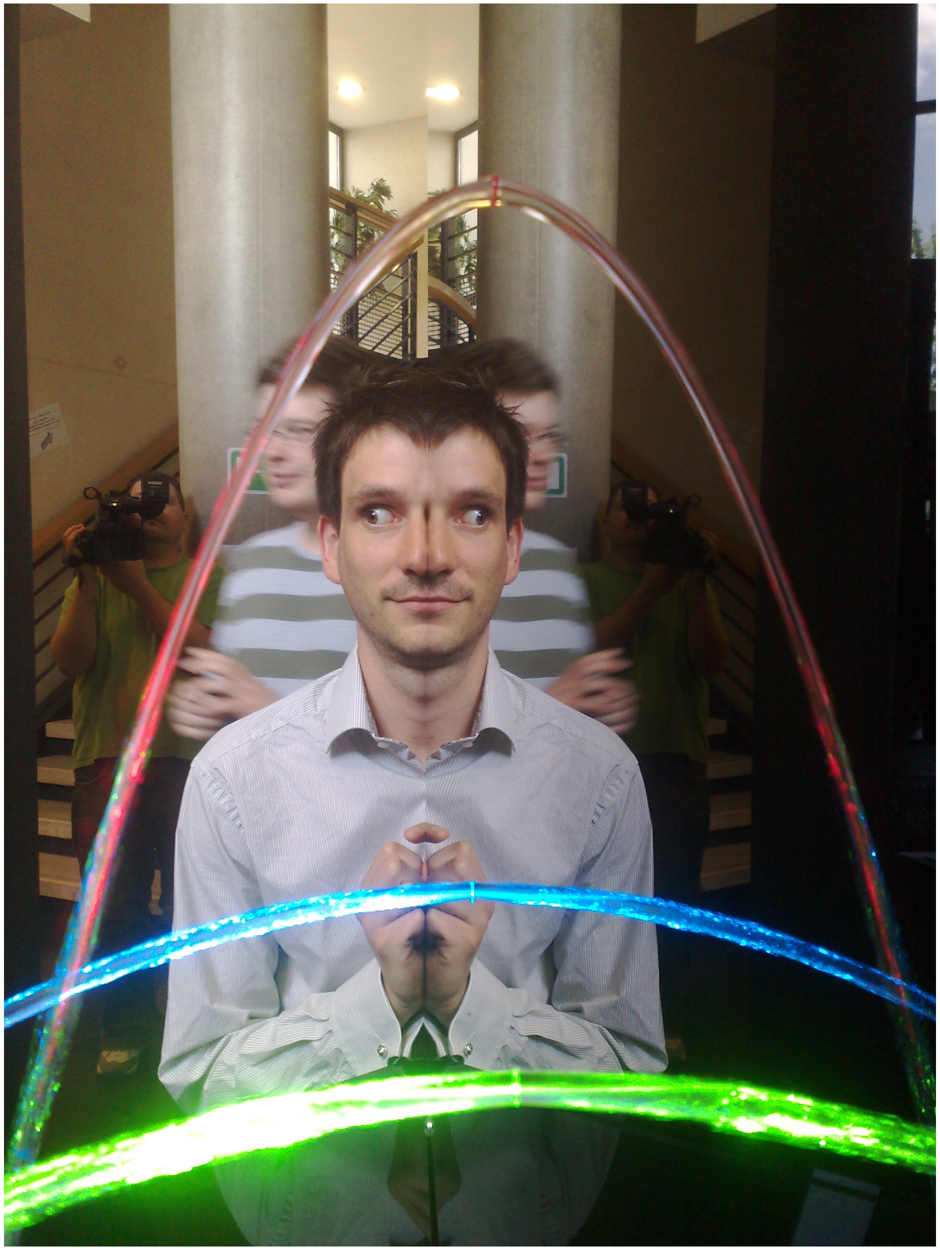

Parity violation in molecular systems

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Thanks to:

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Christian Chardonnet (Paris)
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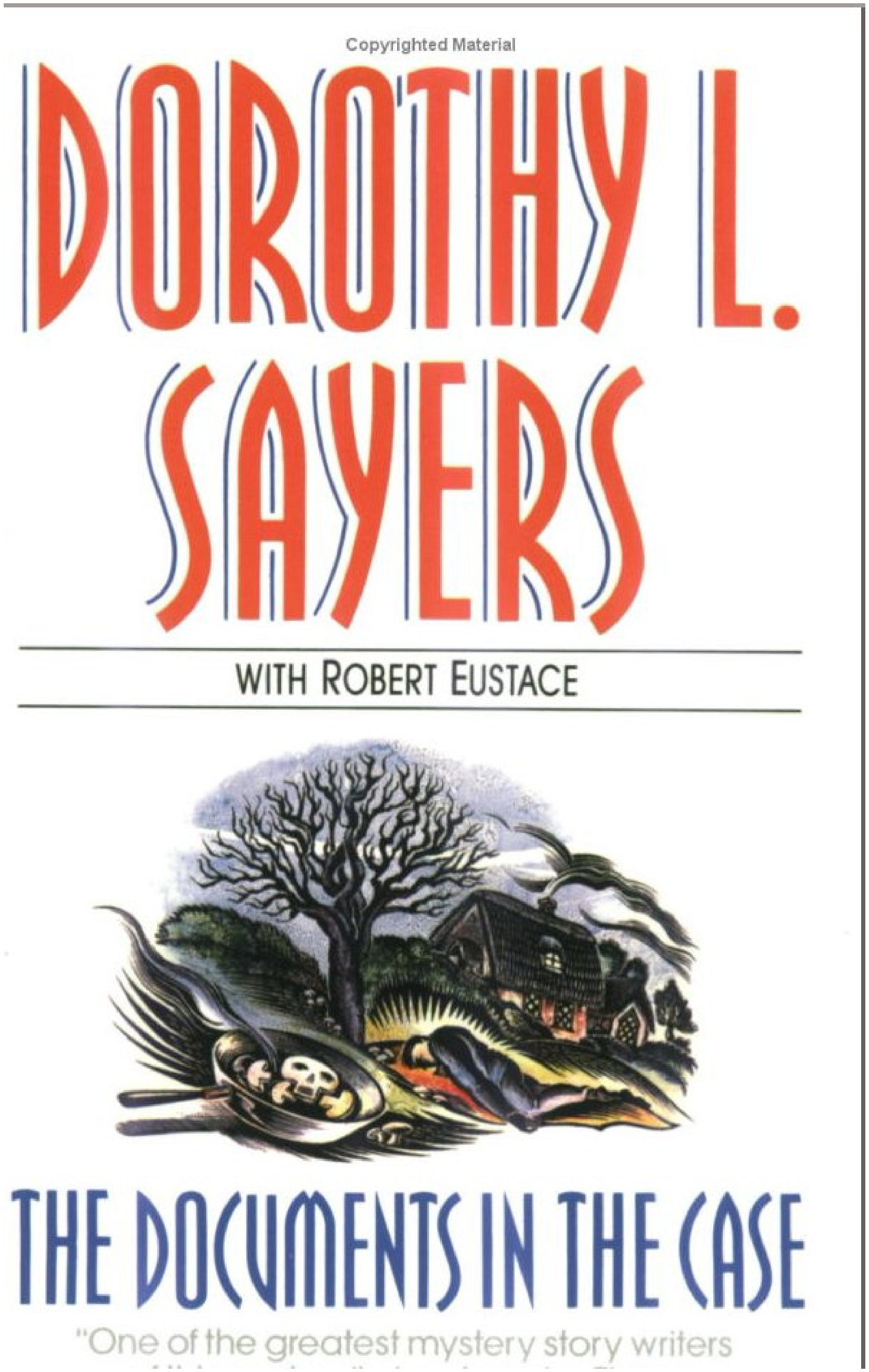
Jeanne Crassous (Rennes)
Benôit Darquié (Paris
Christophe Daussey (Paris)

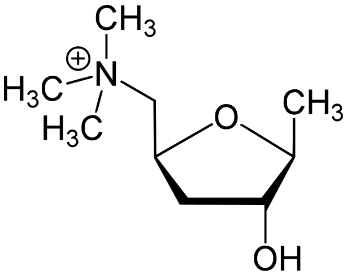
Peter Schwerdtfeger (Auckland)
Pierre Asselin (Paris)
Thérèse Huet (Lille)

What is Life ?



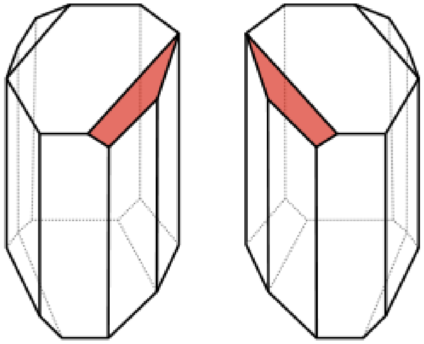
"At present — chemically speaking — the nearest definition I can produce is that it is **a kind of bias** *— a lopsidedness, so to speak."*

"Up to the present, it is only a living substance that has found the trick of transforming a symmetric, optically active compound. At the moment Life appeared on this planet, something happened to the molecular structure of things. They got a **twist***, which nobody has succeeded in reproducing mechanically - at least, not without an exercise of deliberate selective intelligence, which is also, as I suppose you'll allow, a manifestation of Life."*



Pasteur and the universal chiral force

Louis Pasteur manually separated left- and right-handed crystals of chemically synthesized tartaric acid and showed that they were optically active, rotating the plane of light the opposite way.



L'univers est un ensemble dissymétrique, et je suis persuadé que la vie, telle qu'elle se manifeste à nous, est fonction de la dissymétrie de l'univers ou des conséquences qu'elle entraîne.

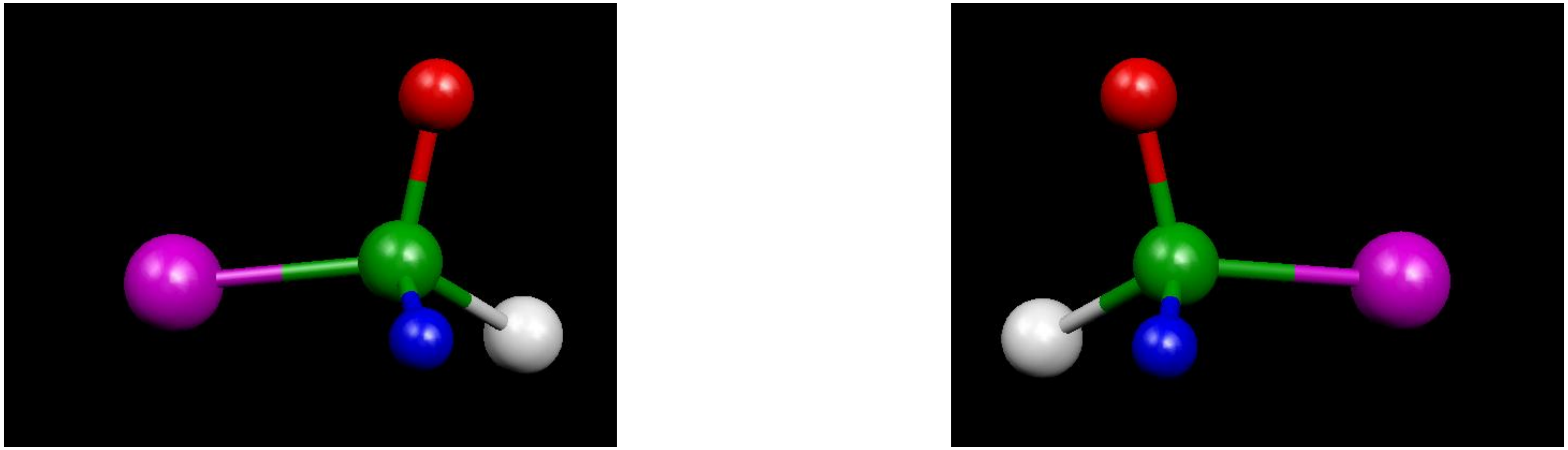

P. Dubois

Biomolecular homochirality:
Life on earth has many homochiral features, e.g. amino acids and sugars consist (almost) exclusively of the L- and the D-form, respectively.

Chiral molecules

The word chirality (handedness) was introduced by Lord Kelvin (1873).
The first paper in chemistry using the word chirality dates from 1962:

Carl Djerassi, Ruth Records, E. Bunnenberg, Kurt Mislow and Albert Moscowitz, J. Am. Chem. Soc. 84 (1962) 870



Enantiomers of chiral molecules are related by the parity operation

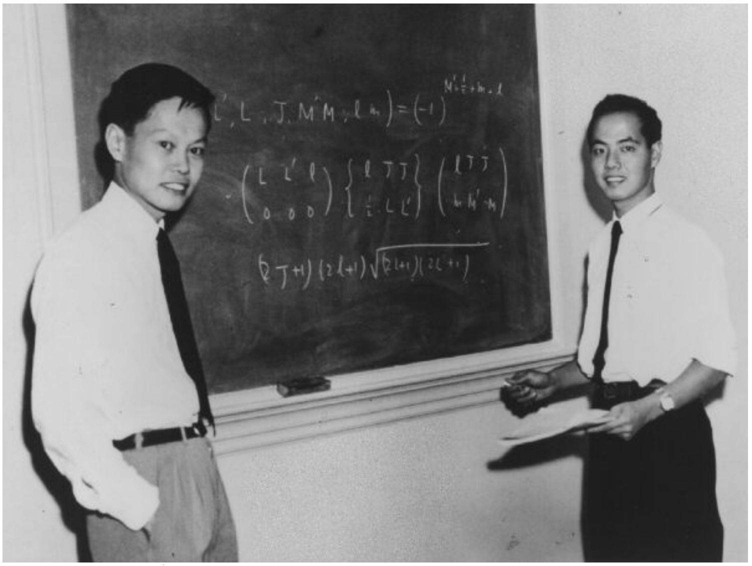
$$\widehat{P}\Psi_L = \Psi_R$$

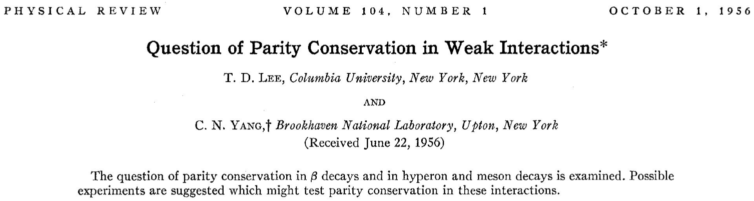
The Hamiltonian of (electromagnetic) quantum chemistry commutes with the parity operator

$$\left[\widehat{H}, \widehat{P}\right] = 0$$

and so the enantiomers are degenerate.

Parity violation in weak interactions





PHYSICAL REVIEW VOLUME 104, NUMBER 1 OCTOBER 1, 1956

Question of Parity Conservation in Weak Interactions*

T. D. Lee, *Columbia University, New York, New York*

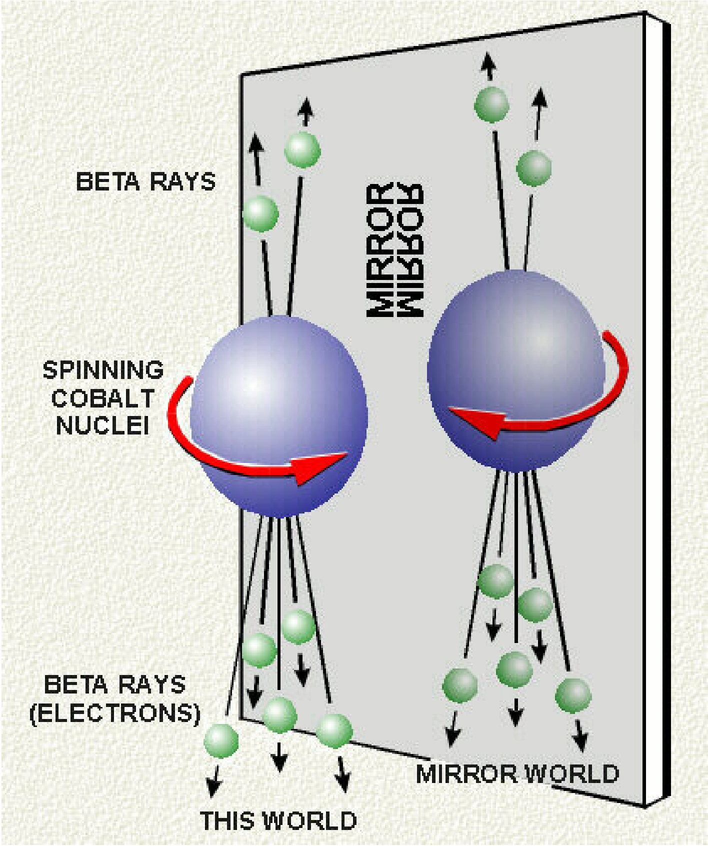
AND

C. N. Yang,† *Brookhaven National Laboratory, Upton, New York*

(Received June 22, 1956)

The question of parity conservation in β decays and in hyperon and meson decays is examined. Possible experiments are suggested which might test parity conservation in these interactions.

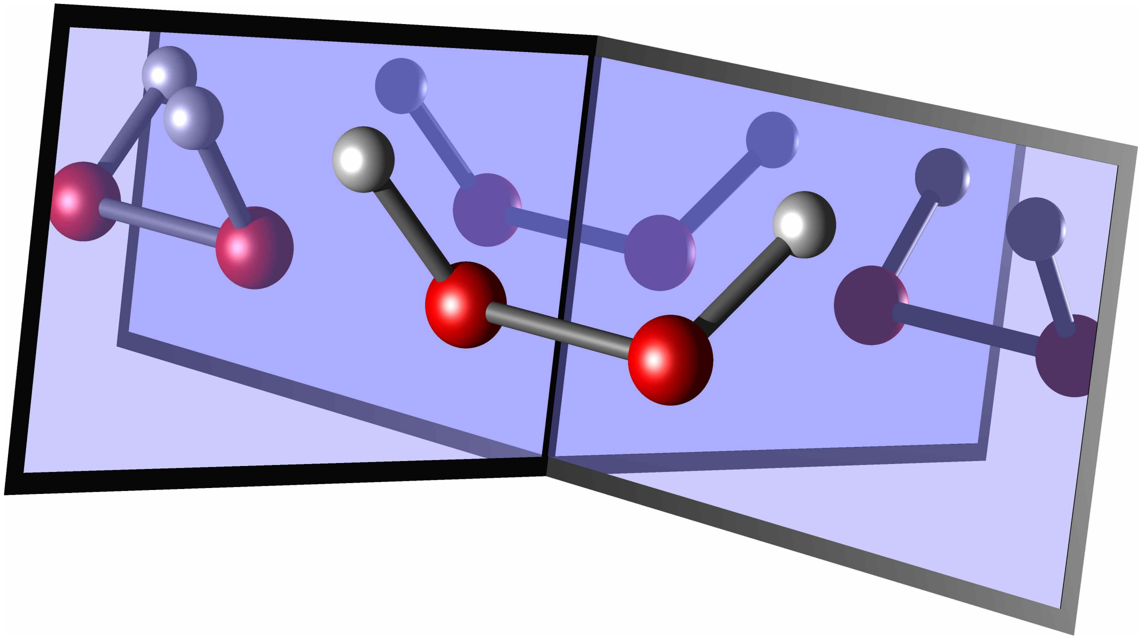
In 1956 Lee and Yang suggested that parity may not be conserved in processes involving the weak force



In 1957 Wu and co-workers observed parity violation in the β-decay of the ^{60}Co nucleus.

Parity-violation in molecular systems

M.Quack, Ang. Chem. Int. Ed. **41**(2002) 4618, J. K. Laerdahl and P. Schwerdtfeger, Phys. Rev. A **60** (1999) 4439



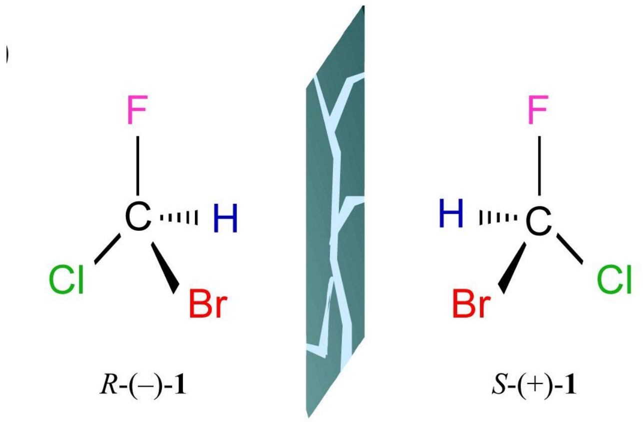
The Hamiltonian of *electroweak* quantum chemistry has a parity-violating (PV) component H_{pv}^{PV} and thus induces a minute energy difference between left- and right-handed molecules

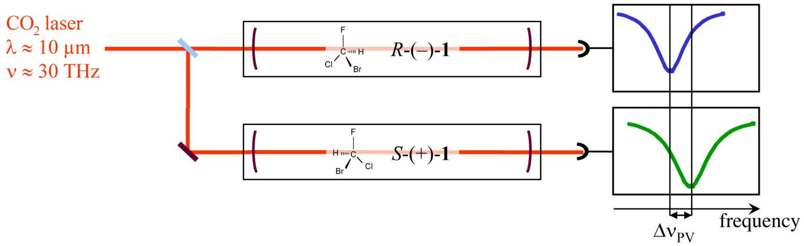
$$E_{pv;L}^{PV} = \left\langle \Psi_L \middle| \hat{H}_{pv}^{PV} \middle| \Psi_L \right\rangle = \left\langle \widehat{P}\Psi_L \middle| \widehat{P}\hat{H}_{pv}^{PV}\widehat{P}^{-1} \middle| \widehat{P}\Psi_L \right\rangle = -\left\langle \Psi_R \middle| \hat{H}_{pv}^{PV} \middle| \Psi_R \right\rangle = -E_{pv;R}^{PV}$$

Could this explain the origin of biochirality ?

Searching for PV effects in vibrational spectra

V. Lethokov, Phys. Lett. A **53** (1975) 275





- C-F stretch:

$$\begin{aligned} \nu_{CF} &= 1077\,\text{cm}^{-1} \\ &= 3.2 \cdot 10^{13}\,\text{Hz} \end{aligned}$$

Experiment:

M. Ziskind, T. Marrel, C. Daussy, C. Chardonnet, Eur. Phys. J. D **20** (2002) 219

- High-resolution spectroscopy:

$$-4.2 \pm 0.6 \pm 1.6\,\text{Hz}$$

- Relative sensitivity: $\Delta\nu/\nu = 4 \cdot 10^{-14}$

Theory:

P. Schwerdtfeger, T. Saue, J. N. P. van Straalen and L. Visscher,
Phys. Rev. A **71** (2005) 012103

- PV shift:

$$\Delta\nu_{RS} = \nu_R - \nu_S = -2.4\,\text{mHz (MP2)}$$

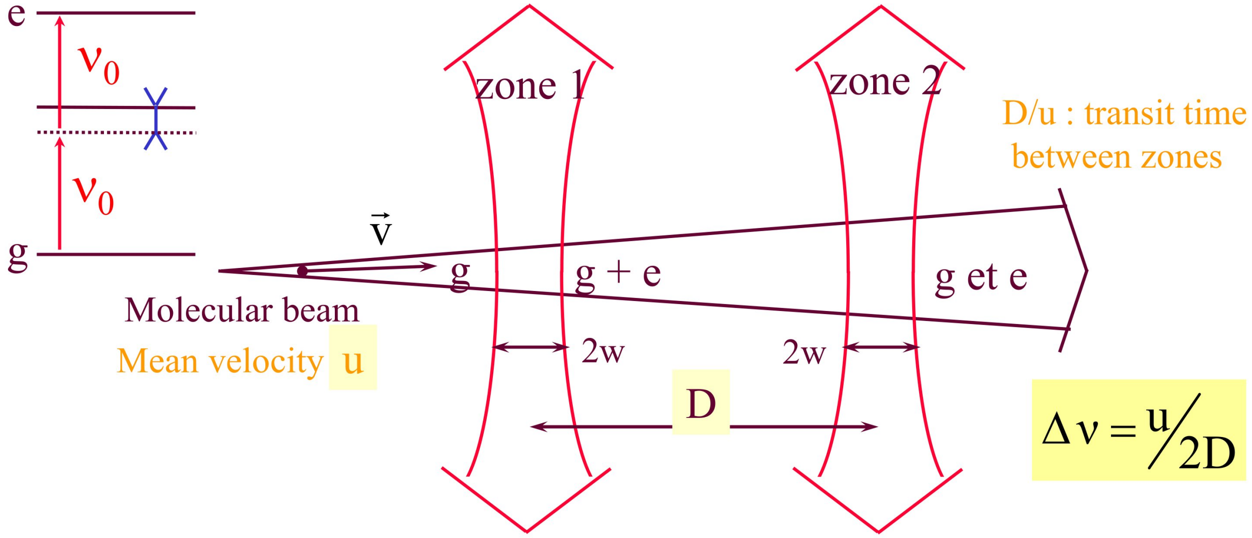
- Relative sensitivity required:

$$\Delta\nu_{RS}/\nu_{CF} = -7.56 \cdot 10^{-17}$$

We need a better experiment and better molecules !

A new experiment

- molecular beam spectroscopy using a two-photon Ramsey fringes experiment
  A. Amy-Klein, L. F. Constantin, R. J. Butcher, G. Charton, and Ch. Chardonnet, Phys. Rev. A 63 (2000) 013404



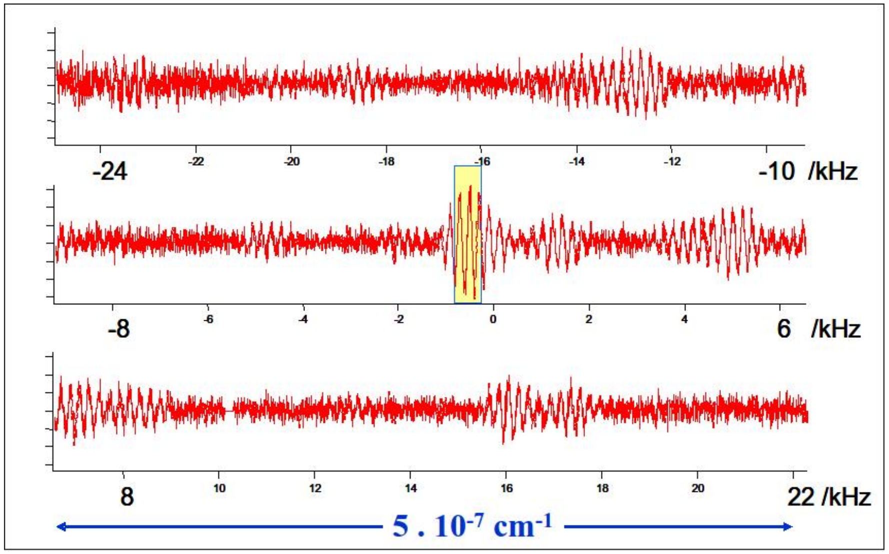
- Lineshape(ν): *Two-photon absorption* $(\nu)\times\left(1+C\cos\left[\frac{2\pi(\nu-\nu_0)}{\Delta\nu}\right]\right)$

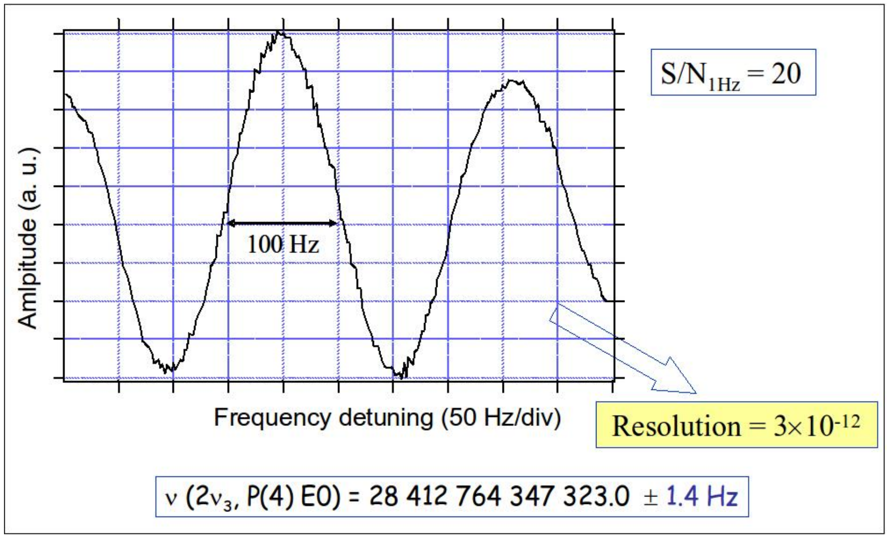
A two-photon Ramsey fringes experiment on SF_6

A. Shelkovnikov, C. Grain, R. J. Butcher, A. Amy-Klein, A. Goncharov, and Ch. Chardonnet,

IEEE Quant. Electron., **40** (2004) 1023,

A. Shelkovnikov, R. J. Butcher, C. Chardonnet, and A. Amy-Klein. Phys. Rev. Lett., **100** (2008) 150801,



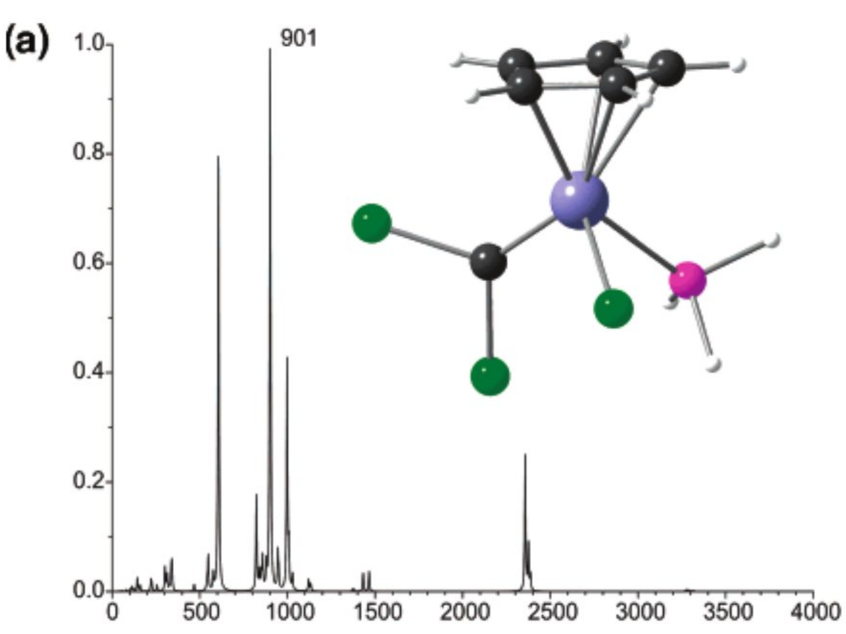


- The LPL team recently developed an experiment of Doppler-free two photon Ramsey fringes on a supersonic beam of SF_6 in which a relative sensitivity below 1 Hz was obtained (10^{-14} in fractional value)

- Taking advantage of the gain expected for a differential experiment, a sensitivity of 0.01 Hz is expected in a similar experiment on parity violation in vibrational shifts.

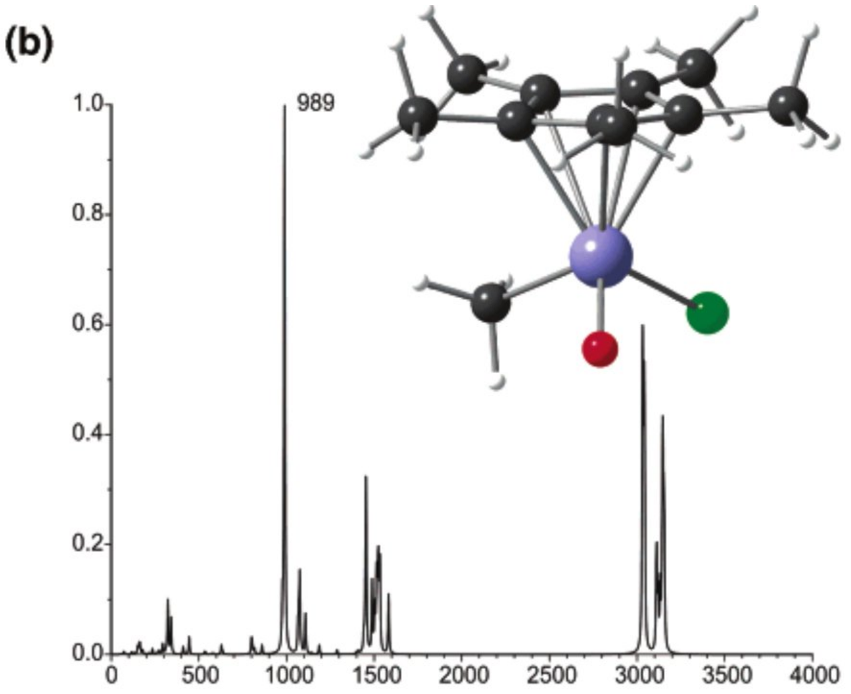
Organometallic compounds

P. Schwerdtfeger and R. Bast, J. Am. Chem. Soc. **126** (2004) 1652



Os(η^5-C$_5$H$_5$)(=CCl$_2$)Cl(PH$_3$)

- Os=C stretch:
  $\nu_{Os-C} = 901\,\text{cm}^{-1}$(B3LYP)
- $\Delta_{RS}(0 \rightarrow 1) = -3.58$ Hz (4c-HF)
- $\Delta\nu_{RS}/\nu_{Os-C} = -4.3 \cdot 10^{-14}$



Re(η^5-Cp*)(=O)(CH$_3$)Cl

- Re=O stretch:
  $\nu_{Re-O} = 989\,\text{cm}^{-1}$(B3LYP)
- $\Delta_{RS}(0 \rightarrow 1) = +1.29$ Hz (4c-HF)
- $\Delta\nu_{RS}/\nu_{Re-O} = +3.7 \cdot 10^{-14}$

Electroweak chemistry

$$E_{PV} = \sum_K E_{PV}^K; \quad E_{PV}^K = \frac{G_F}{2\sqrt{2}} Q_W^K \sum_i \langle \psi_i \, | \gamma_5 \rho_K \, | \, \psi_i \rangle$$

- ✔ Weak charge: $Q_{W;A} = -N_A + Z_A \left(1 - 4\sin^2\theta_W\right); \quad \sin^2\theta_W = 0.2319$
- ✔ Normalized nucleon density: ρ_A
- ✔ $\gamma_5 = \begin{bmatrix} 0_2 & I_2 \\ I_2 & 0_2 \end{bmatrix}$
- ✔ Fermi coupling constant: $G_F = 2.22255 \cdot 10^{-14} \, \mathrm{a.u.}$ very weak !
- ✔ $E_{PV}^K \propto Z_K^5$
- ✔ $E_{PV}^K = 0$, unless spin-orbit coupling is present.

Look for chiral compounds with heavy elements !

The DIRAC code

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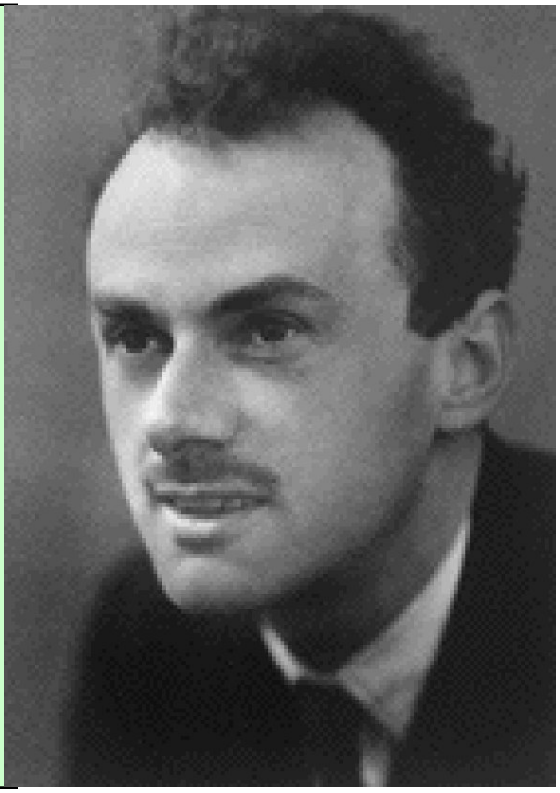
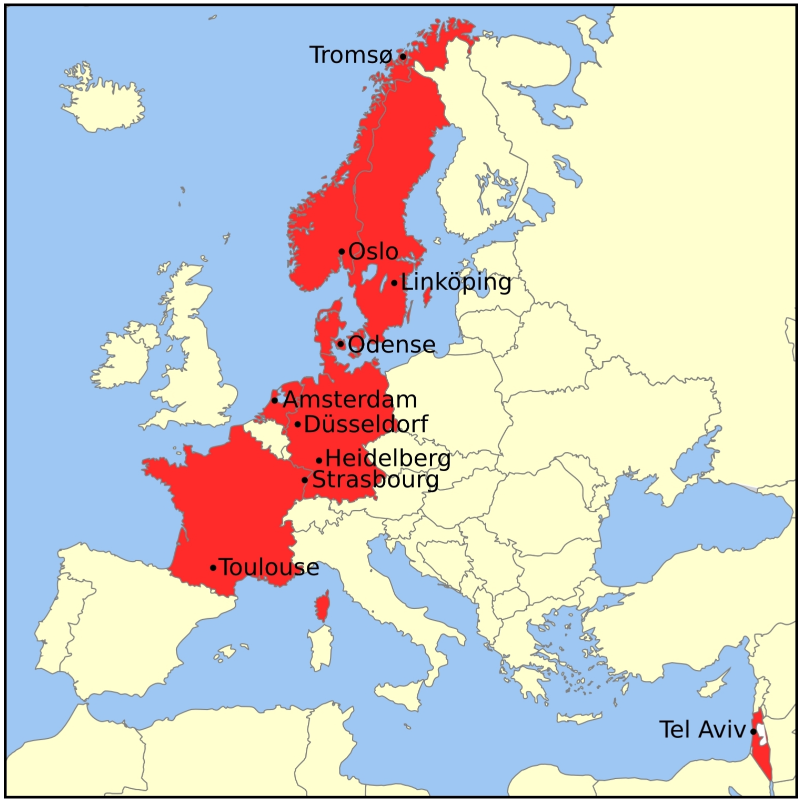
A tomic
• and
M olecular

D irect
I terative
R elativistic
A ll-electron
C alculations





- Web site: `http://wiki.chem.vu.nl/dirac`
- Wave functions: [HF, MP2, RASCI, MCSCF, CCSD(T), FSCCSD]
  + DFT [LDA, GGAs, hybrids]
- HF/DFT: Electric and magnetic properties:
  expectation values, linear and quadratic response functions, single excitation energies

Announcing DIRAC10

Release date: 10/10/10. Check http://wiki.chem.vu.nl/dirac

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A tomic
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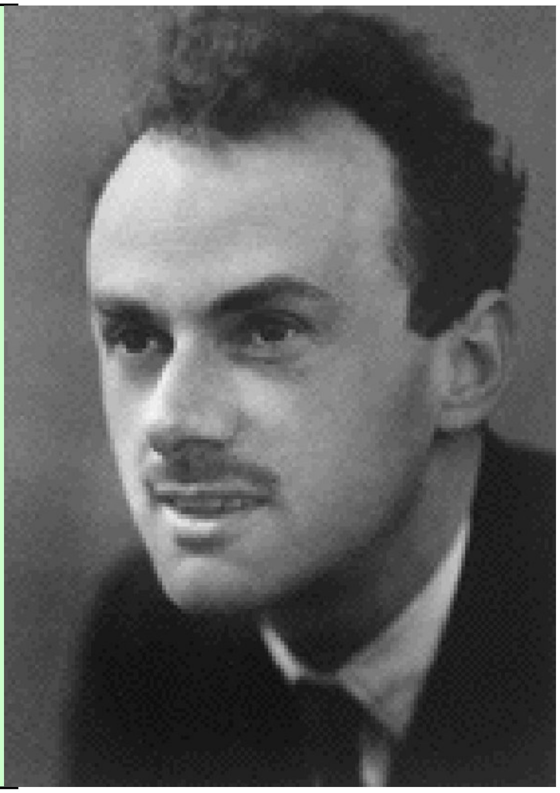


- **Hamiltonians:**
  - X2C+AMFI for 2-electron spin-orbit corrections (SSO/SOO)

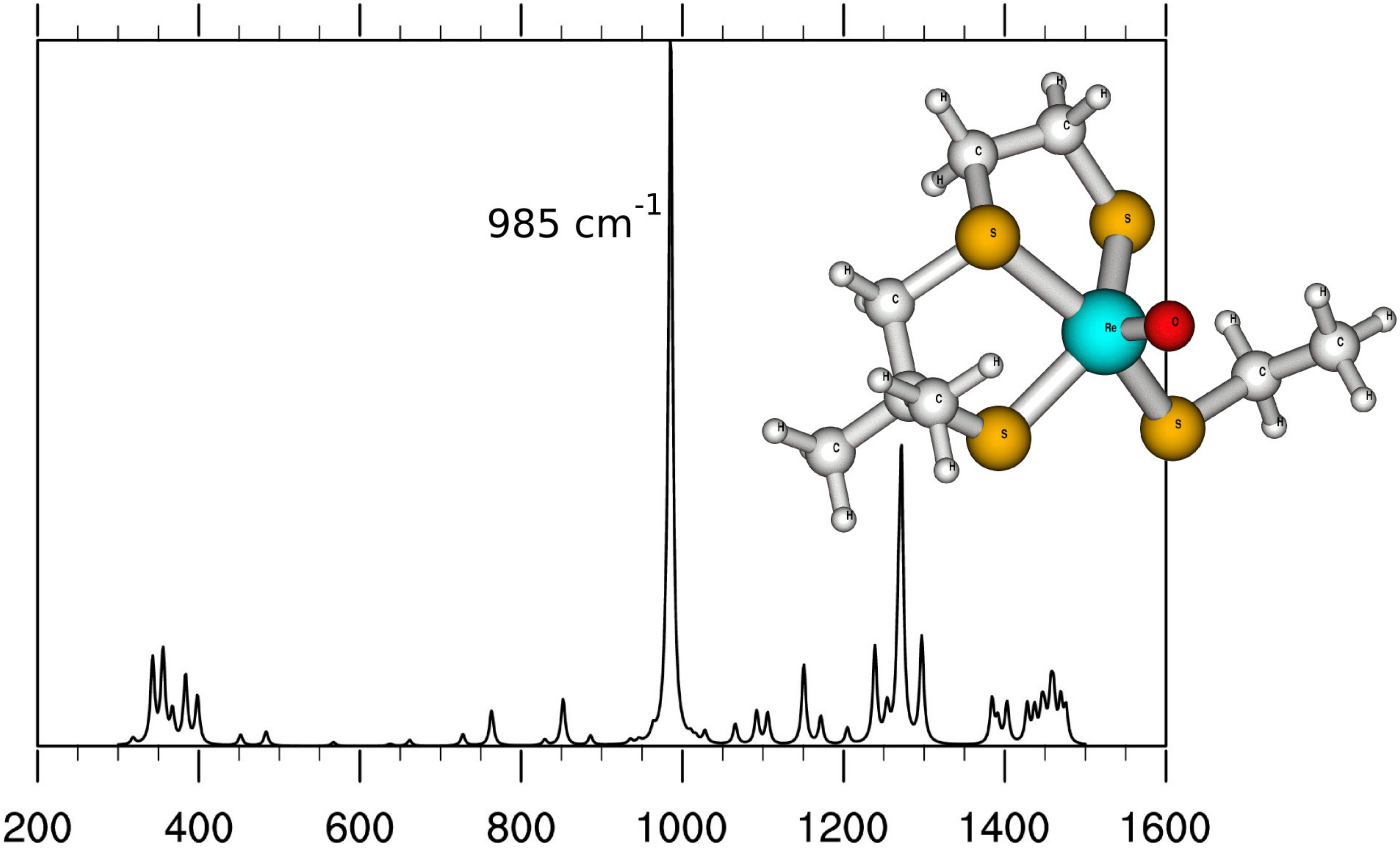
- **Methods:**
  - KR-MCSCF
  - RELADC for correlated calculations of single/double ionization spectra
  - large-scale parallel CI (LUCITA/KRCI)
  - intermediate Hamiltonian formalism for Fock-space CCSD
  - interface to MRCC (M. Kallay)
  - frozen density embedding

- **Properties:**
  - HF/KS excitation energies
  - KS response with noncollinear spin polarization
  - more efficient KS DFT code
  - London orbitals for HF NMR shieldings

- **Analysis:**
  - visualization of unperturbed and perturbed densities
  - projection analysis of expectation values
  - expectation values/transition moments KRCI/GOSCI

Computational procedure

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

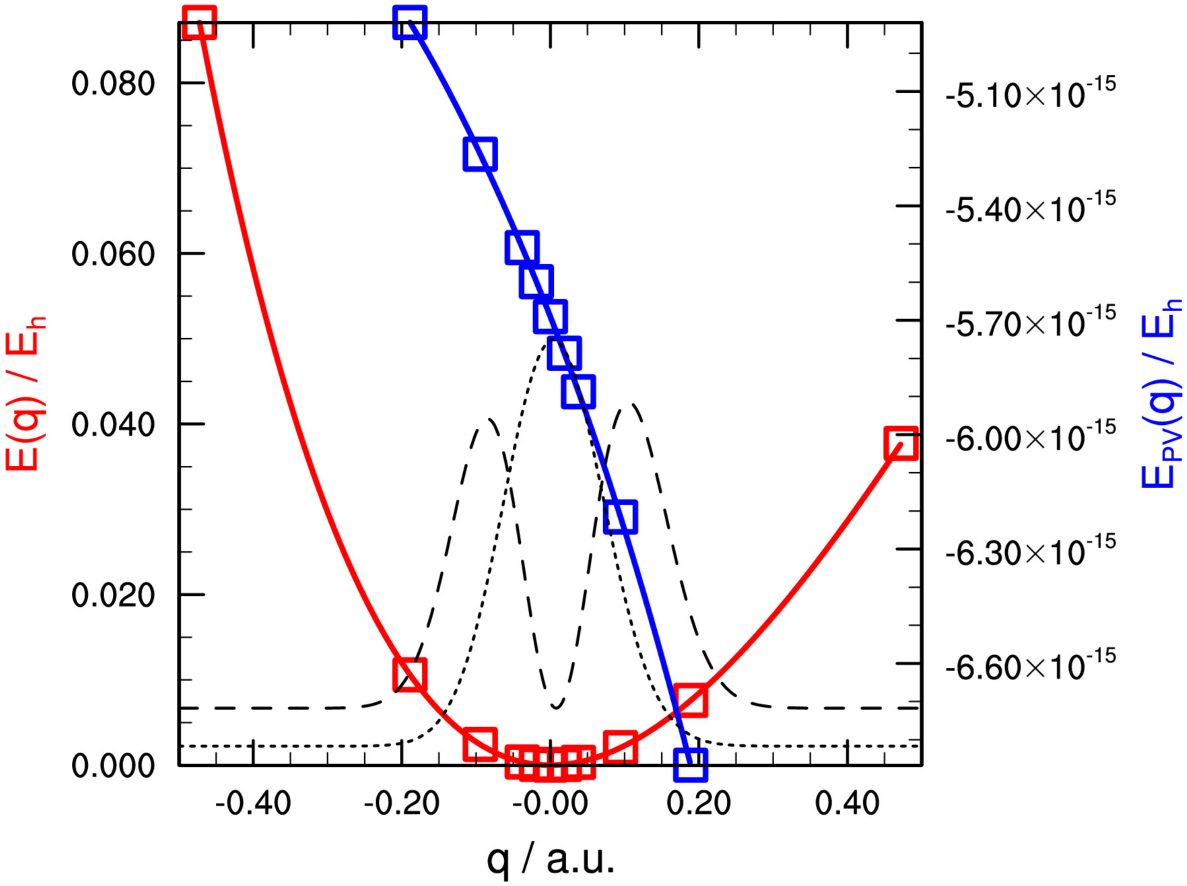


Computational procedure

2. Calculation of 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) $\rightarrow \quad \psi_\nu^{\text{vib}}$

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



Looking for the best candidate

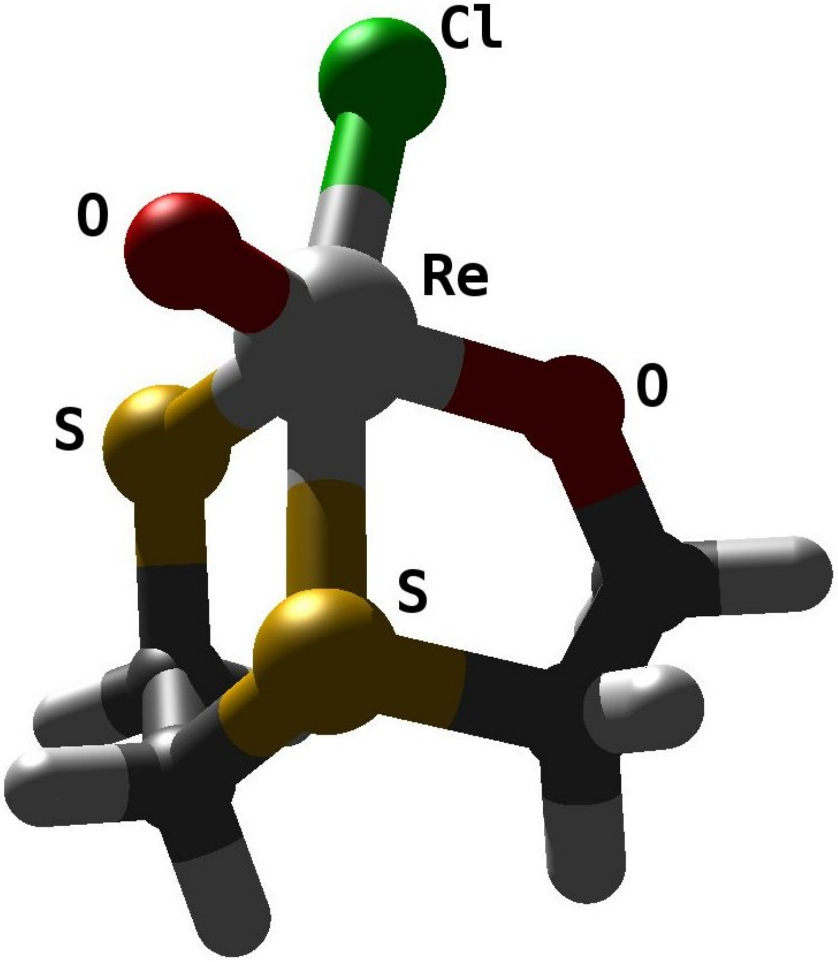
The ideal candidate chiral molecule for the experiment should:

- be available in large enantiomer excess or, ideally, in enantiopure form;
- show a large PV frequency difference of an intense fundamental transition within the CO_2 laser operating range (850-1120 cm^{-1});
- not be too bulky since the sensitivity of the experiment will be largely determined by the partition function of the molecules in a supersonic beam where the internal degrees of freedom are frozen down to about 1 K;
- avoid nuclei with quadrupolar moments;
- preferably sublimate without decomposition for injection into the Fabry-Perot cavity of the experiment, although laser ablation techniques may also be envisaged.

Chiral “3+1” oxorhenium(V) complexes

Frederic De Montigny, Radovan Bast, Andre Severo Pereira Gomes, Guillaume Pilet, Nicolas Vanthuyne, Christian Roussel,

Laure Guy, Peter Schwerdtfeger, Trond Saue and Jeanne Crassous, Phys. Chem. Chem. Phys. **12** (2010) 8792



- Re=O stretch:

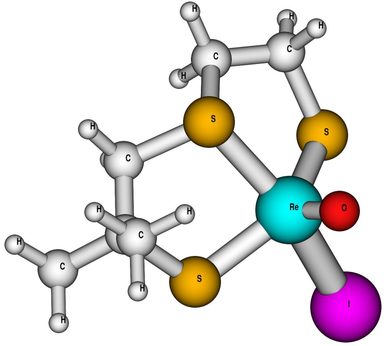
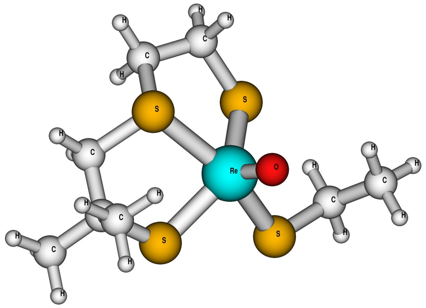
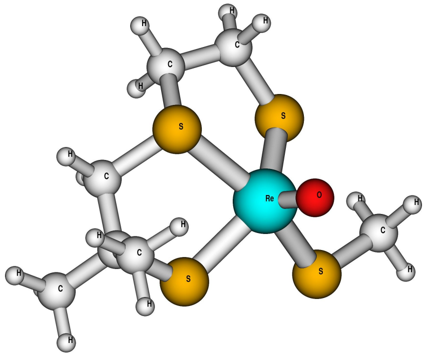
$$\nu_{Re-O} = 1032\,\mathrm{cm}^{-1}$$

- PV shift (HF):

$$\Delta\nu_{RS} = 2055.7\,\mathrm{mHz}$$

- PV shift (B3LYP):

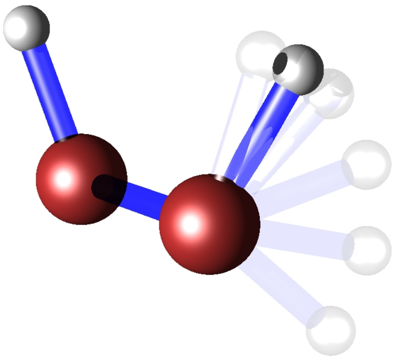
$$\Delta\nu_{RS} = 206.4\,\mathrm{mHz}$$

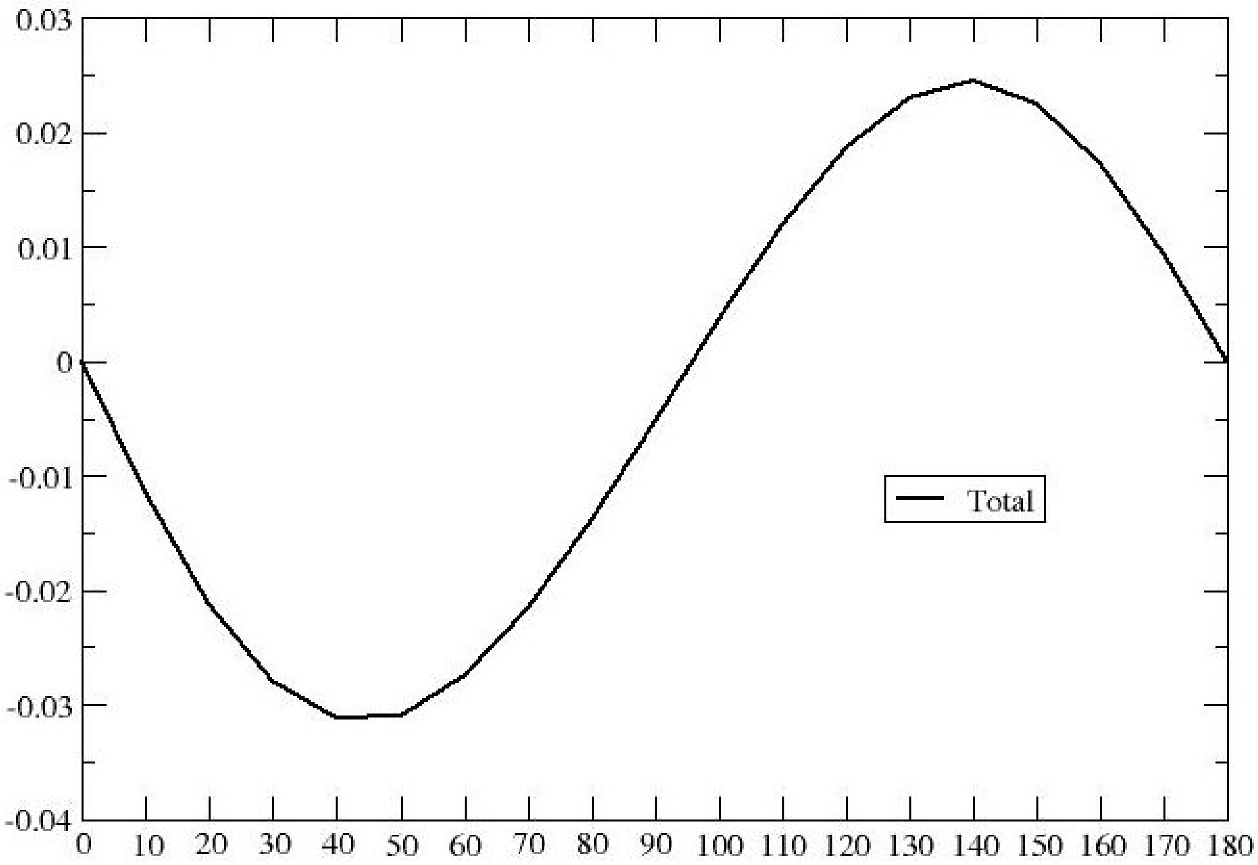
	ν(Re=O)	$\Delta\nu_{RS}$(X2C)		
		HF	B3LYP	
4	1027 cm^{-1}	156.8 mHz	69.0 mHz	
5	1012 cm^{-1}	-1584.9 mHz	-102.5 mHz	
5b	1012 cm^{-1}	-1021.0 mHz	-84.0 mHz	

A significant discrepancy is observed between HF and DFT results and calls upon further analysis.

H_2X_2 (X=O, S, Se, Te, Po) — a toy system

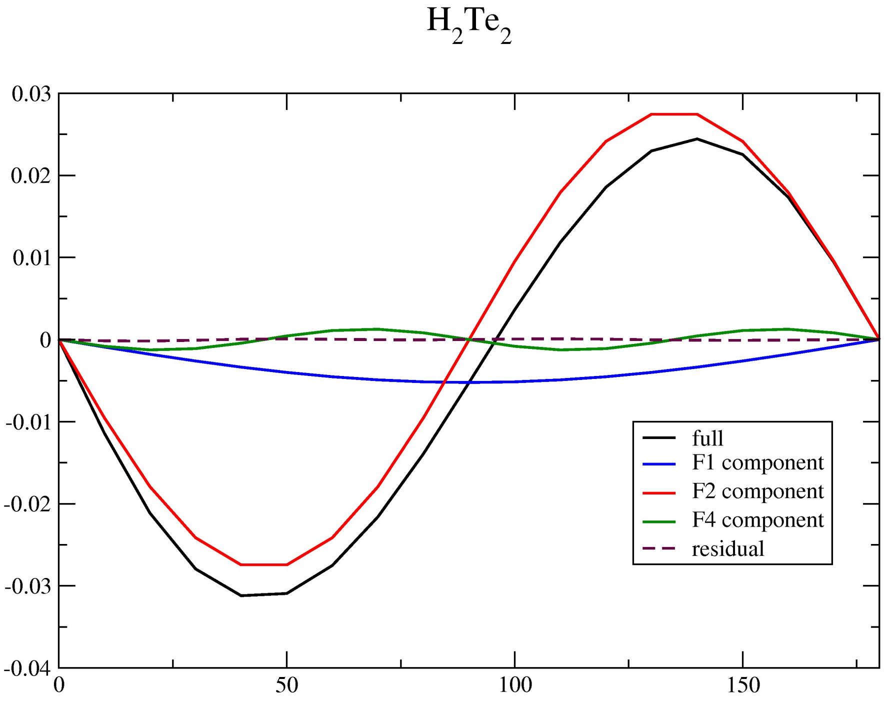
S. F. Mason and G. E. Tranter, Mol. Phys. **53** (1984) 1091





We focus on the PV-contribution E_{PV}^{Te} from one tellurium atom of H_2Te_2 as a function of dihedral angle.

Fourier decomposition

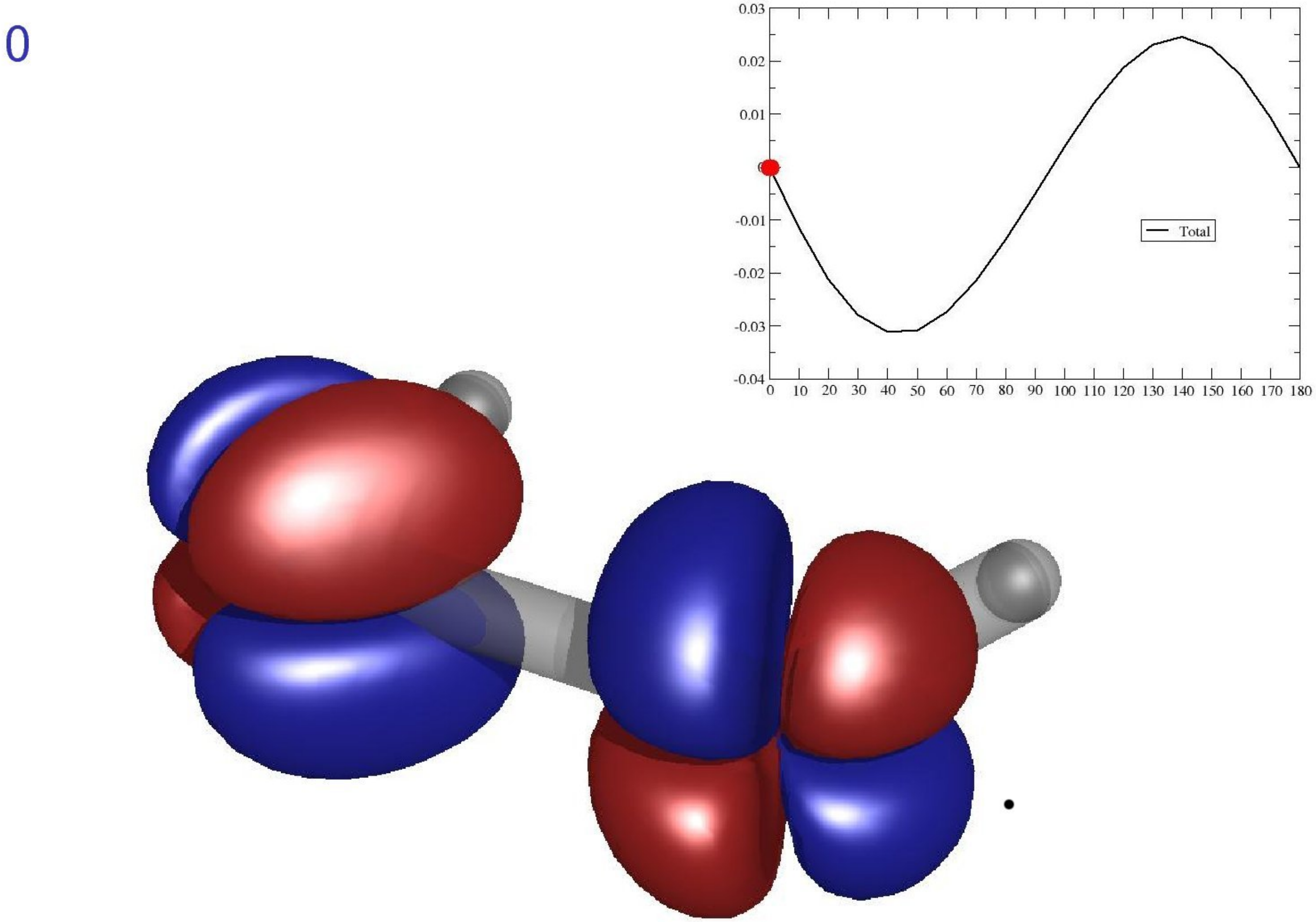


$$K_{PV}^{X}(\gamma) = \sum_{n=1}^{\infty} F_n \sin(n\gamma)$$

F_2	H_2O_2	H_2S_2	H_2Se_2	H_2Te_2	H_2Po_2
HF	-6.492E-06	-7.435E-05	-3.163E-03	-2.787E-02	-7.955E-01
LDA	-7.153E-06	-9.522E-05	-4.335E-03	-3.697E-02	-7.444E-01
BLYP	-6.953E-06	-9.554E-05	-4.204E-03	-3.585E-02	-7.504E-01
B3LYP	-6.889E-06	-9.162E-05	-4.055E-03	-3.488E-02	-7.703E-01

A real-space approach

$$E^A_{PV} = \frac{G}{2\sqrt{2}} Q^A_W \sum_i \langle \psi_i \,|\gamma_5 \rho_A \,|\, \psi_i \rangle = \frac{G}{2\sqrt{2}} Q^A_W \int \gamma^5(\mathbf{r}) \rho_A(\mathbf{r}) d\tau; \quad \gamma_5 = \begin{bmatrix} 0_2 & I_2 \\ I_2 & 0_2 \end{bmatrix}$$



Digression: Visualization of orbitals

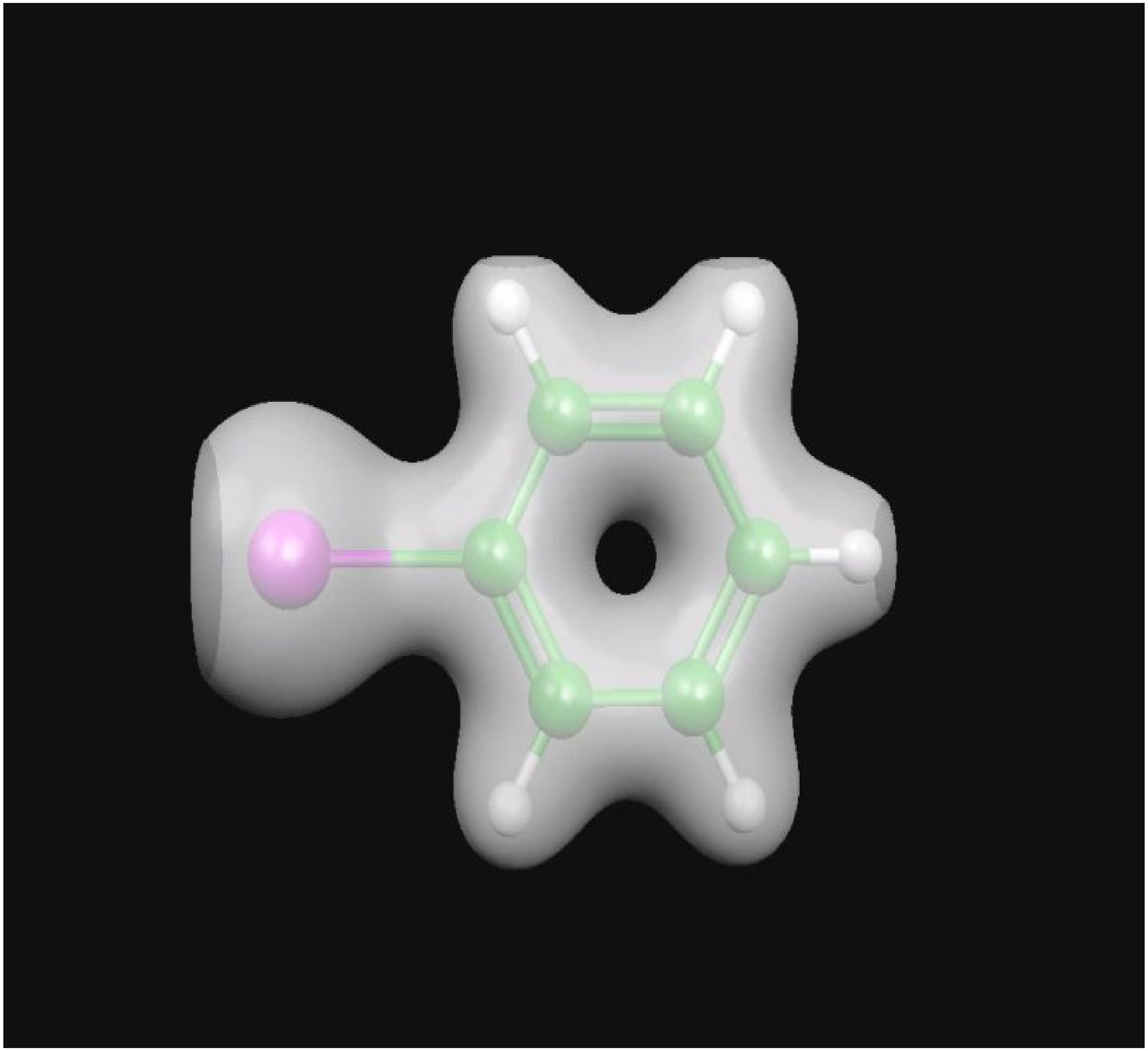
- ✔ Orbitals in Dirac theory are complex vector functions (4-spinors)

$$\psi = \begin{bmatrix} \psi^L \\ \psi^S \end{bmatrix} = \begin{bmatrix} \psi^{L\alpha} \\ \psi^{L\beta} \\ \psi^{S\alpha} \\ \psi^{S\beta} \end{bmatrix}$$

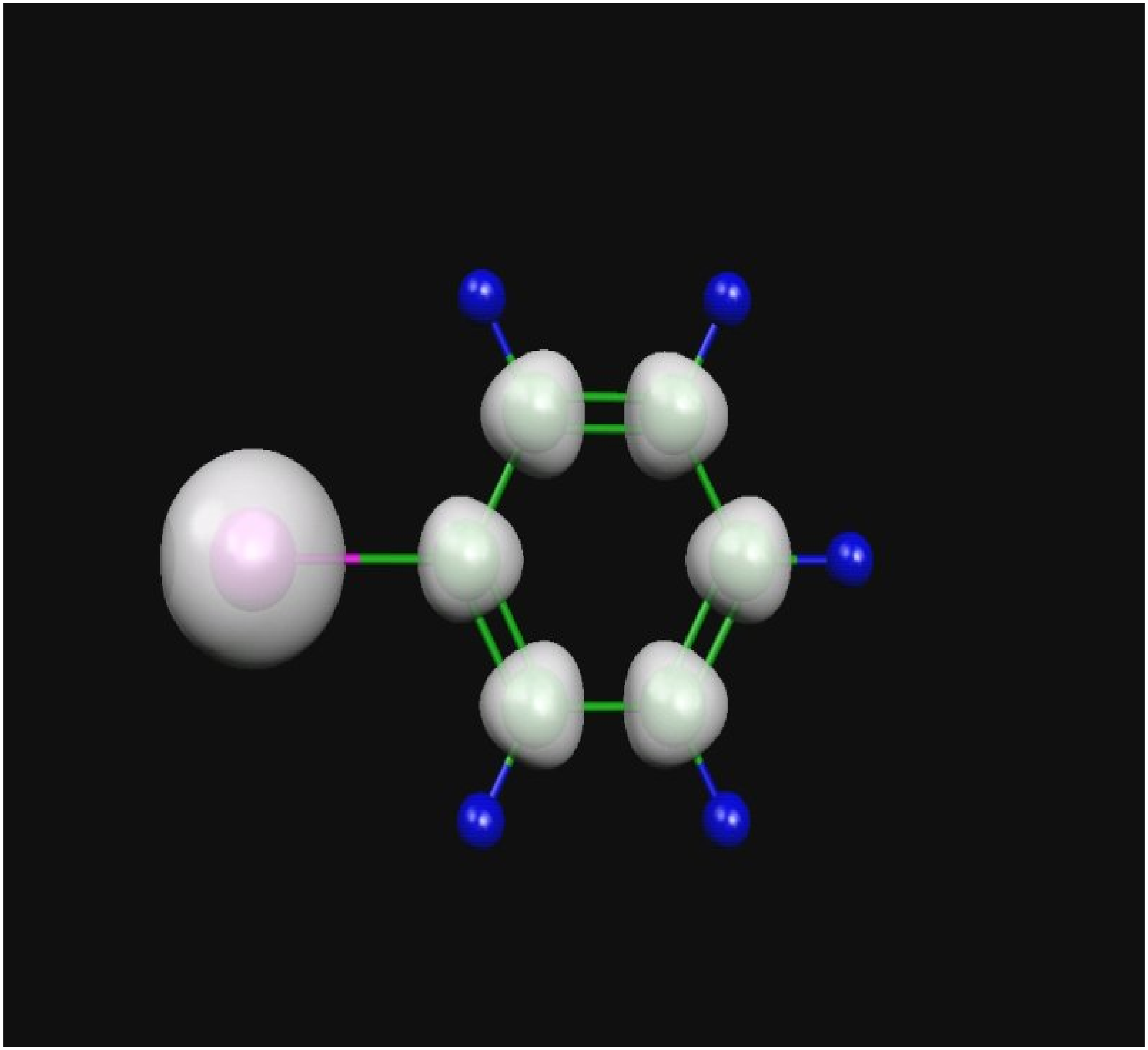
- ✔ The density is a real scalar function

$$\rho(\mathbf{r}) = \rho^L(\mathbf{r}) + \rho^S(\mathbf{r}); \quad \rho^X(\mathbf{r}) = \sum_i^{N_{\mathrm{occ}}} \psi_i^{X\dagger}(\mathbf{r})\psi^X(\mathbf{r}), \quad X = L, S$$

Large component density of iodobenzene (isosurface=0.01)



Small component density of iodobenzene (isosurface=0.0001)



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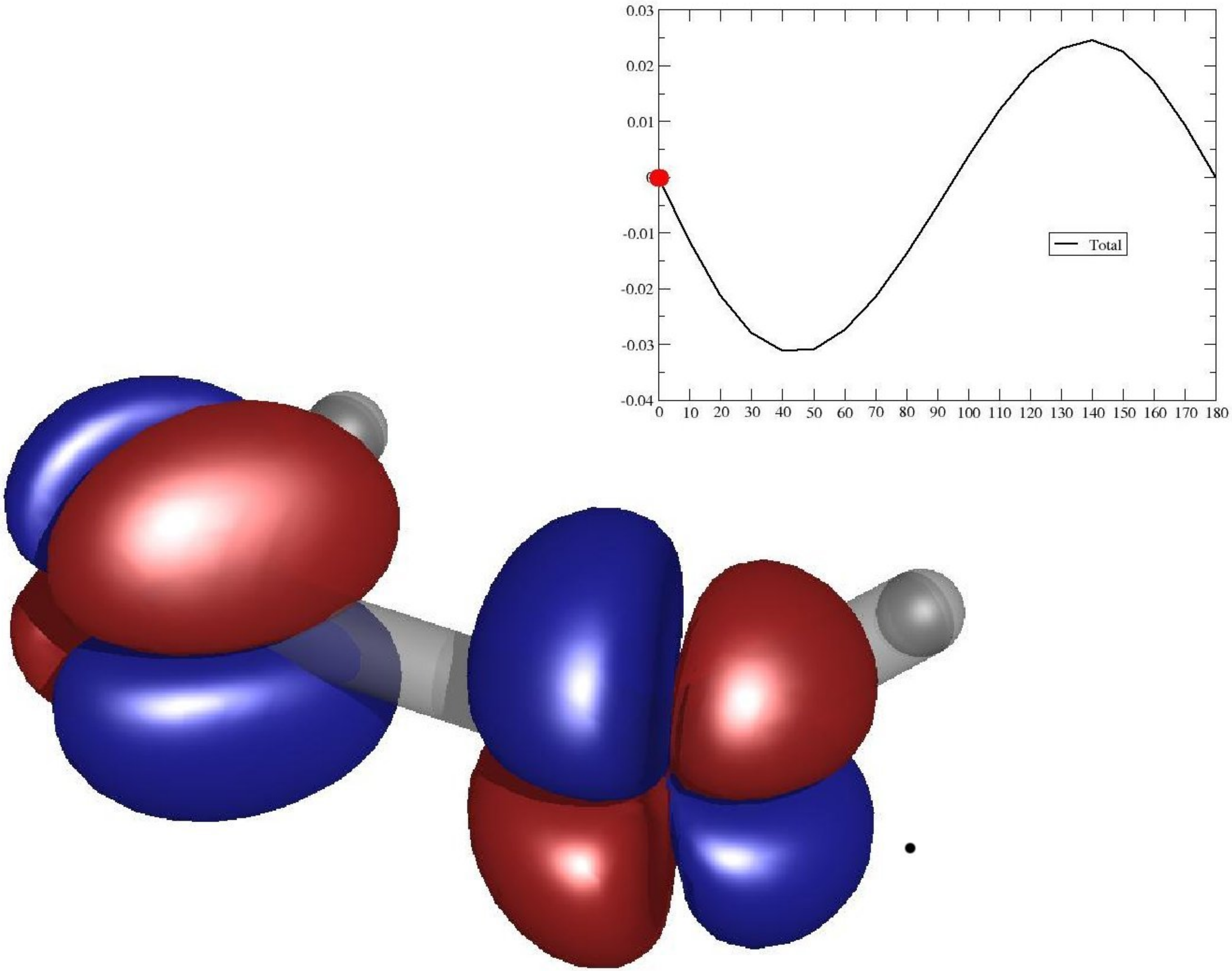

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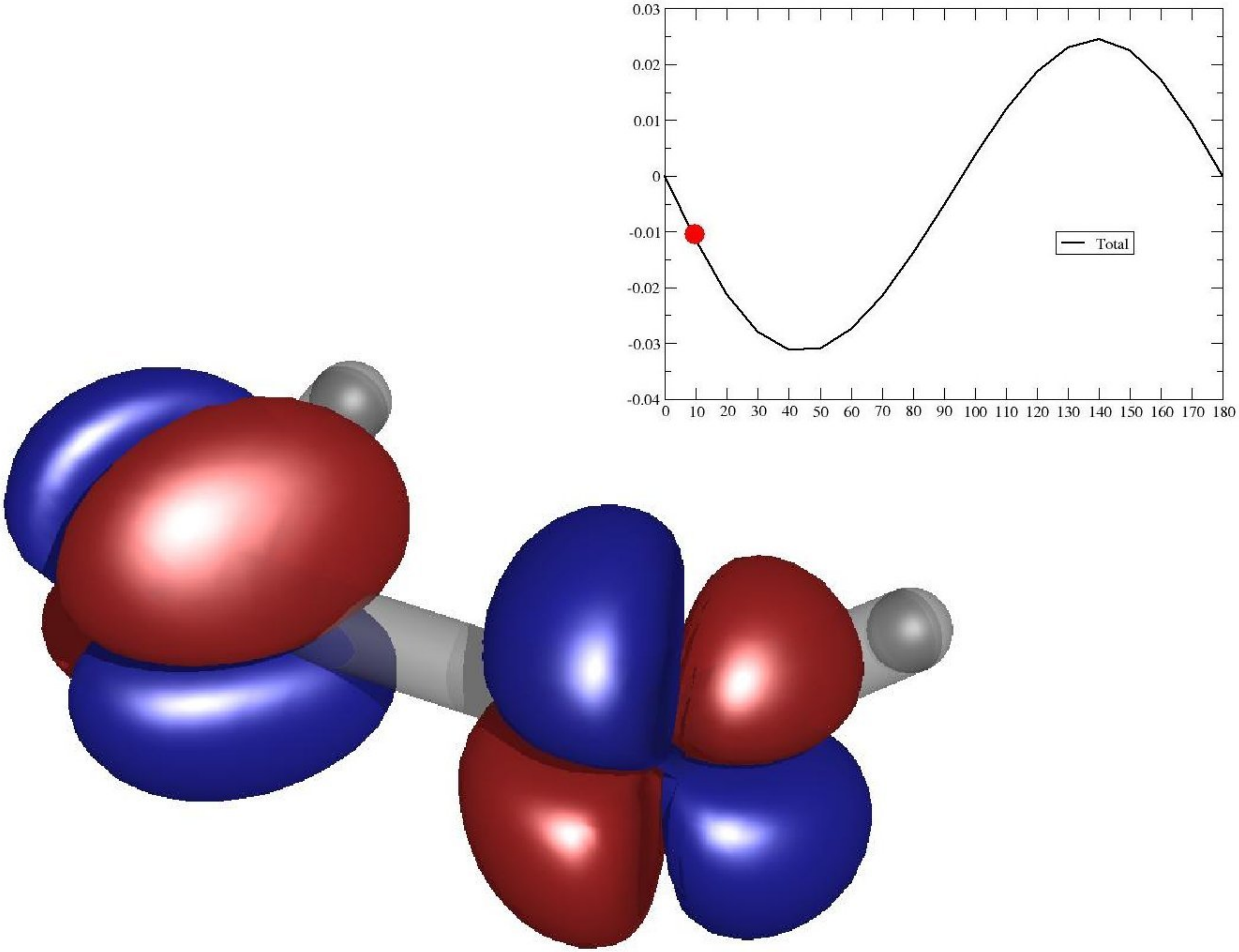
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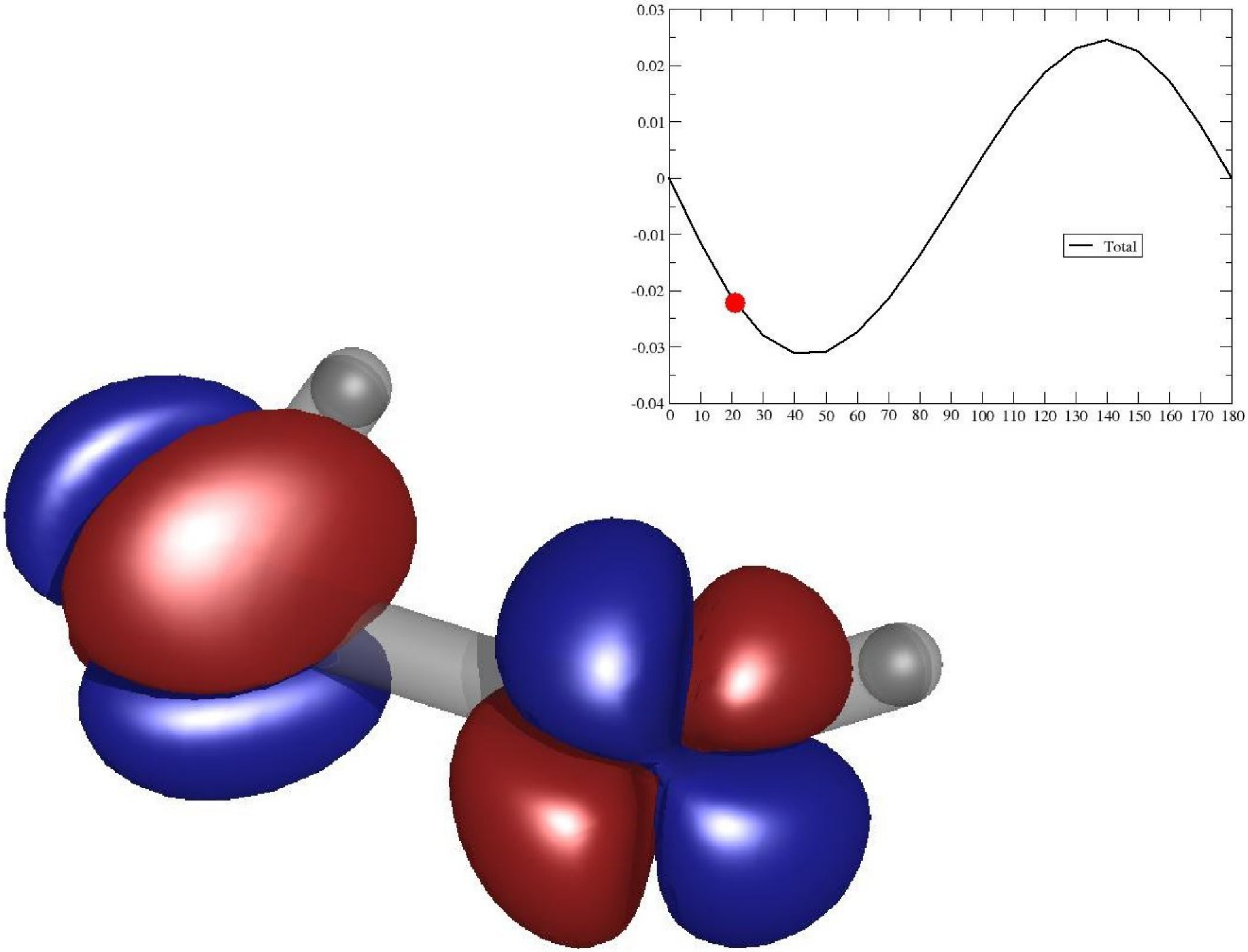
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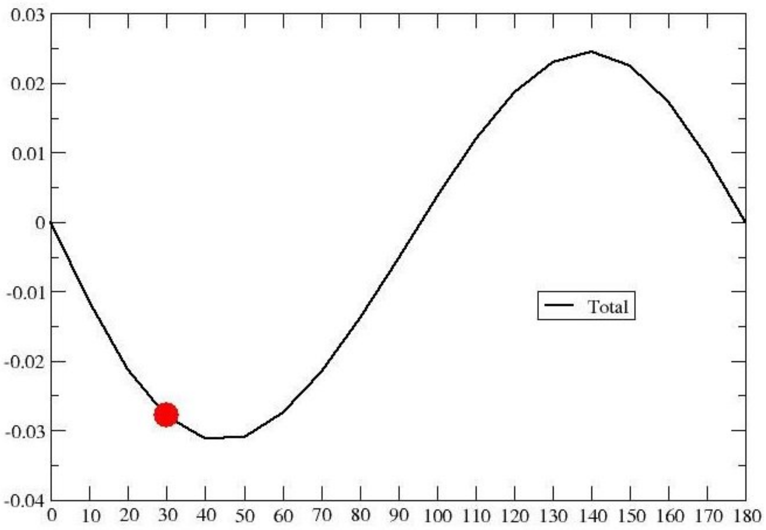

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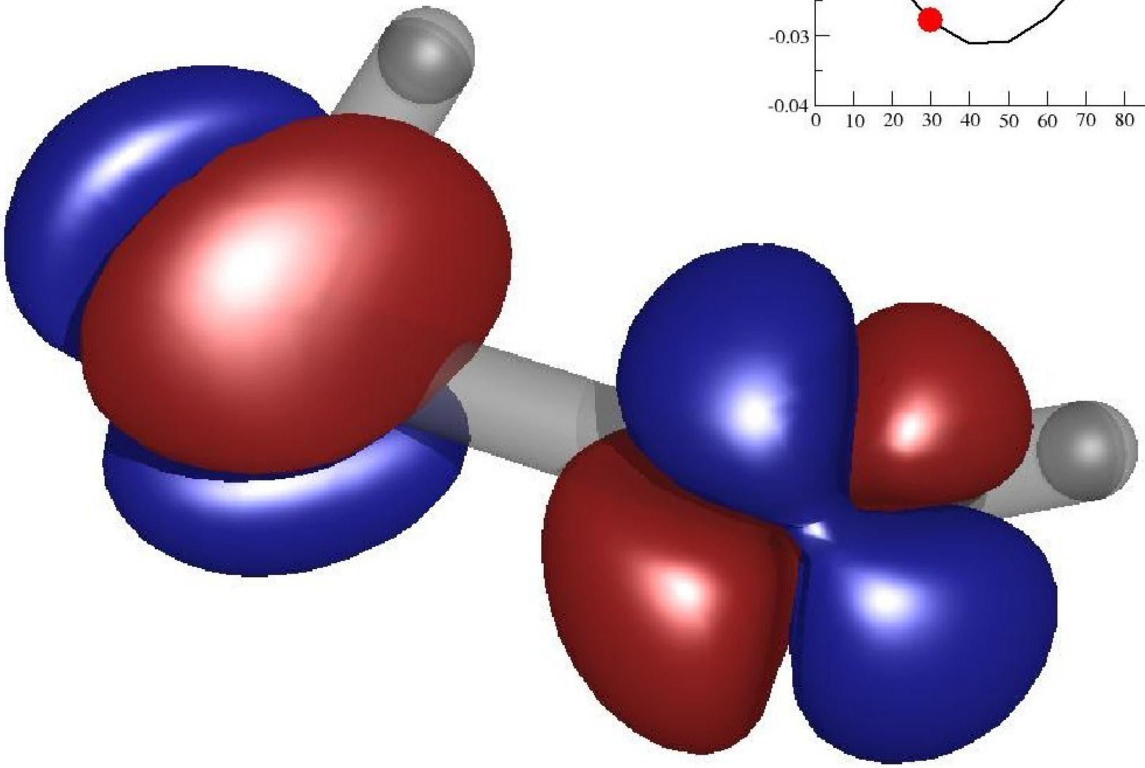

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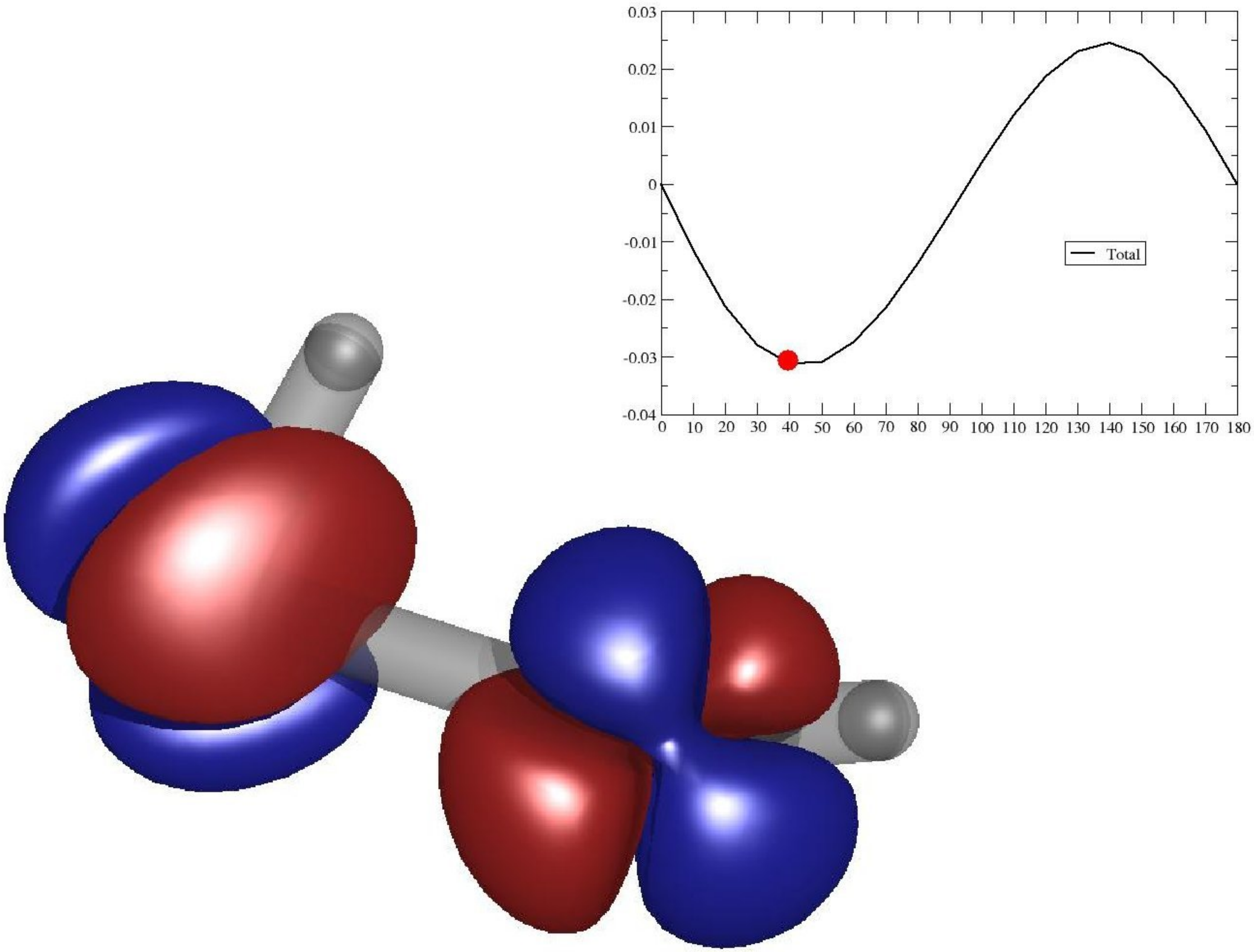

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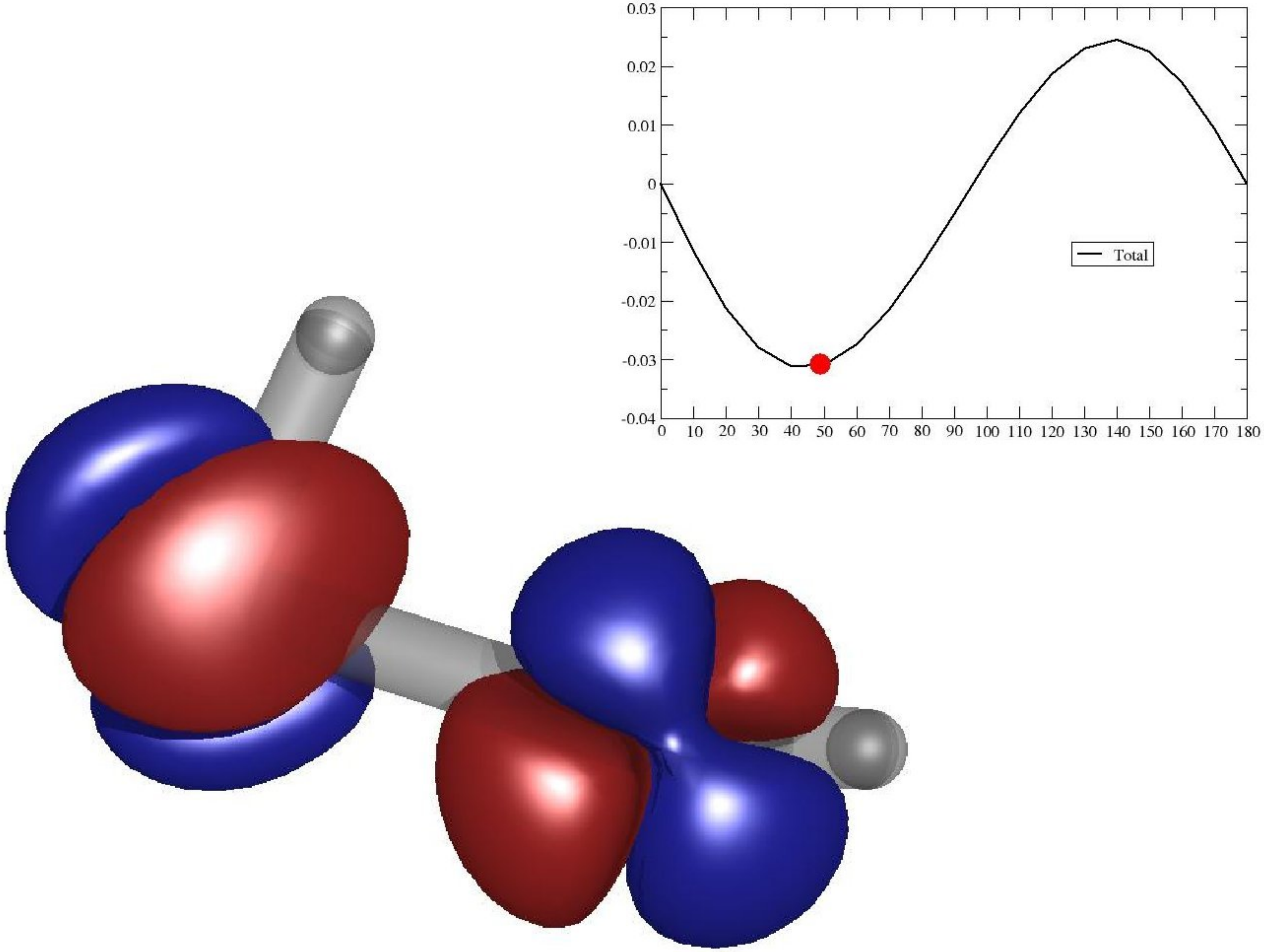
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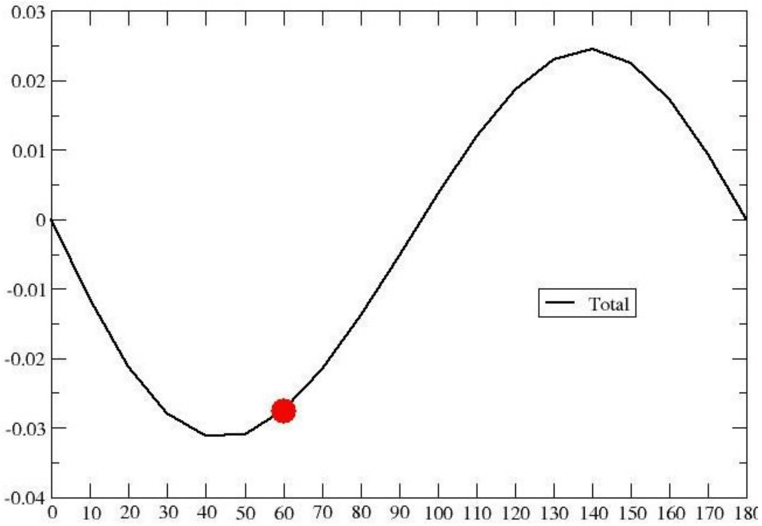
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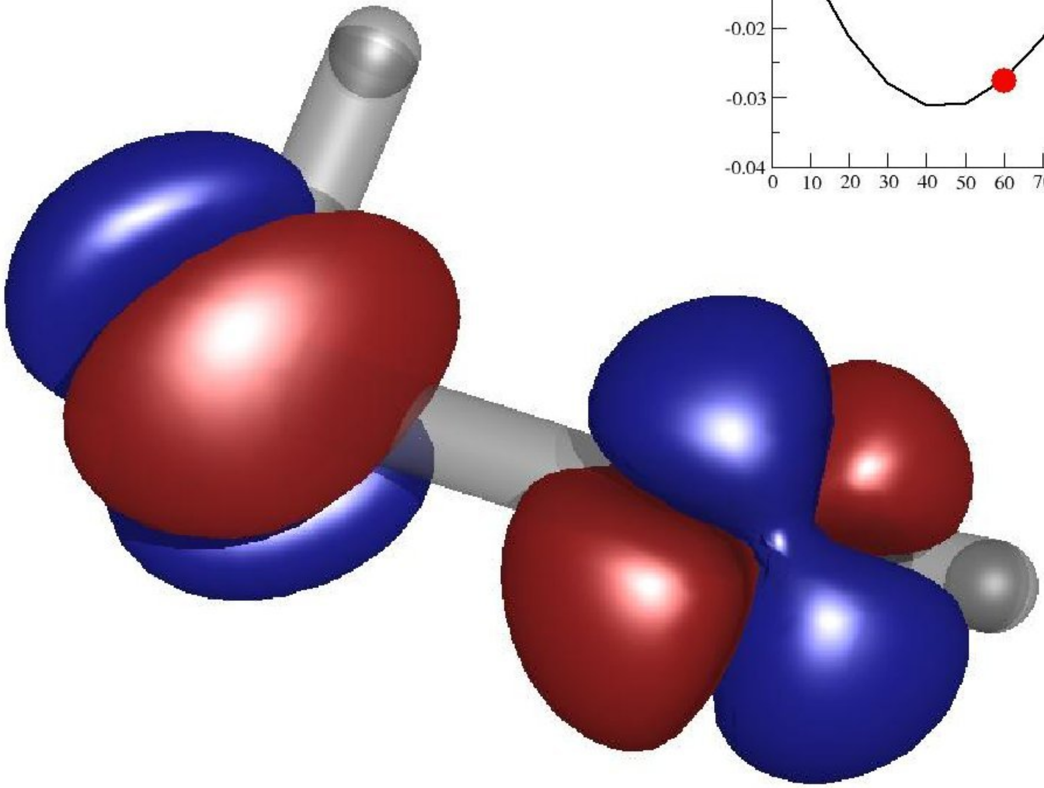

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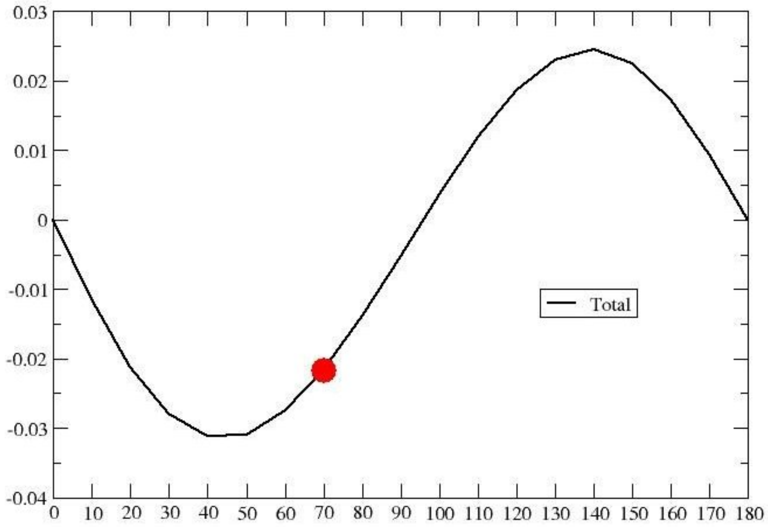
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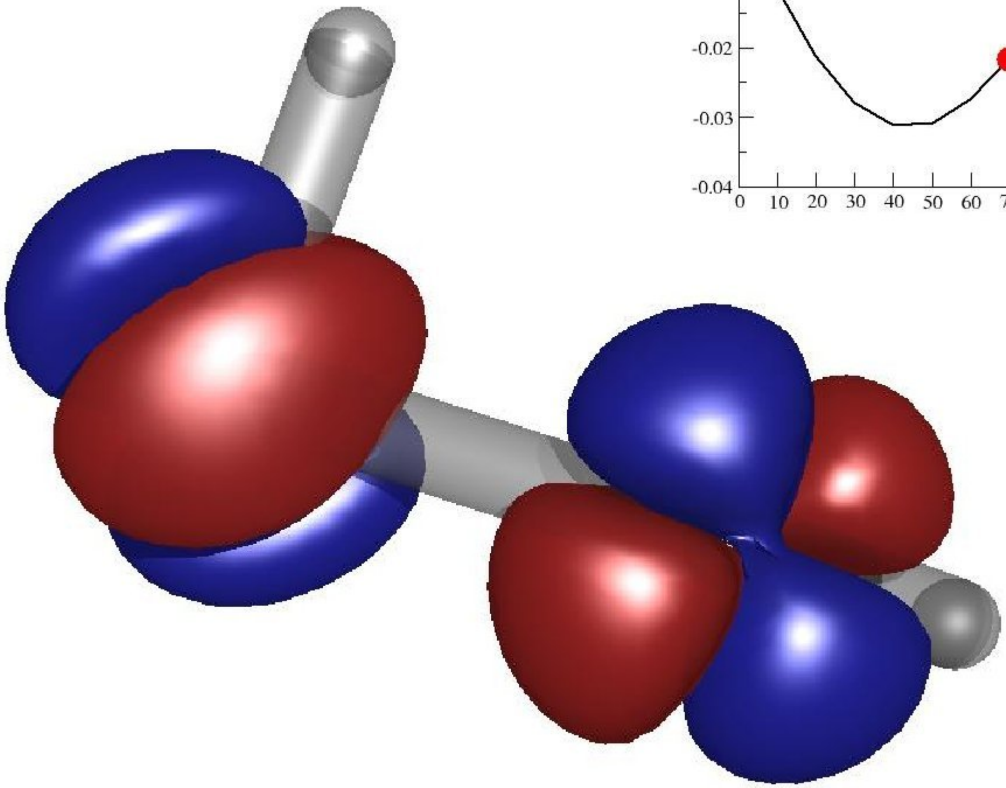

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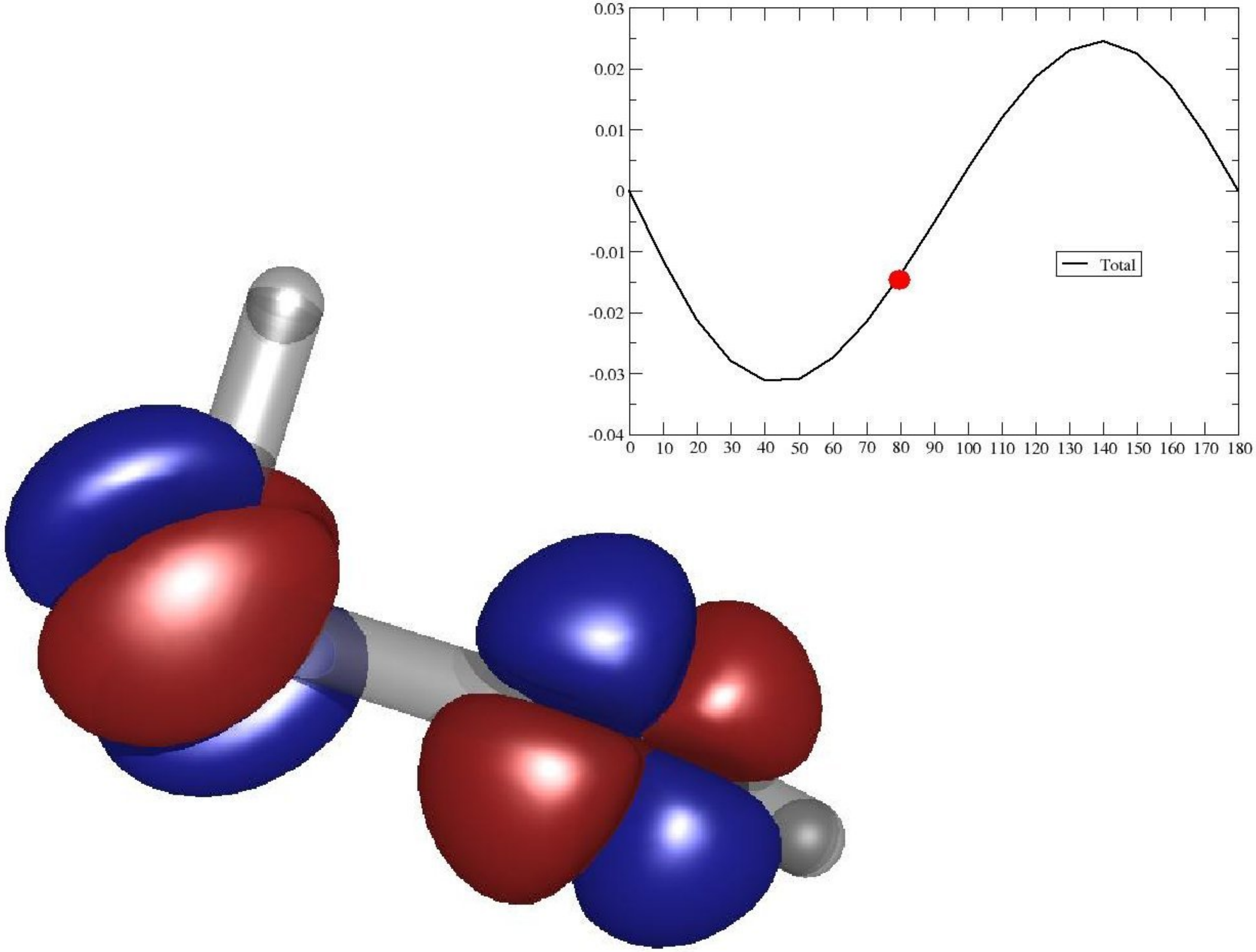
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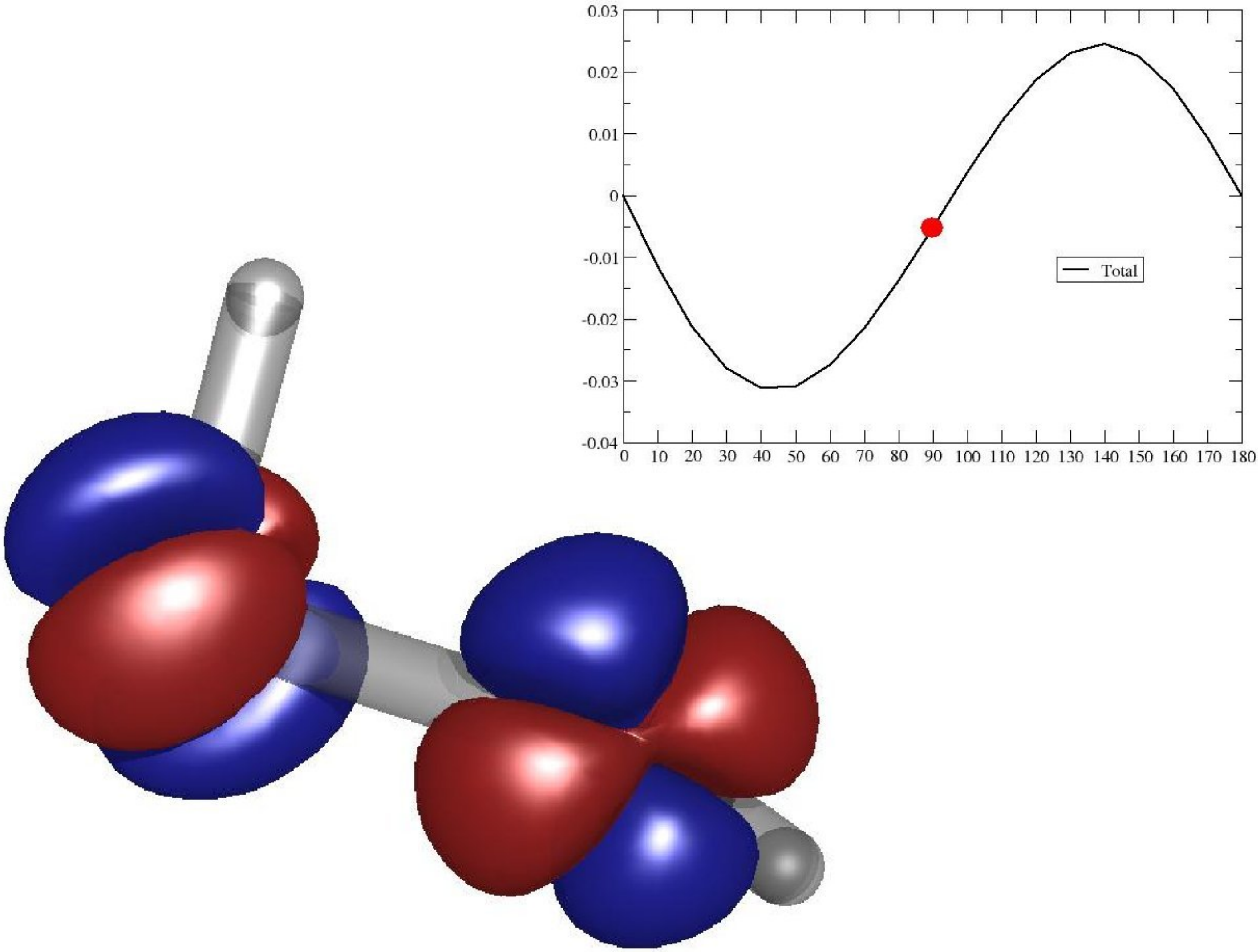
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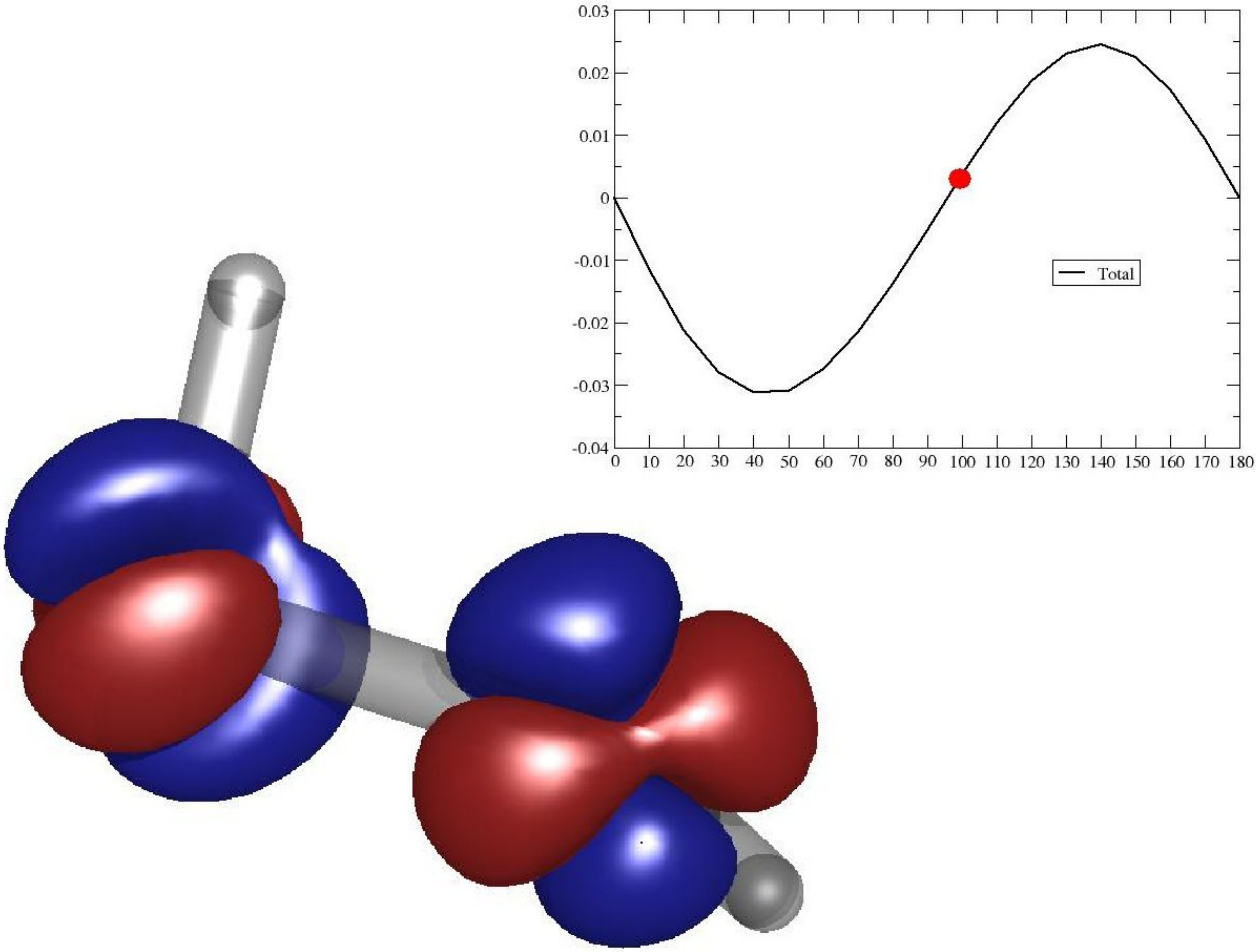
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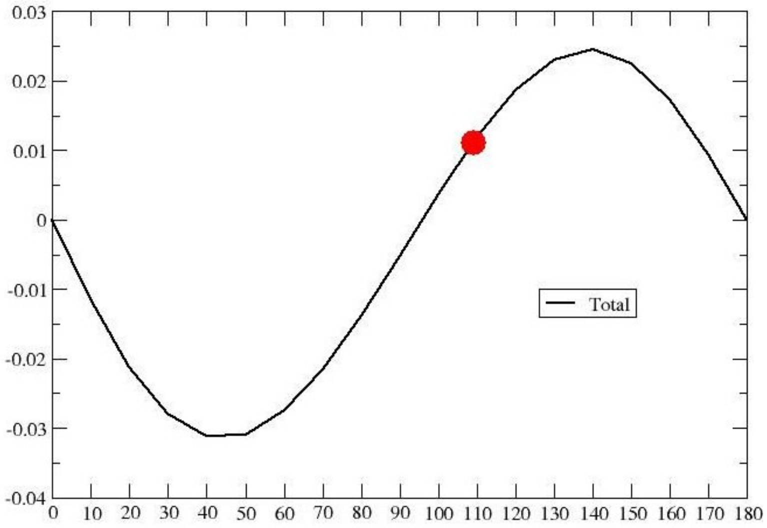
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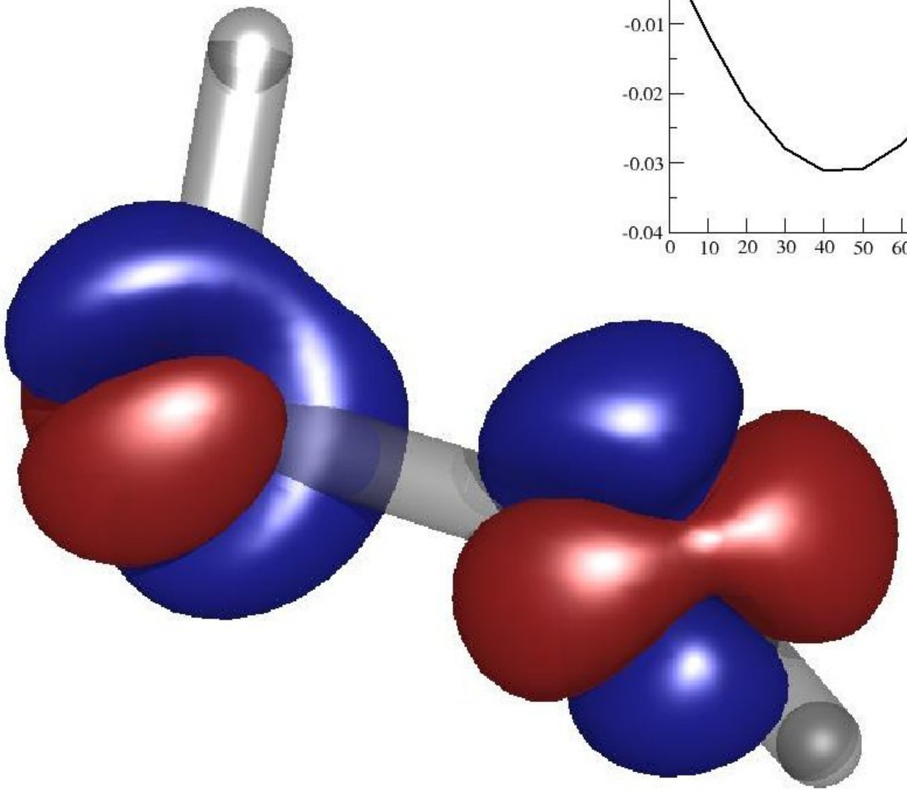

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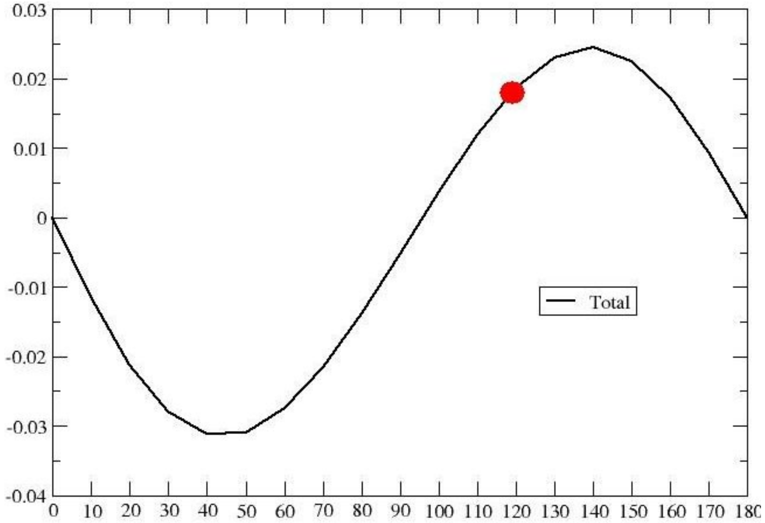
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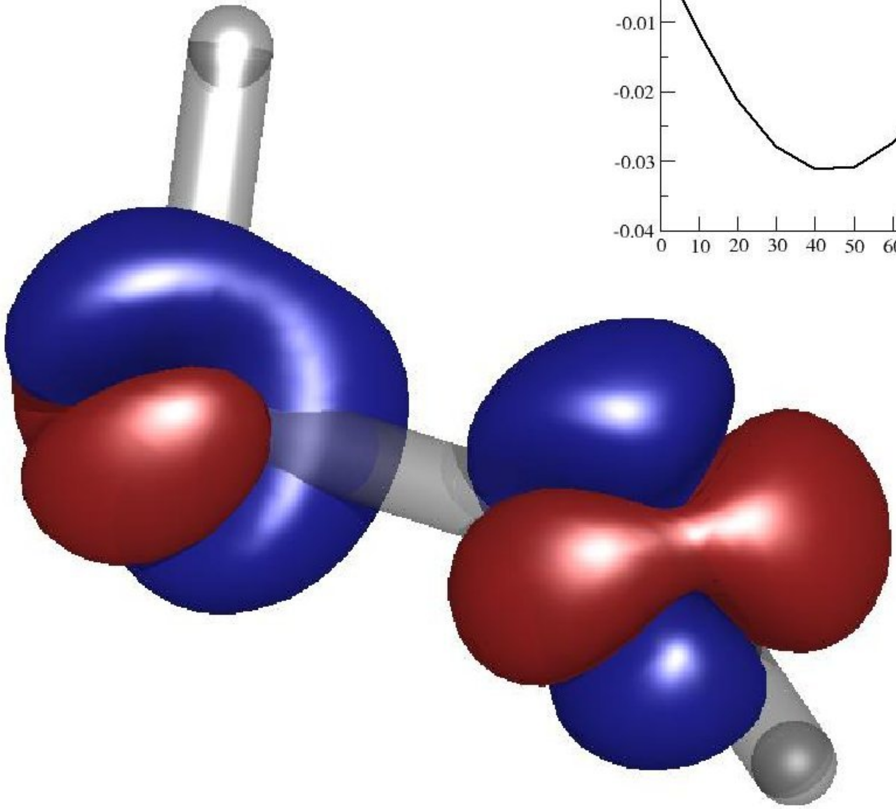

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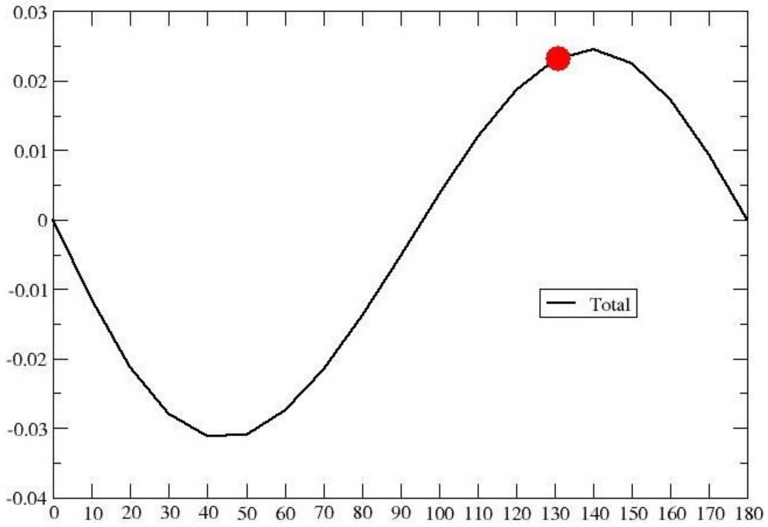
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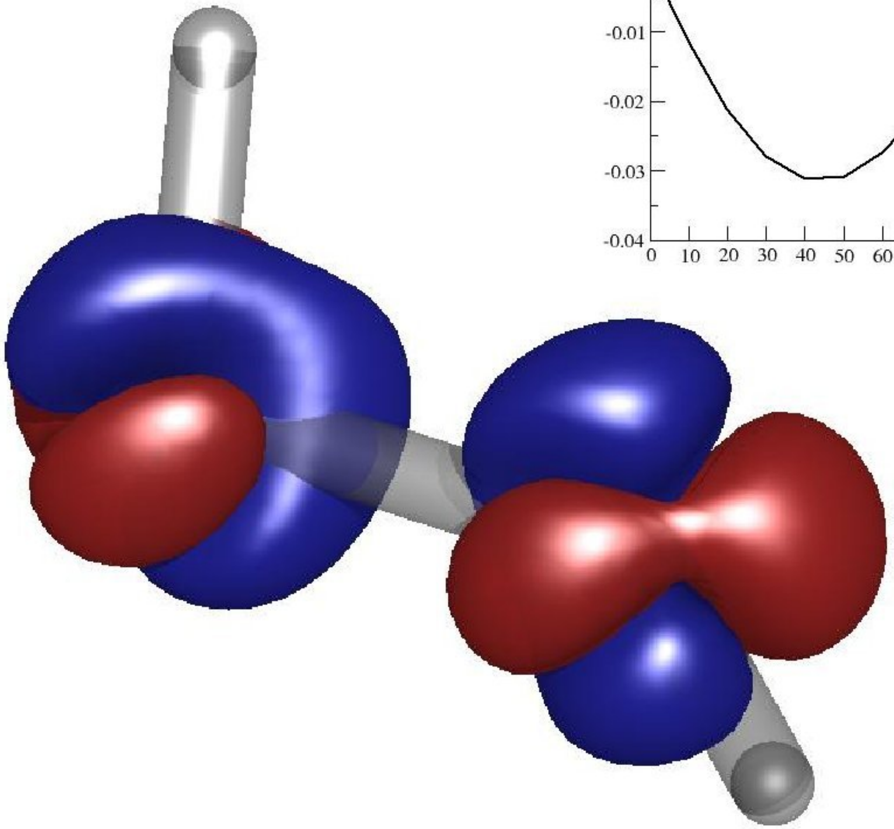

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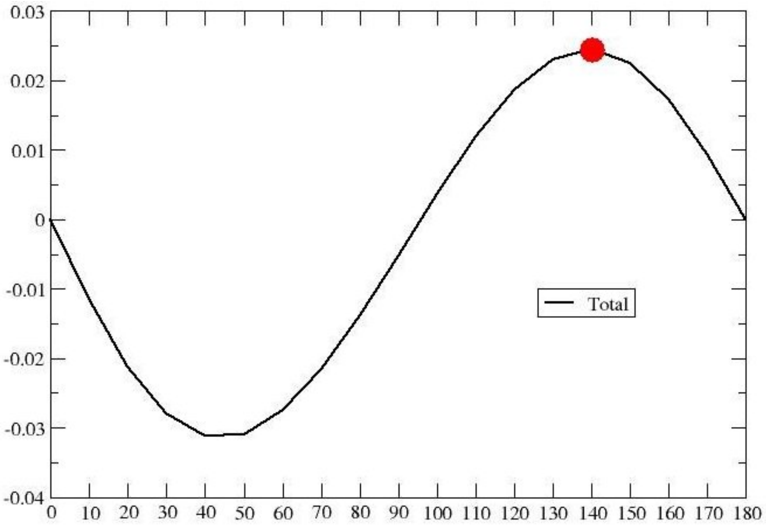
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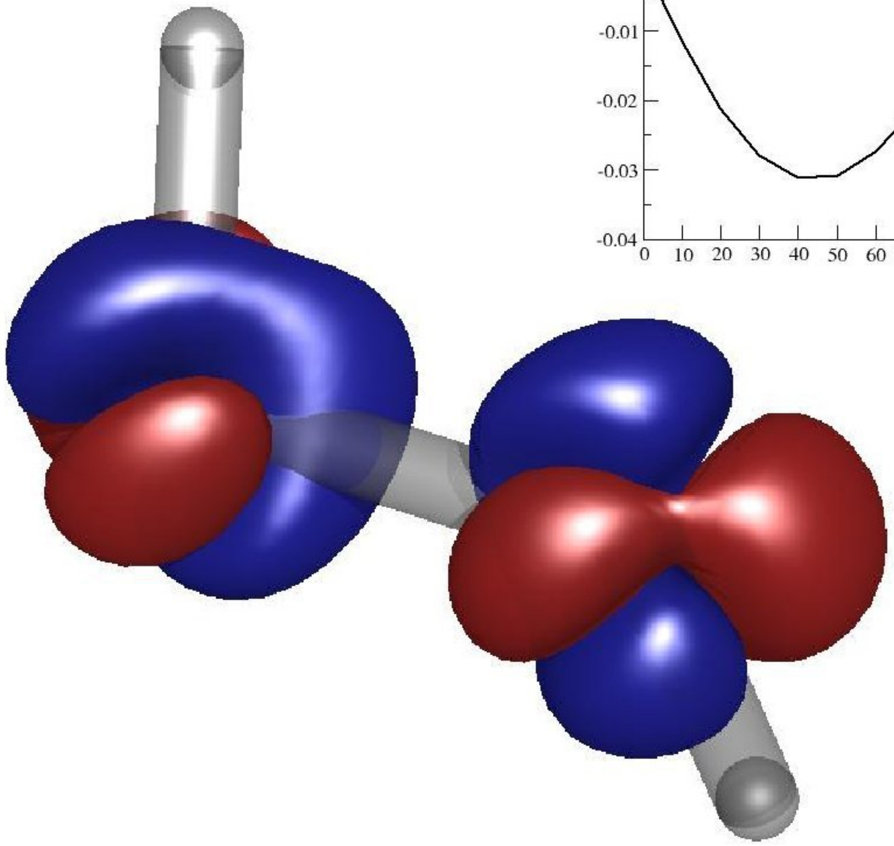

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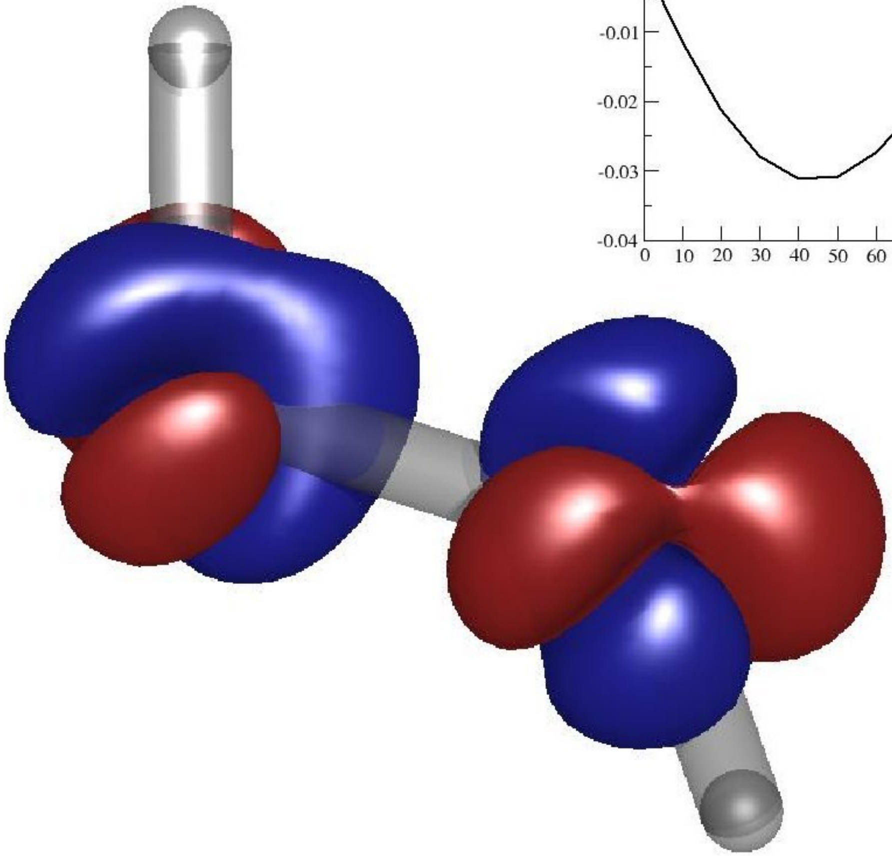

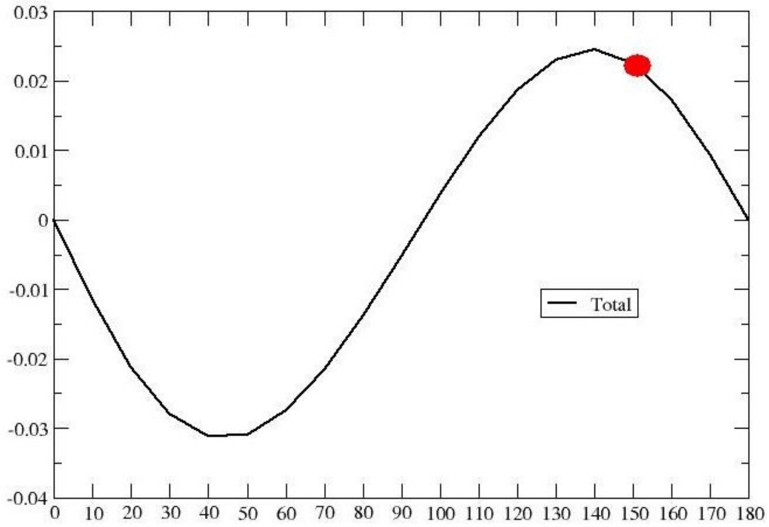

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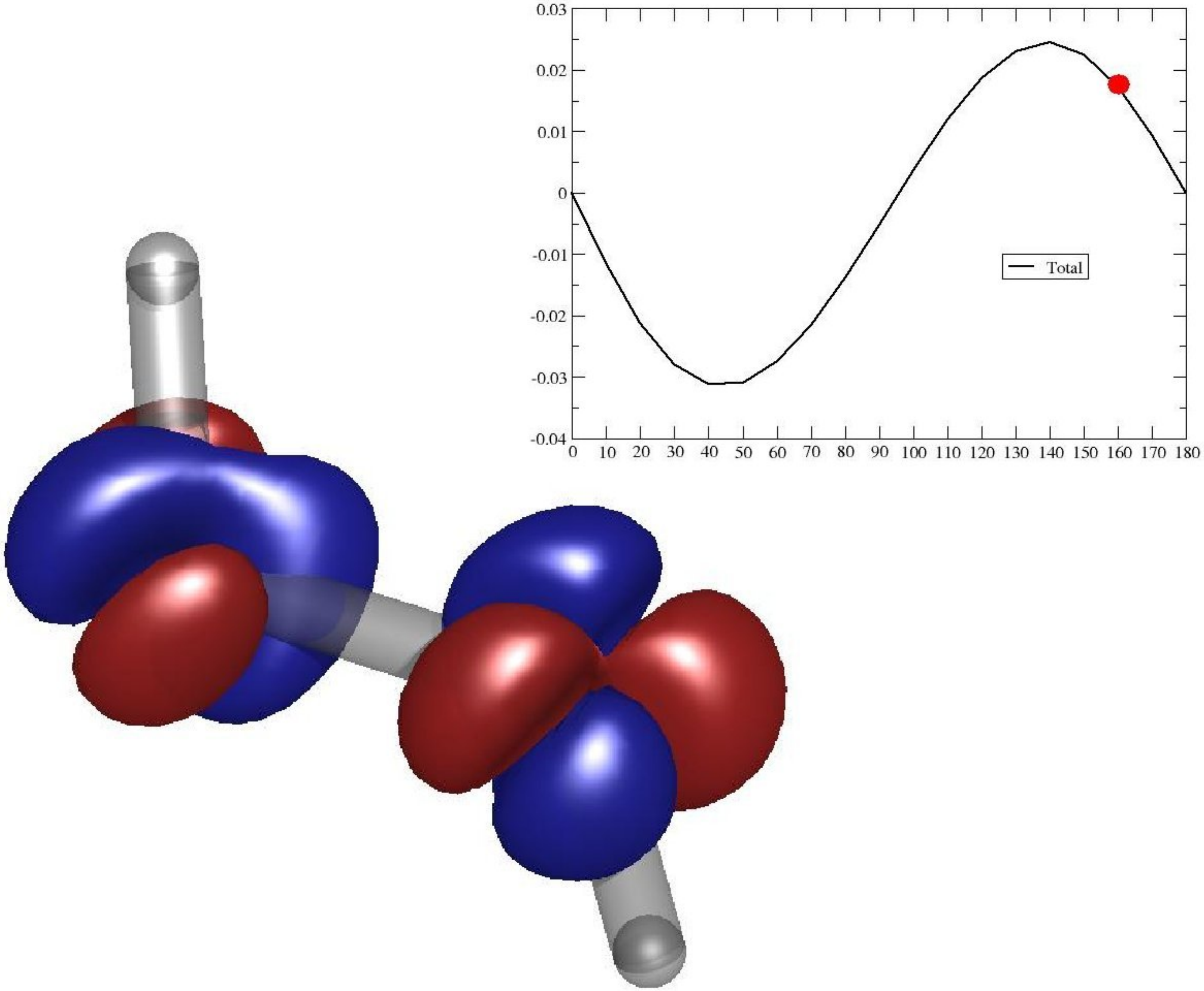
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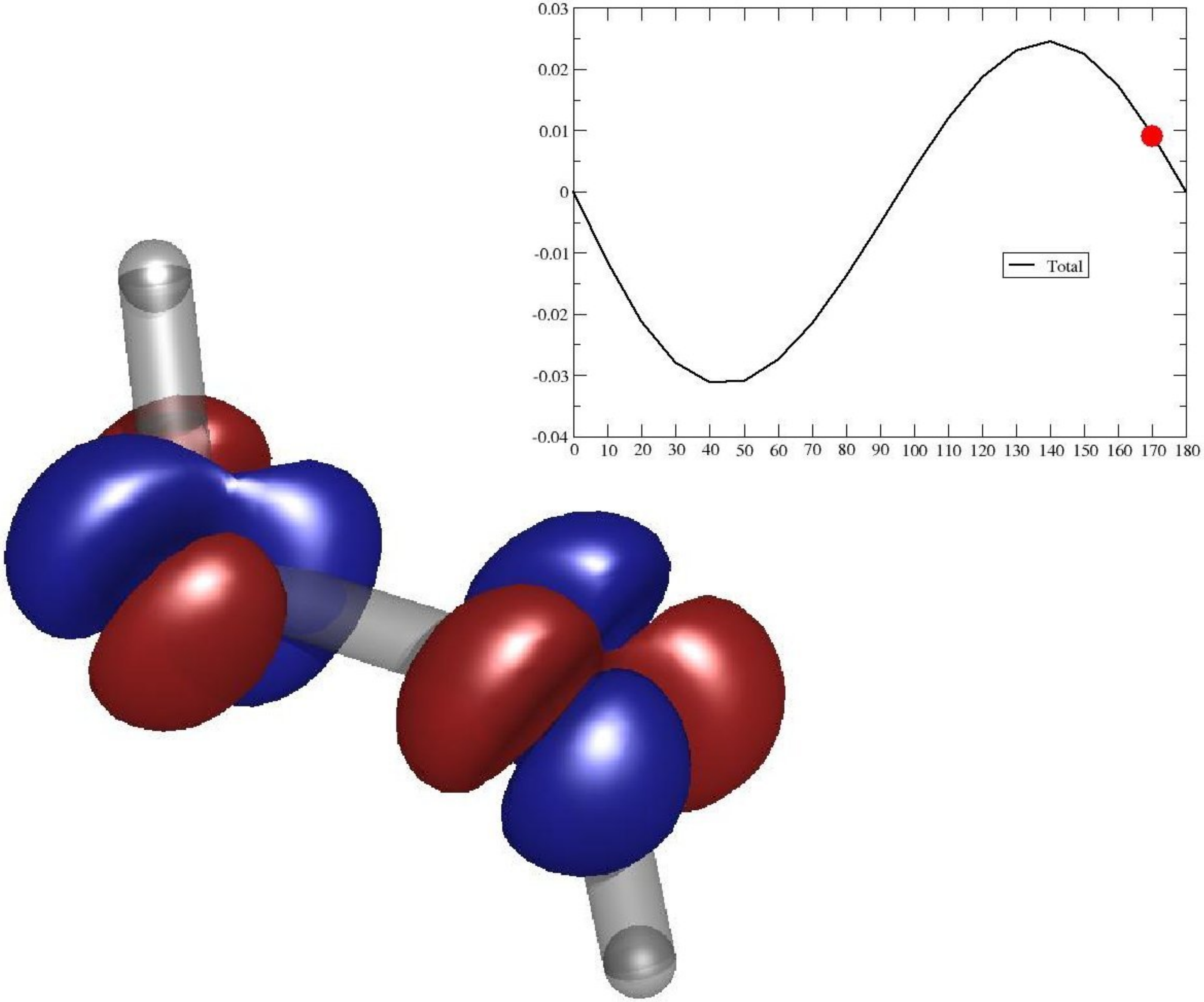
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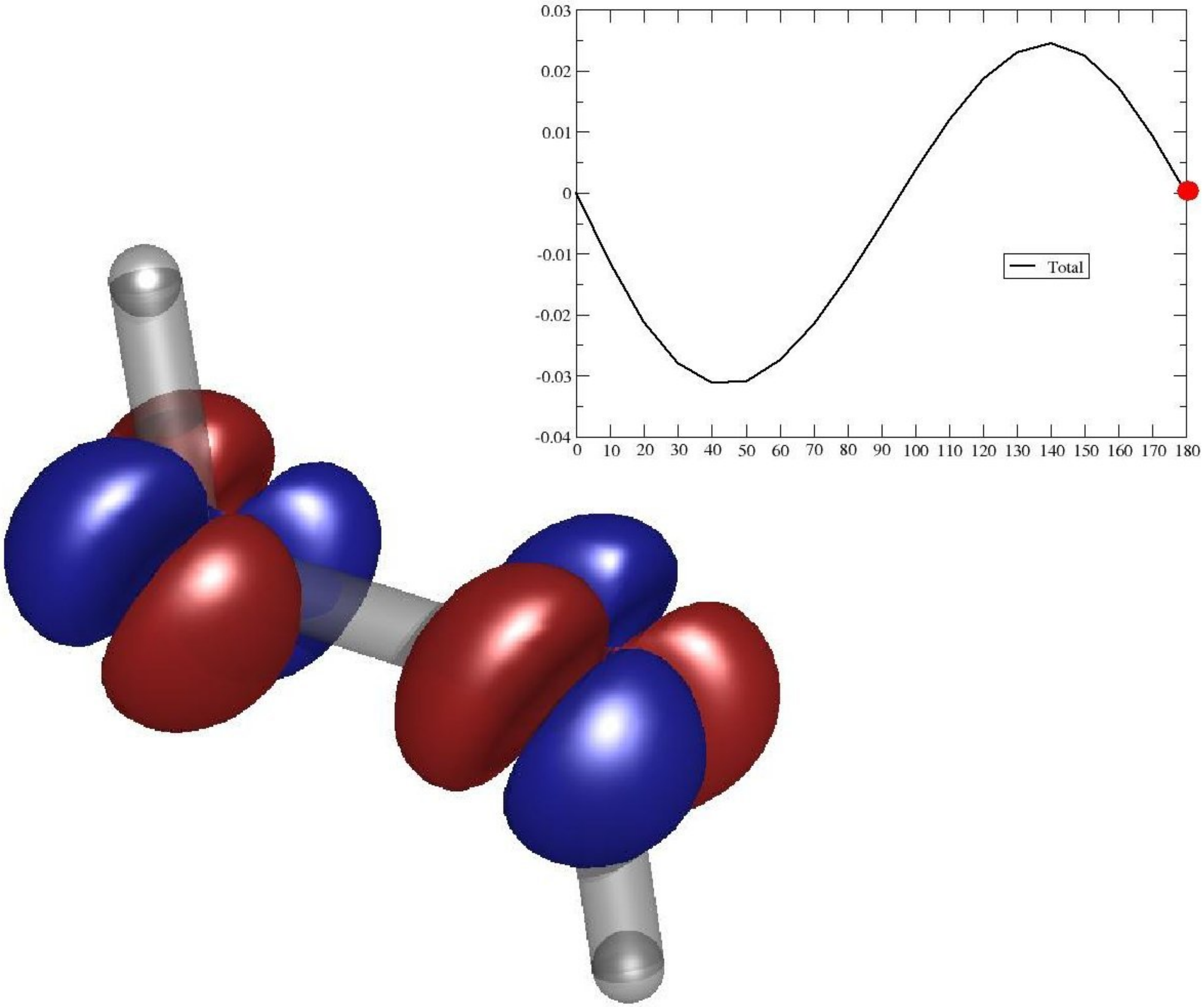
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2D plots of the γ_5 density around the Te nucleus

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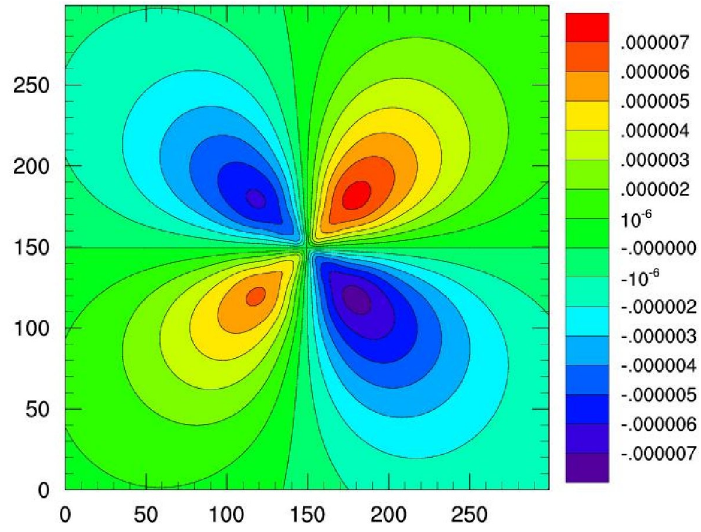

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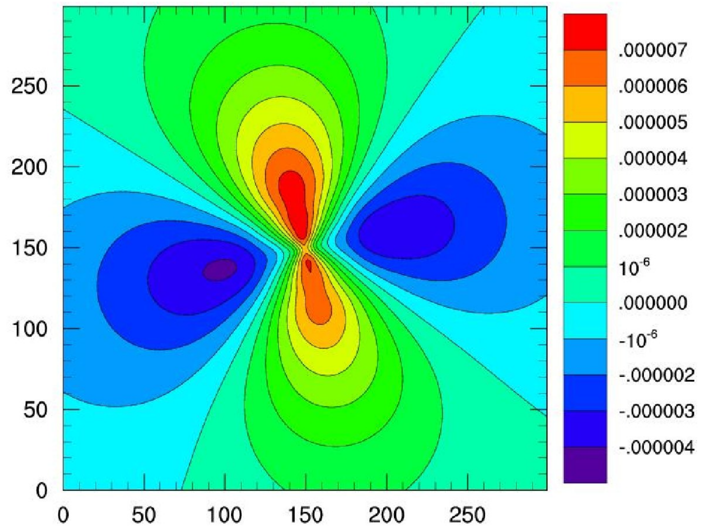

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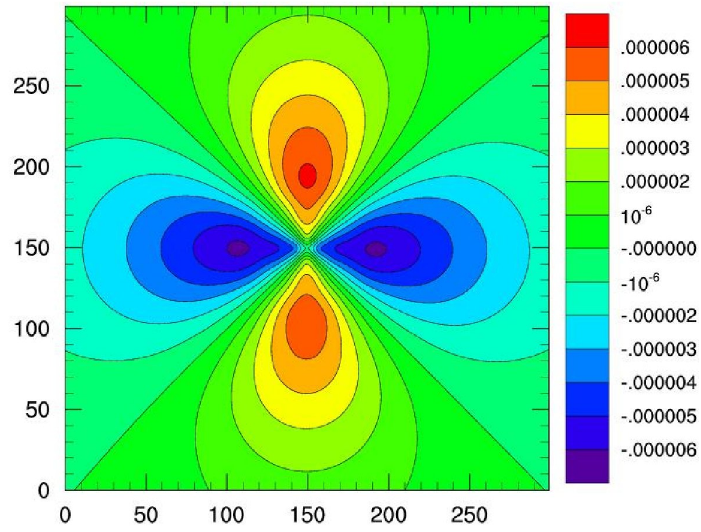

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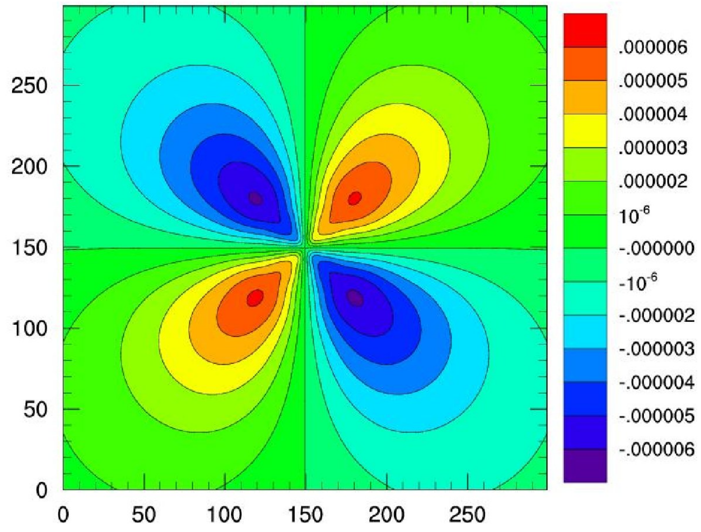


Projection analysis of expectation values

Radovan Bast, Anton Koers, André Severo Pereira Gomes, Miroslav Iliaš, Lucas Visscher, Peter Schwerdtfeger, and Trond Saue, PCCP (2010)

$$E_{PV} = \sum_K E_{PV}^K; \quad E_{PV}^K = \frac{G}{2\sqrt{2}} Q_W^K \sum_i \langle \psi_i | \gamma_5 \rho_K | \psi_i \rangle$$

- ✔ Molecular orbitals (MOs) are expanded in atomic orbitals (AOs):

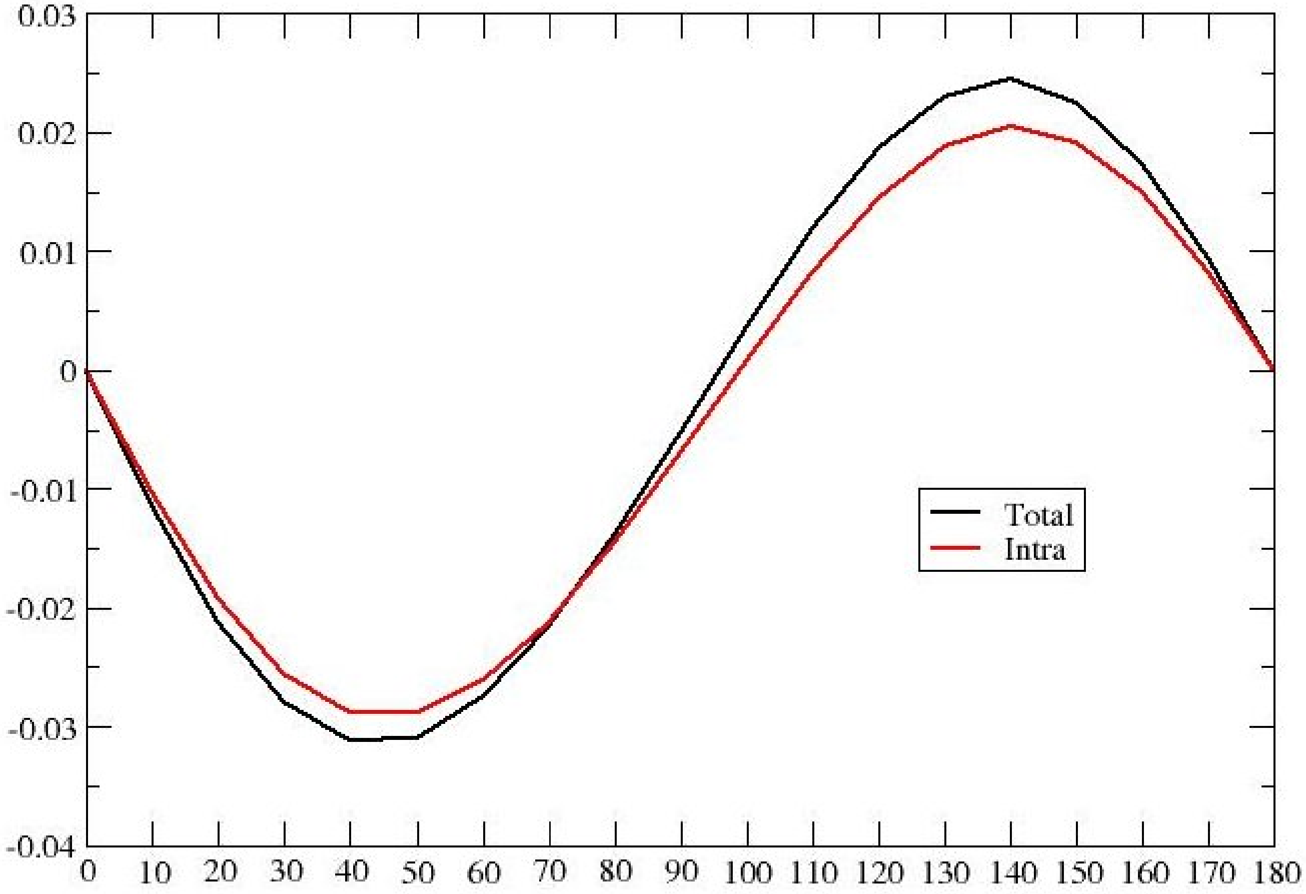
$$|\psi_i\rangle = \sum_{Aj} \left|\psi_j^A\right\rangle c_{ji}^A + \left|\psi_i^{\mathrm{pol}}\right\rangle$$

giving

$$\left\langle \Psi \left| \hat{H}_{PV}^A \right| \Psi \right\rangle = \underbrace{\sum_{ijkB} \left\langle \psi_j^B \left| \hat{H}_{PV}^A \right| \psi_k^B \right\rangle c_{ji}^{B*} c_{ki}^B}_{\text{intra-atomic}} + (\text{inter-atomic:} B \neq C) + (\text{pol})$$

Projection analysis of H_2X_2 compounds

Radovan Bast, Anton Koers, André Severo Pereira Gomes, Miroslav Iliaš, Lucas Visscher, Peter Schwerdtfeger, and Trond Saue, PCCP (2010)

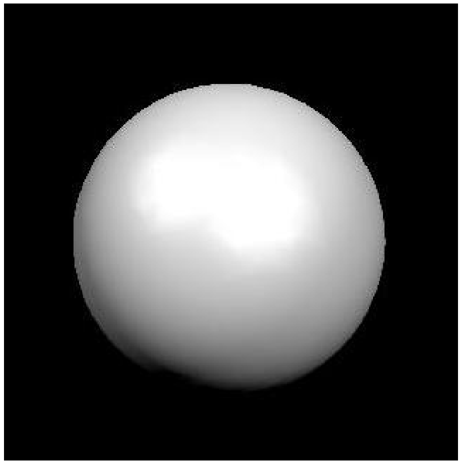


E_{PV}^{Te} is completely dominated by intra-atomic contributions from the same center.

Relativistic atomic orbitals

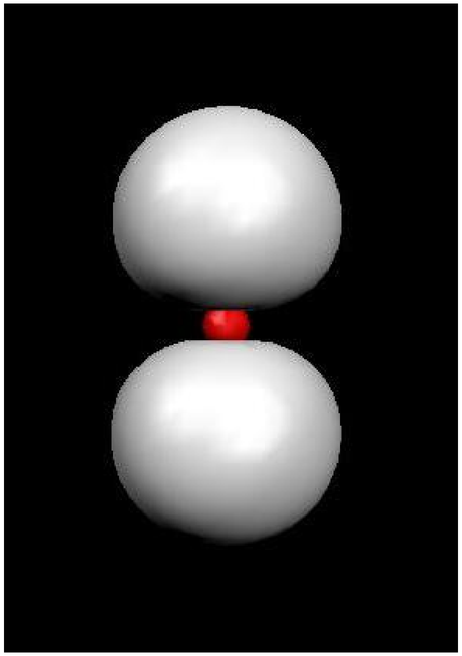
$$\psi^{\mathrm{NR}}(r,\theta,\phi) = R(r)Y_{lm}(\theta,\phi) \Rightarrow \psi^{\mathrm{R}}(r,\theta,\phi) = \left[\begin{array}{c} R^L(r)\chi_{\kappa,m_j}(\theta,\phi) \\ iR^S(r)\chi_{-\kappa,m_j}(\theta,\phi) \end{array} \right]$$

	$s_{1/2}$	$p_{1/2}$	$p_{3/2}$	$d_{3/2}$	$d_{5/2}$
j	1/2	1/2	3/2	3/2	5/2
κ	-1	+1	-2	+2	-3



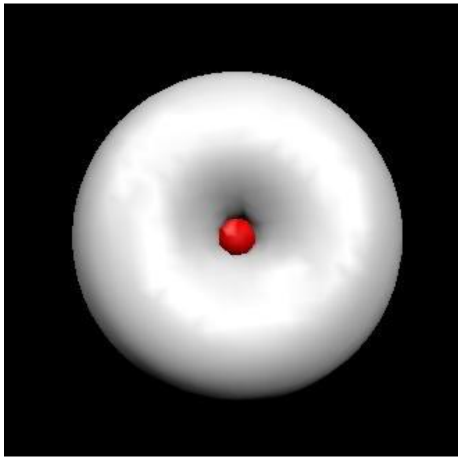
$2(s,p)_{1/2,1/2}$

(z-axis anywhere)



$2(p,d)_{3/2,1/2}$

(z-axis in plane)



$2(p,d)_{3/2,3/2}$

(z-axis out of plane)

Intraatomic contributions

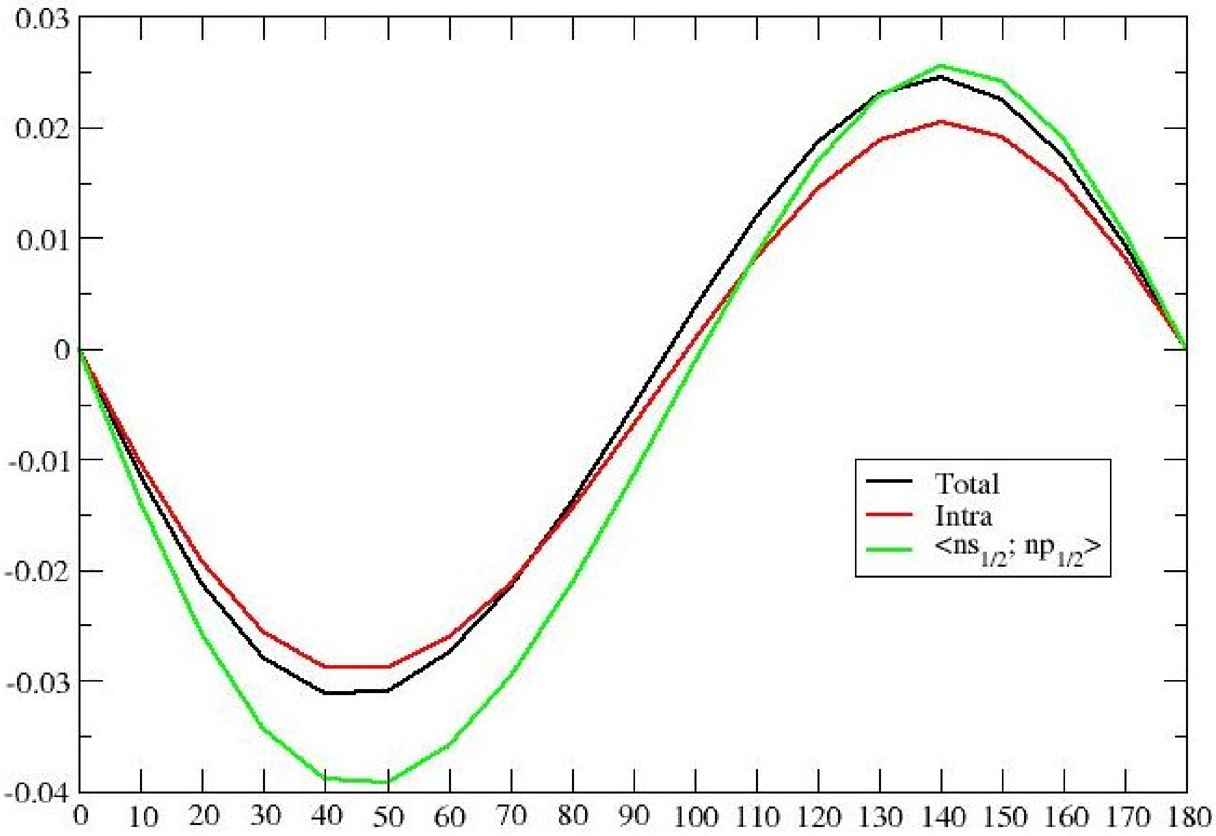
- ✔ Contribution from a pair of atomic orbitals:

$$\left\langle \psi_1^A \left| \hat{H}_{PV}^A \right| \psi_2^A \right\rangle = i\frac{G_F}{2\sqrt{2}} Q_{W;A} \Big[\left\langle R_1^L \left|\rho_A\right| R_2^S \right\rangle_r \left\langle \chi_{\kappa_1,m_1} \mid \chi_{-\kappa_2,-m_2} \right\rangle_{\theta,\phi} - \left\langle R_1^S \left|\rho_A\right| R_2^L \right\rangle_r \left\langle \chi_{-\kappa_1,m_1} \mid \chi_{\kappa_2,m_2} \right\rangle_{\theta,\phi} \Big]$$

- ✔ Angular integration gives: $\kappa_1 = -\kappa_2; \quad m_{j_1} = m_{j_2}$,
  that is, coupling only occurs through pairs $\left(s_{1/2}, p_{1/2}\right)$, $(p_{3/2}, d_{3/2})$, etc.

- ✔ For point nuclei radial integration shows that
  mixing is only possible between $s_{1/2}$ and $p_{1/2}$ orbitals.

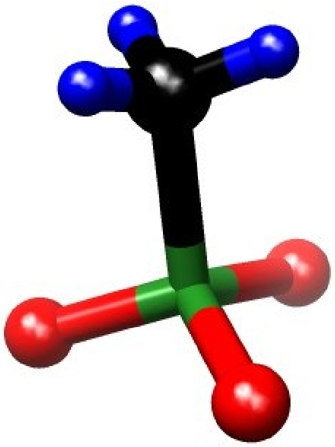
Dominant intra-atomic contribution



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
$<ns_{1/2}\|\widehat{H}^X_{\mathrm{pv}}\|np_{1/2}>$	-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 $p_{1/2}$.

Conclusion and perspectives



- A computational protocol and analysis tools have been developped for the study of parity violation in molecular systems
- Chirality is induced in the second coordinaton sphere of the compounds syntesized so far
- In future work we will concentrate on chiral derivatives of methyltrioxorhenium (MTO)

- PV arises from a specific mixing of valence $s_{1/2}$ and $p_{1/2}$ orbitals on a single center induced by a chiral molecular field
- PV is extremely sensitive to the chemical environment; this is a challenge, *but also means that it is chemically interesting.*

Thanks to:

Radovan Bast (Tromsø)	Jeanne Crassous (Rennes)	Peter Schwerdtfeger (Auckland)
Christian Chardonnet (Paris)	Benôit Darquié (Paris	Pierre Asselin (Paris)
Anne Amy-Klein(Paris)	Christophe Daussey (Paris)	Thérèse Huet (Lille)

Perspective

Buridan's ass

In a conversation between Albert Einstein and the neurobiologist George Wald, Einstein asked:
"Why do you think the natural amino acids are all left-handed?"
Einstein went on to say:
"I have wondered for years how the electron came out to be negative. Negative and positive are perfectly symmetrical principles in physics, so why is the electron negative? All I could think of was, the negative electron won in the fight."
Wald reports that he answered:
"That is exactly what I think of those left-handed amino acids—they won in the fight."