The Search for Parity Violation Effects - Relativistic Coupled Cluster Calculations Chiral Molecules.

\[ H_{pv} = \frac{G_F}{2\sqrt{2}} \sum_{i,n} Q_{W,n} \gamma_i^2 \rho_n (\vec{r}_i) + \frac{G_F}{\sqrt{2}} \sum_{i,n} f_n (I, K) \alpha_i \bar{\alpha}_i \bar{\rho}_n (\vec{r}_i) + \ldots \]

- Timelike component of \((A_e, V_e)\)
- Spacelike component of \((V_e, A_e)\)
Biomolecular Homochirality

Biotic  Hypotheses  Abiotic

Extraterrestrial / Terrestrial
Singular / Multiple Events

Biological Selectivity  Exotic Propositions  Deterministic  Probabilistic

Circular dichroism spectra of D-d(CGCGCG) ( ) and L-d(CGCGCG) ( ) at 0°C. Samples (10 A_{260}/mL) were dissolved in 10 mM sodium phosphate buffer (pH 7) containing (a) 0.1 M NaCl and (b) 4 M NaCl.

H. Urata, K. Shinozaka, E. Ogura, Y. Ueda, M. Akagi,

Breaking mirror image symmetry

at the macroscopic level

L. Pasteur, Acad. Sci, Paris (June 1, 1874)

Life is dominated by dissymmetric actions of whose enveloping and cosmic existence we have some indication. Not only have I refrained from posing as absolute the existence of a barrier between the products in the laboratory and those of life, but I was the first to prove that it was merely an artificial barrier, and I indicated the general procedure necessary to remove it, by recourse to those forces of dissymmetry never before employed in the laboratory.

Convolvulus Arvensis
(Bindweed)

Lonicera Sempervirens
(Trumpet honeysuckle)

Schnirkelschnecke
Movements of the Lower Jaw of Cattle during Mastication.

Among the biological phenomena exhibiting a definite sense of rotation, as, for example, the growth of certain creepers and of the shells of snails, one that does not seem to have been studied and to which we wish to direct attention here, is the masticating motion of cattle. Close investigation shows that the lower jaw of the animal is displaced with respect to the upper jaw, not in a purely horizontal or a purely vertical direction, but simultaneously in both directions with such a phase difference that a clearly evident rotation results. Theoretically this can, of course, take place in two senses, and observation teaches that both possibilities are realised in nature.

Taking the direction of the food as positive, we shall denote as right- and left-circular cows those of which the chewing motion, viewed from the front, turns clockwise and counterclockwise respectively.

This nomenclature is based on the tacit assumption that one and the same cow always maintains its sense of rotation. We could confirm this by a limited number of observations but are aware that more complete data, extending over longer periods of time, are necessary definitely to settle this point. Statistical investigations on cows distributed over the northern part of Slesland, Denmark, led to the result that about fifty-five per cent. were right-circular, the rest left-circular animals. As one sees, the ratio of the two kinds is approximately unity. The number of observations was, however, scarcely sufficient to make sure if the deviation from unity is real. Naturally these determinations allow no generalisation with regard to cows of different nationality.

The fact that both senses of rotation are realised raises the question if simple laws govern the hereditary transmission of the property referred to. Concerning the snails mentioned above, one knows that Mendel's laws in their simplest form apply, while in most other cases the actual occurrence of only one sense of rotation makes such investigations impossible. Particularly it would be interesting to ascertain which of the two modifications is the dominating one.

Pascual Jordan

Ralph de L. Kronig

are, unfortunately, not in a position to bring evidence on this important point, but believe that those having a more intimate acquaintance with cattle will find it easy to give an answer.

University Institute for Theoretical Physics, Copenhagen.
Parity violation in chiral molecules

1975: Due to parity violation, two enantiomers do not have the same absorption spectrum (V.S. Letokhov, Phys. Lett. 53A, 275 (1975))

\[ \Delta \nu_{PV} = \nu_R - \nu_S \neq 0 \]

1976: Proposition to search for parity violation effect in CHFCI\textsubscript{Br} spectrum [O.N. Kompanets et al., Opt. Commun. 19, 414 (1976)]
Electroweak Electronic Structure Theory

\[ \hat{H}_I = \frac{G_F}{\sqrt{2}} \sum_N \left[ c_1^N \bar{\psi}_e \gamma^\mu \gamma^5 \psi_e \bar{\psi}_N \gamma^\mu \psi_N + c_2^N \bar{\psi}_e \gamma^\mu \psi_e \bar{\psi}_N \gamma^\mu \gamma^5 \psi_N + H_{ee} \right] \]

\[ c_1^p = \frac{1}{2} \left( 1 - 4 \sin^2 \theta_W \right) \approx 0.02 \quad , \quad c_1^n = -\frac{1}{2} \quad , \quad c_2^p = -c_2^n = \frac{1}{2} g_A \left( 1 - 4 \sin^2 \theta_W \right) \approx 0.05 \]

vertex factors

\[ G_F = 1.16637 \times 10^{-11} \text{ MeV}^{-2} = 2.22255 \times 10^{-14} \text{ a.u.} \]

Leptonic weak interactions are described by the leptonic currents (V-A coupling)

\[ J_\mu (x) = \sum_l \bar{\psi}_l (x) \gamma_\mu (1 - \gamma_5) \psi_{l'} (x) \]

Coupling to the WN field:

\[ L_I (x) = -\frac{g}{\cos \theta_W} \left[ J_3^\mu (x) - \sin^2 \theta_W j^\mu (x)/e \right] Z_\mu (x) \]

\[ \gamma \text{ Parity conserving} \]

\[ \text{Z}_0 \text{ carries a handedness} \]

\[ \text{Parity violating} \]

\[ M_Z = 90 \text{ GeV} \]
time-like component \((A_e, V_N)\): 

\[
\hat{H}_1 \equiv \frac{G_F}{\sqrt{2}} \gamma^5 \left[ Z c_1^p \rho_p(r) + N c_1^n \rho_n(r) \right] \quad \rho_p(r) \approx \rho_n(r) \\
\hat{H}_1 \equiv \frac{G_F}{2 \sqrt{2}} Q_w \rho(r) \gamma^5
\]

Weak charge 

\[Q_w = -N + Z (1 - 4 \sin^2 \theta_w) \approx -N, \quad \int \rho(r) d^3r = 1\]

Nuclear spin-dependent part, space-like component \((V_e, A_N)\): 

\[
\hat{H}_2 \equiv \frac{G_F}{\sqrt{2}} \bar{\alpha} \left[ c_2^p \sum_p \sigma_p + c_2^n \sum_n \sigma_n \right] \rho(r)
\]

+ nuclear anapole

\[
H_{PV} = \frac{G_F}{2 \sqrt{2}} \sum_{i,M} Q_{W,M} \gamma_i^5 \rho_M(\vec{r}_{iM}) + \frac{G_F}{\sqrt{2}} \sum_{i,N} \left( f_{NC} + f_{HF} + f_A \right) \bar{\alpha}_i \vec{I}_M \rho_M(\vec{r}_{iM}) + ...
\]

\[f_{NC} = c_2^N \frac{1/2 - K_M}{I_M(I_M + 1)}, \quad f_{HF} = \kappa_{HF} / I_M, \quad f_A = \kappa_A \frac{K_M}{I_M(I_M + 1)}\]

\[K_M = (-1)^{I-1+1/2}(I_M + 1/2), \quad \kappa_{HF} = -\frac{1}{3} Q_w \frac{\alpha \mu_N}{m_p R_M}
\]

\[\kappa_A = 2.9 g_p + 0.18 g_n + 0.36 g_{pn} - 0.02 g_{np}\]


Point charge versus finite extension of the nucleus: Choice of \( \rho_M(\vec{r}_{iM}) \)

\[
M_{PV}^n = \sum_i M_{PV}^{n,i} = \sum_i \langle \psi_i | \gamma_i^S \rho_n(\vec{r}_{in}) | \psi_i \rangle
\]

Diagram showing a plot of \( M_{PV}^S \) (a.u.) versus nuclear r.m.s. radius (fm), with data points and a curve indicating a decrease as the radius increases. Annotation at \( \tau = 45^\circ \) with a note on "Experimental r.m.s. radius."
Finite nucleus influence on the Coulomb potential

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

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

\[ n_N(r) = n_0 e^{-\left(\frac{r}{R}\right)} \]

\[ V_{\text{nucl}}(r) / 10^6 \text{ au} \]

\[ -2mc^2 \]

\[ Z = 80 \]

\[ A = 200 \]

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

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

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

Vacuum polarization + electron self-energy:  \[ h_{QED}(i) = h_{VP}(i) + h_{SE}(i) \]

The stationary Dirac-equation

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

Programs: For atoms: GRASP; for molecules: DIRAC, UTCHEM, BERTHA
The Nonrelativistic Formalism (Schrödinger Picture)

The unitary transformation from the Dirac- to the Schrödinger picture:

\[ H_{tr} = U H U^{-1}, \quad U = \sqrt{1 + XX}^1, \quad X = \left( 2mc^2 + E - V \right)^{-1} c\sigma p \]

\[ \varphi_S = \left( 2mc^2 + E - V \right)^{-1} c\sigma p \varphi_L, \quad \Phi = U \varphi_L, \quad (\Phi, \Phi) = 1 \]

1) Diagonal perturbation operators \( f \):

\[
\begin{pmatrix}
V - E + f & c\varphi \\
\varphi & -2mc^2 + V - E + f
\end{pmatrix}
\begin{pmatrix}
\varphi_L \\
\varphi_S
\end{pmatrix} = 0
\]

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

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

\[ f^S = f + \frac{1}{8c^2} \Delta f + ... \]

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 \( f \):

\[
\begin{pmatrix}
V - E & c\varphi + f \\
\varphi + f & -2mc^2 + V - E
\end{pmatrix}
\begin{pmatrix}
\varphi_L \\
\varphi_S
\end{pmatrix} = 0
\]

\[ f^S = \frac{1}{2mc} [\sigma \pi, f]_+ + ... \]

\[ H_{eN}^{PNC} = \frac{G_F}{4mc \sqrt{2}} \sum_{i,M} Q_{W,i} \{ \sigma, p_i, \rho_{M} (r_{iM}) \}^+ \]

Bouchiat-Hamiltonian
Relativistic Electronic Structure Theory.

P.Schwerdtfeger (editor) In honour of Pekka Pyykkö’s 60th birthday

Ch. 1 Tour Historique Jean-Paul Desclaux
Ch. 2 The Dirac Operator Bernd Thaller
Ch. 3 Relativistic Self-Consistent Fields Ian P. Grant, Harry M. Quiney
Ch. 4 Nuclear Charge Density Distributions in Quantum Chemistry Dirk Andrae
Ch. 5 Basis Sets for Relativistic Calculations Knut Faegri Jr., Kenneth G. Dyall
Ch. 6 Post Dirac-Fock-Methods – Electron Correlation Lucas Visscher
Ch. 7 Post Dirac-Fock-Methods – Properties Trond Saue
Ch. 8 QED Theory of Atoms Leonti N. Labzowsky, Igor Goidenko
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Ch. 12 Perturbation Theory of Relativistic Effects Werner Kutzelnigg
Ch. 13 Perturbation Theory Based on Quasi-Relativistic Hamiltonians Dage Sundholm
Ch. 14 Relativistic Effective Core Potentials Michael Dolg
Ch. 15 Relativistic Solid State Theory Niels E. Christensen
Reviews

Parity Nonconservation in Chiral Molecules

\[ \Delta E_{PV} = 2E_{PV} \]

\[ E = E_0 - E_{PV} \]

\[ E = E_0 + E_{PV} \]

**Not detected yet !!!**

Vib-Rot Spectroscopy: Ch.Chardonnet, Ch.J.Bordé, C. Daussy (Paris)
Mössbauer Spectroscopy: R.N.Compton (Tennessee)
Dynamics in excited electronic states: M.Quack (Zürich)
Spectroscopy: R.N.Compton (Tennessee)

\[ \Delta E = 300 \text{ Hz} \]
Usually theoreticians and experimentalists are happiest when they agree with each other. This means, to give an example, that when a new experimental number becomes available, all theoretical groups immediately announce that the number can be calculated by the group’s current theory - no matter what the number is, and no matter what the theory is. Effectively this, of course, forces our theoretical friends always to obtain the same final results, even if some of the intermediate steps may be different. Clearly this is not very satisfactory for them. Electroweak effects in molecules offer a solution to this problem: As such effects cannot be measured at the moment, the theoreticians may feel free to obtain whatever number they like. Together with modern cosmology it has become almost a “Theoreticians Liberation Movement”.
The Search for PNC effects in Chiral Compounds

9.22 µm R(28) CO₂ laser line for the vibrational excitation of d- and l-camphor: Negative outcome Δν < 300 kHz

\[ \Delta \nu / \nu = 10^{-19} \] (exp. In 1977: \[ \Delta \nu / \nu \neq 10^{-8} \])

Nonlinear Laser Spectroscopy on Vibrational Transitions in CHFClBr and CHFClI - The Paris Experiments


Ch. Chardonnet and co-workers
Histogram (Test 2000)

Mean value: -4.2 Hz
Standard deviation: 16 Hz
780 measurements

\[ \frac{\sigma}{\sqrt{N}} = 0.6 \text{Hz} \]

Conclusion of these first tests

Result:

\[
\frac{\Delta \nu^{PV}}{\nu} < 2.5 \times 10^{-13}
\]

Improvement of 5 orders of magnitude

Limitations:

• Sensitivity limited by collisions \( \approx 2.5 \times 10^{-13} \)

• Linewidth \( \sim 60 \text{ kHz} \)

• Calculated effect \((1-3) \sim 2.4 \text{ mHz} \ (8 \times 10^{-17})\)

Molecular beam

no collisional effect

Ramsey Fringes spectroscopy

Linewidth : 100-1000 times narrower

New molecule with stronger effect

Temporal variation of the SF$_6$ two-photon transition frequency

Data from 10 November 2004 to 28 June 2006

Frequency drift:
1.2 mHz/day (+/- 0.35 mHz)

Flambaum:
$$\frac{\delta R_{Cs/SF_6}}{R_{Cs/SF_6}} = 2.83 \frac{\delta \alpha}{\alpha} + 0.61 \frac{\delta (m_q / \Lambda_{QCD})}{m_q / \Lambda_{QCD}}$$
Results from our theoretical calculations

Implementation into the the relativistic *ab-initio* electronic structure program DIRAC

DHF calculations on H$_2$O$_2$, H$_2$S$_2$, H$_2$Se$_2$, H$_2$Te$_2$, and H$_2$Po$_2$ in order to test the $Z^5$-law

\[ E_{pv}^n = \frac{G_F}{2\sqrt{2}} \sum_i Q_{w,\mu} M_{\nu,i}^{pv} = \frac{G_F}{2\sqrt{2}} Q_{w,\mu} \sum_i \langle \psi_i | \gamma^\nu \rho_\mu(r_i) | \psi_i \rangle \]

\[ \Delta E_{pv} = 3.11 \cdot 10^{-21} \cdot Z^{6.18} \text{ [kJ/mol]} \]

\[ \Delta E_{pv} [10^{-n} \text{ kJ/mol}] \]

\[ y = 6.178x - 20.507 \]

\[ \tau = 45^\circ \]

Is PNC a core- or valence property?

\[ M_{n,i}^{PV} = \langle \psi_i | \gamma_i^5 \rho_n (r_i) | \psi_i \rangle \]

Po: \( Z = 84 \)

Po core-orbitals

\( M_{PV} \) contribution

\( M_{PV} \) accumulated

valence-orbitals

\( n_e = 170 \)
Is DFT reliable? 4-component DFT calculations

\[
\frac{2\sqrt{2}}{G_F} E_{pv} \quad [\text{mH}]
\]
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 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

$$\Sigma_y = \begin{pmatrix} \sigma_y & 0 \\ 0 & \sigma_y \end{pmatrix}, \quad \hat{K} (\lambda_1 \psi_1 + \lambda_2 \psi_2) = \lambda_1^* \hat{K} \psi_1 + \lambda_2^* \hat{K} \psi_2$$

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

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

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 coupled cluster (KRCC)

- Closed shell KR-CCSD including perturbative triples, CCSD(T), is implemented in DIRAC (Luuk Visscher) 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 the coupled cluster amplitudes we derive the relations

\[
\begin{align*}
    t_i^a &= t_i^{\bar{a}*}, \\
    t_i^a &= -t_i^{\bar{a}*} \\
    t_{ij}^{ab} &= t_{ij}^{\bar{a}\bar{b}*}, \\
    t_{ij}^{\bar{a}\bar{b}} &= t_{ij}^{ab*}, \\
    t_{ij}^{a\bar{b}} &= t_{ij}^{\bar{a}b*}, \\
    t_{ij}^{ab} &= -t_{ij}^{\bar{a}\bar{b}*}
\end{align*}
\]

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.

- The situation becomes more complicated for open-shell cases, see K. G. Dyall, K. Faegri Jr., *Introduction to relativistic quantum theory*, Oxford, 2007. An alternative is Fock-space coupled cluster (Kaldor, Eliav)
There is no analytical DC-CCSD yet as it is difficult to implement efficiently. Therefore, the finite-difference method for correlation energies is used (PNC perturbation), e.g. a two-point interpolation for the correlation contribution (HF value from expectation value).

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

\[
H_{\text{PV}}^n = \lambda \sum_i \gamma_i n^5(p_{n}(r_i))
\]

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. For the PNC operator we choose the perturbation for each element carefully and analyze its numerical stability.

Problem: The kinetic balance condition changes by addition of the PV operator

\[
\varphi_s = \left(2mc^2 + E - V \right)^{-1} c(\bar{\sigma} \bar{p} + \lambda h_{PV}) \varphi_L
\]

which if neglected could lead to variational instabilities.
How accurate are these results?

Basis set convergence, Electron correlation, Missing Breit and QED interactions

\[ H_{PV}^n (\lambda) = \lambda \sum_i \gamma_i^5 \rho_i (r_i) \rightarrow \Delta_{cor} M_{PV}^n = \frac{\partial E_{cor}}{\partial \lambda} \bigg|_{\lambda=0} \]

\[ E_{cor} = E - E_{HF} \]

\[ M_{PV}^n_{n=0} \]

<table>
<thead>
<tr>
<th>( \lambda )</th>
<th>DHF</th>
<th>MP2</th>
<th>CCSD(T)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>( 4.313 \times 10^{-5} )</td>
<td>( 3.651 \times 10^{-5} )</td>
<td>( 3.836 \times 10^{-5} )</td>
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<td>0.01</td>
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<td>( 5.330 \times 10^{-6} )</td>
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<td>0.001</td>
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<td>( 4.963 \times 10^{-6} )</td>
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<tr>
<td>0.0002</td>
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<td>( 4.963 \times 10^{-6} )</td>
<td>( 5.246 \times 10^{-6} )</td>
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<tr>
<td>analytic</td>
<td>( 5.801 \times 10^{-6} )</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

Compare to real \( \lambda \): \( \sim -10^{-14} \) to \( -10^{-12} \) (!)

C-F stretching mode is in the CO$_2$ laser frequency range

Molecules investigated: CHFClBr, CHFClI, CHFBrI, CHClBrI, CFCIBrI, SiHFClBr, GeHFClBr, SnHFClBr, PbHFClBr

- normal mode analysis
- local mode treatment: anharmonic vibrational analysis using a Morse potential in normal coordinates

$$E_{PV,n} = E_{PV}(0) + \frac{1}{2} \left( \frac{\hbar}{\mu \omega} \right) V^{[2]}(0) + \left( \frac{1}{\mu \omega^2} \right) V^{[3]}(0) E_{PV}^{[1]}(0) \left( n + \frac{1}{2} \right) + ...$$

Buckingham formula
Anharmonic Vibrational Analysis for CHFClBr
Quartic $q$-FF, aug-cc-pvtz basis sets for all atoms, VPT

<table>
<thead>
<tr>
<th>Property</th>
<th>Mode</th>
<th>MBPT2 Harmonic</th>
<th>MBPT2</th>
<th>B3LYP</th>
<th>PW91</th>
<th>CCSD(T) +AH+BS1</th>
<th>Exp.</th>
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<tr>
<td>$E_{ZPVE}$</td>
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<td>4668.5</td>
<td>4621.6</td>
<td>4494.1</td>
<td>4352.7</td>
<td>4585.4</td>
<td>-</td>
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<td>$\nu^{(1)}$</td>
<td>CH str</td>
<td>3185.8</td>
<td>3053.6</td>
<td>3011.6</td>
<td>2930.9</td>
<td>3032.8</td>
<td>3025.5</td>
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<td>$\nu^{(2)}$</td>
<td>FCH bend</td>
<td>1339.4</td>
<td>1309.4</td>
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<tr>
<td>$\nu^{(3)}$</td>
<td>(Cl,Br)CH bend</td>
<td>1246.5</td>
<td>1224.1</td>
<td>1185.3</td>
<td>1137.5</td>
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<td>1202.8</td>
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<td>$\nu^{(4)}$</td>
<td>CF str</td>
<td>1093.5</td>
<td>1065.3</td>
<td>1047.2</td>
<td>1008.2</td>
<td>1073.6</td>
<td>1077.2</td>
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<td>$\nu^{(5)}$</td>
<td>CCl str</td>
<td>808.7</td>
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<td>CBr str</td>
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<td>FCCl bend</td>
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<td>427.4</td>
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<td>404.4</td>
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<tr>
<td>$\nu^{(8)}$</td>
<td>FCBr bend</td>
<td>319.7</td>
<td>316.4</td>
<td>302.9</td>
<td>293.7</td>
<td>312.4</td>
<td>313.0</td>
</tr>
<tr>
<td>$\nu^{(9)}$</td>
<td>ClCCl bend</td>
<td>228.9</td>
<td>227.2</td>
<td>215.1</td>
<td>209.0</td>
<td>222.9</td>
<td>223.6</td>
</tr>
<tr>
<td>rms</td>
<td></td>
<td>10.2</td>
<td>20.8</td>
<td>58.7</td>
<td>4.2</td>
<td>-</td>
<td></td>
</tr>
</tbody>
</table>

### Theory: Stretching frequencies

<table>
<thead>
<tr>
<th></th>
<th>$\omega_e$ (GHz)</th>
<th>$x_e\omega_e$ (GHz)</th>
<th>$\omega_{PV}$ (mHz)</th>
<th>$\nu_{PV}$ (mHz)</th>
<th>$\Delta E_{PV}$ (mHz)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>CHFClBr</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C-F</td>
<td>36,000</td>
<td>270</td>
<td>0.9</td>
<td>-1.0</td>
<td></td>
</tr>
<tr>
<td>C-Cl</td>
<td>25,900</td>
<td>54</td>
<td>-2.4</td>
<td>-3.5</td>
<td></td>
</tr>
<tr>
<td>C-Br</td>
<td>21,500</td>
<td>57</td>
<td>0.2</td>
<td>0.5</td>
<td></td>
</tr>
<tr>
<td><strong>CHFBBrI</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C-F</td>
<td>35,300</td>
<td>280</td>
<td>15.7</td>
<td>-17.9</td>
<td>1047</td>
</tr>
<tr>
<td>C-Br</td>
<td>22,800</td>
<td>18</td>
<td>-55.3</td>
<td>-90.0</td>
<td></td>
</tr>
<tr>
<td>C-I</td>
<td>18,300</td>
<td>6</td>
<td>0.2</td>
<td>3.9</td>
<td></td>
</tr>
<tr>
<td><strong>CHClBrI</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C-Cl</td>
<td>24,600</td>
<td>120</td>
<td>7.6</td>
<td>-19.5</td>
<td>659</td>
</tr>
<tr>
<td>C-Br</td>
<td>21,600</td>
<td>9</td>
<td>-33.6</td>
<td>-39.5</td>
<td></td>
</tr>
<tr>
<td>C-I</td>
<td>16,700</td>
<td>3</td>
<td>-1.6</td>
<td>-0.9</td>
<td></td>
</tr>
</tbody>
</table>

NB: For DFT vibrational transitions remain basically unaffected

![Graph showing vibrational transitions with different methods: HF, PW86, LDA, B3LYP, BLYP, MP2.](image-url)
Relativistic CC: Weak field perturbation

\[ M_{n=Cl}^{PV} (\lambda) = \lambda \sum_{i} \gamma_{i} \rho_{n} (r_{i}) \]

Numerical instabilities

Graph showing the dependence of \( M_{n=Cl}^{PV} \) on perturbation strength \( \lambda \).
Results for CHFCI\textsubscript{Br}

\[ M_n^{PV} = \sum_i M_{n,i}^{PV} = \sum_i \langle \psi_i | \gamma_i^5 \rho_n(r_i) | \psi_i \rangle \]

<table>
<thead>
<tr>
<th></th>
<th>C</th>
<th>F</th>
<th>Cl</th>
<th>Br</th>
</tr>
</thead>
<tbody>
<tr>
<td>DHF</td>
<td>0.0576</td>
<td>0.6803</td>
<td>-1.8454</td>
<td>1.6832</td>
</tr>
<tr>
<td>WFP-DHF</td>
<td>0.057</td>
<td>0.680</td>
<td>-1.846</td>
<td>1.683</td>
</tr>
<tr>
<td>WFP-MP2</td>
<td>0.066</td>
<td>0.665</td>
<td>-1.375</td>
<td>0.935</td>
</tr>
<tr>
<td>WFP-CCSD</td>
<td>0.062</td>
<td>0.632</td>
<td>-1.417</td>
<td>1.075</td>
</tr>
<tr>
<td>WFP-CCSD(T)</td>
<td>0.063</td>
<td>0.628</td>
<td>-1.314</td>
<td>0.931</td>
</tr>
</tbody>
</table>

Parity violation matrix elements \( M_n^{PV} \) (in \( 10^{-5} \) au) at different levels of correlation, uncontracted cc-pVDZ basis sets are used for all atoms of CHFCI\textsubscript{Br}.
The Search for a better candidate: Using the $Z^5$-law
Moving towards the 1 Hz region


$\Delta \nu_{R-S} (mHz) = 158$

$\Delta \nu_{R-S} (mHz) = 219$

One order of magnitude improvement
Choosing even heavier chiral centers

B3LYP

\[ \Delta \nu_{R-S} = +1.09 \text{ Hz} \]
\[ \Delta v_{R-S} = -1.15 \text{ Hz} \]

SeOCII: A promising new candidate

![Molecular structure of SeOCII](image)

**TABLE I: Dipole moments $\mu$ (in Debye) and parity violating contributions $E_{PV}$ (in atomic units) for each atom at the equilibrium geometry of $S$-SeOCII.**

<table>
<thead>
<tr>
<th>Atom</th>
<th>DHF</th>
<th>DKS-LDA</th>
<th>DKS-B3LYP</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\mu$</td>
<td>2.889</td>
<td>2.019</td>
<td>2.264</td>
</tr>
<tr>
<td>Se</td>
<td>$-3.541 \times 10^{-16}$</td>
<td>$-3.945 \times 10^{-16}$</td>
<td>$-3.964 \times 10^{-16}$</td>
</tr>
<tr>
<td>O</td>
<td>$2.770 \times 10^{-18}$</td>
<td>$2.860 \times 10^{-18}$</td>
<td>$3.054 \times 10^{-18}$</td>
</tr>
<tr>
<td>Cl</td>
<td>$-2.084 \times 10^{-18}$</td>
<td>$4.510 \times 10^{-18}$</td>
<td>$2.330 \times 10^{-19}$</td>
</tr>
<tr>
<td>I</td>
<td>$-1.041 \times 10^{-15}$</td>
<td>$-6.943 \times 10^{-16}$</td>
<td>$-7.964 \times 10^{-16}$</td>
</tr>
<tr>
<td>Total</td>
<td>$-1.394 \times 10^{-15}$</td>
<td>$-1.082 \times 10^{-15}$</td>
<td>$-1.190 \times 10^{-15}$</td>
</tr>
<tr>
<td>in Hz</td>
<td>-9.17</td>
<td>-7.12</td>
<td>-7.83</td>
</tr>
</tbody>
</table>
**TABLE** : Calculated harmonic vibrational frequencies $\omega$, corresponding fundamental vibrational transitions $\nu$ (in cm$^{-1}$) from an anharmonic analysis, and PV-induced frequency shifts $\Delta \nu_{PV}$ (in mHz) to the vibrational transitions ($n = 0 \rightarrow m$) for all six modes of S-SeOClII.

<table>
<thead>
<tr>
<th>Mode</th>
<th>$\omega$</th>
<th>$\nu$</th>
<th>0→1</th>
<th>0→2</th>
<th>0→3</th>
<th>0→4</th>
<th>0→5</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\nu_1$ Cl-Se-I bend</td>
<td>100</td>
<td>99</td>
<td>-55.2</td>
<td>-121.6</td>
<td>-197.9</td>
<td>-282.1</td>
<td>-371.3</td>
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<tr>
<td>$\nu_2$ O-Se-I bend</td>
<td>167</td>
<td>166</td>
<td>112.4</td>
<td>230.2</td>
<td>351.6</td>
<td>474.5</td>
<td>596.6</td>
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<tr>
<td>$\nu_3$ O-Se-Cl bend</td>
<td>237</td>
<td>235</td>
<td>-40.6</td>
<td>-81.3</td>
<td>-122.1</td>
<td>-163.0</td>
<td>-204.1</td>
</tr>
<tr>
<td>$\nu_4$ Se-I stretch</td>
<td>246</td>
<td>245</td>
<td>-55.4</td>
<td>-105.4</td>
<td>-150.3</td>
<td>-190.5</td>
<td>-226.2</td>
</tr>
<tr>
<td>$\nu_5$ Se-Cl stretch</td>
<td>346</td>
<td>357</td>
<td>-3.5</td>
<td>-6.9</td>
<td>-10.1</td>
<td>-13.2</td>
<td>-16.2</td>
</tr>
<tr>
<td>$\nu_6$ Se-O stretch</td>
<td>978</td>
<td>968</td>
<td>-55.5</td>
<td>-110.6</td>
<td>-165.4</td>
<td>-219.7</td>
<td>-273.6</td>
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</tbody>
</table>
Mössbauer Spectroscopy

<table>
<thead>
<tr>
<th>ΔE (eV)</th>
<th>singlet</th>
<th>triplet</th>
<th>quintet</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.98</td>
<td>1.87</td>
<td>3.01</td>
</tr>
<tr>
<td>2</td>
<td>2.00</td>
<td>1.88</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>2.01</td>
<td>1.90</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>2.12</td>
<td>1.95</td>
<td></td>
</tr>
</tbody>
</table>

Ground state? (TDDFT/PW91, ADF)

In closed-shell systems parity violation effect in Mössbauer transitions are suppressed significantly:

Consider the Dirac bispinor $\Psi$,

$$\Psi^K = K \Psi, \quad K = -i \sigma_2 C = \gamma^1 \gamma^3 C, \quad K^\dagger K = 1, \quad [K,D] = 0$$

with $K$ being time reversal Kramers operator. $K$ commutes with the $\gamma^i$ Matrix but anticommutes with the $\sigma_i$-matrices in the Dirac equation. Hence we obtain:

$$\langle \Psi^K | H_{pv}^1 | \Psi^K \rangle = \langle \Psi | H_{pv}^1 | \Psi \rangle \quad \text{and} \quad \langle \Psi^K | H_{pv}^2 | \Psi^K \rangle = -\langle \Psi | H_{pv}^2 | \Psi \rangle$$

where

$$H = \frac{G_F}{2\sqrt{2}} \sum_{i,n} Q_{W,n} \gamma_5^i \rho_n(\tilde{r}_i) - \frac{G_F}{\sqrt{2}} \sum_{i,n} \lambda_n (1 - 4 \sin^2 \theta_W) \tilde{\alpha}_i \tilde{\gamma}_n \rho_n(\tilde{r}_i) + \ldots$$

---

Open-shell systems are needed!

The Salam Hypothesis:

At a certain critical temperature, $T_c$, a phase transition occurs into the more stable chiral state, i.e., a racemic mixture of amino acids (sugars) condenses into the most stable enantiomeric form. According to all calculations carried out so far the most stable enantiomeric form is the L-form of amino acid (D-form of sugar)

It should be feasible to detect Bose-Einstein condensation by experimental methods. First estimates result in a critical temperature of $T_c = 5 - 250$ K.

**Problem:** How can you get through a 300 kJ/mol barrier for the inversion process in a short time?

Observation of the Salam Phase Transition for D- and L-alanine and -valine by DSC, DC SQUID magnetic susceptibility, Raman, and $^1$H / $^{13}$C NMR measurements.

The DSC experiment:
The Raman experiment:

- C-H deform.
- C-H stretch.
The Tennessee Response


- DC, ORD, DSC, Raman and NMR measurements.

The DSC experiment:

![Graph](image-url)
Wang's observation cannot be confirmed.
Neutron diffraction investigations of $L$- and $D$-alanine at different temperatures: the search for structural evidence for parity violation

Chick C. Wilson,°ab Dean Myles,cd Minakshi Ghosh,ec Louise N. Johnsoned and Wenging Wangf

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b ISIS Facility, CLRC Rutherford Appleton Laboratory, Chilton, Didcot, Oxon, UK OX11 0QX. E-mail: C.C.Wilson@chem.gla.ac.uk
c EMBL Grenoble Outstation, Institut Laue-Langevin, 38042 Grenoble, France
d Structural Biology Centre, Oak Ridge National Laboratory, One Bethel Valley Road, Oak Ridge, TN 37831, USA
e Laboratory of Molecular Biophysics, Department of Biochemistry, University of Oxford, South Parks Road, Oxford, UK OX1 3QU
f Department of Applied Chemistry, College of Chemistry and Molecular Engineering, Peking University, Beijing, 100871, China

Single crystal neutron diffraction has been used in an investigation of the structures of the amino acids $L$- and $D$-alanine. The aim of the study was to look for proposed phase transitions around $T_c \approx 270$ K. Measurements of both structures at 295 K and 60 K—the neutron structure of $D$-alanine being determined for the first time—show no significant structural basis for this phase transition in alanine. Further, confirmatory, investigation of the structure of $D$-alanine at temperatures of 240, 250, 260 and 300 K also showed no significant changes in bond lengths or angles. We can thus offer no structural support to other physical measurements, which are indicative of the observable effect of parity violation of the electroweak force in these phase transitions.

Conclusions

- High resolution vibrational spectroscopy has perhaps the best chance for success (CHFClII, CDFClII, of Rn-Re=O).
- NMR experiments are currently underway (Tennessee), it looks more promising now.
- PNC in electronic transitions are also currently investigated (Rennes).
- Theoretical calculations need to become more precise in order to confirm future experimental work (Breit interactions).
- The search for suitable chiral molecules (thermodynamically stable and in the right frequency range) including heavy elements is less than trivial.
- Effects have to be in the > 1 Hz range, also more optimistic estimates of the Paris group for future high resolution experiments are moving towards 10-100 mHz.
- Future prospects: Trapped molecules at ultracold temperatures (1 mK and below), laser which operate between 1-20 μm.
Acknowledgment

James Cook Fellowship, Marsden Grant (Royal Society NZ)

Profs. Trond Saue (Strasbourg), Bob Compton (Tennessee),
Guntram Rauhut (Stuttgart), Vincenzo Barone (Napoli), C. Daussy Paolo Lazzeretti
(Modena) and Ch. Chardonnet (Paris)

Students and Postdoctoral Fellows: Joern Thyssen, Matthias Lein, Radovan Bast,
Johannes Gierlich, Andreas Kuehn, Christian Thierfelder, Detlev Figgen, Jon K.
Laerdahl, Ralf Wesendrup, Tobias Bollwein
Theoretical Chemistry and Physics at Albany
New Zealand is a fun place
With water from the stream Galadriel filled the basin to the brim, and breathed on it, and when was still again she spoke. ‘Here is the mirror of Galadriel’, she said. ‘I have brought you here so that you may look in it, if you will’.

The air was very still, and the dell very dark, and the Elf-lady beside him was tall and pale. ‘What shall we look for, and what shall we see?’ asked Frodo filled with awe.

‘Many things I can command the Mirror to reveal’, she answered, ‘and to some I can show what they desire to see. But the Mirror will also show things unbidden, and those are often stranger and more profitable than things which we wish to behold. What you will see, if you leave the Mirror free to work, I cannot tell. For it shows things that were, and things that are, and things that yet may be. But which it is that he sees, even the wisest cannot always tell. Do you wish to look?’

J.R.R. Tolkien, The Fellowship of the Ring
Hypothesis 1: God is right-handed

Answer to Creationalism (intelligent design):
Contra principia negantem disputari non potest
Hypothesis 2: God is left-handed

Stunning Observations of the Berlin biologist Dr. Siegfried Wachtel (65): “Nature is left-handed.” Green beans grow left-circular, bats leave their caves in left spirals. The DNA molecule - building block of life - is a left-handed double helix. Animals never run clock-wise in the circus ring. Animal tamers: Otherwise they become snappish.” Wounded deer always flee to the left, even if the forest is only a few meters to the right. Seals, which swim towards a wall always turn to the left. Animals in cages which jump against the iron bars always land on their left shoulder.

Dr. Wachtel: “There is no explanation for this. One has to take these phenomena as a natural law.”
Single-gene speciation by left–right reversal

A single gene gives rise to the mirror-image form of a snail's body plan, which could become established as a different species if mating is prevented between snails of different chirality by genital mismatch.\(^1\) Here we use molecular phylogeny to demonstrate the parallel evolution of reversal between left and right lineages of the Japanese land snail *Euhadra*. We find that the different mirror-image forms have evolved in favour of the genetically dominant handedness as a result of single-gene speciation.

Speciation accompanying the left–right reversal of the entire ontogeny (chiral speciation) is unique to snails and can be visualized by the coiling direction of their shells (Fig. 1a). The chirality (or 'handedness') — occurring as 'sinister' and 'dexter' forms) of snails is determined by the maternal nuclear genotype at a single locus.\(^2\) Because of the physical difficulty of two-way copulation between snails that have opposite coils (Fig. 1b), frequency-dependent selection occurs to eliminate the chiral minority and antagonize chiral speciation. Offspring from each mother all develop with an identical chiral phenotype, regardless of their genotype. This peculiar mode of inheritance could be advantageous in enabling the dominant reversal allele to proliferate in small, isolated populations.\(^2\) Once the mirror-image variant exceeds 50%, selection fixes the reversal. Reproductive isolation by handedness chance of fixation for the dominant allele, as predicted by theory.\(^9\,10\)

The polyphyly of *E. aomoriensis* in mitochondrial-DNA phylogeny could have resulted from parallel evolution of *E. aomoriensis*, or from introgression or ancestral polymorphism of mitochondrial DNA. As the parallel evolution of three dextral lineages has occurred, multiple peripheral populations of *E. quasita* may also have fixed the dextral allele independently. The polyphyly of ancestral species is expected where prompt speciation recurs in peripheral isolates.\(^6\) Incipient single-gene speciation without genome-wide changes must allow *E. aomoriensis* to interbreed with polyphyletic descendants. *E. aomoriensis* may therefore be a unique example of a polyphyletic animal species.

Introgression is impossible unless the reversal allele has persisted in either species under stringent selection. Any introgression must therefore have been limited to a short time before chiral fixation. Ancestral polymorphism would not easily survive chiral speciation in small, isolated populations.

Left–right reversal in reciprocally mating snails can accomplish pre-mating isolation at a single locus, overcoming the majority rule of handedness. Our results indicate that single-gene speciation is possible, at least in hermaphroditic snails, contrary to the traditionally held view.\(^2\)\(^\ref{2,12,13}\)

Rei Ueshima\(^+\), Takahiro Asami\(^\dagger\)
NMR Spectroscopy

Tennessee Experiments (in preparation)

**What molecule?**
- Nuclear spin $I=1/2$ (for $I>1/2$ line broadening due to the NQM)
- One or more heavy atoms because of Z-scaling:
  $^{187}$Os ($\Delta \nu = 10$ Hz), $^{183}$W ($\Delta \nu = 2$ Hz), $^{117,119}$Sn ($\Delta \nu = 3.5$ Hz)

**Problems:**
- PV chemical shift contribution $\sim B$ in large magnetic fields
  Current $B_0$ for a 900 MHz NMR: 21.1 T
- High-resolution NMR (10 mHz)
- Low Z-scaling behaviour.
  - enhancement due to relativistic effects?
  - Not beyond the mHz range at 20 T?
Lazzeretti: Magnetic fields of $10^5$ T needed!

Wiesenfeld: For 205-Tl NMR $\sim 100 \, \mu$Hz/T

New results from the Strasbourg/Auckland collaboration

\[
\Delta \sigma \, [\text{ppm}] = -G_F \frac{(1 - 4 \sin^2 \theta_W)}{2 \gamma_A \sqrt{2} c_0} \left\langle \left\langle c(\alpha_{\epsilon} \rho_A(r_i)) ; c(\alpha \times r_i G) \right\rangle \right\rangle_{\omega=0}
\]

\( \tau = 45^\circ \)

- \( \text{H}_2\text{O}_2 \)
- \( \text{H}_2\text{S}_2 \)
- \( \text{H}_2\text{Se}_2 \)
- \( \text{H}_2\text{Te}_2 \)
- \( \text{H}_2\text{Po}_2 \)
The center of chirality does not necessarily yield the largest PV contribution.

\[ M_{n}^{PV} = \sum_{i} M_{n,i} = \sum_{i} \langle \psi_i | \gamma_i^{5} \rho_n(r_i) | \psi_i \rangle \]

(in au)
Breaking MI-Symmetry

at the microscopic level

Bouchiat-Hamiltonian:

\[ H_{eN}^{\text{PNC}} = \frac{G_F}{4mc\sqrt{2}} \sum_{i,n} Q_{W,n} \{ \sigma_i p_i, \rho_n(r_{in}) \}^+ \]

\[ G_F = 1.16637 \times 10^{-11} \text{ MeV}^2 = 2.22255 \times 10^{-14} \text{ a.u.} \]

\[ \{ P, H_{eN}^{\text{PNC}} \} \neq 0 \]

Lee, Yang, Weinberg, Salam, Glashow
Coupling between the normal modes are important (M. Quack)
Towards the construction of a nine-dimensional hypersurface

<table>
<thead>
<tr>
<th>Property</th>
<th>CCSD(T)</th>
<th>MP2</th>
<th>B3LYP</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>VCI</td>
<td>VPT</td>
<td>VPT</td>
</tr>
<tr>
<td>$E_{ZPE}$</td>
<td>4584.2</td>
<td>4640.0</td>
<td>4494.1</td>
</tr>
<tr>
<td>$\nu_1$</td>
<td>3020.1</td>
<td>3086.8</td>
<td>3011.6</td>
</tr>
<tr>
<td>$\nu_2$</td>
<td>1319.4</td>
<td>1318.9</td>
<td>1293.7</td>
</tr>
<tr>
<td>$\nu_3$</td>
<td>1211.2</td>
<td>1226.3</td>
<td>1185.3</td>
</tr>
<tr>
<td>$\nu_4$</td>
<td>1071.5</td>
<td>1073.3</td>
<td>1047.2</td>
</tr>
<tr>
<td>$\nu_5$</td>
<td>778.4</td>
<td>805.1</td>
<td>731.1</td>
</tr>
<tr>
<td>$\nu_6$</td>
<td>660.8</td>
<td>682.1</td>
<td>636.2</td>
</tr>
<tr>
<td>$\nu_7$</td>
<td>420.8</td>
<td>432.0</td>
<td>413.6</td>
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<tr>
<td>$\nu_8$</td>
<td>311.8</td>
<td>319.7</td>
<td>302.9</td>
</tr>
<tr>
<td>$\nu_9$</td>
<td>222.5</td>
<td>229.2</td>
<td>215.1</td>
</tr>
<tr>
<td>$\Delta_{mean}$</td>
<td>5.6</td>
<td>18.6</td>
<td>20.8</td>
</tr>
<tr>
<td>$\Delta_{max}$</td>
<td>13.2</td>
<td>61.3</td>
<td>55.9</td>
</tr>
</tbody>
</table>
How accurate are these DHF results?

Along the C-F normal coordinate

Basis set convergence
Electron correlation
Missing Breit interaction
$V_{e-A_e}$ Coupling missing etc.
Every symmetry principle implies that some quantity is not observable (E. Noether, Invariante Variationsprobleme, 1918):

- the *kinematical symmetries* (space-time transformations such as translations, rotations and accelerations in three-dimensional physical configuration space)
- the *permutation symmetry* (exchange of identical particles)
- the *gauge symmetry* (describing dynamical symmetries of particle fields)
- the *discrete symmetries* (such as the inversion of charge, parity (left-right))

The link between symmetries in the natural sciences and in mathematics is the representation of symmetries by groups:

- the *purely discrete groups*
- the *purely continuous*, so-called Lie-groups
- the *mixed general Lie-groups*, combining purely discrete subgroups and purely continuous subgroups such as the Galilei or Lorentz groups
**Camphor** $\text{C}_{10}\text{H}_{16}\text{O}$

*Cinnamomum camphora*

$d$-camphor

$l$-camphor

Mirror image symmetry is perfect

Same spectroscopic properties for $|L\rangle$ and $|R\rangle$

**identical IR spectra**
Principle of Parity Conservation

E.Wigner, Z. Phys. 43, 624 (1927)

\[ P: \psi_L \rightarrow \psi_D, \ [P,H] = 0 \]

\[ \vec{r} = (x, y, z) \]

\[ \mathbf{P} \rightarrow -\vec{r} \equiv (-x, -y, -z) \]

\[ \sigma(y,z) \quad \phi_x(180^\circ) \]

Inversion in 3D space
Parity Nonconservation in Atoms is well known

\[ \psi_{s\frac{1}{2}}^{GSW} = \psi_{s\frac{1}{2}} + \varepsilon \psi_{p\frac{1}{2}} \]

\( \varepsilon \) small induces an E1 transition

optical activity in the M1 transition

Experiments:
Bi Novosibirsk 1978 (876 nm)
   Moscow, Oxford
Tl 6P\(_{1/2} \) - 7P\(_{1/2} \) Berkeley 1979
   Seattle
Pb Seattle
Cs 6S\(_{1/2} \) - 7S\(_{1/2} \) Paris, Boulder 1997
   Accuracy of 0.35 % in PNC
Fr 7S\(_{1/2} \) - 8S\(_{1/2} \) Stony Brook
Ba\(^+\) Washington
Dy Berkeley

Conclusion: Theory and experiments agree, Standard model works
Dependence on the HXXH torsional angle

Chirality $\iff$ Nonzero $E_{PV}$
How to obtain ultra-high resolution?

A long-distance optical link to the primary frequency standard

**CO₂ laser** @ 30 THz

**Primary Frequency Standard**

**Cs Fountain**

**Laser Diode** @ 1.55 µm

**Optical fiber** 43 km

**Frequency counter**

**Detector**
Current Program

Vibrational Harmonic Schrödinger Equation

$$H_{\text{Watson}} = -\frac{1}{2} \sum \frac{\partial^2 V}{\partial q_i^2} q_i + V(q_i) + H_{VR}$$

Normal Mode Analysis for CH(D)FClBr

$$q = O_N M^{1/2} X$$

Transformation in normal coordinates

$$V(q_i) = \frac{1}{2} \sum \frac{\partial^2 V}{\partial q_i^2} q_i^2 + \frac{1}{6} \sum \frac{\partial^3 V}{\partial q_i \partial q_j \partial q_k} q_i q_j q_k + \ldots$$

$$H_0 = -\frac{1}{2} \sum \frac{\partial^2}{\partial q_i^2} q_i^2 + \frac{1}{2} \sum \frac{\partial^2 V}{\partial q_i^2} q_i^2$$

$$H' = V_{\text{anharm}} + H_{VR}$$

Test of quality of FF

Perturbation Theory

Quadratic (n=2) 

$$\sum \frac{\partial^2 V}{\partial q_i^2} q_i$$

cubic (n=3)

$$\sum \frac{\partial^3 V}{\partial q_i \partial q_j \partial q_k} q_i q_j q_k$$

quartic (n=4) FF

$$\sum \frac{\partial^4 V}{\partial q_i \partial q_j \partial q_k \partial q_l} q_i q_j q_k q_l$$

$$\left(3N - 7 + n\right)$$ terms

With G. Rauhut (Stuttgart)


New Synthetic Targets
Jeanne Crassous et al., Universtité de Rennes (France)

![Chemical structures](image)

1: Re
2: Re

5: R = CH₃
6: R = tBu