Orbital contributions to magnetically induced ring currents

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Approaches for decomposition of magnetic response properties into orbital contributions

- **Nucleus Independent Chemical Shifts (NICS):**[1]
  - Only total σ and total π contributions can be calculated.
- **Selection Rules + Orbital Analysis:**
  Translationally allowed $\rightarrow$ diatropic contribution,
  Rotationally allowed $\rightarrow$ paratropic contribution,
  - Provides only quantitative contributions.
- **CTOCD-DZ or Ipsocentric Approach:**[2,3]
  - Basis set convergence is slower than with GIAO.

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[1] P. v. R. Schleyer et al. (2001). In: *Org.Lett.* 3.16, pp. 2465–2468.

[2] P. Lazzeretti, M. Malagoli, and R. Zanasi (1994). In: *Chem.Phys.Lett.* 220.3-5, pp. 299–304.

[3] E. Steiner and P.W. Fowler (2004). In: *PCCP* 6.2, pp. 261–272.

GIMIC

- Based on the usage of Gauge Inclusive Atomic Orbitals (GIAO): Results are always gauge independent;
- Takes as input only **one-electron density** and **first-order perturbed density**. Any level of theory which allows to obtain these matrices can be used.
- Can be used for visualization of Magnetically Induced Current Densities (MICD).

Plan: Implementation of orbital contribution calculations by modifying input density matrices.

Decomposition of densities

Level of theory: B3LYP and SCLH22t[4] with def2-TZVP basis set.
One-electron density in AO basis:

$$D_0 = \sum_i^{N_{occ}} D_{0,i} = \sum_i^{N_{occ}} C n_i C^T \tag{1}$$

First-order one-electron density in AO basis[5]:

$$D_\lambda = D_{\lambda,0} + [D_0, X_\lambda]_S = -D_0 S_\lambda D_0 + D_0 S X_\lambda - X_\lambda S D_0 \tag{2}$$

Using the following expressions:

$$C_\lambda = C U_\lambda; \quad X_\lambda = C U_\lambda C^T; \quad U_\lambda = \frac{\partial C(\mathbf{B})}{\partial B_\lambda}, \tag{3}$$

$$D_\lambda = \sum_i^{N_{occ}} D_{\lambda,i} = \sum_i^{N_{occ}} 2(C_\lambda n_i C^T - C n_i C_\lambda^T). \tag{4}$$

The occupied-virtual and virtual-occupied blocks of U_λ are obtained as a result of solving the response equations, and the occupied-occupied block is given by $U_\lambda = -0.5 C^T S_\lambda C$.

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[4] C. Holzer, Y. J. Franzke, and M. Kehry (2021). In: *J. Chem. Theory Comput.* 17.5, pp. 2928–2947.

[5] H. Larsen et al. (2001). In: *J. Chem. Phys.* 115.22, pp. 10344–10352.

Benzene (core orbitals)

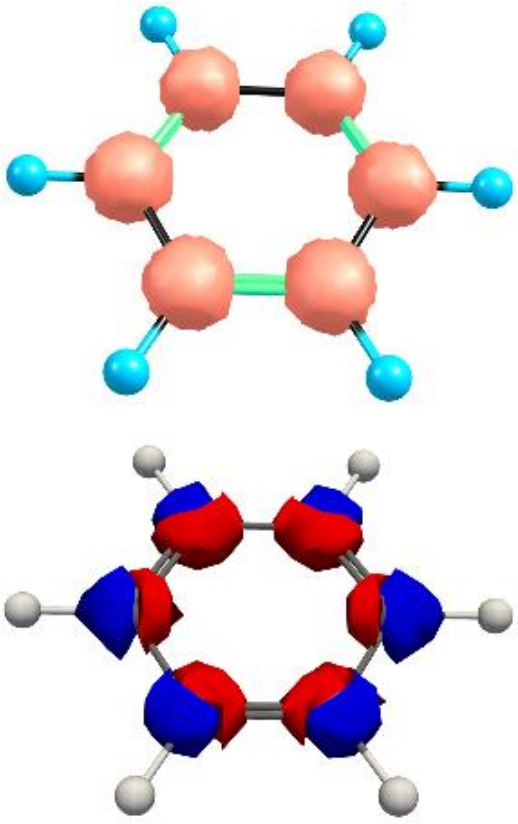


Table 1: Contributions of core orbitals j to the magnetically induced ring current strength J and ring-center shielding tensor σ^0 (negative NICS(0))[6]

Orbital	Occ.	j(sclh22t), nA/T	j(B3LYP), nA/T	σ^0, ppm
$1a_{1g}$	2	0.01	0.02	0.1
$1e_{1u}$	4	-0.02	0.02	-0.64
$1e_{2g}$	4	-0.02	0.06	0.73
$1b_{2u}$	2	-0.02	0.03	-0.06
Total core		**-0.05**	**0.13**	

Figure 1: Visualization of $1a_{1g}$ (top) and magnetically induced current density for it (bottom)

Benzene (σ orbitals)

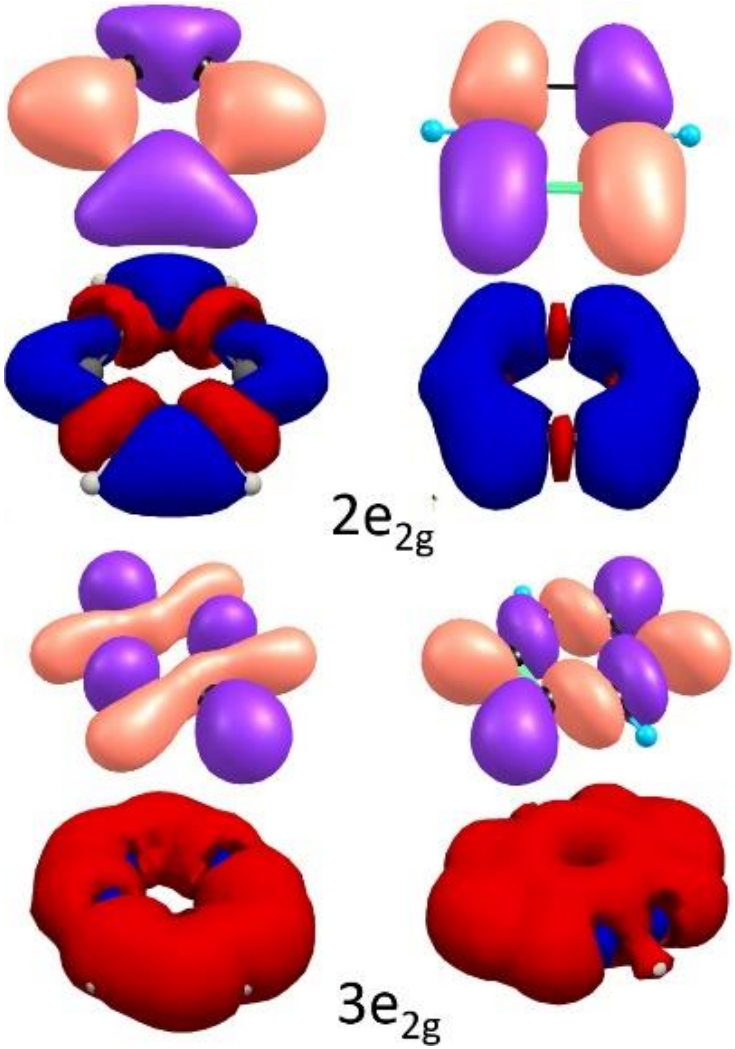


Figure 2: Magnetically induced current density for $2e_{2g}$ (top) and $3e_{2g}$ (bottom)

Table 2: Contributions of σ orbitals j to the magnetically induced ring current strength J and ring-center shielding tensor σ^0 (negative NICS(0))[3]

Orbital	Occ.	j(sclh22t), nA/T	j(B3LYP), nA/T	σ^0, ppm
$2a_{1g}$	2	3.07	2.95	-0.4
$2e_{1u}$	4	4.81	4.97	0.09
$2e_{2g}$	4	5.25	5.37	8.94
$3a_{1g}$	2	2.71	2.78	0.34
$2b_{2u}$	2	-2.1	-2.27	-2.25
$3e_{1u}$	4	-2.63	-2.88	-7.47
$1b_{1u}$	2	4.2	4.21	0.01
$3e_{2g}$	4	-14.78	-14.87	-11.34
Total σ		**0.53**	**0.26**	

[3] E. Steiner and P.W. Fowler (2004). In: *PCCP* 6.2, pp. 261–272.

Benzene (π orbitals)

Table 3: Contributions of π orbitals j to the magnetically induced ring current strength J, and ring-center shielding tensor σ^0 (negative NICS(0))[3]

Orbital	Occ.	j(sclh22t), nA/T	j(B3LYP), nA/T	σ_0, ppm
$1a_{2u}$	2	4.13	4.1	2.92
$1e_{1g}$	4	7.61	7.57	18.9
Total core		-0.05	0.13	
Total σ		0.53	0.26	
Total π		11.74	11.67	
Total J		12.21	12.03	

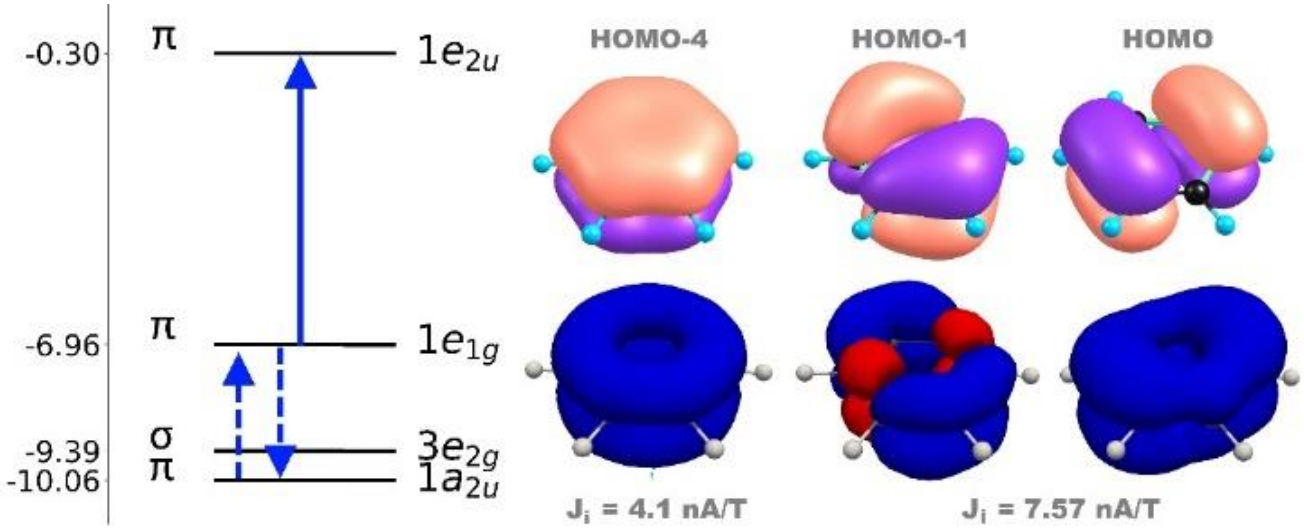


Figure 3: Energy diagram with allowed translational transitions (blue arrow) (left)[3] and magnetically induced current density for $1a_{2u}$ and $1e_{1g}$ (right).

[3] E. Steiner and P.W. Fowler (2004). In: *PCCP* 6.2, pp. 261–272.

Contributions of π orbitals for Benzene and Borazine

Table 4: Contributions of π orbitals, total σ, π, and core orbitals to the magnetically induced ring current strength J for borazine

Orbital	Occ.	Type	j(sclh22t), nA/T	j(B3LYP), nA/T
$1a_2$"	2	π	3.46	3.50
1e"	4	π	-0.62	-0.46
Total core			0.12	0.18
Total σ			0.10	0.01
Total π			2.85	3.03
Total J			**3.06**	**3.23**

[6] R. Ba´ez-Grez and R. Pino-Rios (2022). In: *RSC Adv.* 12.13, pp. 7906–7910.

[7] E Steiner, A Soncini, and PW Fowler (2006). In: *J. Phys. Chem. A* 110.47, pp. 12882–12886.

Contributions of π orbitals for Benzene and Borazine

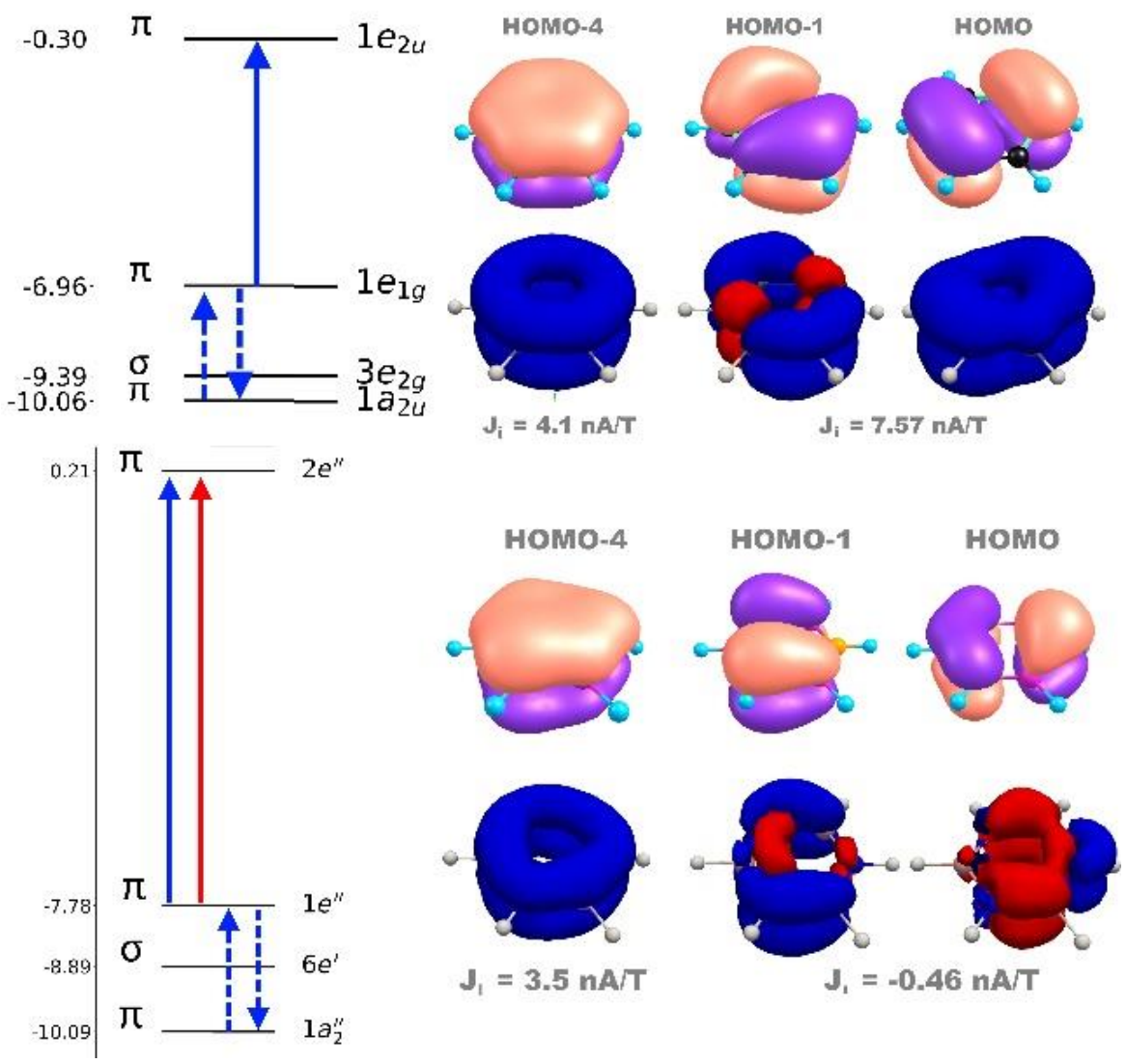


Figure 4: Energy diagrams with allowed transitions: blue arrows for translational transitions and red arrows for rotational transitions, and MICD for π orbitals of benzene (top) and borazine (bottom).

σ-aromaticity of $C_3H_3^+$

Table 5: Orbital contributions j (nA/T) to the magnetically induced ring current strength J of $C_3H_3^+$

Orbital	Occ.	Type	j(sclh22t	j, B3LYP
$1a_1'$	2	core	0.01	0.01
1e'	4	core	0.06	-0.01
$2a_1'$	2	σ	2.97	2.73
2e'	4	σ	4.24	4.64
$3a_1'$	2	σ	0.17	0.48
$1a_2''$	2	π	3.95	3.92
3e'	4	σ	-0.79	-1.16
Total core			**0.07**	**0.00**
Total σ			**6.59**	**6.69**
Total π			**3.95**	**3.92**
Total J			**10.61**	**10.61**

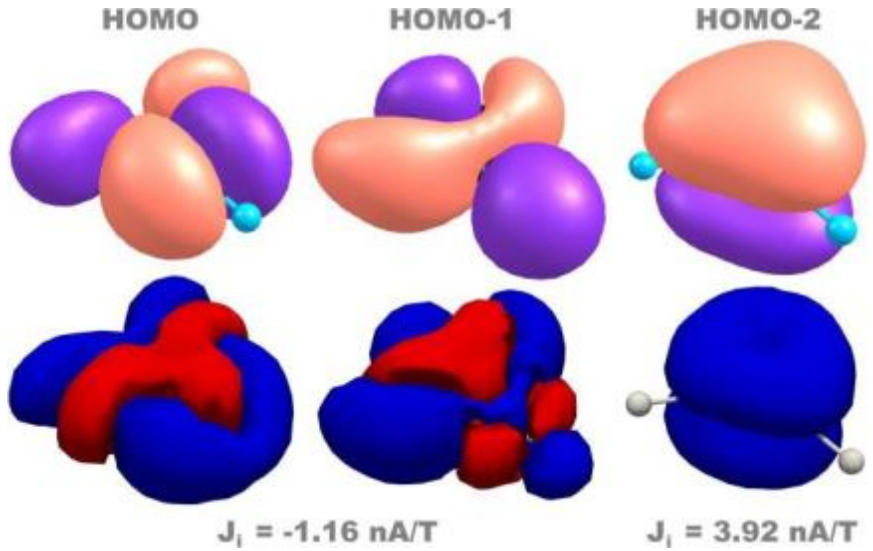


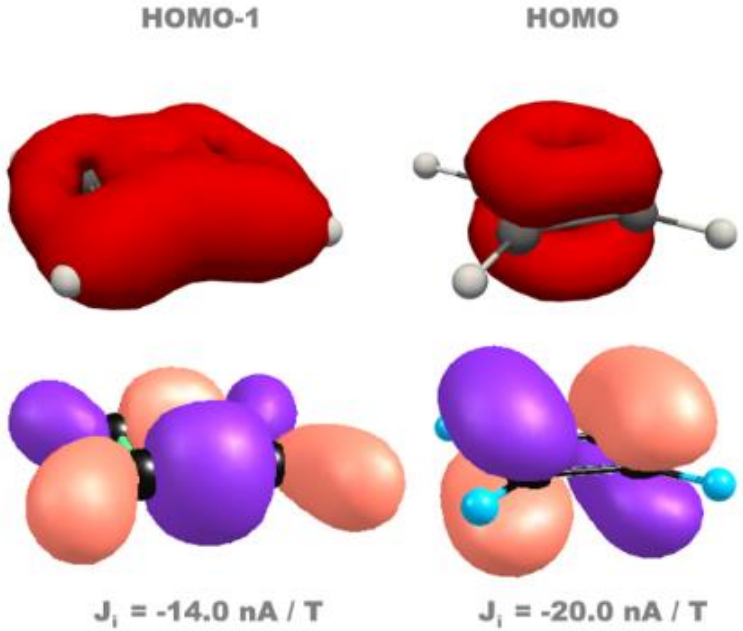
Figure 5: MICD and contributions j for frontier orbitals of $C_3H_3^+$

[8] D. Cremer and J. Gauss (1986). In: *J.Am.Chem.Soc.* 108.24, pp. 7467–7477.

σ-aromaticity of cyclobutadiene

Table 6: Orbital contributions for frontier orbitals *j* to the magnetically induced ring current strength *J* of cyclobutadiene.

Orbital	Occ.	Type	*j*(sclh22t), nA/T	*j*(B3LYP), nA/T
HOMO-2 ($1b_{1u}$)	2	π	3.933	4.043
HOMO-1 ($3b_{2u}$)	2	σ	-13.945	-14.141
HOMO ($1b_{2g}$)	2	π	-20.03	-20.673
Total *J*			**-19.96**	**-20.69**
Total core			**0.035**	**0.03**
Total σ			**-3.9**	**-4.088**
Total π			**-16.097**	**-16.63**



[8] D. Cremer and J. Gauss (1986). In: *J.Am.Chem.Soc.* 108.24, pp. 7467–7477.

σ-aromaticity of cyclooctatraene

Table 7: Contributions of the HOMO to the magnetically induced ring current strength *J* (nA/T) for cyclooctatetraene in planar conformation (D4h)

Orbital	Occ.	Type	*j*(sclh22t), nA/T	*j*(B3LYP), nA/T
HOMO	2	π	-50.603	-50.713
Total core			-0.145	0.246
Total σ			-0.294	-0.684
Total π			-39.792	-39.792
Total J			**-40.231**	**-40.230**

Table 8: Contributions of the HOMO to the magnetically induced ring current strength *J* (nA/T) for cyclooctatetraene in tub conformation (D2d)

Orbital	Occ.	Type	*j*(sclh22t), nA/T	*j*(B3LYP), nA/T
HOMO	2	π	-11.113	-12.899
Total core			0.199	0.179
Total σ			5.925	6.163
Total π			-7.896	-9.593
Total J			**-1.772**	**-3.251**

σ-aromaticity of cyclooctatraene

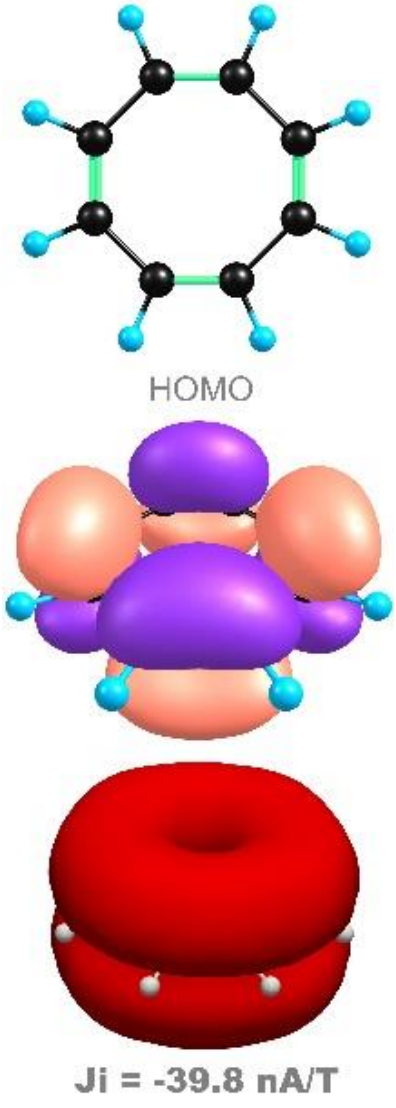


Figure 8: MICD and contribution for HOMO of COT in planar conformation.

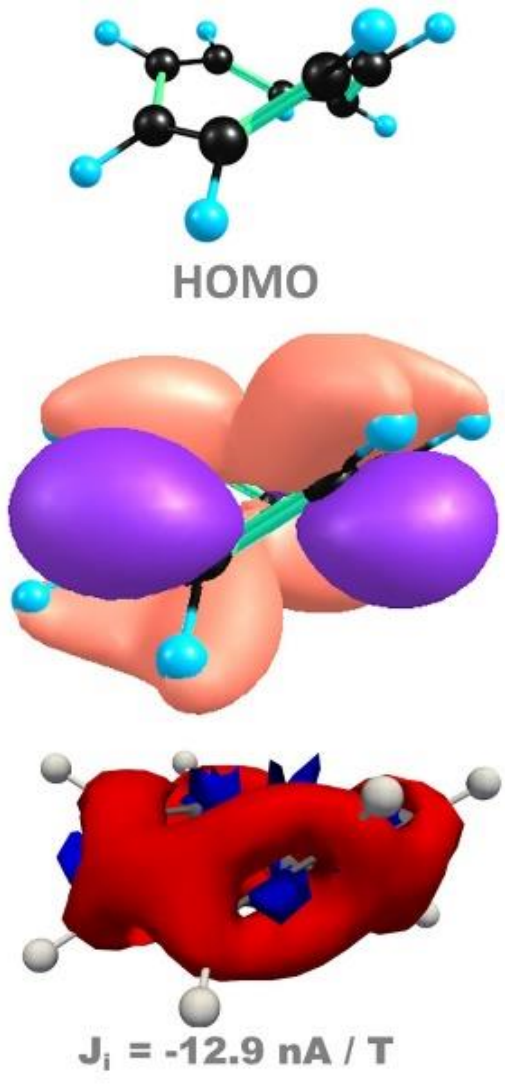


Figure 7: MICD and contribution for HOMO of COT in tub conformation.

Porphyrin

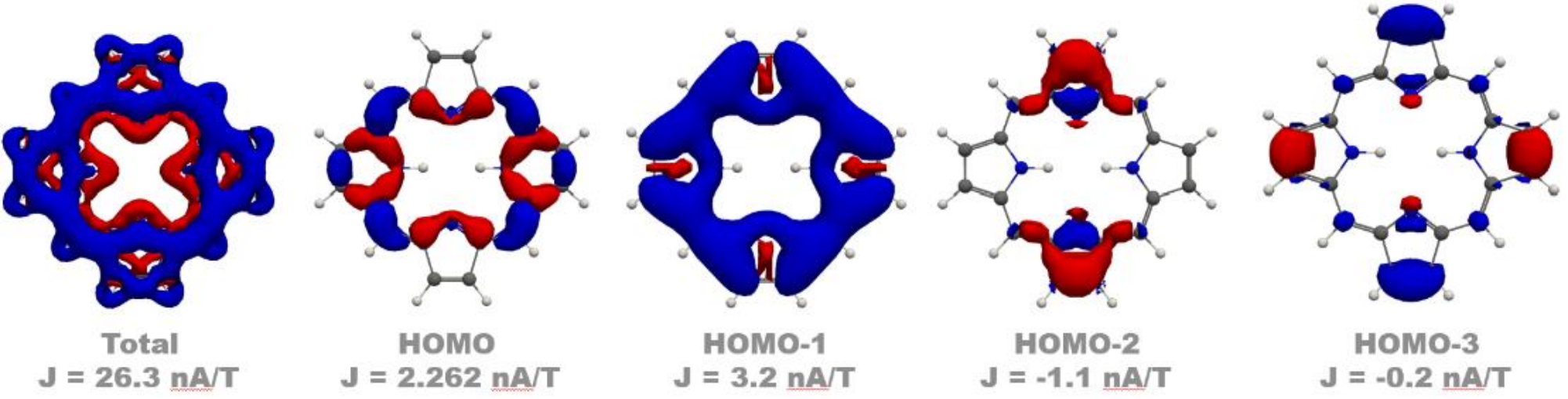


Figure 9: MICD and contribution for frontier orbitals of porphyrin

Table 9: Contributions for the frontier orbitals of porphyrin to the magnetically induced ring current strength J (nA/T)

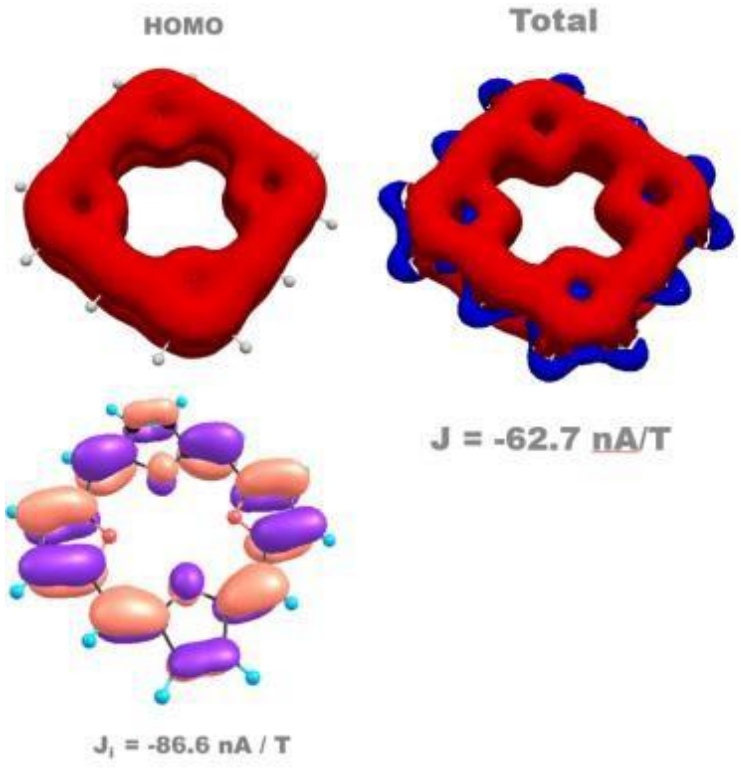
Orbital	Occ.	Type	j(sclh22t), nA/T	j(B3LYP), nA/T
HOMO-3	2	π	-0.242	-0.156
HOMO-2	2	π	-1.079	-1.069
HOMO-1	2	π	3.210	3.179
HOMO	2	π	2.488	2.262
Total core			0.396	0.473
Total σ			0.143	-0.157
Total π			26.650	26.257

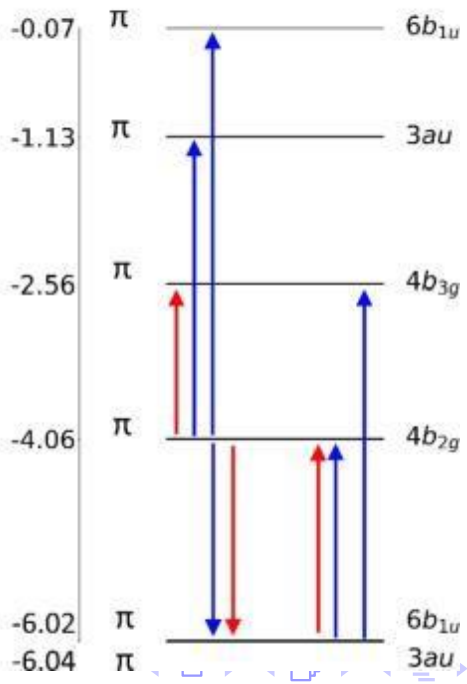
[9] E. Steiner and P.W. Fowler (2002). In: *ChemPhysChem* 3.1, pp. 114–116.

Planar antiaromatic molecules: Isophlorine

Table 10: Contributions of the HOMO to the magnetically induced ring current strength J (nA/T) for isophlorin

Orbital	Occ.	Type	j(sclh22t), nA/T	j(B3LYP), nA/T
HOMO	2.0	π	-70.06	-86.62
Total			**-47.73**	**-62.72**
Total core			0.48	0.54
Total σ			-1.67	-1.63
Total π			-46.53	-61.63

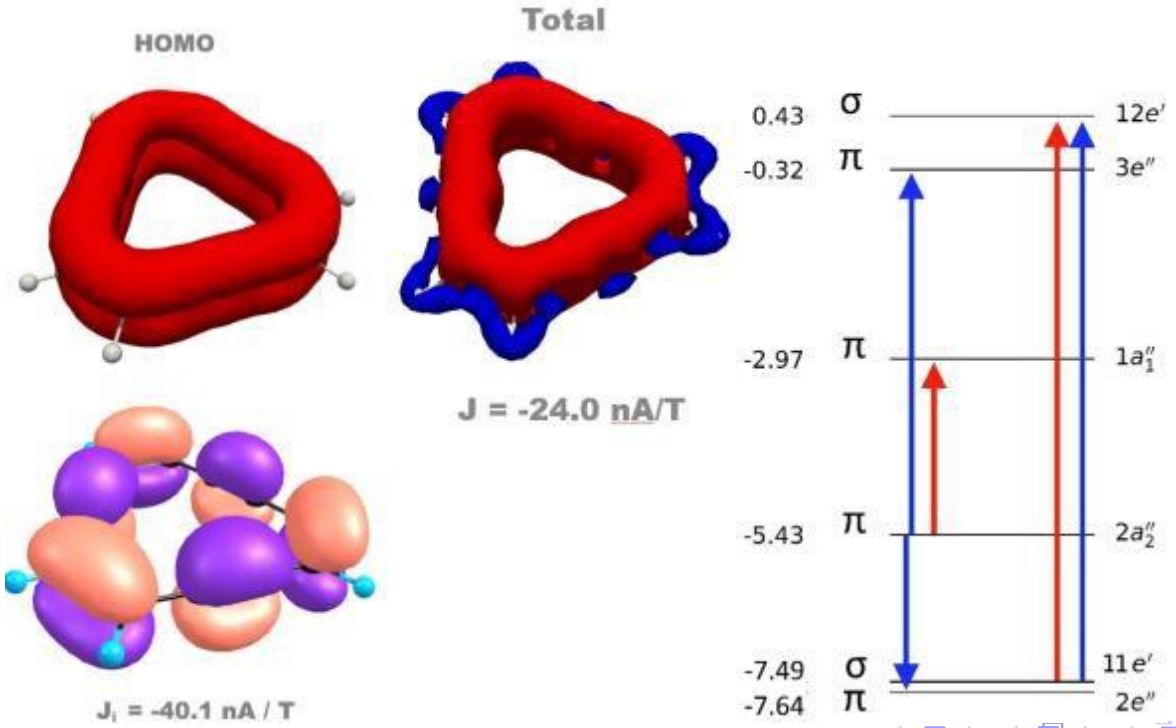




Planar antiaromatic molecules: Hexadehydroannulene

Table 11: Contributions of the HOMO to the magnetically induced ring current strength J (nA/T) for hexadehydroannulene

Orbital	Occ.	Type	j(sclh22t), nA/T	j(B3LYP), nA/T
HOMO	2.0	π	-33.539	-40.111
Total			**-18.656**	**-23.934**
Total core			1.378	3.332
Total σ			-1.554	-3.361
Total π			-18.481	-23.903



Conclusion

Table 12: Total core, σ and π contriputions for 10 considered molecules

Type	H_2P	Benzene	$C_3H_3^+$	Borazine	1,4-Cyclohexadiene	COT (D2d)	COT (D4h)	cyclobutadiene	Hexadehydroannulene	Isophlorine
core	0.5	-0.1	0.1	0.2	-0.3	-0.2	0.2	0.0	3.3	0.5
σ	-0.2	0.5	6.6	0.0	-0.1	6.8	-0.7	-3.9	-3.4	-1.6
π	26.3	11.7	3.9	3.0	0.4	-9.8	-39.8	-16.1	-23.9	-61.6
Total	26.6	12.0	10.6	3.2	-0.6	-3.3	-40.2	-20.0	-23.9	-62.7

1. For the studied planar and not strained antiaromatic molecules, the HOMO gives the largest paratropic contribution to the ring current strength, which is not observed for the studied aromatic molecules.
2. The contribution from the "σ" orbitals increases when the molecular structure deviates from planarity or experiences strain.
3. The magnitude of the magnetically induced ring currents obtained with sclh22t is less than or equal to the magnitude of the currents obtained with B3LYP.

Thank you for your attention!