
\]

\[
\Pi_{\mu \nu}^{SL} = \left< \chi_{\mu}^{S} \mid -i \bar{\sigma} \cdot \vec{V} \right| \chi_{\nu}^{L} \rangle \quad \Pi_{\nu \mu}^{SL} = \Pi_{\nu \mu}^{LS^\dagger} \quad S_{\mu \nu}^{SS} = \left< \chi_{\mu}^{S} \right| \chi_{\nu}^{S} \rangle
\]

- For Cartesian Gaussian type basis sets \(\chi(x, y, z) = x^n y^l z^m e^{-\mu r^2}\) computer time is saved by using “dual-family” basis sets as

\[
\tilde{\nabla} \chi(x, y, z) = x^n y^l z^m e^{-\mu r^2} \left( \frac{\mu}{x} - 2 \mu x, \frac{l}{y} - 2 \mu y, \frac{m}{z} - 2 \mu z \right)
\]

Same exponents for all even \(l\), and for all odd \(l\)

How important are Breit and other QED contributions for EFGs?

- Pernpointner studied the Gaunt interaction in TlH
  \[(J. \text{Phys. B: At. Mol. Phys.} \ 35, \ 383 \ (2002))\]

\[
\Delta n(\vec{r}) = n_c(\vec{r}) - n_{CG}(\vec{r})
\]

\[
g_{CG}(i, j, \frac{\omega_{ij}}{c} \rightarrow 0) \approx r_{ij}^{-1} \left(1 - \tilde{\alpha}_i \tilde{\alpha}_j \right)
\]

<table>
<thead>
<tr>
<th>Method</th>
<th>C</th>
<th>CG</th>
</tr>
</thead>
<tbody>
<tr>
<td>$q_{\text{DHF}}^{\text{Tl}}$</td>
<td>-1.7953</td>
<td>-1.7945</td>
</tr>
<tr>
<td>$\Delta q_{\text{MP2}}^{\text{Tl}}$</td>
<td>0.06533</td>
<td>0.06529</td>
</tr>
<tr>
<td>$\Delta q_{\text{CCSD}}^{\text{Tl}}$</td>
<td>0.08642</td>
<td>0.08632</td>
</tr>
<tr>
<td>$\Delta q_{\text{(T)}}^{\text{Tl}}$</td>
<td>0.02041</td>
<td>0.02040</td>
</tr>
</tbody>
</table>

- Pyykkö et al. studied VP+SE for AuH

<table>
<thead>
<tr>
<th>Method</th>
<th>at Au</th>
</tr>
</thead>
<tbody>
<tr>
<td>$q_{\text{DHF}}$</td>
<td>-2.3340</td>
</tr>
<tr>
<td>$\Delta q_{\text{CCSD(T)}}$</td>
<td>3.9721</td>
</tr>
<tr>
<td>$\Delta q_{G}$</td>
<td>-0.0226</td>
</tr>
<tr>
<td>$\Delta q_{\text{VP+SE/DHF}}$</td>
<td>-0.0460</td>
</tr>
</tbody>
</table>
### Relativistic Electronic Structure Theory


P. Schwerdtfeger (editor)

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(or why density functionals are bad news for EFGs)

Q: Can we get away relativistic Kohn-Sham density functional theory?
The EFG is a core property, so DFT is fine (common belief in solid-state community).

\[ E \text{ [cm}^{-1}] \]

\[ r \text{ [Å]} \]

Case 1: Main Group: Gallium Halides ($^{69}$Ga)

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

Graph showing the relationship between $C_{\text{NQCC}}[\text{MHz}]$ and $q[\text{a.u.}]$ with data points for different gallium halides such as GaF, GaCl, GaBr, GaI, GaH, GaLi, and GaI. The figure includes lines representing different computational methods such as HF, MP2, LDA, BPW91, BPE, and B3LYP with experimental results indicated as 'exp.'
Case 2: Early Transition Element: Scandium Halides ($^{45}\text{Sc}$)

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

$C_{NQCC}[\text{MHz}]$ vs $q[\text{a.u.}]$ for Scandium Halides:
- ScF
- ScCl
- ScBr
- ScI
- ScH
- ScLi

Calculations using various methods:
- HF
- MP2
- LDA
- BPW91
- BPE
- B3LYP
Case 3: Late Transition Element: Copper Halides (${}^{63}\text{Cu}$)

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

wrong slope
do not go through origin
CuF: Orbital Contributions

Possible (not the most elegant and accurate) solutions:

- Changing the Hartree-Fock contribution to the hybrid functional (semi-empirical!)

\[
E_{X}^{local}(a) = aE_{X}^{Slater} + (1 - a)E_{X}^{HF}
\]

For Cu we get \( a = 0.583 \) (mB3LYP)

For \( CuF_3 \) works reasonably well for \( CuF_3 \)

- Introducing long-range corrections

\[
\frac{1}{r_{12}} = \left( \text{erf} (\gamma r_{12}) \right) \frac{1}{r_{12}} + \left[ 1 - \text{erf} (\gamma r_{12}) \right] \frac{1}{r_{12}}
\]

(Stoll, Savin 1982)

\[\text{DFT} \quad \text{HF/CCSD}\]

Kramers restricted MP and CC calculations

Dirac relativistic SCF calculations are more computer time expensive compared to nonrelativistic or 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

\[
\hat{K} = -i \Sigma_y \hat{C}
\]

with \( \Sigma_y = \begin{pmatrix} \sigma_y & 0 \\ 0 & \sigma_y \end{pmatrix} \),

\[
\hat{K} \left( \lambda_1 \psi_1 + \lambda_2 \psi_2 \right) = \lambda_1^* \hat{K} \psi_1 + \lambda_2^* \hat{K} \psi_2 , \quad \hat{K} \hat{H}_D \hat{K}^\dagger = \hat{H}_D
\]

and \( \psi \) and \( \hat{K} \psi \) are energy degenerate (in covariant form: \( \hat{K} = i \gamma_1 \gamma_3 \gamma_0 \)).
For fermions one can show that \( \langle \hat{K}\psi | \hat{K}\psi \rangle = 1 \) and \( \langle \hat{K}\psi | \psi \rangle = 0 \)

hence \( \psi \) and \( \hat{K}\psi \equiv \bar{\psi} \) are linearly independent, they form a degenerate pair (Kramers pair)

In correlation methods one needs to transform the one- and two-electron integrals into the molecular spinor basis, e.g. (Esser, Butcher, Schwarz 1981)

\[
(pq|rs) = \sum_{X,Y} \sum_{\mu\nu\kappa\lambda} a_{\mu p}^{X*} a_{\nu r}^{X*} a_{\kappa r}^{Y*} a_{\lambda s}^{Y*} (\mu^X \nu^X | \kappa^Y \lambda^Y )
\]

For the Dirac-Coulomb Hamiltonian we have the integral classes (LL|LL), (LL|SS), (SS|LL) and (SS|SS). For the Gaunt term additional (LS|SL) and (LS|LS) classes of integrals appear. Kramers symmetry gives

\[
(pq||rs) = (pq|rs) - (ps|rq) = (\bar{pq}||\bar{rs})^*
\]

A Kramers restricted integral transformation is 24 times more expensive than the nonrelativistic integral transformation.
Kramers restricted MBPT2 (KRMP2)

- The nonrelativistic expression for the MP2 (MBPT2) expression is

\[
E_{\text{Corr.}}^{\text{MP2}} = \frac{1}{4} \sum_{I,J} \sum_{A,B} \mathcal{E}_I + \mathcal{E}_J - \mathcal{E}_A - \mathcal{E}_B \left| (IA||JB) \right|^2
\]

- The Kramers restricted relativistic MP2 expression is

\[
E_{\text{Corr.}}^{\text{MP2}} = \frac{1}{4} \sum_{I,J} \sum_{A,B} \mathcal{E}_I + \mathcal{E}_J - \mathcal{E}_A - \mathcal{E}_B \left| (IA||JB) \right|^2 + 2 \left| (IA||JB) \right|^2 + \left| (IA||JB) \right|^2 + \left| (IA||JB) \right|^2 + \left| (IA||JB) \right|^2
\]

- This can be brought into a more compact form and has been implemented by L. Visscher into DIRAC. The energy expression is roughly 12 times more expensive than the nonrelativistic code. A direct MP2 code has also been implemented into DIRAC (Visscher, Saue).

- Energy derivative for properties \( P \):

\[
\frac{dE_{\text{Corr.}}^{\text{MP2}}}{d\lambda} = \sum_{I,J} D^{(2)}_{IJ} P_{IJ} + \sum_{A,B} D^{(2)}_{AB} P_{BA} + \sum_{A,I} Z^*_{IA} P_{AI} + \sum_{X,I} Z^*_{IX} P_{XI} + \sum_{A,X} Z^*_{AX} P_{XA}
\]

\[\text{PE-PE relax} \quad \text{PE-NE relax}\]

Kramers restricted coupled cluster (KRCC)

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

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

with

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

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

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

Closed shell KR-CCSD including perturbative triples, CCSD(T), is implemented in DIRAC. CC to higher order is implemented in UTCHEM.

Utilizing Kramers symmetry for the closed-shell case:

$$[\hat{K}, e^{\hat{T}}] = 0$$
The wave operator is thus symmetric under time reversal. For example, if we apply the time-reversal operator to the term we obtain

\[ \hat{K} \hat{T}_i = \hat{K} \sum_{ii} \sum_{a\bar{a}} \left[ t_i^a \hat{E}_i^a + t_i^{\bar{a}} \hat{E}_i^{\bar{a}} + t_i^a \hat{E}_i^{a} + t_i^{\bar{a}} \hat{E}_i^{\bar{a}} \right] \]

\[ = \sum_{ii} \sum_{a\bar{a}} \left[ \hat{K}t_i^a \hat{E}_i^a + \hat{K}t_i^{\bar{a}} \hat{E}_i^{\bar{a}} + \hat{K}t_i^a \hat{E}_i^{a} + \hat{K}t_i^{\bar{a}} \hat{E}_i^{\bar{a}} \right] \]

\[ = \sum_{ii} \sum_{a\bar{a}} \left[ t_i^a \hat{E}_i^{a} - t_i^{\bar{a}} \hat{E}_i^{\bar{a}} - t_i^a \hat{E}_i^{a} + t_i^{\bar{a}} \hat{E}_i^{\bar{a}} \right] \]

which gives the relation \( t_i^a = t_i^{\bar{a}} \), \( t_i^{\bar{a}} = -t_i^a \)

Similar for the two-electron amplitudes,

\[ t_{ij}^{ab} = t_{ij}^{\bar{a}\bar{b}} \], \( t_{ij}^{\bar{a}\bar{b}} = t_{ij}^{ab*} \), \( t_{ij}^{ab} = t_{ij}^{\bar{a}\bar{b}*} \), \( t_{ij}^{\bar{a}\bar{b}} = -t_{ij}^{ab*} \)

This leads to a simplified expression for the \( N \)-electron amplitudes. The energy expression for KR-CCSD becomes roughly 32 times more expensive than the nonrelativistic code.

There is no analytical property DC-CCSD yet as it is difficult to implement efficiently. Therefore, the finite-difference method for correlation energies is used (either PCNQM or EFG perturbation), e.g. a two-point interpolation for the correlation contribution (HF value from expectation value)

\[
\left( \frac{\partial E_{\text{cor}}(\lambda)}{\partial \lambda} \right)_0 \approx \frac{E_{\text{cor}}(\lambda + \lambda) - E_{\text{cor}}(\lambda - \lambda)}{2\lambda}
\]

There are numerical limitations of the finite field method: Field strength must be chosen much higher than the physical value as long as the linear response regime remains valid. However, for the NHM this was not feasible.

Very tight \( p \)-basis functions lead to very large matrix elements which cancel out, but may lead to numerical instabilities. Similar arguments for the choice of the active space in the correlation treatment.
Electron correlation contribution from the PCNQM model

\[
\Delta E_{\text{int}} = 3 \frac{3}{2} \zeta d^2 q_{zz} = \frac{3}{2} \zeta q_{zz}
\]

\((d=10^{-3}\text{ a.u.})\)
Four-component CCSD(T) EFGs (a.u.) at the halogen center for the HX molecules compared to the scalar relativistic and nonrelativistic calculations by Kellö and Sadlej and to DFT results obtained by Malkin et al.

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

- The $^{57}\text{Fe}$ ($I=3/2^-$ excited state) nuclear quadrupole moment
  
  - Needed in Mössbauer spectroscopy (ground state: $I=1/2^-$)
  - Accepted NQM for $^{57}\text{Fe}$ 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

Nuclear shell-structure calculations

$^{57}\text{Fe}$: $26p^+$, proton shell: $1s^2, 1p^6, 1d^{10}, 2s^2, 1f^{6}_{7/2}$
$31n$, neutron shell: $1s^2, 1p^6, 1d^{10}, 2s^2, 1f^{8}_{7/2}, 2p^3$

- The $Q_s(54\text{Fe} 10^+)/Q_s(57\text{Fe} 3/2^-) = 3.63 \pm 0.22$ is known (M. Hass et al., Nucl. Phys. A 414, 316 (1984)).

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

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

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

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

Fe(CO)$_5$:

$q_T = q_{CCSD(T)} + \Delta q_{\text{rest.space}} + \Delta q_{\text{Basis}} + \Delta q_{\text{Solid-State}} + \Delta q_{\text{Struct}} + \Delta q_{\text{relativistic}}$

$1.439 + 0.082 + 0.476(?) + -0.036 + 0.074 + 0.065$

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

$Q_s \text{[mb]} = 98.93 \frac{\Delta[\text{mm/s}]}{q[\text{a.u.}]} = 0.12 \text{ b}$
<table>
<thead>
<tr>
<th>Method</th>
<th>$\text{Fe(CO)}_5$</th>
<th>$\text{Fe(CO)}_5 \text{ LB}$</th>
<th>$\text{Fe(Cp)}_2$</th>
<th>$\text{Fe(Cp)}_2 \text{ LB}$</th>
</tr>
</thead>
<tbody>
<tr>
<td><em>ab-initio</em></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>HF</td>
<td>1.394</td>
<td>1.522</td>
<td>3.157</td>
<td>3.407</td>
</tr>
<tr>
<td>MP2</td>
<td>3.593</td>
<td>4.069</td>
<td>1.563</td>
<td>1.649</td>
</tr>
<tr>
<td>RSMP2</td>
<td>3.511</td>
<td></td>
<td>1.560</td>
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<tr>
<td>RSMP3</td>
<td>-0.740</td>
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<td>3.385</td>
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<tr>
<td>RSMP4</td>
<td>9.484</td>
<td></td>
<td>-0.250</td>
<td></td>
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<tr>
<td>RCCCSSD</td>
<td>1.339</td>
<td></td>
<td>1.831</td>
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</tr>
<tr>
<td>RCCCSSD(T)</td>
<td>1.439</td>
<td></td>
<td>1.496</td>
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<tr>
<td><em>DFT</em></td>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Xα</td>
<td>1.148</td>
<td>1.322</td>
<td>1.374</td>
<td>1.522</td>
</tr>
<tr>
<td>HFS</td>
<td>1.092</td>
<td>1.260</td>
<td>1.363</td>
<td>1.498</td>
</tr>
<tr>
<td>LDA</td>
<td>1.154</td>
<td>1.323</td>
<td>1.359</td>
<td>1.504</td>
</tr>
<tr>
<td><em>GGA</em></td>
<td></td>
<td></td>
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</tr>
<tr>
<td>BHFS</td>
<td>1.187</td>
<td>1.361</td>
<td>1.434</td>
<td></td>
</tr>
<tr>
<td>BLYP</td>
<td>1.203</td>
<td>1.372</td>
<td>1.425</td>
<td>1.563</td>
</tr>
<tr>
<td>BPW91</td>
<td>1.203</td>
<td>1.371</td>
<td>1.377</td>
<td>1.516</td>
</tr>
<tr>
<td><em>Hybrid</em></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>B3LYP</td>
<td>1.393</td>
<td>1.575</td>
<td>1.854</td>
<td>2.022</td>
</tr>
<tr>
<td>B3PW91</td>
<td>1.395</td>
<td>1.577</td>
<td>1.806</td>
<td></td>
</tr>
<tr>
<td>BHH</td>
<td>1.547</td>
<td>1.732</td>
<td>2.429</td>
<td>2.640</td>
</tr>
<tr>
<td>BHH-LYP</td>
<td>1.573</td>
<td>1.758</td>
<td>2.488</td>
<td>2.699</td>
</tr>
</tbody>
</table>

Compare to GGA-PAW EFGs of Blaha and Schwarz:
Fe($\text{CO})_5$: 1.05 a.u., FeCp$_2$: 1.10 a.u.

P. Schwerdtfeger, T. Söhnel, M. Pernpointner, J. K. Laerdahl, F. E. Wagner, 
The $^{197}$Au ($I=3/2^+$) nuclear quadrupole moment

The figure shows a plot of the Moessbauer quadrupole splitting ($q$ in a.u.) versus the nuclear quadrupole moment ($Q_s$) for various compounds. The equation $Q_s = 0.612(8)$ b is used to fit the data. The authors used the PAW method (WIEN98) with the GGA functional (PBE) for this analysis.

The compounds listed include:
- $\text{CsAuO}$
- $\text{K}_2\text{Au}_3$-
- $\text{Au}^{(1)}$
- $\text{NaAu}_2$
- $\text{CsAuSe}$
- $\text{KAuSe}$
- $\text{K}_2\text{Au}_3$-
- $\text{Au}^{(II)}$
- $\text{AuCl}$
- $\text{K}_2\text{Au}_5$-
- $\text{Au}^{(II)}$
- $\text{Na}_3\text{AuO}_2$
- $\text{Na}_3\text{Au}_2\text{Cl}_6$-
- $\text{Au}^{(I)}$
- $\text{LiAu}_3$
- $\text{K}_2\text{Au}_3$-
- $\text{Au}^{(II)}$
- $\text{Li}_3\text{AuO}_3$
- $\text{Au}_2\text{O}_3$
- $\text{Li}_3\text{AuO}_3$
- $\text{RbAuF}_4$
- $\text{KAuTe}$
- $\text{CsAuTe}$

The authors are:
- 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,

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

\[ Q_s[b] = 3.76 \text{(B3LYP)}, \ 0.23 \text{ (DHF)}, \ -0.44 \text{ (LDA)}, \ -0.79 \text{ (PW86)}, \ -0.99 \text{ (BLYP)} \]

compare to best estimate from muonic experiments: +0.55 b
But: Take larger range of EFGs

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 \( +0.547(16) \text{ b} \))


<table>
<thead>
<tr>
<th>Molecule</th>
<th>( q_{\text{nuc}} )</th>
<th>( q_{\text{NRHF}} )</th>
<th>( \Delta q_{\text{DHF}} )</th>
<th>( \Delta q_{\text{corr}}^{\text{CCSD(T)}} )</th>
<th>( \Delta q_{\text{zpV}} )</th>
<th>( q_{\text{total}} )</th>
<th>( Q_s(b) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>AuF</td>
<td>0.378</td>
<td>-5.636</td>
<td>+0.643</td>
<td>+4.765</td>
<td>-0.019</td>
<td>+0.131</td>
<td>-1.729</td>
</tr>
<tr>
<td>AuCl</td>
<td>0.474</td>
<td>-4.544</td>
<td>+0.634</td>
<td>+3.062</td>
<td>-</td>
<td>-0.374</td>
<td>-0.110</td>
</tr>
</tbody>
</table>

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

<table>
<thead>
<tr>
<th>Molecule</th>
<th>( q_{\text{nuc}} )</th>
<th>( q_{\text{NRHF}} )</th>
<th>( \Delta q_{\text{DK}} )</th>
<th>( \Delta q_{\text{corr}}^{\text{CCSD}} )</th>
<th>( \Delta q_{\text{corr}}^{\text{+T(CCSD)}} )</th>
<th>( q_{\text{total}} )</th>
<th>( Q_s(b) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>FAuCO</td>
<td>0.755</td>
<td>-10.145</td>
<td>-1.845</td>
<td>+3.852</td>
<td>+0.605</td>
<td>-6.777</td>
<td>+0.632</td>
</tr>
</tbody>
</table>

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))

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

The Colorado attempt


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

The Tel-Aviv attempt


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

The Amsterdam attempt


KR-CCSD(T) for AuF, XeAuF, KrAuF, ArAuF, OCAuF, and AuH
$Q_s = +0.510(13) \text{ b}$
The Helsinki-Bratislava-Auckland response

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

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

<table>
<thead>
<tr>
<th>Molecule</th>
<th>$q_{\text{nuc}}$</th>
<th>$q_{\text{MP2}}$</th>
<th>$q_{\text{CCSD}}$</th>
<th>$q_{\text{CCSD(T)}}$</th>
<th>$\Delta q_{\text{Gaunt}}$</th>
<th>$\Delta q_{\text{vib}}$</th>
<th>$\Delta q_{\text{QED}}$</th>
<th>$q_{\text{total}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>AuH</td>
<td>-2.241</td>
<td>2.526</td>
<td>1.236</td>
<td>1.744</td>
<td>-0.023</td>
<td>0.053</td>
<td>-0.045</td>
<td>1.510</td>
</tr>
</tbody>
</table>

$Q = +0.509$ b

Problem: Uncertainty in QED, Large triples contribution in CCSD, one may have to do CCSDTQ
The nuclear hexadecapole moment of $^{127}\text{I}$ ($I=5/2^+$)

**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) $24 \pm 5$ kHz for $^{123}\text{Sb}$ (SbBr$_3$)
- Hewitt and William (1963) $13 \pm 30$ kHz for $^{123}\text{Sb}$ (Sb)
- Goutou (1983) $110 \pm 61$ kHz (SbCl$_3$)
- Ni and Sears (1991) 2.8 Hz $^{127}\text{I}$ (KI)
- Cederberg *et al* (1999) $15.1 \pm 3.0$ Hz for $^{127}\text{I}$ (LiI) (J.Cederberg et al, *J. Chem. Phys.* 110, 2431 (1999)).

**However:**

**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.

\[ V_{zzzz}^{(127\text{I})} = 7.274 \text{ a.u.} \quad \text{in LiI} \]

Nuclear structure calculations:

Surface of a deformed nucleus:

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

\[ a_{20} = \beta_2 \cos \gamma \quad a_{22} = \frac{1}{\sqrt{2}} \beta_2 \sin \gamma \]

Axial deformation parameters:

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

\[ M_0 (2) = Q_0 \quad M_0 (4) = H_0 \]

\[ M_0 (\lambda) = \left( \frac{16\pi}{2(\lambda + 1)} \right)^{1/2} \int d\vec{r} \ n_N (\vec{r}) r^2 Y_{\lambda0} (\vartheta, \varphi) \]

Final results:

<table>
<thead>
<tr>
<th></th>
<th>Experimental</th>
<th>Calculated</th>
<th>Used NQM(NHM)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NQCC [MHz]</td>
<td>$-194.351212(17)$</td>
<td>$-172$</td>
<td>$-0.70$ b</td>
</tr>
<tr>
<td>NHCC [Hz]</td>
<td>$-15.1(30)$</td>
<td>$+0.060$</td>
<td>$+0.006$ b$^2$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$+0.020$</td>
<td>$+0.002$ b$^2$</td>
</tr>
</tbody>
</table>


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 $^{133}\text{Cs}$, $^{99,101}\text{Ru}$, $^{191,193}\text{Ir}$ and $^{139}\text{La}$
New Zealand is a fun place
CuCl: Charge Distribution

\[ \rho(z,0,0) \]

CuCl

HF
BBHH-LYP
B3LYP
HFS

Cu
Cl

R [a.u.]
# Order of magnitudes

<table>
<thead>
<tr>
<th></th>
<th>Second row</th>
<th>Sixth row</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Nuclear radius</strong></td>
<td>2.48 fm</td>
<td>5.52 fm</td>
</tr>
<tr>
<td><strong>$E^0$</strong></td>
<td>$-8.8 \times 10^2$ a.u.</td>
<td>$-2.1 \times 10^4$ a.u.</td>
</tr>
<tr>
<td><strong>$\Delta E^2,\text{isotropic}$</strong></td>
<td>$3.5 \times 10^{-6}$ a.u.</td>
<td>$5.9 \times 10^0$ a.u.</td>
</tr>
<tr>
<td><strong>$\Delta E^2,\text{anisotropic}$</strong></td>
<td>$1.8 \times 10^{-10}$ a.u.</td>
<td>$8.0 \times 10^{-8}$ a.u.</td>
</tr>
</tbody>
</table>

(from L. Visscher *(ICCMSE 2006)*)

$\Delta E^{\lambda,\text{anisotropic}}$ can be treated perturbatively

Electric field gradient tensor at nucleus $N$:

$$q_{\alpha\beta} = \left\langle V^{\text{el},(2)}_{\alpha\beta}\left(\vec{R}_N\right)\right\rangle + V^{\text{nuc},(2)}_{\alpha\beta}(\vec{R}_N)$$

For $n$ electrons:

$$\left\langle V^{\text{el},(2)}_{\alpha\beta}\left(\vec{R}_N\right)\right\rangle = \left\langle \Psi \right| \sum_{i=1}^{n} \frac{3(\vec{r}_{i\alpha} - \vec{R}_{N\alpha})(\vec{r}_{i\beta} - \vec{R}_{N\beta}) - \left|\vec{r}_i - \vec{R}_N\right|^2 \delta_{\alpha\beta}}{\left|\vec{r}_i - \vec{R}_N\right|^5} \left|\Psi\right\rangle$$
Nuclear deformations

MAXIMUM DEFORMATION: Super- or hyper-deformed nuclei:
$^{152}$Dy $Q=18.9$ b; $^{149}$Gd $Q=16.5$ b


(1 barn = $10^{-28}$ m$^2$)