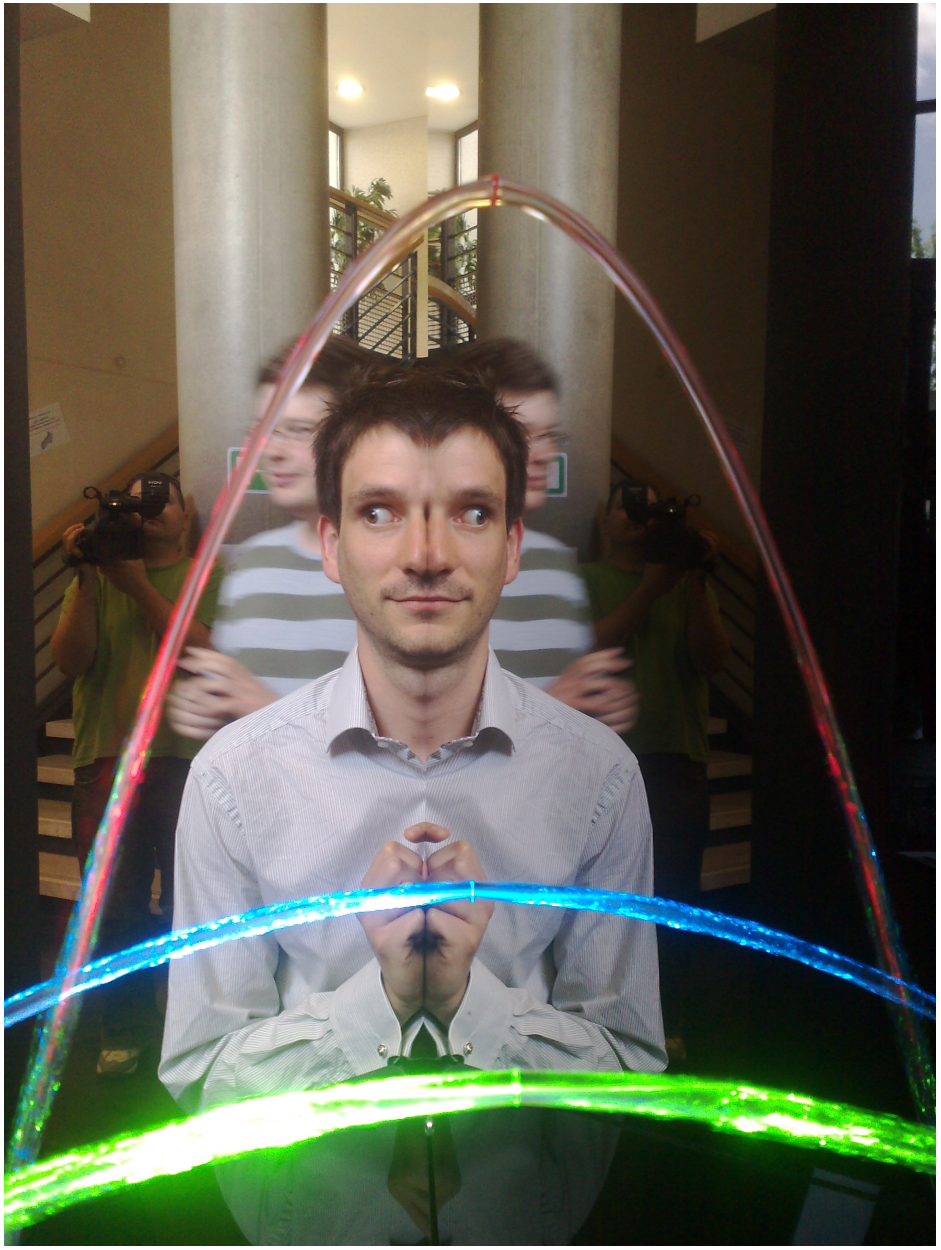

Parity violation in molecular systems:

what we can learn from theory

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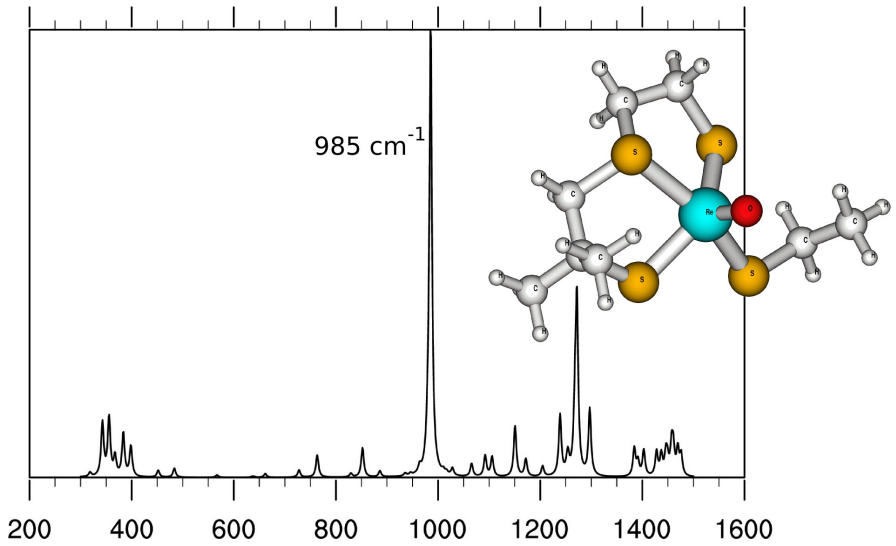
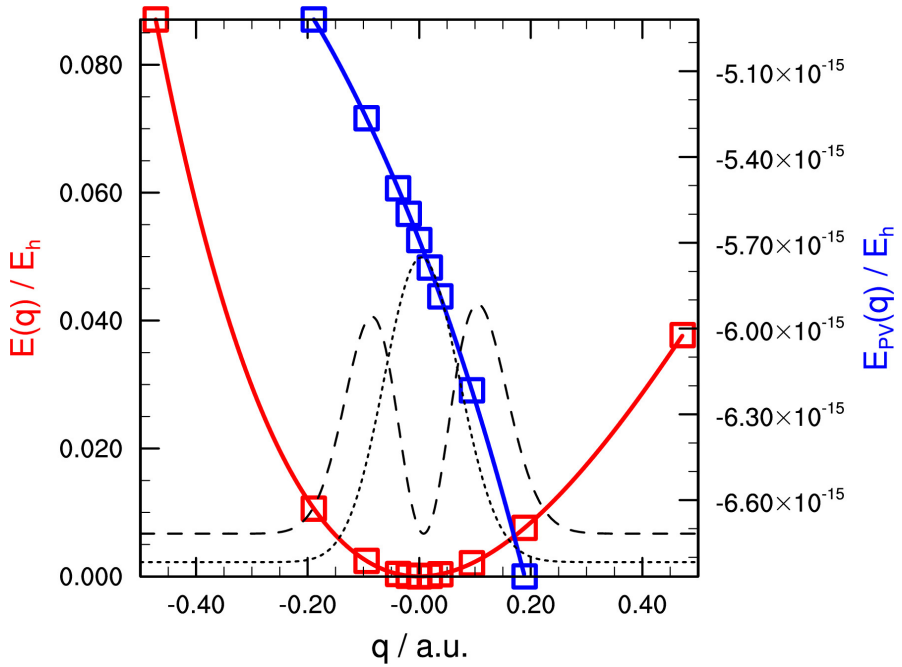
Reminder: Computational procedure



1. **Geometry optimization + rovibrational analysis** (gaussian/B3LYP): the infrared spectrum is simulated using calculated frequencies and intensities



2. Calculation of total energy $E(q)$ and PV energy contribution $E_{PV}(q)$ along selected vibrational mode (DIRAC/X2C/B3LYP or HF)

3. Numerical solution of vibrational problem (Numerov-Cooley) $\rightarrow$ ψ_ν^{vib}

4. Integration of $E_{PV}(q)$ with vibrational solutions: $E_{PV}(\nu) = \left\langle \psi_\nu^{\text{vib}} \left| E_{PV}(q) \right| \psi_\nu^{\text{vib}} \right\rangle$

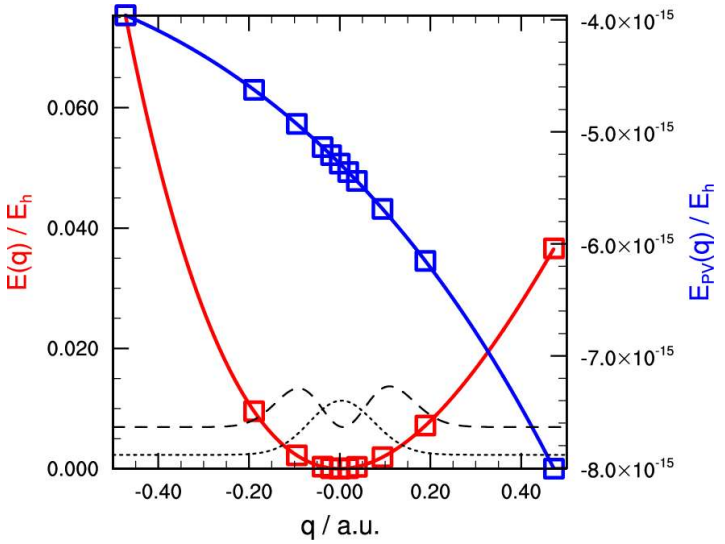
Reminder: Perturbational approach

- Series expansion:

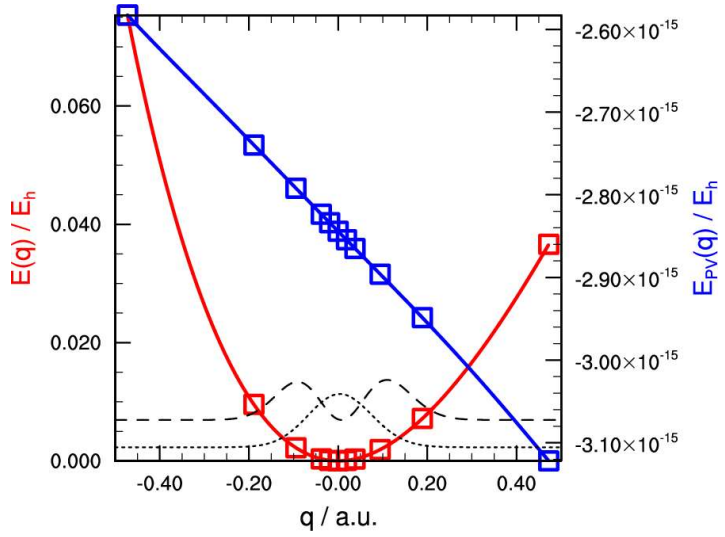
$$E(q) = V(q=0) + V^{[1]}q + \frac{1}{2}V^{[2]}q^2 + \ldots \quad E_{PV}(q) = P(q=0) + P^{[1]}q + \frac{1}{2}P^{[2]}q^2 + \ldots$$

- PV shift

$$\Delta\nu_{RS} = \frac{\hbar}{\sqrt{\mu V^{[2]}}} \left\{ P^{[2]} - \frac{V^{[3]}}{V^{[2]}} P^{[1]} \right\}$$



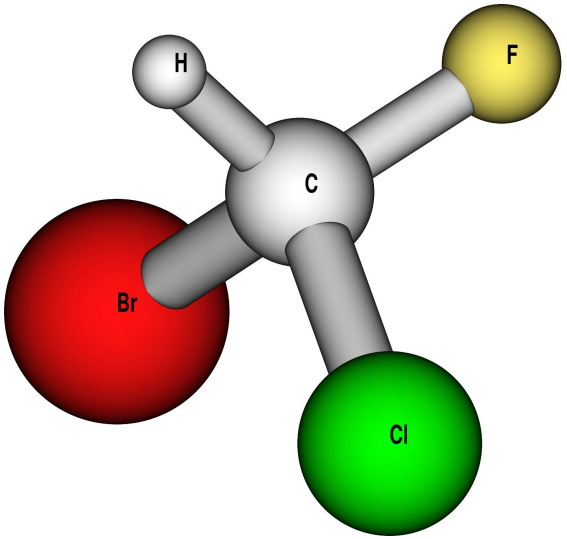
5b (HF): $\Delta_{RS} = -1020.7$ mHz
(harmonic: -390.4 mHz)



5b (B3LYP): $\Delta_{RS} = -84$ mHz
(harmonic: $+0.02$ mHz)

PV shifts for all normal modes of CHFClBr

B3LYP			Displacement (mHz)		Attribution
	$\bar{\nu}(\mathrm{cm}^{-1})$	μ (amu)	Total	Harmonic	
1	217.7	26.6781	-1.186		Bending Cl - C - Br
2	307.2	21.0297	9.85	2.184	Bending F - C - Br
3	418.9	17.6804	-5.774	-2.126	Bending Cl - C - F
4	642.2	5.6584	-5.807	-3.65	Stretching C - Br
5	744.2	8.1195	12.489	9.715	Stretching C - Cl
6	1092.3	11.3289	3.432	-1.876	Stretching C - F
7	1215.3	1.0943	1.261	0.942	Bending H - C - Br
8	1328.0	1.1154	-3.436	-1.638	Bending F - C - H
9	3150.4	1.0885	-1.649	-0.097	Stretching H - C

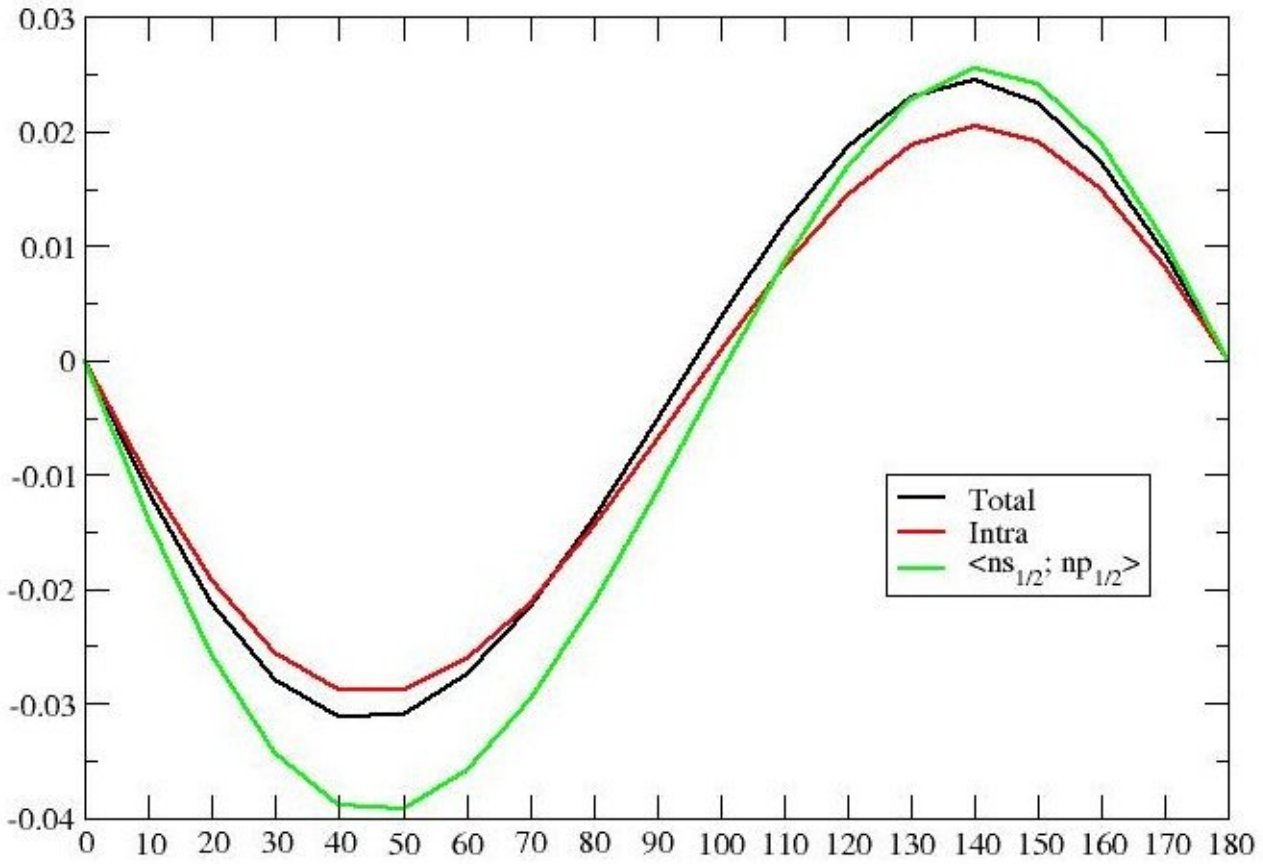


Sampling point must be adapted to curvature of potential curve; use classical turning points

$$x_{max} = \sqrt{\frac{2\hbar}{\mu\omega}\left(\nu + \frac{1}{2}\right)}$$

Make robust scheme for numerical differentiation.

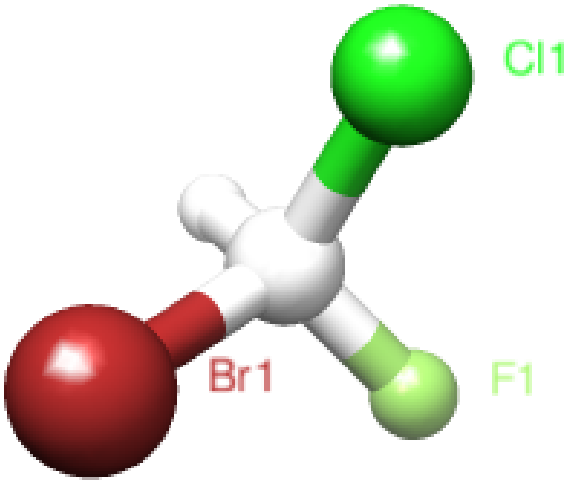
Reminder: Towards deeper understanding



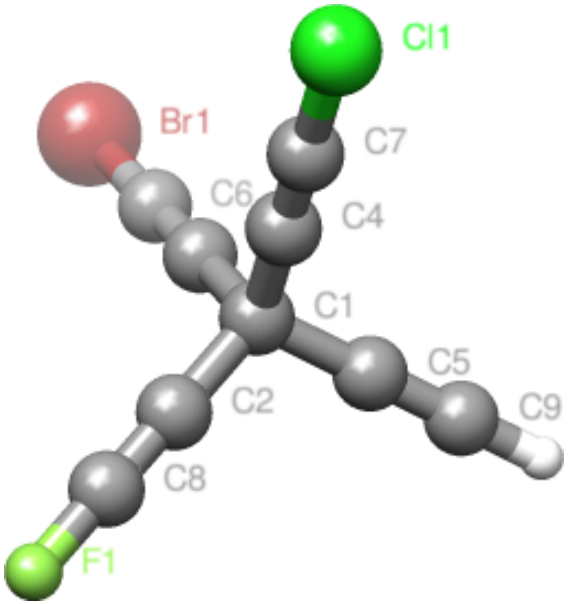
HF	H_2O_2	H_2S_2	H_2Se_2	H_2Te_2	H_2Po_2
Full	**-6.729E-06**	**-7.435E-05**	**-3.163E-03**	**-2.787E-02**	**-7.955E-01**
Intra	-5.879E-06	-6.876E-05	-2.717E-03	-2.459E-02	-6.334E-01
$<ns_{1/2}\|\widehat{H}^X_{\rm pv}\|np_{1/2}>$	-8.819E-06	-8.548E-05	-3.773E-03	-3.216E-02	-7.728E-01

A non-zero contribution requires an imaginary phase in the mixing coefficient between $s_{1/2}$ and $p_{1/2}$.

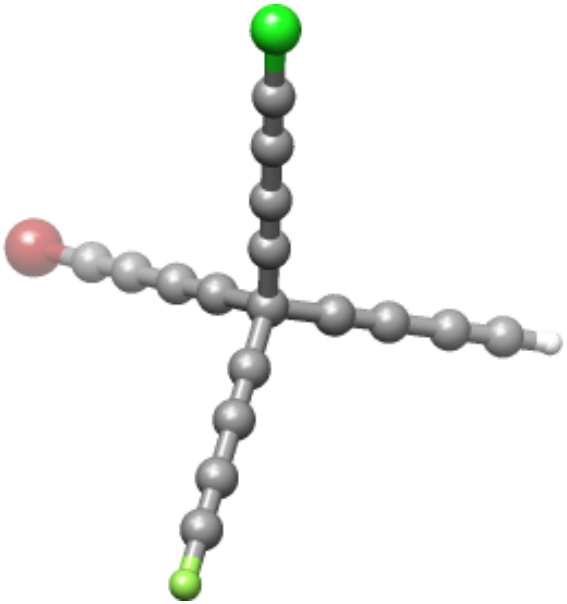
Exploring the chiral field: carbomers



r(C1-Br): 1.945 Å
r(C1-Cl): 1.766 Å
r(C1-F): 1.346 Å
r(C1-H): 1.087 Å
Total energy: -3206.489586 E_h
HOMO-LUMO gap:
0.248490 E_h
Total EPV $=$ 1.001E-18 E_h
EPV (central carbon C1): 5.523E-20 E_h

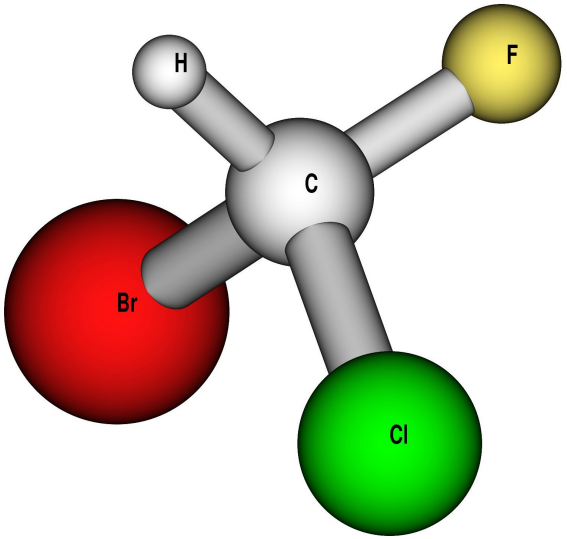


r(C1-Br): 4.469 Å
r(C1-Cl): 4.316 Å
r(C1-F): 3.947 Å
r(C1-H): 3.744 Å
Total energy: -3510.990470 E_h
HOMO-LUMO gap:
0.242571 E_h
Total EPV $=$ 1.629E-20 E_h
EPV (central carbon C1): 2.905E-23 E_h

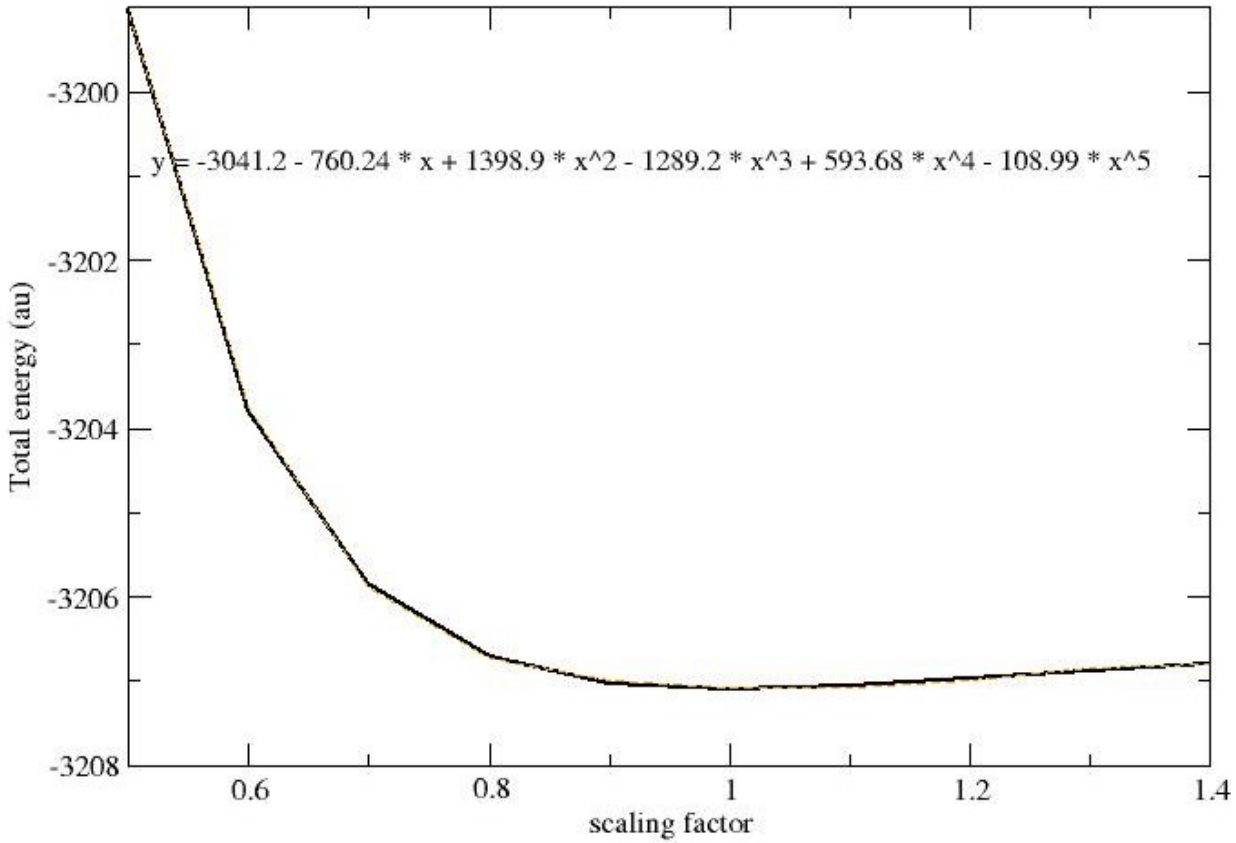


r(C1-Br): 7.035 Å
r(C1-Cl): 6.882 Å
r(C1-F): 6.517 Å
r(C1-H): 6.319 Å
Total energy: -3815.623118 E_h
HOMO-LUMO gap:
0.198085 E_h
Total EPV $=$ -9.436E-23 E_h
EPV (central carbon C1): -3.737E-25 E_h

Exploring the chiral field: CHFClBr

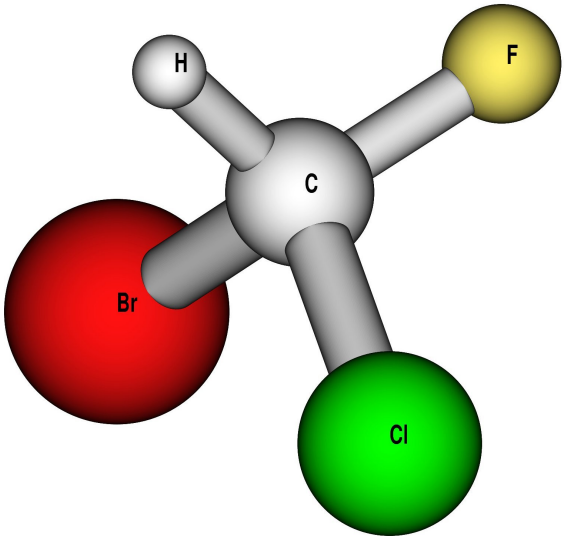


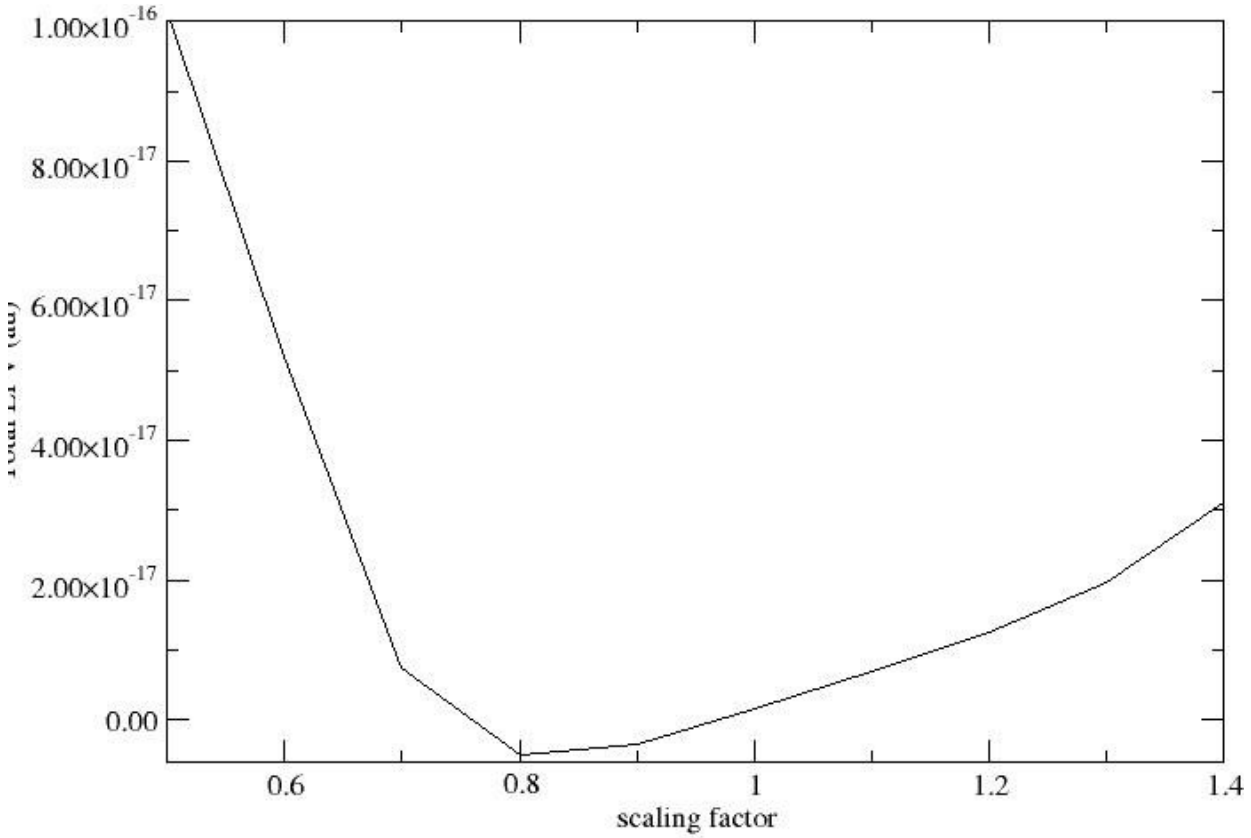
We start from CCSD(T) optimized geometry and scale all bond lengths



The total electronic energy shows a minimum near scaling factor 1.0.

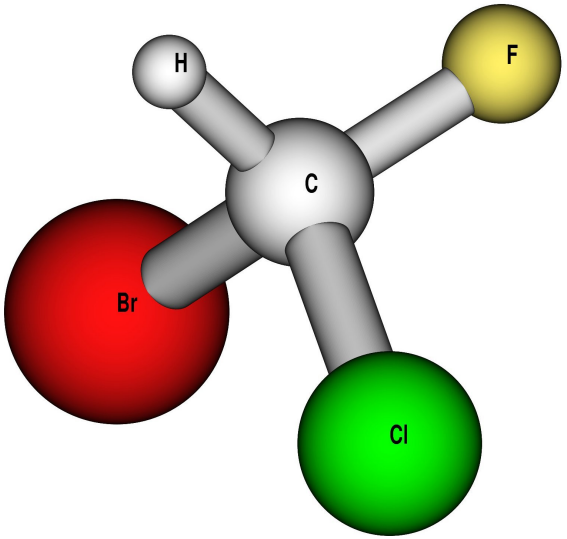
Exploring the chiral field: CHFClBr

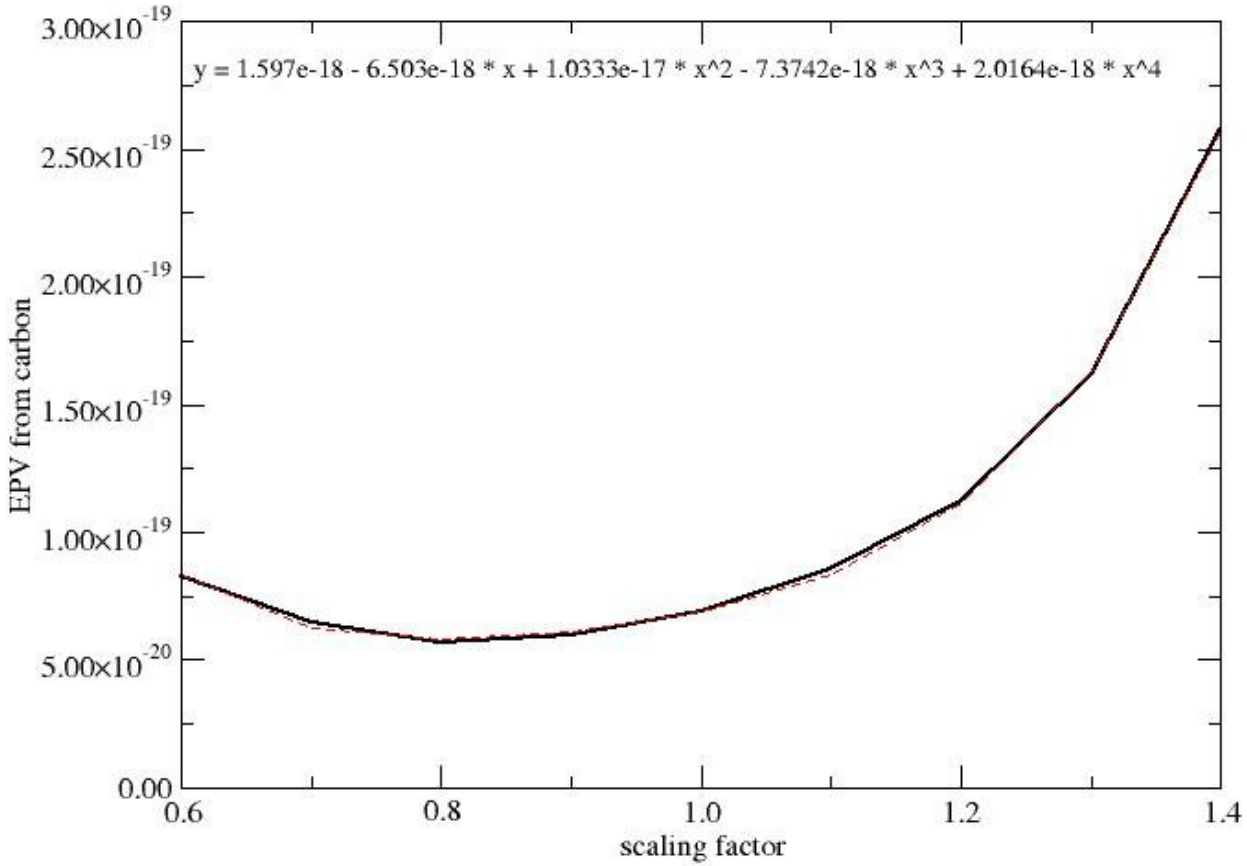




The total E_{PV} energy is not the most interesting quantity since the change in the chiral field for all atoms except the central carbon atom is rather complicated.

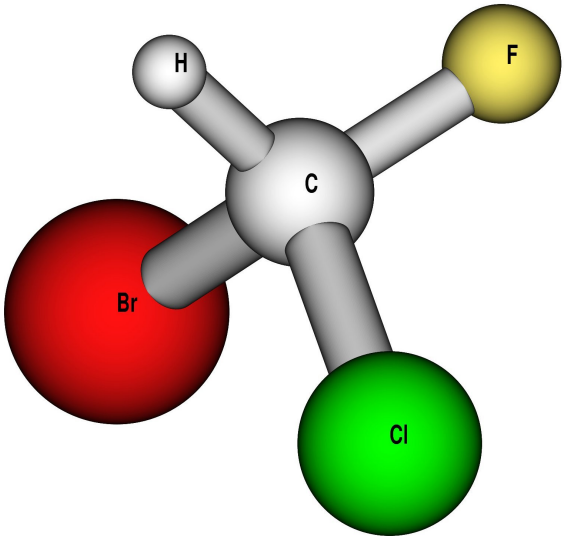
Exploring the chiral field: CHFClBr

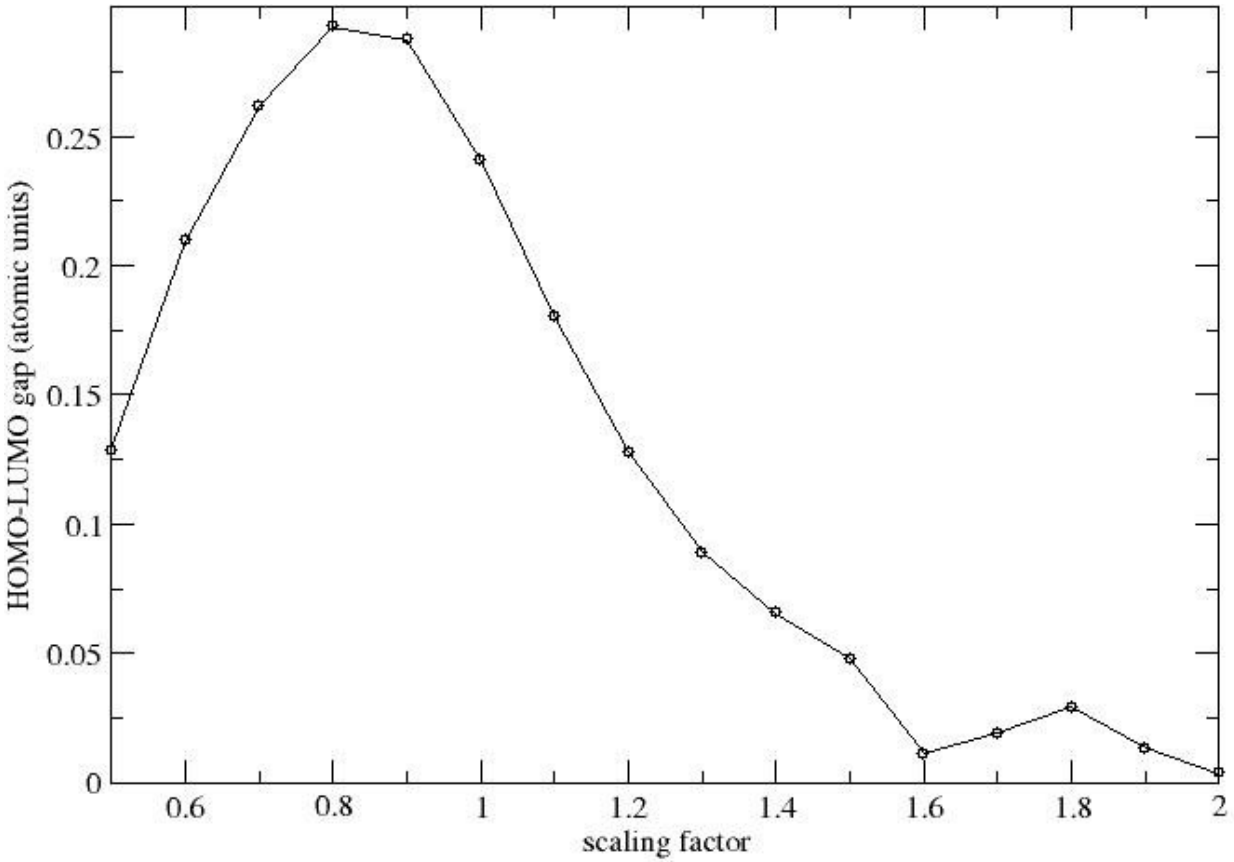




More interesting is the contribution to the E_{PV} energy from the central carbon atom. Surprisingly it increases within the range of validity of the model and goes through a minimum around s=0.82.

Exploring the chiral field: CHFClBr





The bond stretching will inevitably lead to a breakdown of the SCF model. Indeed one observes that the HOMO-LUMO gap closes and the SCF did not converge beyond scaling factor 1.4 Further studies requires the calculation of E_{PV} using a method which can break bonds, e.g. MCSCF.