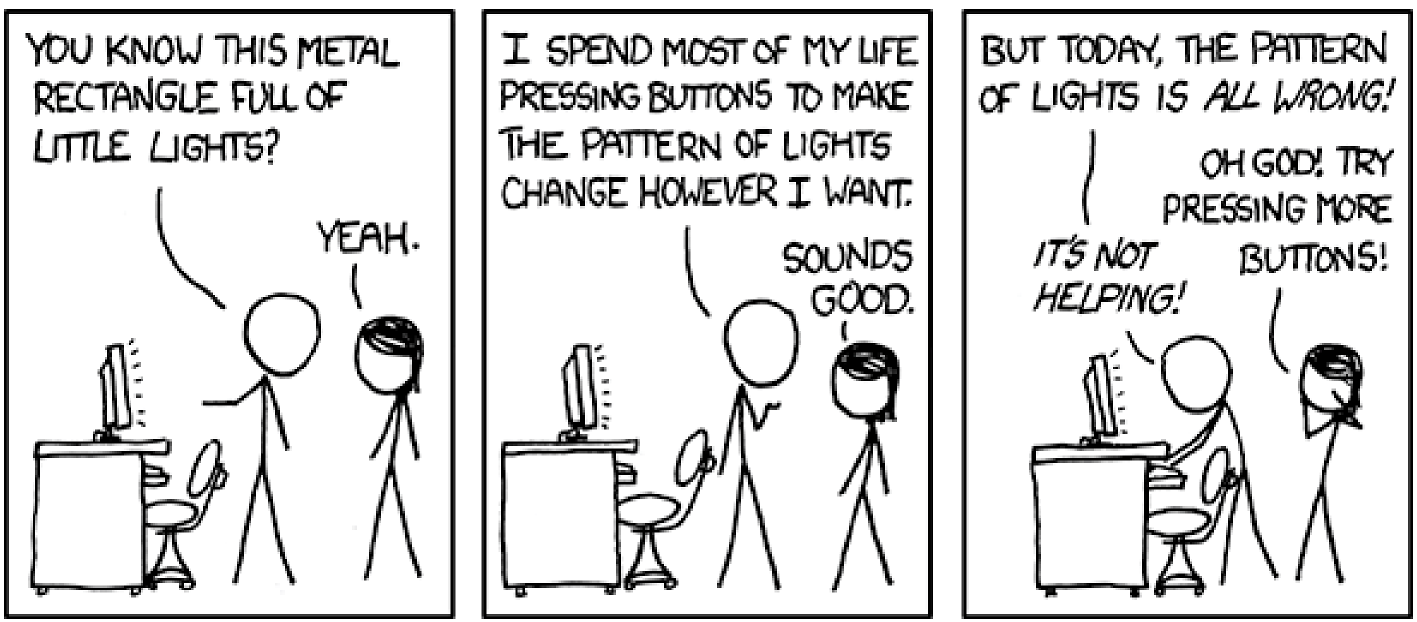
Current densities as a tool for analysis of magnetic properties in the relativistic domain:

Heavy-Atom-Light-Atom effect in the NMR spectroscopy

Stanislav Komorovský

12.9. 2024



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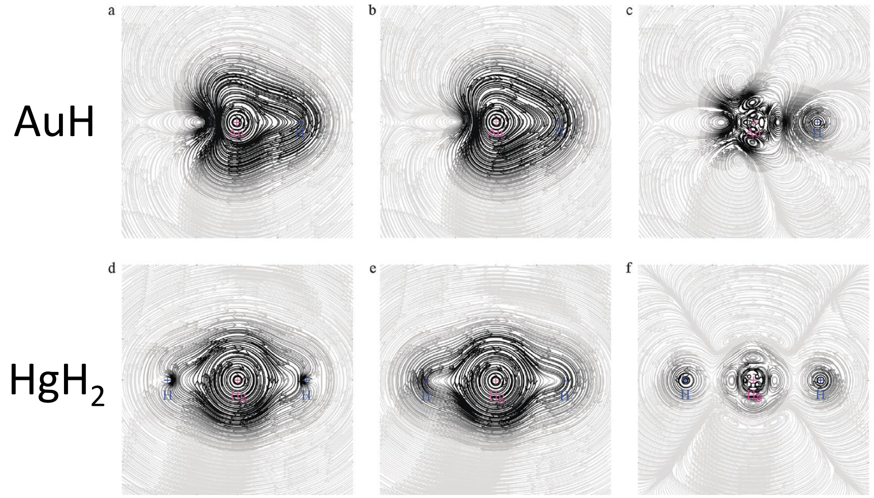
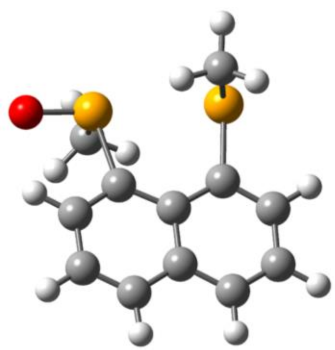
xkcd https://xkcd.com/722/

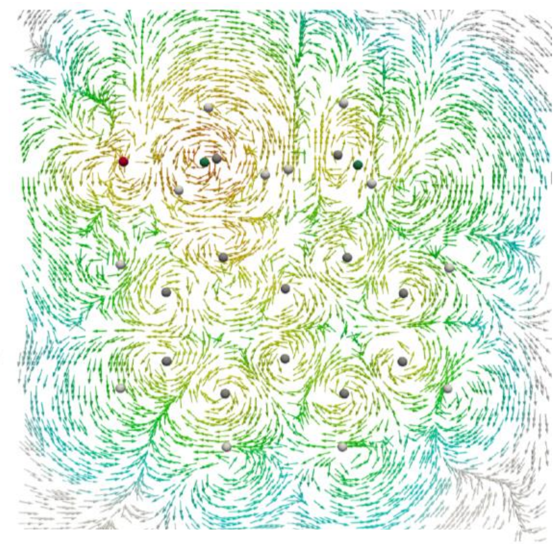
My currents

R. J. F. Berger, M. Repisky, and S. Komorovsky, *Chem. Commun.* **51**, 13961 (2015).



S. Komorovsky, K. Jakubowska, P. Świder, M. Repisky, M. Jaszuński, *J. Phys. Chem. A* **124**, 5157–5169 (2020).





D. Misenkova, F. Lemken, M. Repisky, J. Noga, O. L. Malkina, and S. Komorovsky, *J. Chem. Phys.* **157**, 164114 (2022).

$$g_{uv} = -\frac{1}{S}\sum_{c=1}^{n}\left\{\int \left[\vec{r}_c \times \vec{j}_c(\vec{r}_c, \vec{J}_v, 0)\right]_u d^3\vec{r}_c - \left[(\vec{r}_0 - \vec{r}_{0c}) \times \int \vec{j}_c(\vec{r}_c, \vec{J}_v, 0)\, d^3\vec{r}_c\right]_u\right\},$$

Dirac-Kohn-Sham equation

$$\left(c\vec{\boldsymbol{\alpha}} \cdot \vec{p} + \vec{\boldsymbol{\alpha}} \cdot \vec{A} + c^2\boldsymbol{\beta}' - V^{\text{nuc}}\mathbf{1} + V^{C}\mathbf{1} + \boldsymbol{V}^{\text{ex}}_{4\times4} + \boldsymbol{V}^{\text{xc}}_{4\times4}\right)\boldsymbol{\varphi}_i = \varepsilon_i\boldsymbol{\varphi}_i$$

$$\vec{\alpha} = \begin{pmatrix} 0 & \vec{\sigma} \\ \vec{\sigma} & 0 \end{pmatrix} \qquad \beta' = \begin{pmatrix} 0 & 0 \\ 0 & -2 \end{pmatrix} \qquad \boldsymbol{V}^{\text{xc}}_{4\times4}[\rho_0, \vec{\rho}] = \begin{pmatrix} \boldsymbol{V}^{\text{LL}}_{2\times2} & 0 \\ 0 & \boldsymbol{V}^{\text{SS}}_{2\times2} \end{pmatrix}$$

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Pauli current density

Time-dependent
Kohn-Sham equation:

$$\vec{\pi} = \vec{p} + \frac{1}{c}\vec{A}$$

$$i\dot{\varphi}_i = \left[\frac{(\vec{\sigma}\cdot\vec{\pi})^2}{2} + V_{2\times 2}\right]\varphi_i$$

$$-i\dot{\varphi}_i^\dagger = \left[\frac{(\vec{\sigma}\cdot\vec{\pi})^2}{2}\varphi_i\right]^\dagger + \varphi_i^\dagger V_{2\times 2}$$

Continuity equation:

$$q\dot{\rho}_0 = -\vec{\nabla}\cdot\vec{j}$$

$$q\left(\dot{\overline{\varphi_i^\dagger\varphi_i}}\right) = q\left(\varphi_i^\dagger\dot{\varphi}_i + \dot{\varphi}_i^\dagger\varphi_i\right) = \cdots = -\frac{q}{2}\vec{\nabla}\cdot\left\{\varphi_i^\dagger\vec{p}\,\varphi_i - \left[\vec{p}\,\varphi_i^\dagger\right]\varphi_i + i(\vec{p}\times\vec{\rho})\right\}$$

Pauli current density in the presence of magnetic fields:

$$\vec{j} = -\mathrm{Im}\{\varphi_i^\dagger\vec{\nabla}\varphi_i\} - \frac{1}{2}\left(\vec{\nabla}\times\vec{\rho}\right) - \frac{1}{c}\vec{A}\rho_0$$

orbital spin (Pauli) magnetic

Four-component current density within DFT

Time-dependent Dirac-Kohn-Sham equation:

$$i\dot{\varphi}_i = \left(c\vec{\alpha}\cdot\vec{p} + \vec{\alpha}\cdot\vec{A} + c^2\beta + V_{4\times4}\right)\varphi_i$$

$$-i\dot{\varphi}_i^\dagger = [c\vec{\alpha}\cdot\vec{p}\,\varphi_i]^\dagger + \varphi_i^\dagger\vec{\alpha}\cdot\vec{A} + c^2\varphi_i^\dagger\beta + \varphi_i^\dagger V_{4\times4}$$

$$\vec{\alpha} = \begin{pmatrix} 0 & \vec{\sigma} \\ \vec{\sigma} & 0 \end{pmatrix}$$

$$\beta = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

Continuity equation: $$q\dot{\rho}_0 = -\vec{\nabla}\cdot\vec{j}$$

$$q\dot{\left(\varphi_i^\dagger\varphi_i\right)} = \cdots = -q\nabla_j\left[\varphi_i^\dagger c\alpha_j\,\varphi_i\right]$$

Four-component electron current density: $$\vec{j} = -\varphi_i^\dagger c\vec{\alpha}\varphi_i$$

J. Chem. Phys. **128**, 104101 (2008)

J. Chem. Phys. **132**, 154101 (2010)

J. Phys. Chem. A **124**, 5157 (2020)

$$\varphi_{mi} = \mathrm{X}_{m,n\eta}^{\mathrm{RMB-GIAO}} C_{n\eta,i}^{0}$$

$$\mathrm{X}_{m,n\eta}^{\mathrm{RMB-GIAO}} = \begin{pmatrix} 1 & 0 \\ 0 & \frac{1}{2c}\vec{\sigma}\cdot\left(\vec{p} + \frac{1}{c}\vec{A}\right) \end{pmatrix}_{mn} \omega_\eta(\vec{B})\,\chi_\eta$$

Gordon decomposition

Time-independent Dirac-Kohn-Sham equation:

$$\left(c\vec{\alpha}\cdot\vec{p} + \vec{\alpha}\cdot\vec{A} + c^2\beta + V_{4\times4}\right)\varphi_i = \varepsilon_i\varphi_i \qquad \varphi_i = \frac{1}{c^2}\beta\left[\varepsilon_i - \left(c\vec{\alpha}\cdot\vec{p} + \vec{\alpha}\cdot\vec{A} + V_{4\times4}\right)\right]\varphi_i$$

Four-component current density:

$$\vec{j} = -\varphi_i^\dagger c\vec{\alpha}\varphi_i \qquad \vec{\alpha} = \begin{pmatrix} 0 & \vec{\sigma} \\ \vec{\sigma} & 0 \end{pmatrix} \qquad \beta = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

Gordon decomposition of four-component current density:

$$\vec{j} = -\mathrm{Im}\{\varphi_i^\dagger\vec{\nabla}\beta\varphi_i\} - \frac{1}{2}\left(\vec{\nabla}\times\vec{\rho}^G\right) - \frac{1}{c}\vec{A}\rho_0^G$$

$$\rho_0^G = \varphi_i^\dagger\beta\varphi_i \qquad \vec{\rho}^G = \varphi_i^\dagger\vec{\Sigma}\beta\varphi_i \qquad \vec{\Sigma} = \begin{pmatrix} \vec{\sigma} & 0 \\ 0 & \vec{\sigma} \end{pmatrix}$$

Pauli (non-relativistic) current density:

$$\vec{j} = -\mathrm{Im}\{\varphi_i^\dagger\vec{\nabla}\varphi_i\} - \frac{1}{2}\left(\vec{\nabla}\times\vec{\rho}\right) - \frac{1}{c}\vec{A}\rho_0$$

$$\rho_0 = \varphi_i^\dagger\varphi_i \qquad \vec{\rho} = \varphi_i^\dagger\vec{\sigma}\varphi_i$$

Calculation of magnetic properties

Energy within Dirac-Kohn-Sham theory: $E = \langle \varphi_i | c\vec{\alpha}\cdot\vec{p} + \vec{\alpha}\cdot\vec{A}(\lambda) + c^2\beta | \varphi_i \rangle + E^{2\mathrm{e}}$

Four-component current density: $\vec{j} = -\varphi_i^\dagger c\vec{\alpha}\varphi_i$ $\qquad \lambda = B_u, \mu_u^M$

$$\frac{dE}{d\lambda} = \int \varphi_i^\dagger \vec{\alpha}\varphi_i \cdot \frac{d\vec{A}}{d\lambda}\,\mathrm{dV} \quad = -\frac{1}{c}\int \vec{j}\cdot\frac{d\vec{A}}{d\lambda}\,\mathrm{dV}$$

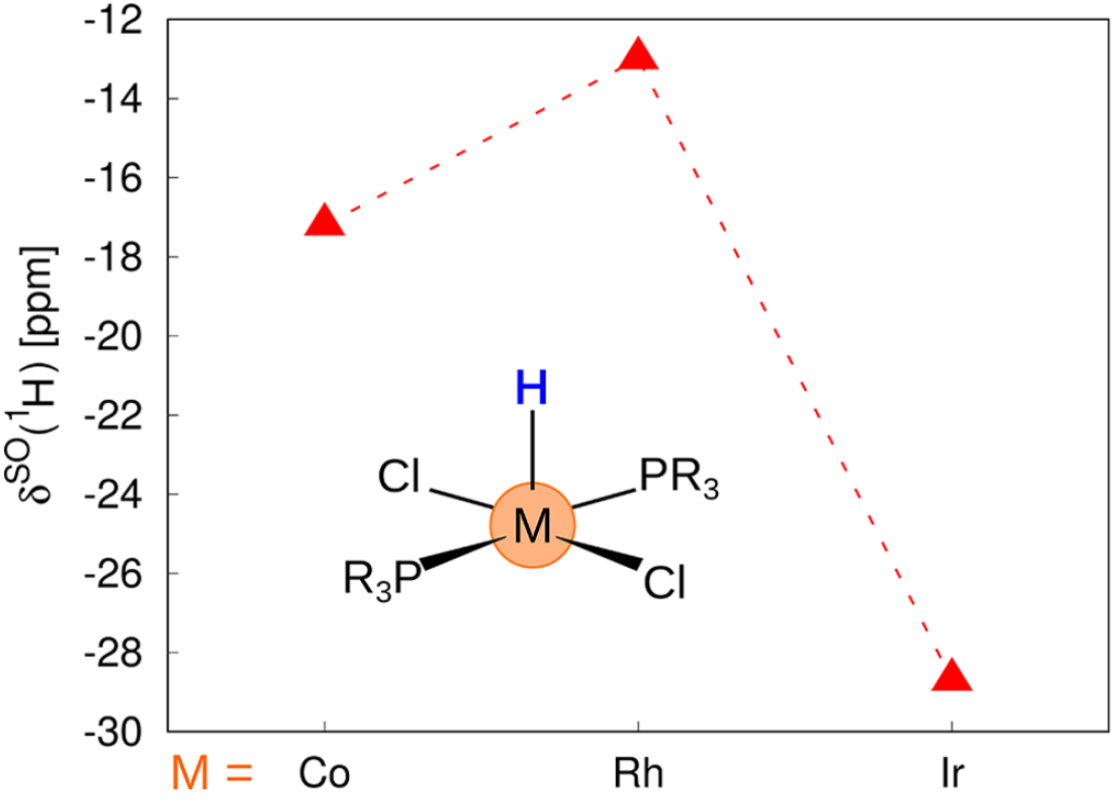
EPR g-tensor: $g_{uv} = 4c\left.\frac{dE(J_v)}{dB_u}\right|_0 = -4\int \vec{j}^0(J_v)\cdot\left.\frac{d\vec{A}}{dB_u}\right|_0 \mathrm{dV}$ $\qquad \vec{A}^B = \frac{1}{2}(\vec{B}\times\vec{r}_G)$

NMR shielding tensor: $\sigma_{uv}^M = \left.\frac{dE}{dB_u d\mu_v^M}\right|_0 = -\frac{1}{c}\int \left.\frac{d\vec{j}}{dB_u}\right|_0 \cdot \left.\frac{d\vec{A}}{d\mu_v^M}\right|_0 \mathrm{dV}$ $\qquad \vec{A}^M = \frac{\vec{\mu}^M\times\vec{r}_M}{r_M^3}$

$$\vec{j} = -\mathrm{Im}\{\varphi_i^\dagger\vec{\nabla}\beta\varphi_i\} - \frac{1}{2}(\vec{\nabla}\times\vec{\rho}^G) - \frac{1}{c}\vec{A}\rho_0^G$$

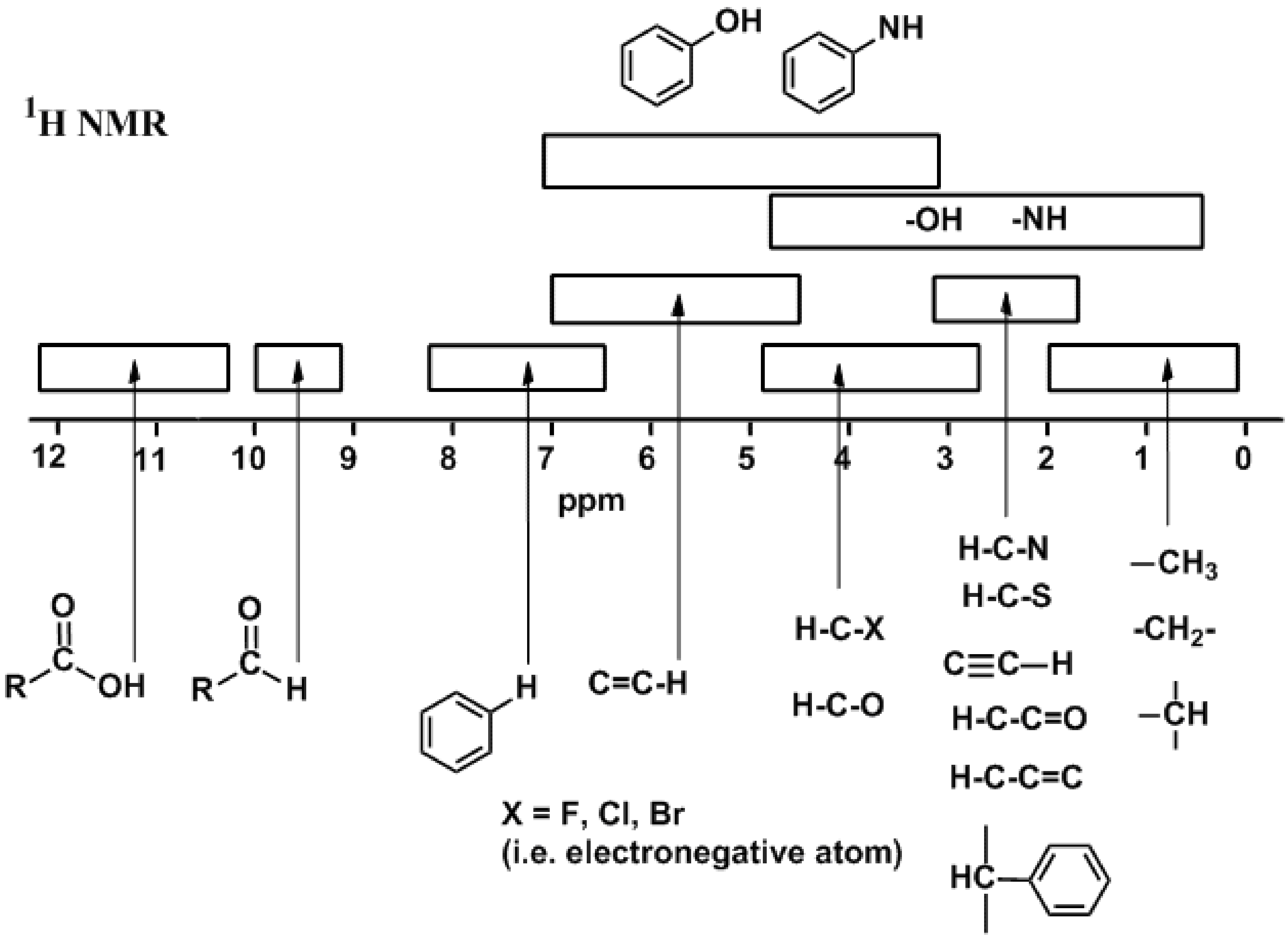
Heavy-Atom-Light-Atom effect

HALA

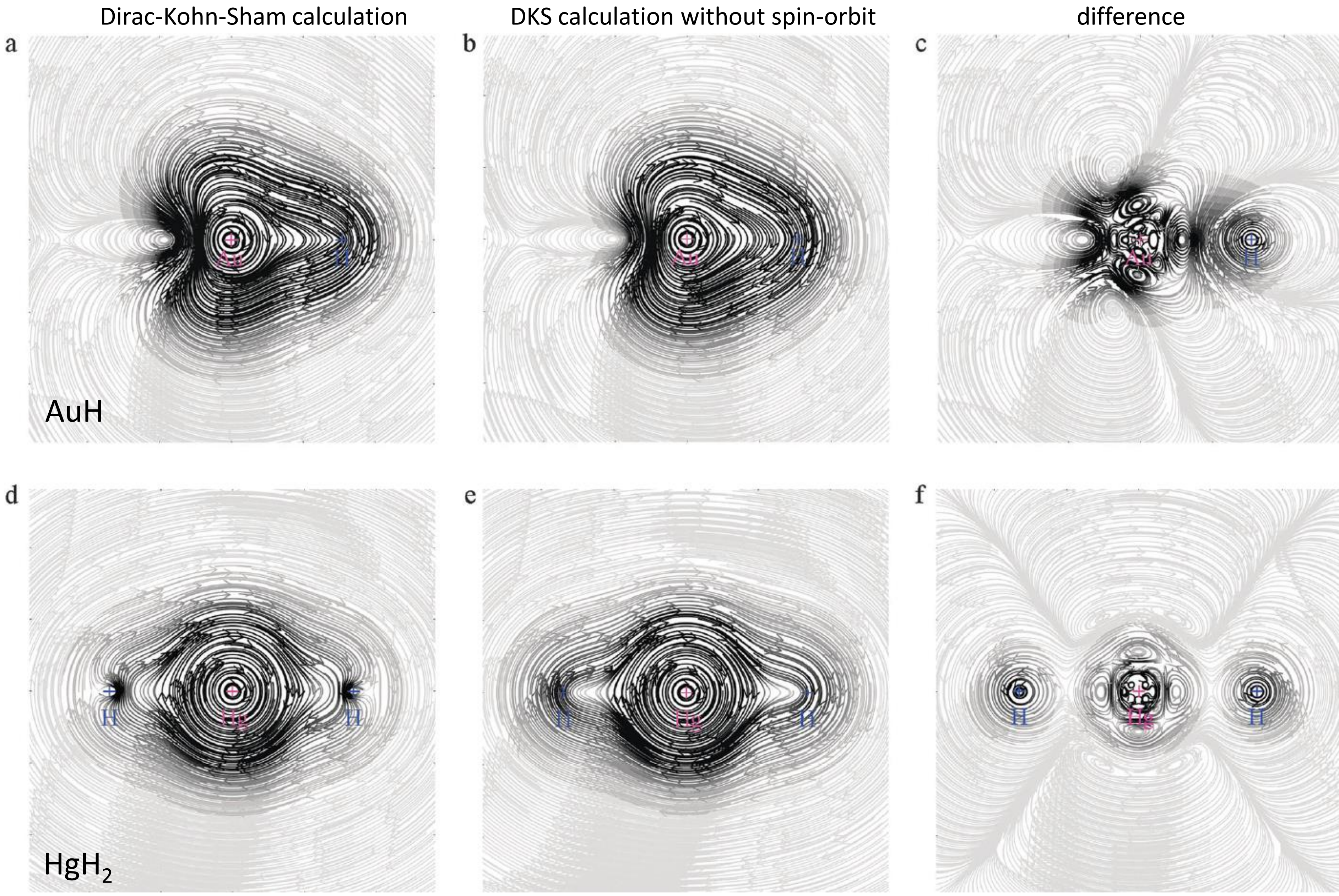


J. Vicha, J. Novotny, S. Komorovsky, M. Straka, M. Kaupp, and R. Marek, *Chem. Rev.* **120**, 7065−7103, (2020).

Typical ^{1}H NMR in organic compounds



Current density induced by an external uniform magnetic field



R. J. F. Berger, M. Repisky, and S. Komorovsky, Chem. Commun. **51**, 13961 (2015).

Heavy-Atom-Light-Atom effect

NMR shielding tensor:

$$\vec{r}_M = \vec{r} - \vec{R}_M$$

$$\sigma_{zv}^{\mathrm{SO},M} = -\frac{1}{c}\int \vec{j}^{\,\mathrm{SO},B_z} \cdot \left.\frac{d\vec{A}}{d\mu_v^M}\right|_0 \mathrm{dV} = -\frac{1}{c}\int \left[\frac{\vec{r}_M}{r_M^3} \times \vec{j}^{\,\mathrm{SO},B_z}\right]_v \mathrm{dV}$$

Model of circular current centred on $\vec{R}_M$:

$$\vec{j}^{\,\mathrm{SO},B_z} = \mp\left(\vec{z} \times f(r_M)\,\vec{r}_M\right) \qquad f(r_M) > 0$$

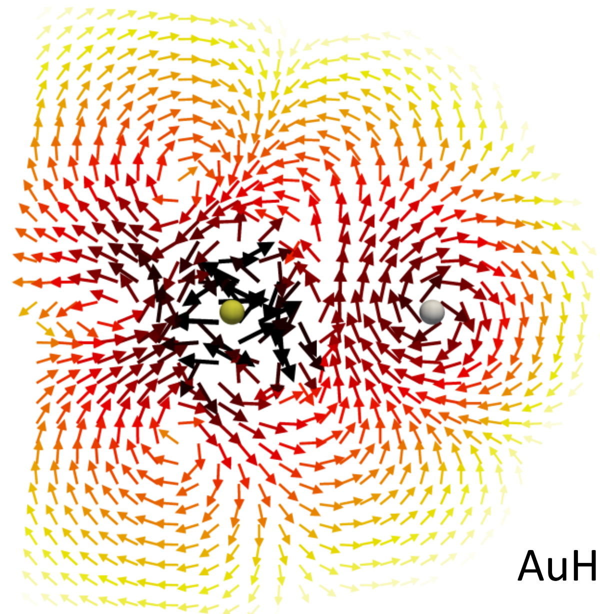
$$\sigma_{zz}^{\mathrm{SO},M} = \pm\frac{1}{c}\int \left[\vec{z}\left(\frac{\vec{r}_M}{r_M^3} \cdot f(r_M)\,\vec{r}_M\right) - f(r_M)\,\vec{r}_M\left(\frac{\vec{r}_M}{r_M^3} \cdot \vec{z}\right)\right]_z \mathrm{dV}$$

$$= \pm\frac{1}{c}\int \frac{f(r_M)}{r_M}\mathrm{dV}$$

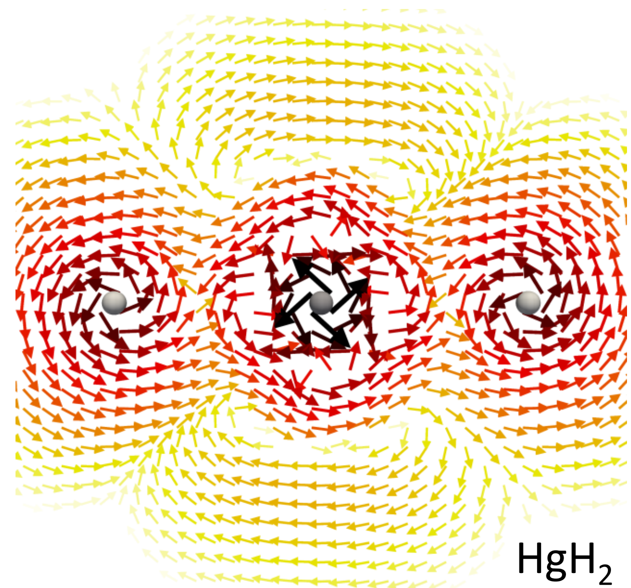
Clockwise: $-\left(\vec{z} \times f(r_M)\,\vec{r}_M\right)$ to shielding $\sigma_{zz}^{\mathrm{SO},M} > 0$

Anti-clockwise: $+\left(\vec{z} \times f(r_M)\,\vec{r}_M\right)$ to deshielding $\sigma_{zz}^{\mathrm{SO},M} < 0$

spin-orbit induced current



AuH



HgH_2

Magnetically and spin-orbit induced spin-density

Only spin-current has nonzero linear SO contribution:

$$\vec{j} = -\mathrm{Im}\{\varphi_i^\dagger \vec{\nabla}\beta\varphi_i\} - \frac{1}{2}\left(\vec{\nabla}\times\vec{\rho}^{\,G}\right) - \frac{1}{c}\vec{A}\rho_0^G$$

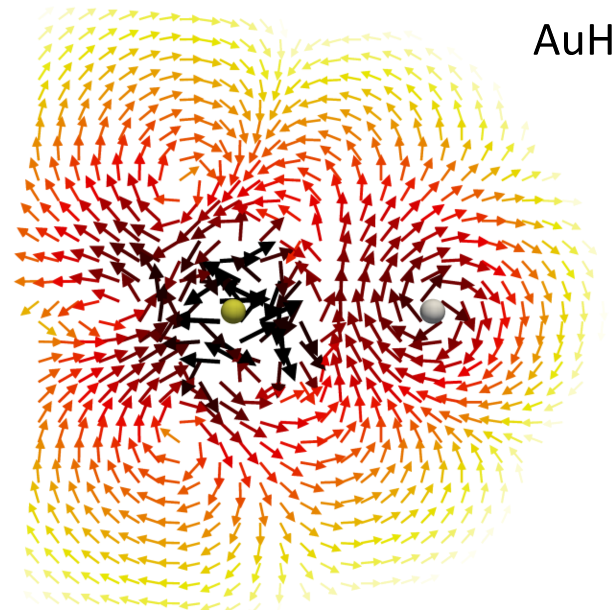
$$\vec{j}^{\,\mathrm{SO},B_z} = -\frac{1}{2}\left(\vec{\nabla}\times\vec{\rho}^{\,\mathrm{SO},B_z}\right)$$

Non-spherical part of

$\left|\vec{\rho}^{\,\mathrm{SO},B_z}\right|(\vec{r}_M)$

$$\sigma_{zz}^{\mathrm{SO},M} = -\frac{1}{c}\int\left[\frac{\vec{r}_M}{r_M^3}\times\vec{j}^{\,\mathrm{SO},B_z}\right]_z \mathrm{dV} = \frac{8\pi}{6c}\rho_z^{\mathrm{SO},B_z}(M) + \cdots$$

spin-orbit induced current

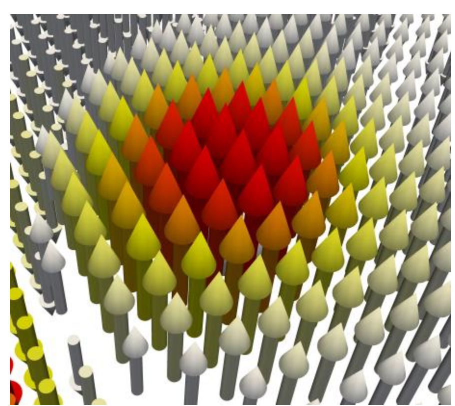


Model of spin-density with only z-component nonzero:

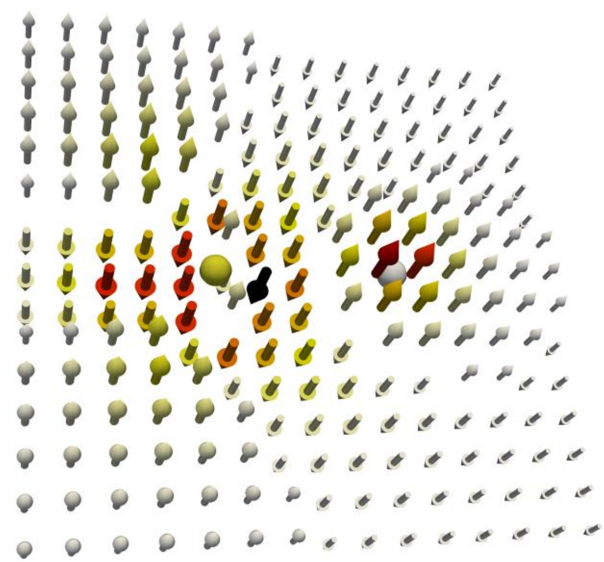
$$\vec{\rho}^{\,\mathrm{SO},B_z} = f(r_M)\vec{z} \qquad f(r_M) > 0 \qquad \max(f) = f(R_M)$$

$$\vec{j}^{\,\mathrm{SO},B_z} = -\frac{1}{2}\left(\vec{\nabla}\times f(r_M)\vec{z}\right)$$

$$= -\frac{|f'(r_M)|}{2r_M}\left(\vec{z}\times\vec{r}_M\right)$$



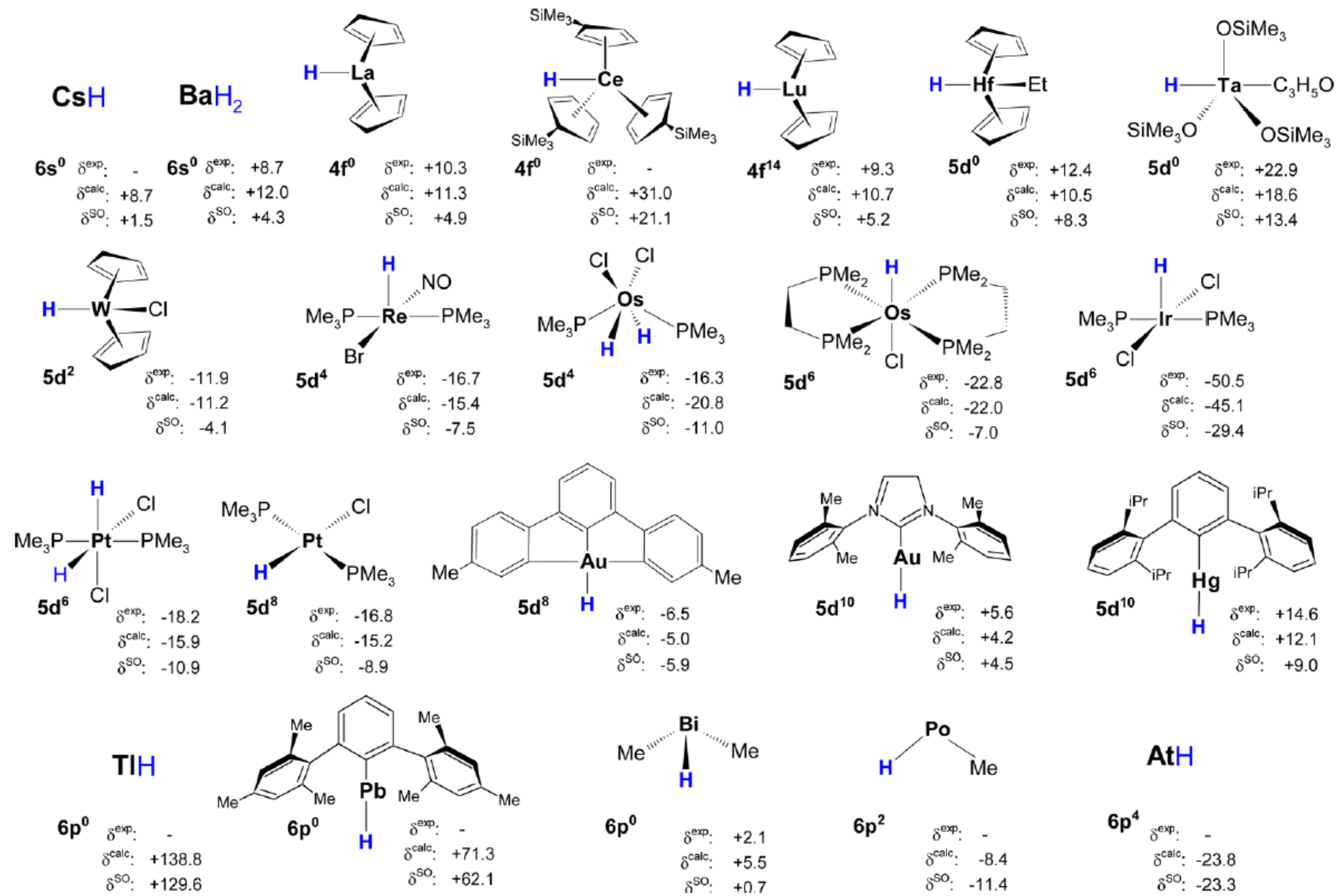
magnetically induced spin-density



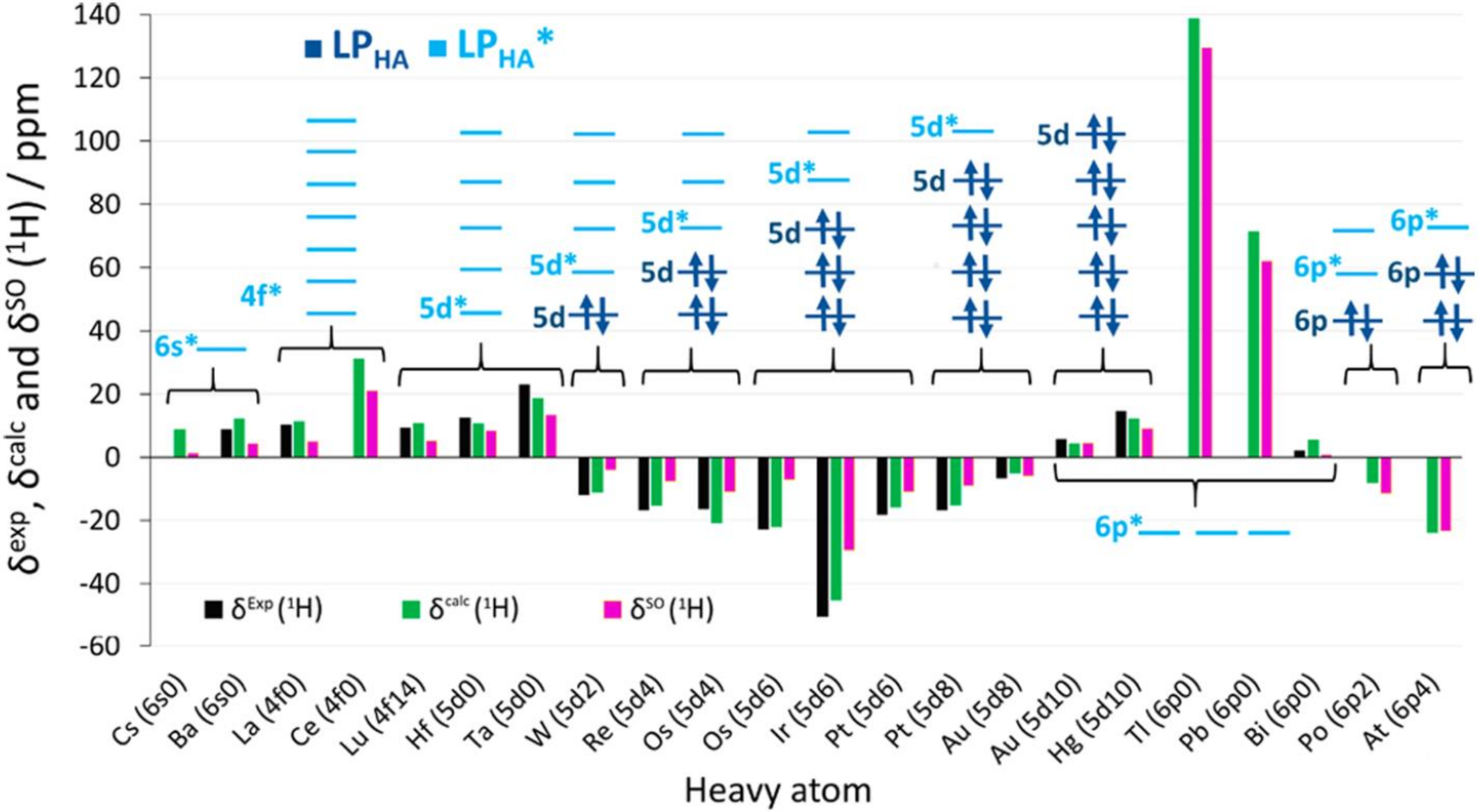
J. Novotny, J. Vicha, P. L. Bora, M. Repisky, M. Straka, S. Komorovsky, and R. Marek, *J. Chem. Theory Comput.* **13**, 3586−3601 (2017).

J. Vicha, S. Komorovsky, M. Repisky, R. Marek, and M. Straka, *J. Chem. Theory Comput.* **14**, 3025 (2018).

J. Vicha, J. Novotny, S. Komorovsky, M. Straka, M. Kaupp, and R. Marek, *Chem. Rev.* **120**, 7065−7103, (2020).



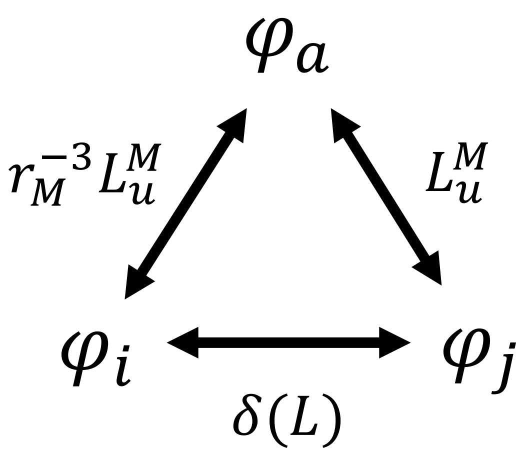
Trends across the periodic table

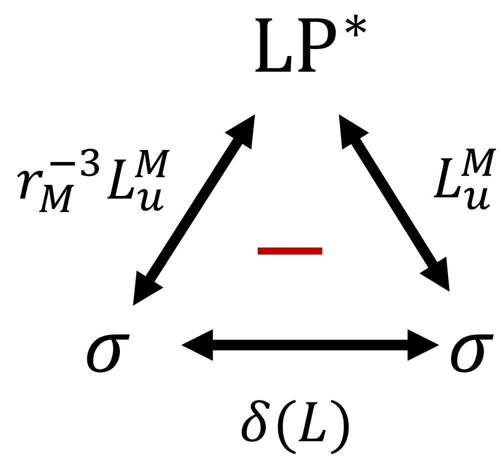


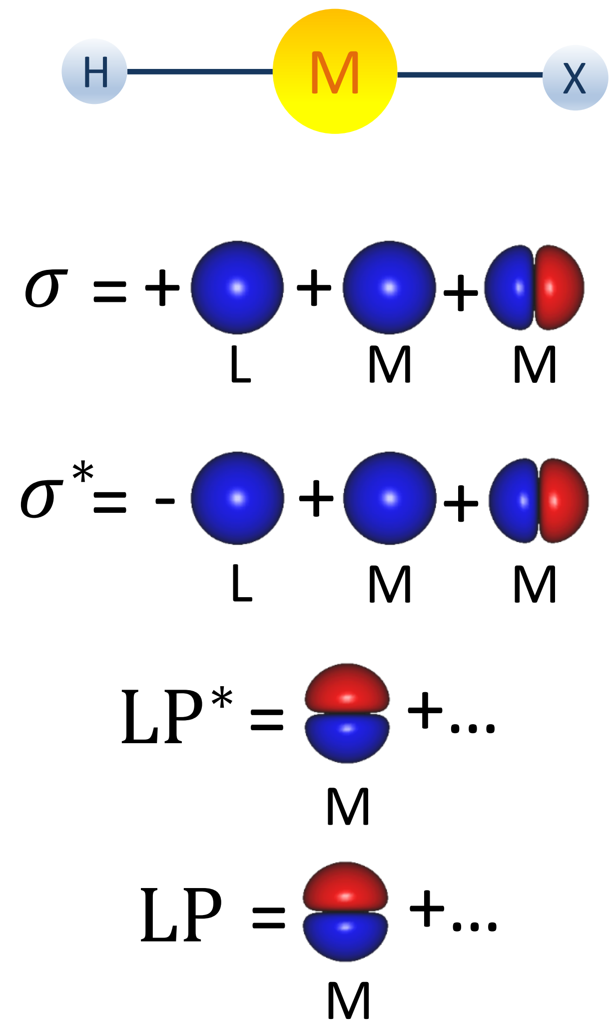
J. Chem. Theory Comput. **14**, 3025 (2018)

The dominant relativistic contribution is the coupling between SO/FC/OZ

$$\sigma_{uu}^{\mathrm{SO/FC^{\Delta}}}(L) \approx -\frac{1}{c^4}\sum_{i=1}^{\mathrm{occ}}\sum_{j=1}^{\mathrm{occ}}\sum_{a=1}^{\mathrm{vac}} \frac{\langle\varphi_a|r_M^{-3}L_u^M|\varphi_i\rangle\langle\varphi_i|\delta(L)|\varphi_j\rangle\langle\varphi_j|L_u^M|\varphi_a\rangle}{(\varepsilon_i-\varepsilon_a)(\varepsilon_j-\varepsilon_a)} + \cdots$$







$$\mathrm{sgn}\langle\varphi_i|L_u^M|\varphi_a\rangle = \mathrm{sgn}\langle\varphi_i|r_M^{-3}L_u^M|\varphi_a\rangle$$

$$\langle\varphi_a|r_M^{-3}L_u^M|\varphi_i\rangle\langle\varphi_j|L_u^M|\varphi_a\rangle > 0$$

$$(\varepsilon_i-\varepsilon_a)(\varepsilon_j-\varepsilon_a) > 0$$

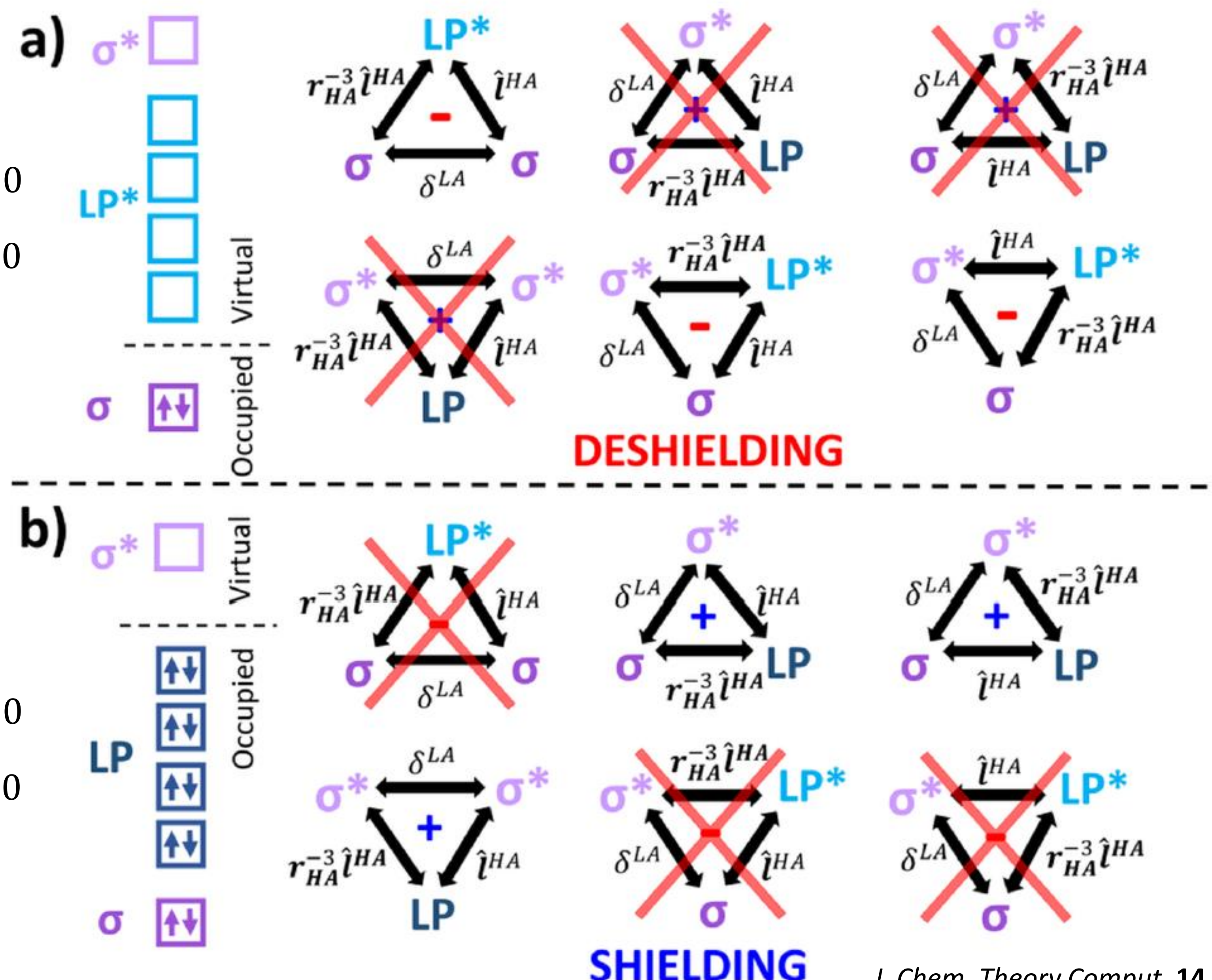
Two border cases

$\sigma^{SO} < 0$

$\delta^{SO} > 0$

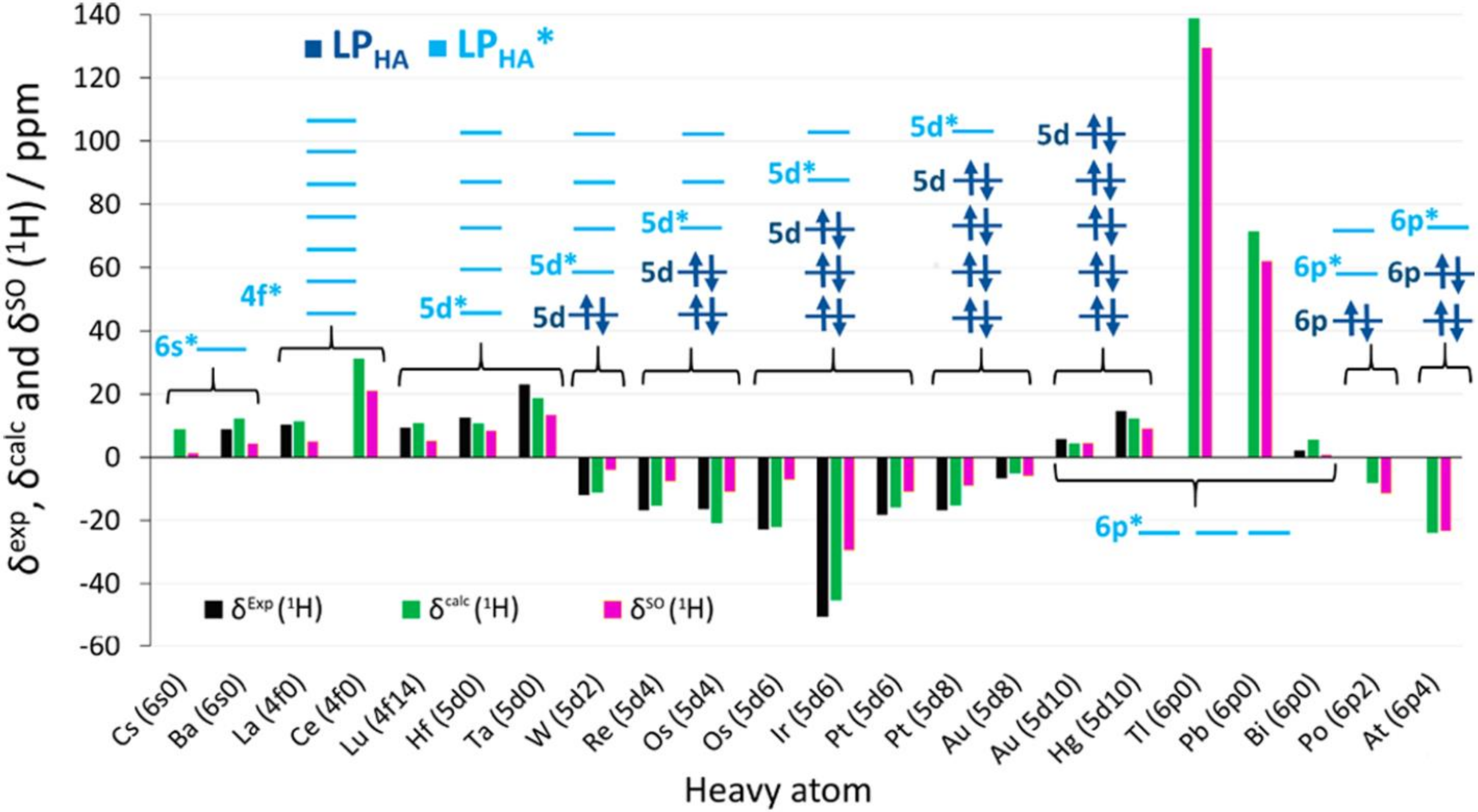
$\sigma^{SO} > 0$

$\delta^{SO} < 0$



J. Chem. Theory Comput. **14**, 3025 (2018)

Trends across the periodic table

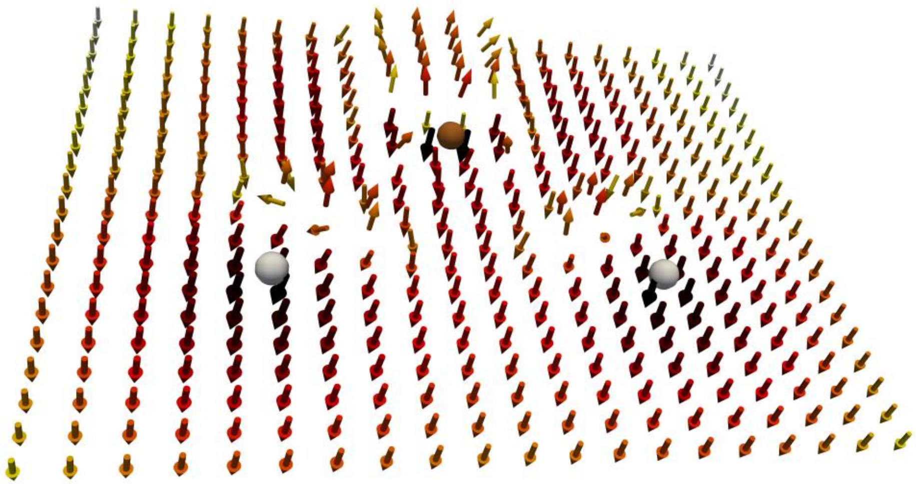


J. Chem. Theory Comput. **14**, 3025 (2018)

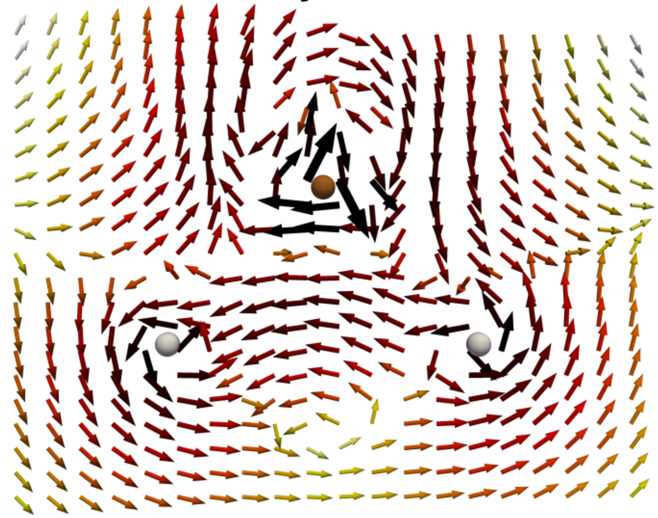
Competing case of both occupied and unoccupied valence orbitals

H2Po

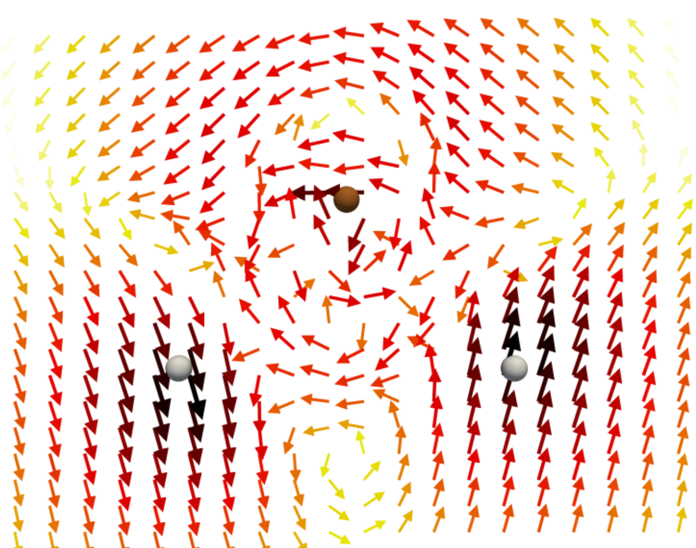
$\vec{\rho}^{\,SO,B_z}$

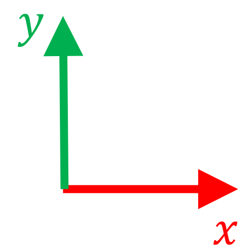


$\vec{j}^{\,SO,B_z}$

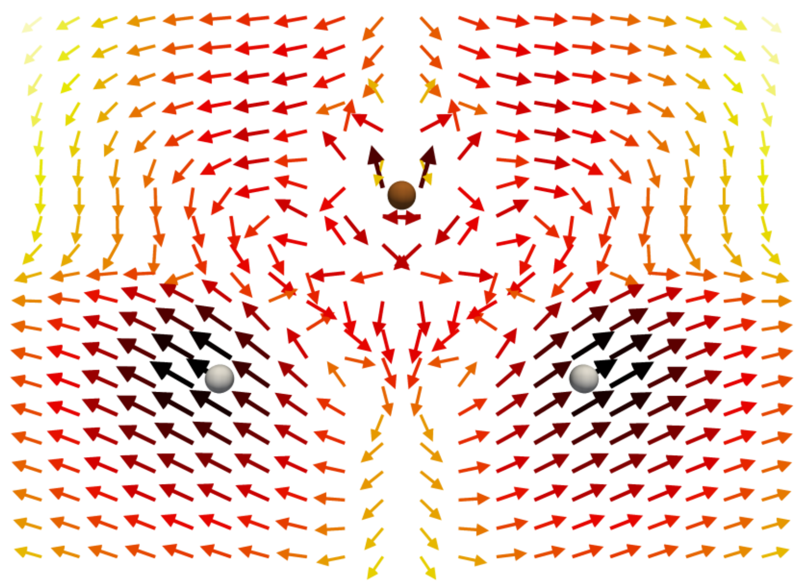


$\vec{\rho}^{\,SO,B_x}$





$\vec{\rho}^{\,SO,B_y}$



$$\sigma_{xx}^{SO,M} \sim \rho_x^{SO,B_x}(M)$$

$$\sigma_{yy}^{SO,M} \sim \rho_y^{SO,B_y}(M)$$

$$\sigma_{zz}^{SO,M} \sim \rho_z^{SO,B_z}(M)$$

Summary

Partially occupied heavy atom valence shells

induce relativistic **shielding** at the light atom nuclei,

while **empty** heavy atom valence shells

induce relativistic **deshielding**.

Acknowledgment

ReSpect

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Thank you
69.633353, 18.020557