COMMUNICATION

How does relativity affect magnetically induced currents?†

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Magnetically induced probability currents in molecules are studied in relativistic theory. Spin–orbit coupling (SOC) enhances the curvature and gives rise to a previously unobserved current cusp in AuH or small bulge-like distortions in HgH$_2$ at the proton positions. The origin of this curvature is magnetically induced spin-density arising from SOC in the relativistic description.

Under terrestrial conditions magnetic fields are omnipresent and even in environments free of external magnetic fields nuclear magnetic moments are present. The electronic probability current density vector field ($\mathbf{j_B}$) is the fundamental property for the description of the magnetic response of a molecule to an external magnetic field $\mathbf{B}$. Various programs for the computation of numerical approximations to $\mathbf{j_B}$ have been developed,[1–3] and exemplary studies have been reviewed some years ago.[4] Other magnetic response properties like the magnetic susceptibility, induced magnetic multipole-moments or even chemical shieldings can directly be calculated from $\mathbf{j_B}$.[5] $\mathbf{j_B}$ can be determined experimentally, as it was shown in two conceptional studies using polarized neutron diffraction.[6,7] Two of us (SK, MR) have developed in the framework of the program ReSpect[8] methods for a fully relativistic four-component treatment (FR) capable of calculating $\mathbf{j_B}$ in polyatomic molecules. In this current version of ReSpect also a physically consistent determination of the influence of solely the relativistic spin–orbit coupling (SOC) contribution to $\mathbf{j_B}$ is possible. This is one of the first investigations where particular SOC contributions to FR molecular currents are reported. The only other work where a FR method was employed to analyze the SOC contribution to $\mathbf{j_B}$ involved the Sternheim approximation[9] to the diamagnetic contribution of

the response current.[10] Later Sulzer and coworkers overcame this approximation by using the simple magnetic balance approach but they have not regarded the specific nature of the SOC contributions they yielded.[11] In this work we use a computationally efficient solution based on the restricted magnetic balance framework.[12] We have chosen gold(I) hydride (AuH) and mercury(II) bishydride (HgH$_2$) as subjects of this study due to their simplicity and since they are in the non-relativistic (NR) framework single reference singlets.

Not taking SOC into account (computational details are provided in the ESI†), AuH sustains one large gold centered diatropic (inductively weakening the external field $\mathbf{B}$) current loop (see Fig. 1b) with a distinct extension directed to the proton. At the FR level (Fig. 1a) the current topology remains unchanged, however, it appears that the current loops contain considerably more curvature around the atomic cores and most notably a kind of current cusp appears at the position of the proton, which without regarding SOC effects (non-SOC) is passed over by a smooth current. Such a cusp structure in molecular ring currents, to the best of our knowledge is previously unobserved. The current difference plot (FR minus non-SOC, Fig. 1c) shows that this cusp originates solely from SOC, causing a strongly localized ring current around the proton. It can be easily seen that a ring current of suitable orientation when added to a smooth current field with little curvature yields a total current of such a cusp shape. However, it is required that the strength of the ring current contribution in the area of the cusp is approximately constant and equal in strength to the smooth current field contribution. Apparently, these conditions are met in the case of AuH. In a homogeneous magnetic field of 1 T strength the total current of the SOC induced vortex around the hydrogen atom integrates to 1.6 nA (see the ESI† for computational details). This additional diatropic vortex causes an SOC induced high field chemical shift of the proton of about −19 ppm compared to the non-SOC calculation (FR shielding: 54 ppm, non-SOC shielding: 35 ppm). The corresponding difference (FR minus non-SOC) of only the z components of the shielding tensor, which can be directly

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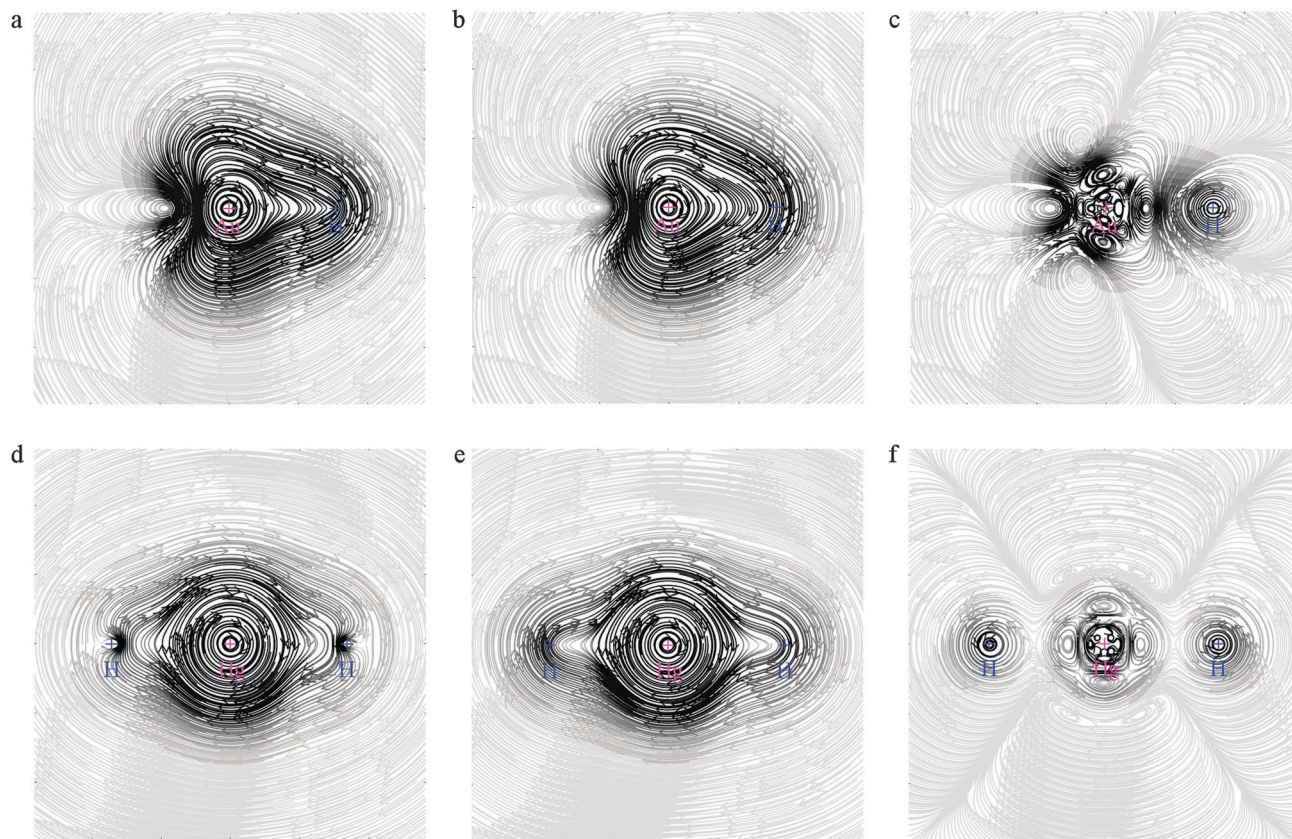
Fig. 1 Streamline plots in AuH and HgH$_2$. B is set perpendicular to the plot plane, all atoms are in the plane. Diatropic currents (weakening B) show clockwise and paratropic currents (enhancing B) have anti-clockwise orientation. The line shading intensity is proportional to the current strengths. (a) AuH, fully relativistic; (b) AuH, without spin–orbit coupling; (c) AuH, difference plot from (a) and (b); (d) HgH$_2$, fully relativistic; (e) HgH$_2$, without spin–orbit coupling; (f) HgH$_2$, difference plot from (d) and (e).

(without taking into account directional averaging) related to the integrated and plotted $\mathbf{j_B}$ field, is −30 ppm. To quantify the additional curvature of the current field in the region around the hydrogen atom one can calculate the radius of a circular loop of an infinitely thin wire, causing a field of −30 ppm of 1 T (3.0×10^{-5} T) at the center of the loop (hydrogen atom position) and sustaining a current of 1.6 nA using the Biot–Savart law. This yields a loop radius of 0.35 Å or a curvature (reciprocal radius) of 2.9 Å^{-1}.

At the molecular currents of HgH$_2$ at the non-SOC level of theory (Fig. 1e), we find very similar conditions to those in AuH with the exception that the extension of the currents to the proton positions is slightly more pronounced than in AuH. Going to the full relativistic level of theory we again see that more curvature is introduced into the streamlines (Fig. 1d). Unlike in AuH here a drop-shaped deformation of the currents, directed to the center of the molecule, is induced by SOC effects. Again its origins can be readily seen in the difference plot in Fig. 1f (FR minus non-SOC), showing small SOC induced localized current loops on the proton positions. In contrast to the situation in AuH these additional local current loops in HgH$_2$ are paratropic (inductively enhancing the external field B), leading to drop-shaped perturbations rather than the cusp-shaped ones seen in AuH. An integration (see the ESI† for computational

details) of these SOC induced local current vortices yields a local paramagnetic contribution of −1.5 nA (in a magnetic field of 1 T). At the SOC level of theory the isotropic ^{1}H chemical shieldings (10 ppm) are found to be down field shifted by +17 ppm as compared to their non-SOC equivalents (27 ppm). An analogous consideration of the curvature as for AuH yields a loop radius of 0.41 Å or a curvature of 2.4 Å^{-1}.

For an explanation of these findings the following can be considered: $\mathbf{j_B}$ in a single charged spin-free particle in the NR framework contains a sum of two terms which are conventionally called diamagnetic and paramagnetic terms, together these might be called 'Pauli-current'§ ($\mathbf{j_B^{Pauli}}$). In the case of a many-particle system described in an effective single particle picture like HF or Kohn–Sham DFT with the total spin equal to zero, like for example a closed shell molecule, $\mathbf{j_B}$ reduces to the sum of Pauli-current terms of each particle. In the NR framework there are simple MO selection rules allowing for a prediction and a chemical interpretation of these currents,[13,14] and the physics of the NR contribution to the molecular currents appears to be well understood. For systems with non-zero spin, and again in the NR case, $\mathbf{j_B}$ is the sum of the Pauli-current terms plus a 'spin-current' term $\mathbf{j^{spin}}$:

$$\mathbf{j_B^{NR}} = \mathbf{j_B^{Pauli}} + \mathbf{j^{spin}} \tag{1}$$

Hereby $\mathbf{j}^{spin}$ is the curl of the density of the magnetic moment $\mathbf{\mu}^{spin}$ arising from spin:

$$\mathbf{j}^{spin} = \text{rot } \mathbf{\mu}^{spin} \qquad (2)$$

The density of the magnetic moment arising from spin, $\mathbf{\mu}^{spin}$, is directly proportional to the spin-density¶ distribution $\mathbf{\rho}^{spin}$ of the system:

$$\mathbf{\mu}^{spin} = -e/m\, \mathbf{\rho}^{spin} \qquad (3)$$

This means that $\mathbf{\mu}^{spin}$ (or $\mathbf{\rho}^{spin}$) is represented by a current field $\mathbf{j}^{spin}$ and both are related by eqn (2). In classical electrodynamics (using $\mathbf{j}$ instead of $\mathbf{j}^{spin}$, and $\mathbf{B}$ instead of $\mathbf{\mu}^{spin}$) eqn (2) is Ampères law. It relates currents to the magnetic field they induce. It can be shown that in the NR case, eqn (1) also holds for a system of n-electrons with non-zero total spin in an effective one-particle picture (summing up one-particle terms).

We are here interested in a fully relativistic description including spin–orbit effects of currents in a magnetic field $\mathbf{j}_{\mathbf{B}}^{FR}$ for "closed shell" molecules (*i.e.* singlet states in the NR picture). Treating SOC and $\mathbf{B}$ as a perturbation and using an effective one-particle description, it can be shown[15] that up to second order terms, the total current

$$\mathbf{j}_{\mathbf{B}}^{FR} \approx \mathbf{j}_{\mathbf{B}}^{Pauli} + \mathbf{j}_{\mathbf{B},SOC}^{spin} + \mathbf{j}_{\mathbf{B},scalar} \qquad (4)$$

where $\mathbf{j}_{\mathbf{B},SOC}^{spin}$ is a spin-current which is induced into the closed shell, spin-zero system by the presence of both the magnetic field and SOC, while $\mathbf{j}_{\mathbf{B},scalar}$ is the scalar relativistic remainder of the induced current density. Note that first order SO effects contribute exclusively *via* $\mathbf{j}^{spin}$ to the response current density, while scalar relativistic effects contribute *via* $\mathbf{j}^{spin}$ and $\mathbf{j}^{Pauli}$ like terms (in the sense of the Gordon decomposition of the four-component current[16]). Due to the short range of the SOC effect the perturbations of the singlet wave function in the first instance are spatially in close proximity to the heavy nuclei causing the SOC effect, but when such perturbations occur within a covalent bond between the heavy atom and a light atom the perturbation extends also to a spatial region around the bound light atom. This is a key mechanism of the so-called heavy-atom–light-atom (HALA) effect.[17–19] In the presence of an external magnetic field B and under consideration of SOC a non-zero and non-constant spin-density is induced into the wave function. The spin-current that directly corresponds to this induced spin-density is, in very good approximation, the only spin–orbit contribution to the currents (see the ESI† for details of term partitioning)

$$\mathbf{j}_{\mathbf{B}}^{FR} - \mathbf{j}_{\mathbf{B}}^{non\text{-}SOC} \approx \mathbf{j}_{\mathbf{B},SOC}^{spin} = -(e/m)\, \text{rot } \mathbf{\rho}_{\mathbf{B},SOC}^{spin} \qquad (5)$$

(where we have used the same definitions as for eqn (4) and $\mathbf{j}_{\mathbf{B}}^{non\text{-}SOC} = \mathbf{j}_{\mathbf{B}}^{Pauli} + \mathbf{j}_{\mathbf{B},scalar}$). Thus studying pure SOC influences on magnetically induced currents in 'closed-shell' molecules can be reduced to studying the SOC induced spin-density in the

magnetic field $\mathbf{\rho}_{\mathbf{B},SOC}^{spin}$. The SOC coupling mechanism explains why the effects are confined to a surrounding of the nuclei and why they can extend to covalently bond lighter atoms as we have observed in AuH and HgH_2.

We have developed computational methods to calculate four-component relativistic magnetically induced molecular ring currents. Case studies on AuH and HgH_2 illustrate that spin–orbit coupling influences the shape of induced currents leading to intriguing curvature and strongly localized ring current contributions to hydrogen atoms bound to gold and mercury. In this way we have revealed the ring current picture of the HALA effect. SOC induced currents in the magnetic field can be traced back directly to an induced spin-density *via* a relation resembling Ampères law. In general a non-zero and non-constant spin-density arises in 'closed shell' molecules due to the presence of both a magnetic field and SOC.

Notes and references

§ Alternative definitions of the term 'Pauli current' are in use. This one might be justified by the notion that it is the current terms which arise already from the Pauli equation.[20,21]

¶ Which is defined as $\mathbf{\rho}^{spin} = \hbar/2\, \langle\mathbf{\sigma}\rangle$, integrating over spin coordinates.

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