Improvements on Magnetically Induced Current Density and Derived Properties:

- Open Shell Systems
- Divergenceless Induced Current Density

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Electric and Magnetic Properties

In the presence of the time-independent external perturbation,for example, spatially nonuniform electric and magnetic fields $\boldsymbol{E}$ and $\boldsymbol{B}$, and of an intramolecular permanent magnetic dipole moment $\boldsymbol{\mu}_I$ on nucleus I, it is expedient to represent the energy of the molecule in a singlet electronic state as

$$
\begin{aligned}
W_a =& W_a^{(0)} - \mathcal{M}_\alpha^{(0)} E_\alpha - \frac{1}{2}\alpha_{\alpha\beta} E_\alpha E_\beta - \frac{1}{6}\beta_{\alpha\beta\gamma} E_\alpha E_\beta E_\gamma - \frac{1}{24}\gamma_{\alpha\beta\gamma\delta} E_\alpha E_\beta E_\gamma E_\delta + \\
&- \frac{1}{120}\delta_{\alpha\beta\gamma\delta\epsilon} E_\alpha E_\beta E_\gamma E_\delta E_\epsilon - \alpha_{\alpha,\beta\gamma} E_\alpha E_{\gamma\beta} - \alpha_{\alpha,\beta\gamma\delta} E_\alpha E_{\delta\gamma\beta} + \\
&- \frac{1}{2}\alpha_{\alpha\beta,\gamma\delta} E_{\beta\alpha} E_{\delta\gamma} - \alpha_{\alpha\beta,\gamma\delta\epsilon} E_{\beta\alpha} E_{\epsilon\delta\gamma} - \frac{1}{2}\chi_{\alpha\beta} B_\alpha B_\beta + \\
&- \frac{1}{24}\eta_{\alpha\beta\gamma\delta} B_\alpha B_\beta B_\gamma B_\delta - \chi_{\alpha,\beta\gamma} B_\alpha B_{\gamma\beta} - \chi_{\alpha,\beta\gamma\delta} B_\alpha B_{\delta\gamma\beta} + \\
&- \frac{1}{2}\chi_{\alpha\beta,\gamma\delta} B_{\beta\alpha} B_{\delta\gamma} - \chi_{\alpha\beta,\gamma\delta\epsilon} B_{\beta\alpha} B_{\epsilon\delta\gamma} + \sigma'_{\alpha\beta}\mu_{I\alpha} B_\beta + \\
&- \frac{1}{2}\chi_{\alpha\beta\gamma} B_\alpha B_\beta E_\gamma - \frac{1}{4}\chi_{\alpha\beta\gamma\delta} B_\alpha B_\beta E_\gamma E_\delta + \sigma'_{\alpha\beta\gamma}\mu_{I\alpha} B_\beta E_\gamma + \cdots
\end{aligned}
$$

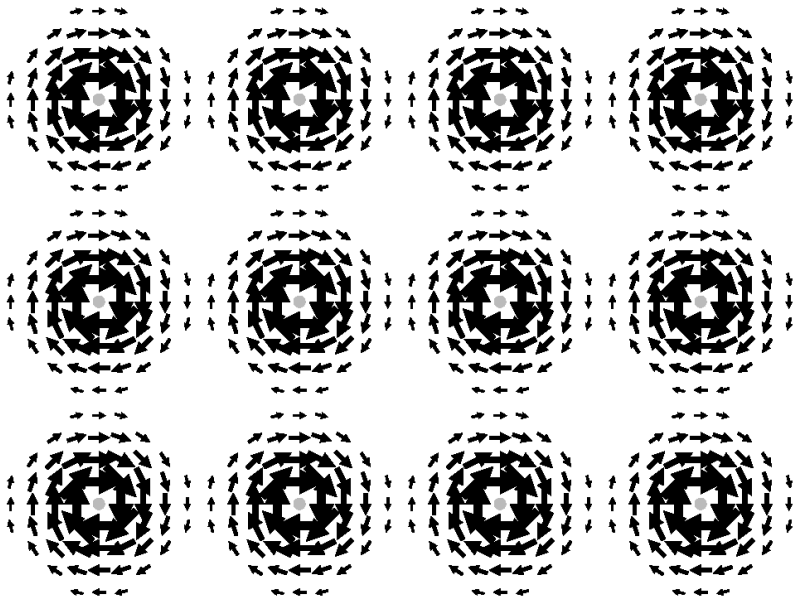
where W is the energy and Einstein implicit sum over repeated Greek indices is adopted.

The intrinsic molecular properties can then be expressed as partial derivatives in the limit of vanishing fields. For instance,

$$
\begin{aligned}
\mathcal{M}_{\alpha}^{(0)} &= -\left(\frac{\partial W}{\partial E_{\alpha}}\right)_{E_{\alpha}\to 0} \\
m_{\alpha}^{(0)} &= -\left(\frac{\partial W}{\partial B_{\alpha}}\right)_{B_{\alpha}\to 0} \\
\alpha_{\alpha\beta} &= -\left(\frac{\partial^2 W}{\partial E_{\alpha}\partial E_{\beta}}\right)_{E_{\alpha}\to 0} \\
\beta_{\alpha\beta\gamma} &= -\left(\frac{\partial^3 W}{\partial E_{\alpha}\partial E_{\beta}\partial E_{\gamma}}\right)_{E_{\alpha}\to 0} \\
\chi_{\alpha\beta} &= -\left(\frac{\partial^2 W}{\partial B_{\alpha}\partial B_{\beta}}\right)_{B_{\alpha}\to 0} \\
\sigma_{\alpha\beta}^{I} &= \left(\frac{\partial^2 W}{\partial \mu_{I\alpha}\partial B_{\beta}}\right)_{\mu_{I\alpha},B_{\beta}\to 0}
\end{aligned}
\tag{1}
$$

The Induced Current Density Picture

When the magnetic field is applied a current is generated.



An easy approach to derive magnetic properties is to use the quantum mechanical induced current density tensor at first order $\mathcal{J}_\alpha^{B_\delta}$ defined as

$$\mathcal{J}_\alpha^{B_\beta}(\boldsymbol{r}) = \frac{\partial}{\partial B_\beta} J_\alpha^{\boldsymbol{B}}(\boldsymbol{r}) \qquad J_\alpha^{\boldsymbol{B}}(\boldsymbol{r}) = -\frac{e}{m_e} \Re \left[\hat{\pi}_\alpha \gamma \left(\boldsymbol{r}; \boldsymbol{r}' \right) \right]_{\boldsymbol{r}'=\boldsymbol{r}}$$

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NMR Chemical Shifts and Magnetizabilites

In the case of a **closed shell** molecule the NMR chemical shift can be computed using the Biot-Savart law according to

$$\sigma_{\alpha\beta}^{\boldsymbol{IB}} = \left.\frac{\partial^2 W^{\boldsymbol{IB}}}{\partial \mu_{I_\alpha} \partial B_\beta}\right|_{\boldsymbol{\mu}_I, \boldsymbol{B}\to\boldsymbol{0}} = -\frac{\mu_0}{4\pi}\epsilon_{\lambda\alpha\gamma}\int \frac{r_\gamma - R_{I\gamma}}{|\boldsymbol{r}-\boldsymbol{R}_I|^3}\mathcal{J}_\lambda^{B_\beta}(\boldsymbol{r})\, d^3r$$

and the magnetizability as

$$\begin{aligned}
\chi_{\mu\lambda}^{\boldsymbol{B}} = -\left.\frac{\partial^2 W^{\boldsymbol{BB}}}{\partial B_\mu \partial B_\lambda}\right|_{\boldsymbol{B}\to\boldsymbol{0}} &= \frac{1}{4}\epsilon_{\alpha\beta\gamma}\frac{\partial^2 B_\beta B_\delta}{\partial B_\mu \partial B_\lambda}\int r_\gamma\, \mathcal{J}_\alpha^{B_\delta} d^3r = \\
&= \frac{1}{4}\epsilon_{\alpha\beta\gamma}\left(\delta_{\lambda\beta}\delta_{\mu\delta} + \delta_{\lambda\delta}\delta_{\mu\beta}\right)\int r_\gamma \mathcal{J}_\alpha^{B_\delta} d^3r = \\
&= \frac{1}{4}\epsilon_{\alpha\lambda\gamma}\int r_\gamma \mathcal{J}_\alpha^{B_\mu} d^3r + \frac{1}{4}\epsilon_{\alpha\mu\gamma}\int r_\gamma \mathcal{J}_\alpha^{B_\lambda} d^3r = \\
&= \frac{1}{4}\int (\epsilon_{\lambda\gamma\alpha}\mathcal{J}_\alpha^{B_\mu} + \epsilon_{\mu\gamma\alpha}\mathcal{J}_\alpha^{B_\lambda}) r_\gamma\, d^3r
\end{aligned}$$

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Hückel's rule would suggests a paratropic current for the two coupled 4n annulenes which form the belt in both EB[6]CPP (**1**) and MB[6]CPP (**2**);

DFT

The calculation confirms the presence of a paratropic belt-current (PBC).

Can the PBC be verified also from experimental data ?

HOW

Disentangling the contributions to the proton magnetic shielding in:

- Curvature effect;
- Genuine belt-current.

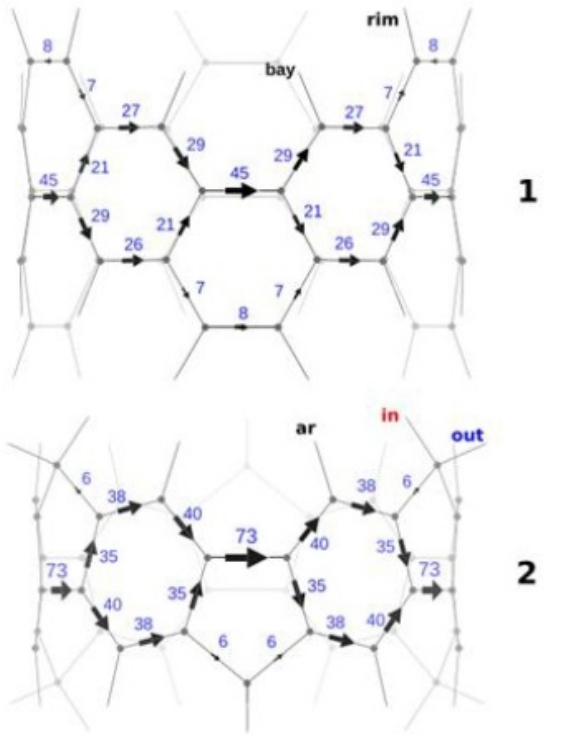

Figure 1. Net C–C bond current strengths for a magnetic field parallel to the main symmetry axis and pointing from bottom to top. Values aside each arrow represent the percentage relationship with respect to the benzene current strength. Circulation from left to right are globally paratropic/antiaromatic.

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ANISOTROPY EFFECT

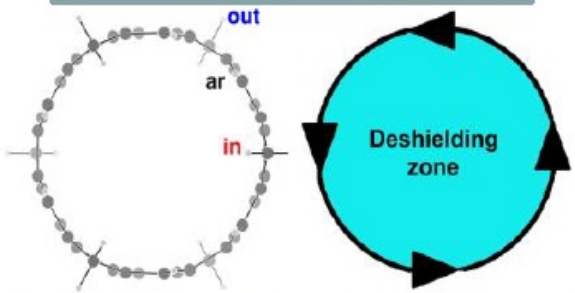

Figure 2. Left: top view of 2. Right: schematic representation of the paratropic current flowing in a tiny wire having the nanobelt radius.

Scheme 1. Fluorene 3, Folded Fluorene 4, Half Nanobelts 5 and 6

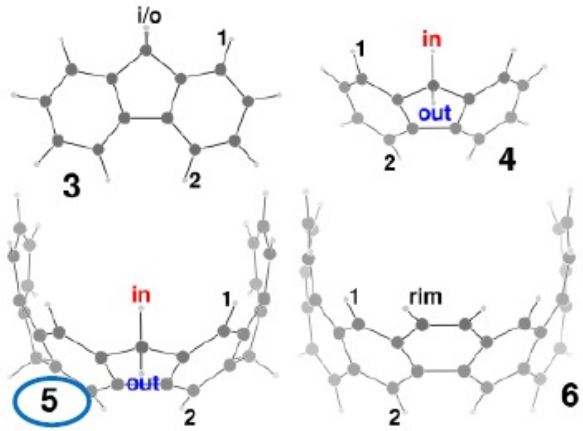

Table 1. CSGT-BCP ^{1}H NMR δ's in ppm at the DFT/6-311+G(2d,p)//DFT/6-31G(d) Level

DFT	1-H_{rim}	1-H_{bay}	2-H_{ar}	2-H_{in}	2-H_{out}
B3LYP	7.55	8.39	8.08	4.01	4.21
M06-2X	7.45	8.35	7.82	3.76	4.21
B97-2	7.56	8.40	8.11	4.08	4.22
expt[9,10]	7.51	8.26	7.86	4.09	4.29

0.20 ppm

Table 2. CSGT-BCP ^{1}H NMR δ's in ppm at the B97-2/6-311+G(2d,p) Level

up down

mol	H_{ar1}		H_{ar2}	H_{in}	H_{out}
3	7.56	up	7.87	3.78	3.78
4	7.39		7.50	3.18	4.28
5	7.27		7.29	3.01	4.11

1.1 ppm

Consolidated data

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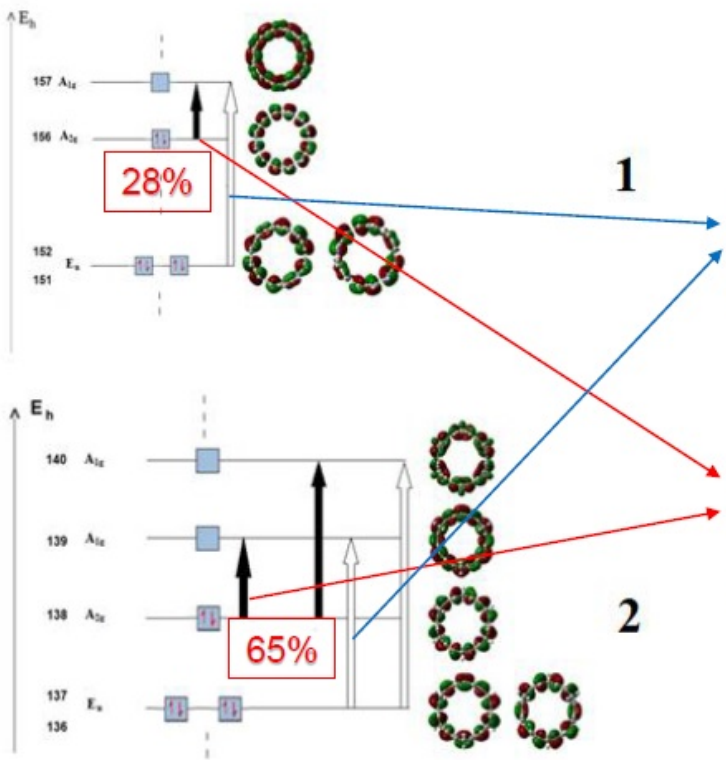


D_{3d}

$E_u \otimes A_{1g} = E_u$ transforming as (T_x; T_y), active for B_z giving a diatropic contribution; HOMO-1 → LUMO

$A_{2g} \otimes A_{1g} = A_{2g}$ transforming as R_z, active for B_z giving a paratropic contribution; HOMO→LUMO

Figures S12 and S13: Contributions to total current density for 1 and 2 respectively given only from frontier orbitals. White arrows indicate a diamagnetic current while black arrows a paramagnetic current.

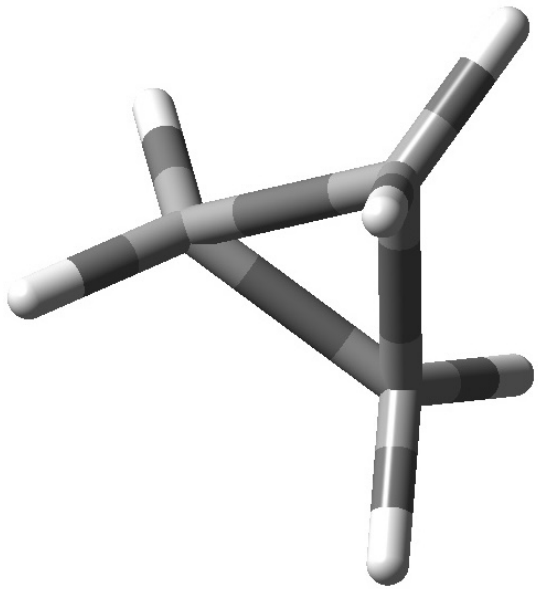


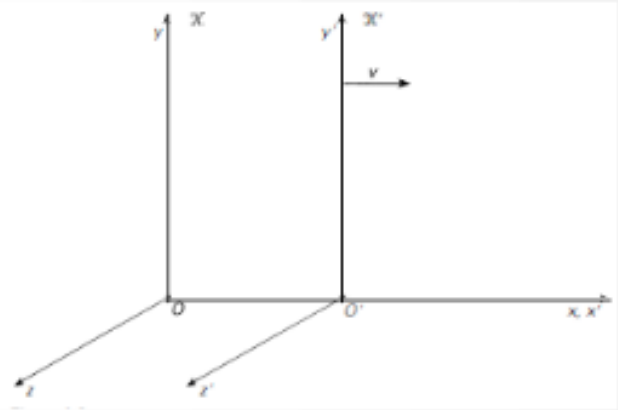
Table: Magnetizability of Cyclopropane in $10^{-29}\mathrm{JT}^{-2}$ calculated at B972/6-31G(d)//B972/6-311+G(2d,p) level of theory

	calc	exp[a]	exp[b]
$\chi_{\parallel}$	-77.8	-75 ± 2	-77.9 ± 1.8
$\chi_{\perp}$	-58.9	-60 ± 2	-58.7 ± 1.5

[a] JACS **1983**, 105, 5569; [b] J. Phys. Chem. **1985**, 89, 1309.

Open-Shell Molecules

LORENTZ TRANSFORMATION AND SPECIAL RELATIVITY



$$x' = \frac{x - \left(\frac{v}{c}\right)ct}{\sqrt{1 - \frac{v^2}{c^2}}},$$
$$y' = y,$$
$$z' = z,$$
$$ct' = \frac{ct - \left(\frac{v}{c}\right)x}{\sqrt{1 - \frac{v^2}{c^2}}},$$

From K to K'

$$x = \frac{x' + vt'}{\sqrt{1 - \frac{v^2}{c^2}}},$$
$$y = y',$$
$$z = z',$$
$$t = \frac{t' + \frac{vx'}{c^2}}{\sqrt{1 - \frac{v^2}{c^2}}},$$

From K' to K

1. Physical laws have the same form in all inertial reference systems;
2. The speed of light in vacuum c has the same value in all inertial reference systems.

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Relativistic Corrections

To handle in the correct phenomenological way spin effects, our starting point is the Dirac Hamiltonian for an electron in a nonvanishing electromagnetic field

$$\hat{H}_D = c\boldsymbol{\alpha} \cdot \hat{\boldsymbol{\pi}} + \beta m_e c^2 + \left[\hat{V} - e\Phi\right] \boldsymbol{I}_4 \tag{2}$$

where

$$\boldsymbol{\alpha} = \begin{pmatrix} 0 & \hat{\boldsymbol{\sigma}} \\ \hat{\boldsymbol{\sigma}} & 0 \end{pmatrix} \qquad \boldsymbol{\beta} = \begin{pmatrix} \boldsymbol{I}_2 & 0 \\ 0 & -\boldsymbol{I}_2 \end{pmatrix} \tag{3}$$

with $\boldsymbol{I}_n$ an identity matrix of dimensions $n \times n$ and $\hat{\boldsymbol{\sigma}}$ that is a vector operator collecting the Pauli matrices

$$\hat{\sigma}_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \quad \hat{\sigma}_y = \begin{pmatrix} 0 & -\mathrm{i} \\ \mathrm{i} & 0 \end{pmatrix} \quad \hat{\sigma}_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \tag{4}$$

The eigenvectors of $\hat{\sigma}_z$ are commonly indicated by

$$|\alpha\rangle \equiv \begin{pmatrix} 1 \\ 0 \end{pmatrix} \quad |\beta\rangle \equiv \begin{pmatrix} 0 \\ 1 \end{pmatrix}$$

To have a simpler description of this Hamiltonian a diagonalization procedure, called Foldy–Wouthuysen transformation of the Dirac Hamiltonian can be used. This procedure consists to put $\hat{H}_D$ into block diagonal form

$$\hat{H}_D \simeq \begin{pmatrix} \hat{h}_1 & 0 \\ 0 & \hat{h}_2 \end{pmatrix} \tag{5}$$

and to take the positive energy wavefunction part. Using this technique it is possible to obtain for a Coulomb like potential

$$\hat{H}_D \simeq m_e c^2 + \frac{\hat{\pi}^2}{2m_e} \boldsymbol{I}_2 + \frac{g\mu_\beta}{\hbar} \hat{\boldsymbol{s}} \cdot \boldsymbol{B} + \left[\hat{V} - e\Phi\right] \boldsymbol{I}_2 + \frac{\hat{\pi}^4}{8m_e^3 c^2} \boldsymbol{I}_2 + \frac{e}{2m_e^2 c^2} \hat{\boldsymbol{s}} \cdot \left[\hat{\boldsymbol{E}} \times \hat{\boldsymbol{\pi}}\right] \tag{6}$$

that is an approximated Breit-Pauli Hamiltonian where electric field operator is

$$\hat{\boldsymbol{E}} = \frac{Z_a\, e}{4\pi\varepsilon_0} \frac{\boldsymbol{r}}{|\boldsymbol{r}|^3} \tag{7}$$

μ_β is the Bohr magneton and g is the electron spin g-factor.

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The generalization of the previous Hamiltonian in the case of a molecular system is straightforward. Indeed, in the Born–Oppenheimer approximation, for applied static and uniform magnetic and eletric fields we have

$$\hat{H} = \sum_{k}^{n} \frac{\hat{\boldsymbol{\pi}}_k^2}{2m_\mathrm{e}} + \sum_{k}^{n} \frac{g\mu_\beta}{\hbar} \hat{\boldsymbol{s}}_k \cdot [\boldsymbol{\nabla} \times \boldsymbol{A}_k] + \sum_{k,a}^{n,N} \frac{e}{2m_\mathrm{e}^2 c^2} \hat{\boldsymbol{s}}_k \cdot \left[\hat{\boldsymbol{E}}_k^a \times \hat{\boldsymbol{\pi}}_k\right] - \sum_{k}^{n} e\Phi_k$$
$$+ \frac{e^2}{8\pi\varepsilon_0} \sum_{k,j}^{n,n}{}' \frac{1}{r_{kj}} - \frac{e^2}{8\pi\varepsilon_0} \sum_{a,k}^{N,n} \frac{Z_a}{r_{ak}} + \frac{e^2}{8\pi\varepsilon_0} \sum_{a,a'}^{N,N}{}' \frac{Z_a Z_{a'}}{R_{aa'}} \tag{8}$$

where here $\hat{\boldsymbol{E}}_k^a$ is the electric field operator defined as

$$\hat{\boldsymbol{E}}_k^a = \frac{Z_a\, e}{4\pi\varepsilon_0} \frac{\boldsymbol{r}_k - \boldsymbol{R}_a}{|\boldsymbol{r}_k - \boldsymbol{R}_a|^3} \tag{9}$$

In this section we have introduced a simplified expression of the one electron spin-orbit coupling Hamiltonian, that is strictly valid for a Coulomb like potential.

Many Body Induced Current Density

It is possible to introduce the concept of spin density matrix as

$$Q_\alpha(\boldsymbol{r};\boldsymbol{r}') = \int_{\eta_1'=\eta_1} \hat{s}_\alpha(1)\gamma\left(\boldsymbol{x}_1;\boldsymbol{x}_1'\right) d\eta_1 \tag{10}$$

Putting $\boldsymbol{r} = \boldsymbol{r}'$ we obtain the spin density, described by the axial vector

$$Q_\alpha(\boldsymbol{r}) \equiv Q_\alpha(\boldsymbol{r};\boldsymbol{r}) \tag{11}$$

In the limit of a central field the many body semirelativistic induced current density can be written neglecting the two spin-orbit coupling contribution as

$$\mathbf{J}(\boldsymbol{r}) = -\frac{e}{m_\mathrm{e}}\Re\left[\hat{\boldsymbol{\pi}}\gamma\left(\boldsymbol{r};\boldsymbol{r}'\right)\right]_{\boldsymbol{r}'=\boldsymbol{r}} - \frac{g\mu_\beta}{\hbar}\boldsymbol{\nabla}\times\boldsymbol{Q}(\boldsymbol{r}) - \sum_{a=1}^{N}\frac{e^2}{2m_\mathrm{e}^2c^2}\boldsymbol{Q}(\boldsymbol{r})\times\hat{\boldsymbol{E}}^a$$

The previous equation satisfies in the limit of a complete basis set or for an exact calculation the condition

$$\boldsymbol{\nabla}\cdot\mathbf{J} = 0$$

The non-relativistic current density does not satisfy the continuity equation in an approximate calculation

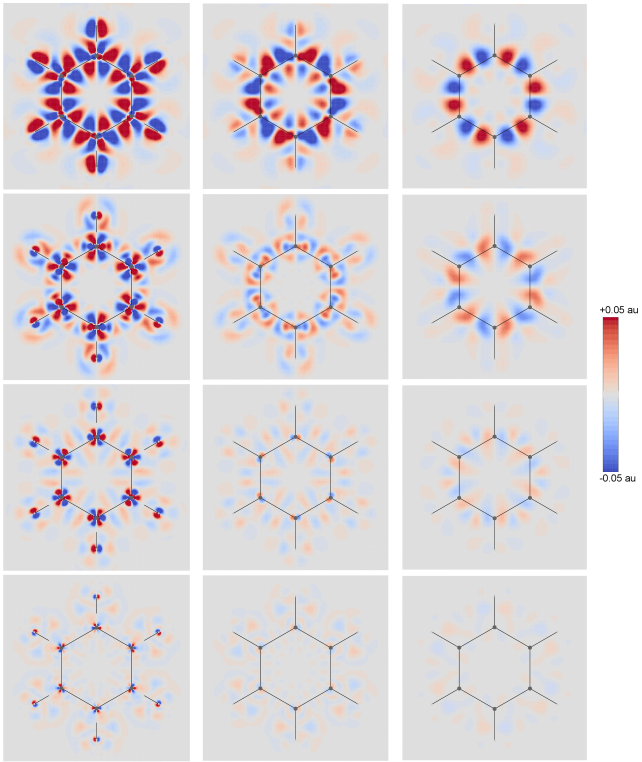

Figure: Diverging color map of $\nabla_\alpha J_\alpha$ induced by a static magnetic field $B_z\epsilon_3$ for the benzene molecule calculated on three different planes, i.e. the molecular plane, -0.5 and -1 a.u. respectively, at BHandHLYP level of theory with four different basis sets.

NMR Chemical Shifts and Magnetizabilites

In the case of open-shell systems another contribution arising from electron spin has to be taken into account when we compute chemical shieldings and magnetizabilities:

$$\sigma_{\alpha\beta}^{\boldsymbol{IS}} = \left.\frac{\partial^2 \langle W^{\boldsymbol{IS}} \rangle}{\partial \mu_{I_\alpha} \partial B_\beta}\right|_{\boldsymbol{\mu_I}, \boldsymbol{B}\to\boldsymbol{0}} = \frac{\mu_0}{4\pi} g \mu_\beta \frac{S(S+1)}{3k_B T} \epsilon_{\lambda\alpha\gamma} \int \frac{r_\gamma - R_{I\gamma}}{|\boldsymbol{r} - \boldsymbol{R}_I|^3} \mathcal{J}_\lambda^{S_\beta}(\boldsymbol{r})\, d^3 r$$

$$\chi_{\mu\lambda}^{\boldsymbol{S}} = -\left.\frac{\partial^2 \langle W^{\boldsymbol{BS}} \rangle}{\partial B_\mu \partial B_\lambda}\right|_{\boldsymbol{B}\to\boldsymbol{0}} = -g\mu_\beta \frac{S(S+1)}{12k_B T} \int (\epsilon_{\lambda\gamma\alpha} \mathcal{J}_\alpha^{S_\mu} + \epsilon_{\mu\gamma\alpha} \mathcal{J}_\alpha^{S_\lambda}) r_\gamma \, d^3 r$$

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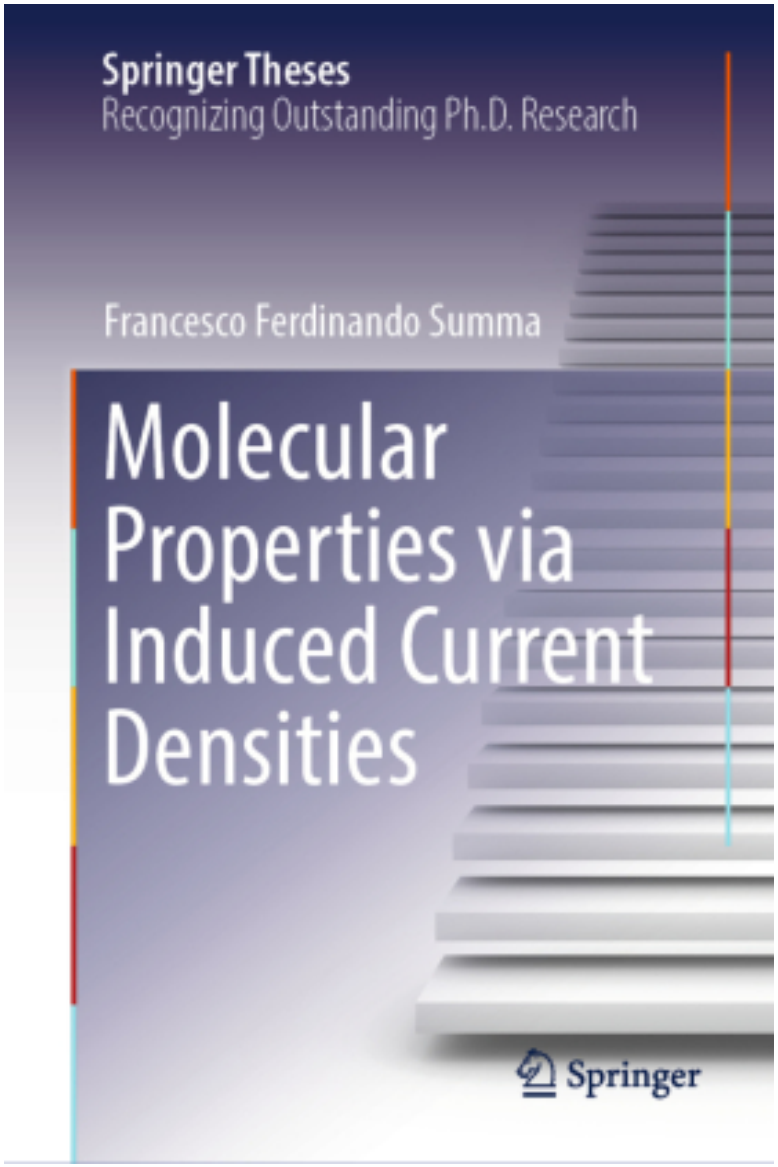

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- Nominated as an outstanding Ph.D. thesis by the University of Salerno, Italy;
- Introduces new density functions that are origin-independent;
- Covers molecular response theory using static and dynamic-induced current densities;

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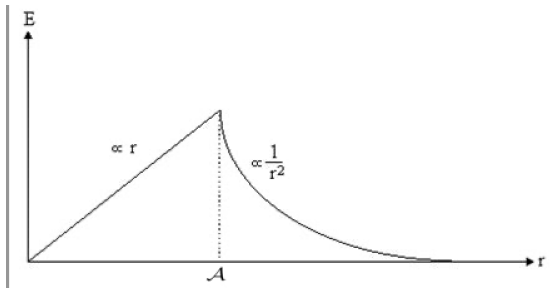
The SOC current introduce a divergence in the spin contribution to nuclear magnetic shieldings, but not in the evaluation of magnetizabilities. A simple way to remove this divergence is to change the electric field operator introduced before with the one adopted for a finite nucleus

$$\begin{cases} \hat{\boldsymbol{E}}_k^a = \frac{Z_a\, e}{4\pi\varepsilon_0} \frac{\boldsymbol{r}_k - \boldsymbol{R}_a}{|\boldsymbol{r}_k - \boldsymbol{R}_a|^3} & \boldsymbol{r}_k \geq \mathcal{A} \\ \hat{\boldsymbol{E}}_k^a = \frac{Z_a\, e}{4\pi\varepsilon_0} \frac{\boldsymbol{r}_k - \boldsymbol{R}_a}{\mathcal{A}^3} & \boldsymbol{r}_k < \mathcal{A} \end{cases} \tag{12}$$



where $\mathcal{A}$ is the atomic radius when the calculation of the spin current density is carried out! The SOC current gives only a small contribution compared to the magnetization current for both properties computed for light atoms.

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Comparison with Pennanen and Vaara Approach

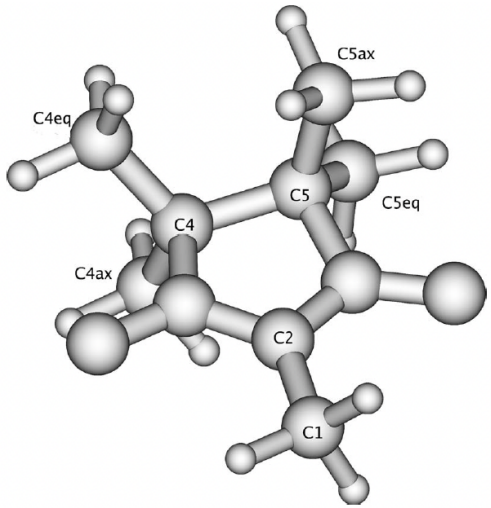


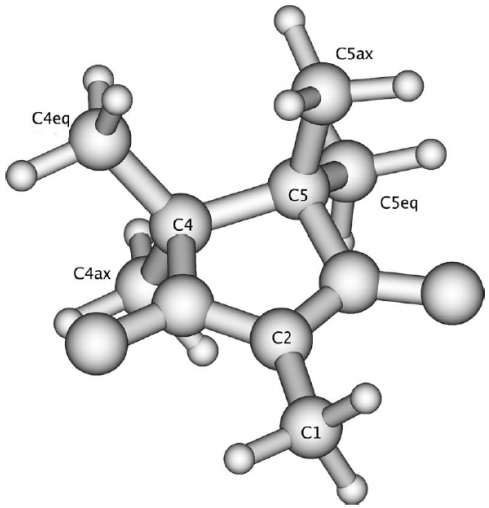
TABLE I. Calculated chemical shifts (in ppm) for the nitroxide compound N6 (compound 6 in Ref. 9) at 298 K.

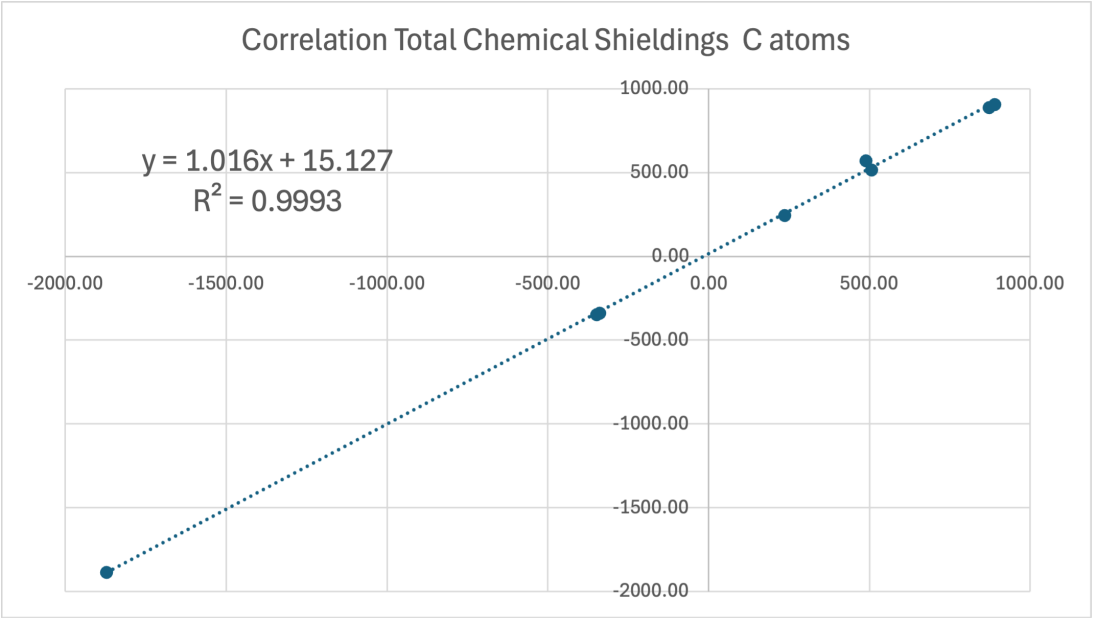
		δ(DFT)				BP86 contributions to shift[a]				
Nucleus[b]	Expt.[c]	BP86	BP86m[d]	PBE	PW91	δ_{orb}[e]	$g_e A_{con}$	$g_e A_{PC}$	$\Delta g_{iso} A_{con}$	$\Delta\tilde{\mathbf{g}}\cdot\mathbf{A}_{dip}$
Cα4$_{ax}$	1135	889.1	1022.9	899.3	889.1	34.6	853.4	−0.3	1.8	0.3
Cα5$_{ax}$	1170	906.7	1038.6	916.0	905.6	34.6	870.8	−0.3	1.9	0.3
Cα4$_{eq}$	573	499.3	505.9	497.1	492.8	28.8	469.5	0.0	1.0	0.0
Cα5$_{eq}$	650	517.6	524.0	515.0	510.4	28.6	488.0	0.0	1.0	0.0
C4	−635	−345.1	−607.1	−371.1	−370.7	89.5	−435.6	1.9	−0.9	0.0
C5	−670	−338.1	−600.9	−363.3	−363.0	88.3	−427.4	1.9	−0.9	0.0
C1′	466	245.9	625.4	253.1	260.8	15.9	229.4	0.0	0.5	0.1
C2	⋯	−1884.9	−3714.5	−2036.4	−1989.3	157.7	−2044.2	3.7	−4.4	2.3
Hα4/5$_{ax}$	−13.1	−9.3	−12.9	−10.2	−10.2	1.4	−10.6	0.0	0.0	0.0
Hα4/5$_{eq}$	−13.9	−11.0	−17.5	−11.7	−12.0	1.5	−12.4	0.0	0.0	0.0
H1′	−230.6	−169.3	−345.2	−170.8	−174.2	2.2	−171.1	0.0	−0.3	0.0

[a]Corresponding terms in Eqs. 7–10 are indicated for each chemical shift contribution.
[b]Labeling of nuclei as in Ref. 4.
[c]Solid-state experimental results from Ref. 9. Signal exchange between respective carbons labeled with 4/5 could not be excluded.
[d]Nonrelativistic **A** from B3LYP calculations with GAUSSIAN03, other terms from BP86.
[e]Orbital shift relative to the calculated shielding constant in tetramethylsilane (TMS), σ_{ref}=188.0 (BP86), 188.0 (PBE), and 187.1 (PW91) for carbon, as well as 31.5 (BP86), 31.4 (PBE), and 31.4 (PW91) for hydrogen. All values in ppm.

T. O. Pennanen, J. Vaara, J. Chem. Phys. 123, 174102 (2005)

Comparison with Pennanen and Vaara Approach





The approach in terms of spin currents is very easy to implement, because the only think we need is the spin density matrix!

T. O. Pennanen, J. Vaara, J. Chem. Phys. 123, 174102 (2005)

Is Possible to Obtain a Divergenceless Current Density Vector Field?

The Helmholtz decomposition theorem states that $\boldsymbol{J}(\boldsymbol{r})$ can be written as the sum of an irrotational vector field and a solenoidal vector field, namely

$$\boldsymbol{J}(\boldsymbol{r}) = -\boldsymbol{\nabla}\phi(\boldsymbol{r}) + \boldsymbol{\nabla} \times \boldsymbol{A}(\boldsymbol{r}) \tag{13}$$

where the scalar and vector potentials are respectively uniquely defined as

$$\phi(\boldsymbol{r}) \equiv \frac{1}{4\pi} \int \frac{\boldsymbol{\nabla}' \cdot \boldsymbol{J}(\boldsymbol{r}')}{|\boldsymbol{r} - \boldsymbol{r}'|} \, d^3 r' \tag{14}$$

$$\boldsymbol{A}(\boldsymbol{r}) \equiv \frac{1}{4\pi} \int \frac{\boldsymbol{\nabla}' \times \boldsymbol{J}(\boldsymbol{r}')}{|\boldsymbol{r} - \boldsymbol{r}'|} \, d^3 r' \tag{15}$$

Since $\boldsymbol{\nabla} \cdot \boldsymbol{\nabla} \times \boldsymbol{A} = 0$ we can immediately identify the solenoidal field $\boldsymbol{\nabla} \times \boldsymbol{A}$ in (13) with $\boldsymbol{J}^{\mathrm{AM}}$ and write

$$\boldsymbol{J}^{\mathrm{AM}}(\boldsymbol{r}) = \boldsymbol{J}(\boldsymbol{r}) + \frac{1}{4\pi} \boldsymbol{\nabla} \int \frac{\boldsymbol{\nabla}' \cdot \boldsymbol{J}(\boldsymbol{r}')}{|\boldsymbol{r} - \boldsymbol{r}'|} \, d^3 r' \tag{16}$$

Now, $\boldsymbol{\nabla}(\frac{1}{r}) = -\frac{\boldsymbol{r}}{|\boldsymbol{r}|^3}$ then

$$\boldsymbol{J}^{\mathrm{AM}}(\boldsymbol{r}) = \boldsymbol{J}(\boldsymbol{r}) + \frac{1}{4\pi}\int \frac{(\boldsymbol{r}' - \boldsymbol{r})}{|\boldsymbol{r}' - \boldsymbol{r}|^3}\boldsymbol{\nabla}' \cdot \boldsymbol{J}(\boldsymbol{r}')\, d^3 r' \tag{17}$$

Last but not least, it is interesting to consider the divergence of the corrective term

$$\begin{aligned}
\boldsymbol{\nabla} \cdot \boldsymbol{J}^{\mathrm{cor}}(\boldsymbol{r}) &= \frac{1}{4\pi}\int \left[\boldsymbol{\nabla} \cdot \frac{(\boldsymbol{r}' - \boldsymbol{r})}{|\boldsymbol{r}' - \boldsymbol{r}|^3}\right] \boldsymbol{\nabla}' \cdot \boldsymbol{J}(\boldsymbol{r}')\; d^3 r' \\
&= -\frac{1}{4\pi}\int 4\pi\delta^3(\boldsymbol{r} - \boldsymbol{r}')\boldsymbol{\nabla}' \cdot \boldsymbol{J}(\boldsymbol{r}')\; d^3 r' \\
&= -\boldsymbol{\nabla} \cdot \boldsymbol{J}(\boldsymbol{r})
\end{aligned} \tag{18}$$

which definitely proves that $\boldsymbol{\nabla} \cdot \boldsymbol{J}^{\mathrm{AM}}(\boldsymbol{r}) = 0$ even in approximate cases.

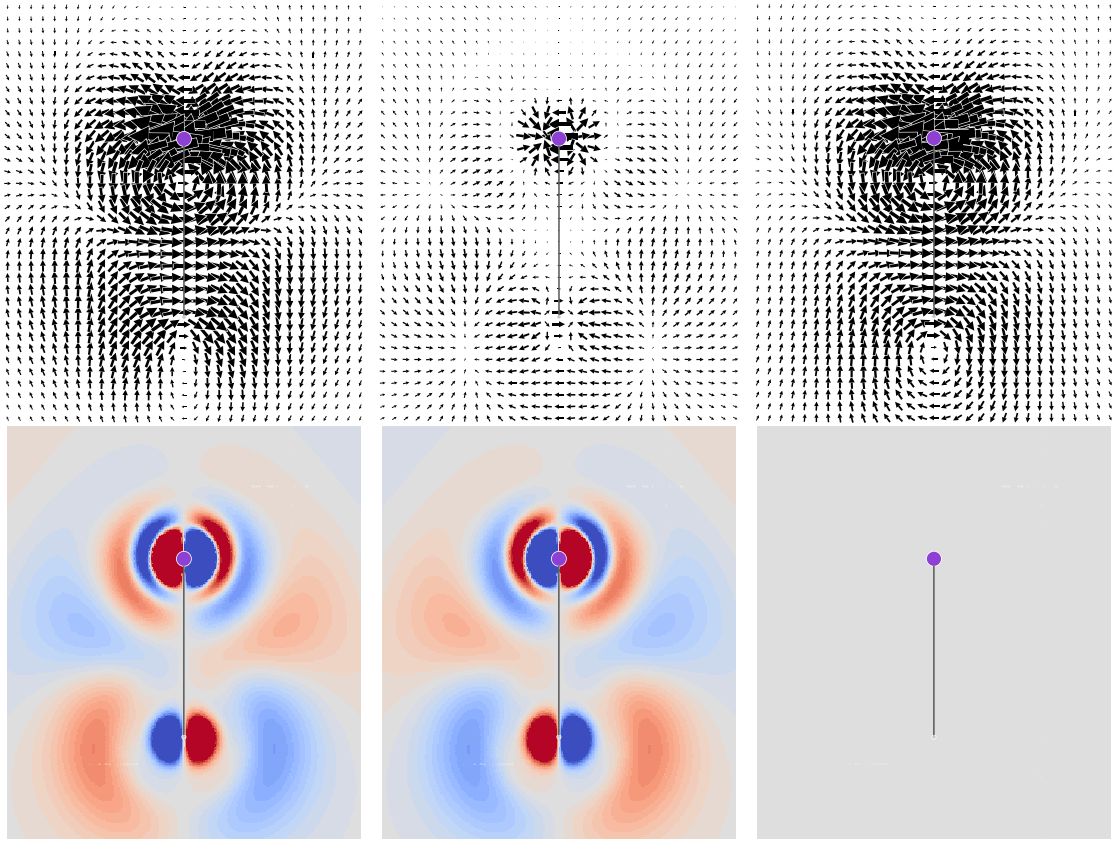


Figure: Current density induced in LiH by a magnetic field perpendicular to the main symmetry axis of the molecule and pointing toward the reader calculated for points over a symmetry plane at CTOCD-DZ1 HF/3-21G level of theory. Top row from left to right: $\boldsymbol{J}(\boldsymbol{r})$, $\boldsymbol{J}^{\mathrm{cor}}(\boldsymbol{r})$, and $\boldsymbol{J}^{\mathrm{AM}}(\boldsymbol{r})$ vector fields, respectively. Bottom row from left to right: $\boldsymbol{\nabla} \cdot \boldsymbol{J}(\boldsymbol{r})$, $\boldsymbol{\nabla} \cdot \boldsymbol{J}^{\mathrm{cor}}(\boldsymbol{r})$, and $\boldsymbol{\nabla} \cdot \boldsymbol{J}^{\mathrm{AM}}(\boldsymbol{r})$ scalar fields, respectively.

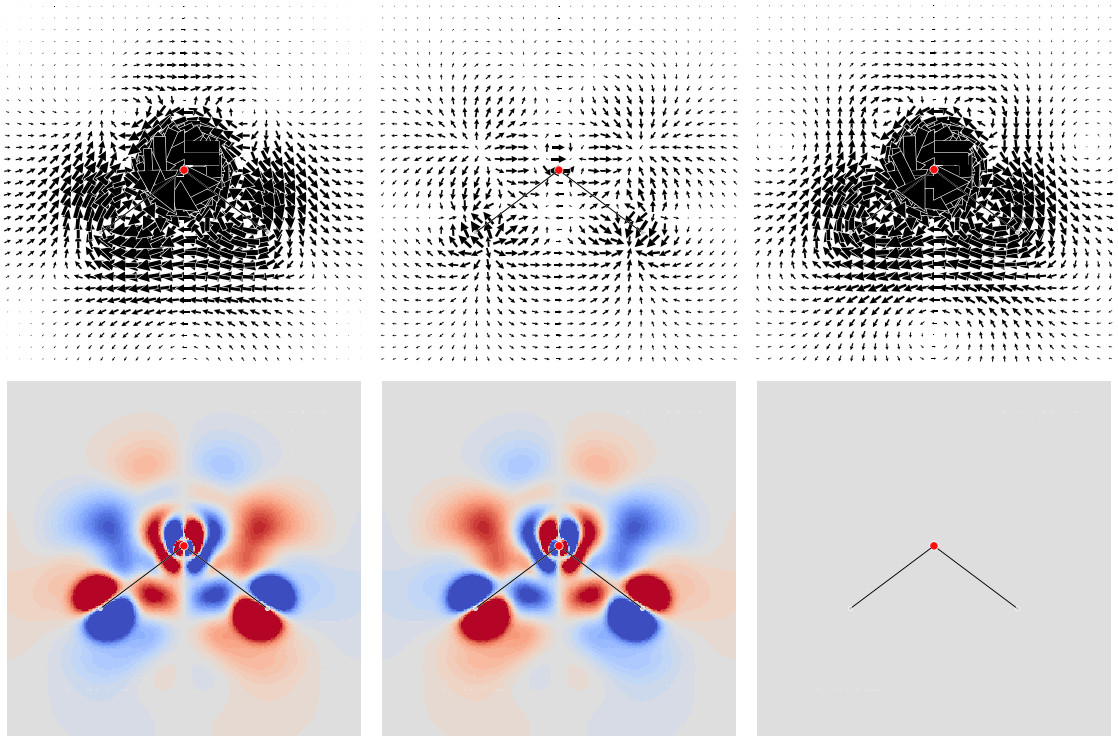


Figure: Current density induced in H_2O by a magnetic field perpendicular to the main symmetry axis of the molecule and pointing toward the reader calculated for points over the molecular plane at CTOCD-DZ1 HF/3-21G level of theory. Top row from left to right: $\boldsymbol{J}(\boldsymbol{r})$, $\boldsymbol{J}^{\mathrm{cor}}(\boldsymbol{r})$, and $\boldsymbol{J}^{\mathrm{AM}}(\boldsymbol{r})$ vector fields, respectively. Bottom row from left to right: $\boldsymbol{\nabla} \cdot \boldsymbol{J}(\boldsymbol{r})$, $\boldsymbol{\nabla} \cdot \boldsymbol{J}^{\mathrm{cor}}(\boldsymbol{r})$, and $\boldsymbol{\nabla} \cdot \boldsymbol{J}^{\mathrm{AM}}(\boldsymbol{r})$ scalar fields, respectively.

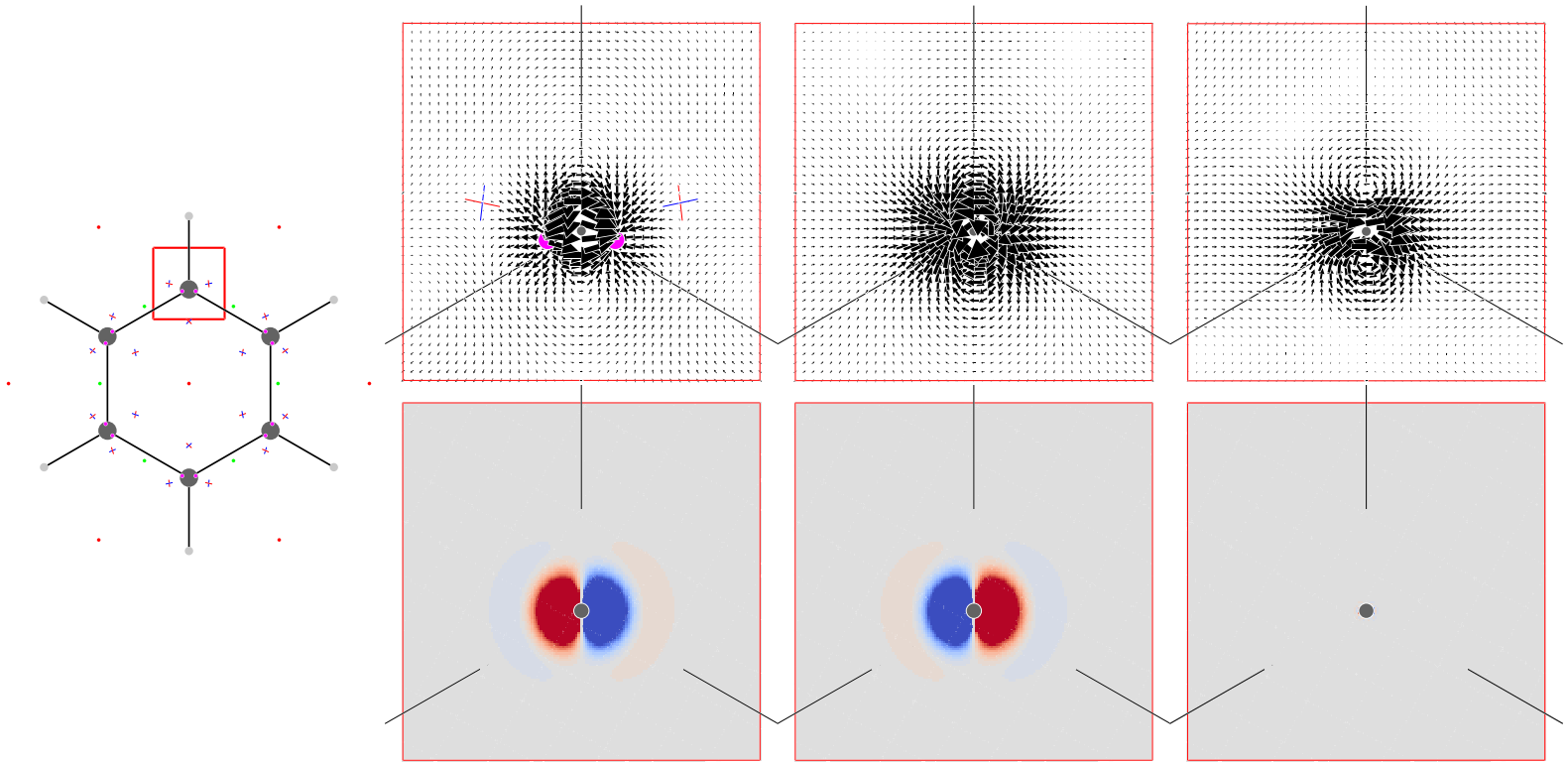


Figure: Current density induced on the molecular plane of the benzene molecule by a magnetic field parallel to the main symmetry axis and pointing toward the reader, calculated using the CO method at the HF level. On the left a section of the stagnation graph (SG) of $\boldsymbol{J}(\boldsymbol{r})$ is shown, where: (2,0) green/red dots mark diatropic/paratropic center lines; (2,0) two-armed crosses mark saddle lines; (3,$\pm$1) three-armed crosses mark isolated saddle points; (3,$\pm$3) magenta dots mark isolated sources and sinks.

Table: Magnetizability tensor components calculated at CTOCD-DZ1 HF level of theory for LiH in a.u.

Basis set	using	$\xi_\perp$	$\xi_\parallel$
STO-3G	$\mathcal{J}$	0.47	-0.69
	$\mathcal{J}^{\mathrm{AM}}$	0.49	-0.69
3-21G	$\mathcal{J}$	-0.23	-1.01
	$\mathcal{J}^{\mathrm{AM}}$	-0.29	-1.01
6-21G	$\mathcal{J}$	-0.34	-1.01
	$\mathcal{J}^{\mathrm{AM}}$	-0.39	-1.01
6-21G*	$\mathcal{J}$	-0.58	-1.27
	$\mathcal{J}^{\mathrm{AM}}$	-0.65	-1.27
aug-pcSseg-2	$\mathcal{J}$	-1.39	-1.93
	$\mathcal{J}^{\mathrm{AM}}$	-1.39	-1.93
aug-pcSseg-4		-1.42	-1.95

The SYSMOIC program is freely available online for three different platforms.Instructions for downloading and using the package are available at:

`http://sysmoic.chem.unisa.it/MANUAL/`

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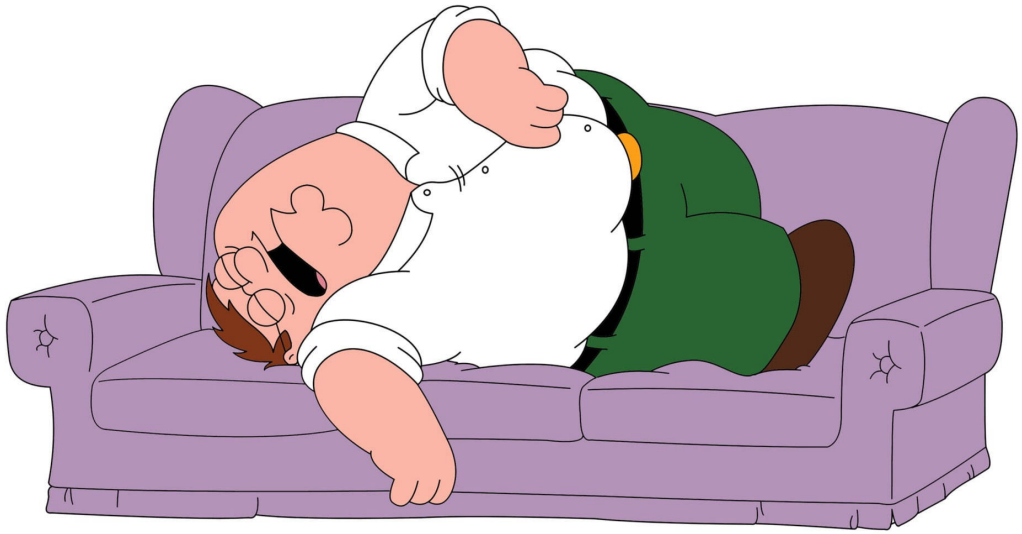

Thanks for your attention!

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