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Electron localization function for non-collinear spins

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We extend the electron localization function — a popular descriptor of molecular bonds and atomic shells — to general non-collinearly magnetized states, open-shell solutions of the Pauli-Schrödinger equation. The description is also improved in paradigmatic, collinear states.

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Introduction. An ongoing effort in physics and chemistry is to turn the concept of bonds among atoms into a quantitative modeling tool to handle understanding and prediction in most general and novel regimes.[1] This quest started before the discovery of quantum mechanics with the Lewis picture of bonding.[2] This was then incarnated in the modern approach by the valence bond (VB) theory of Heitler and London.[3] Which, in turn, inspired the concept of "resonance" by Pauling[4] and, eventually, models of condensed matter in terms of resonant valence bonds by P.W. Anderson[5] and valence shell electron pair repulsion theory.[6] The idea of sharing electrons is also at the base of the so-called molecular orbital theory, which introduces single-particle orbitals delocalized over the molecule.

The Kohn-Sham (KS) formulation of density functional theory (DFT) is a molecular orbital theory and, currently, is also the most applied computational methodology in chemistry and materials science.[7] At the center of the success of KS-DFT is the exchange correlation (xc) energy functional — a functional of the particle density. A pioneering observation by Bader revealed that the Laplacian of the particle density handles the visualization of atomic shells and bonds[8,9] — although not always successfully — and kicked off the challenge of describing bonds within a DFT-like modeling. Two cornerstones of which are the "quantum theory of atoms in molecules and crystals" and the "electron localization function".[10] In this letter we shall focus on the latter.[11]

Following suggestions by Bader,[12,13] Becke and Edgecombe exploited the anti-symmetry of the many-body state to probe the localization of electrons via the information available at the level of a single Slater determinant for (globally) *collinear* states: if an electron is localized at a given point in space, another electron cannot be brought at the same position with the same spin. This behavior can be captured via the same-spin pair density[14] $P_{\sigma\sigma}(\mathbf{r}_1,\mathbf{r}_2) = N(N-1)\int d3d4...dN\ |\Psi(\mathbf{r}_1\sigma,\mathbf{r}_2\sigma,3,...,N)|^2$ where the many-electron wave function $\Psi(1,2,3,...,N)$, for simplicity, is taken as an N-electron Slater determinant; $1,2,...,N$ stands for the combined spatial plus spin variables $(\mathbf{r}_1,\sigma_1),(\mathbf{r}_2,\sigma_2),...,(\mathbf{r}_N,\sigma_N)$. Therefore, the *conditional* probability $P_{\sigma\sigma}(\mathbf{r}_1,\mathbf{r}_2)/n_\sigma(\mathbf{r}_1)$ — where $n_\sigma(\mathbf{r}_1)$ is the spin-electron density — refers to the event of finding a second electron at $\mathbf{r}_2$ given the first electron at $\mathbf{r}_1$. Restricting to collinear states, setting $\mathbf{r}_1 = \mathbf{r}$ and $\mathbf{r}_2 = \mathbf{r}_1 + \mathbf{u}$, and taking the spherical average around $\mathbf{r}_1$, one then readily finds $P_{\sigma\sigma}(\mathbf{r},u)/n_\sigma(\mathbf{r}) = \frac{1}{3}D_\sigma(\mathbf{r})u^2 + \cdots$, where: $D_\sigma(\mathbf{r}) = \left[2\tau_\sigma(\mathbf{r}) - \frac{1}{4}\nabla n_\sigma(\mathbf{r})\cdot\nabla n_\sigma(\mathbf{r})/n_\sigma(\mathbf{r})\right]$ and $\tau_\sigma(\mathbf{r}) = \frac{1}{2}\Sigma_{i=1,N_\sigma}|\nabla\varphi_{i,\sigma}(\mathbf{r})|^2$ is the kinetic energy density of the electrons in the N_σ single-particle orbitals $\varphi_{i,\sigma}(\mathbf{r})$. Next, Becke and Edgecombe defined the spin-dependent electron localization function as follows

$$\mathrm{ELF}_\sigma(\mathbf{r}) \equiv \frac{1}{1+\left[D_\sigma(\mathbf{r})/D_\sigma^{\mathrm{unif}}(\mathbf{r})\right]^2} \tag{1}$$

where $D_\sigma^{\mathrm{unif}}(\mathbf{r}) = \frac{3}{5}\left(6\pi^2\right)^{2/3} n_\sigma^{5/3}(\mathbf{r})$ is $D_\sigma(\mathbf{r})$ evaluated for a homogeneous electron gas with the same local density of the real system. Eq. (1) is a simple scalar quantity comprised between 0 (zero localization), 1/2 (electron gas-like localization) and 1 (full localization). In practice, one usually runs a DFT calculations and evaluates the ratio $D(\mathbf{r})/D^{\mathrm{unif}}(\mathbf{r})$ using the corresponding KS orbitals.

Since its inception, the ELF has become important beyond the purpose of rationalizing chemical structures and synthesis thereof: it provided insights for improving density functional approximations.[15–19] The ELF has also been linked to the ability of density functionals to access local information on the spin-entanglement,[20] to properties of the electronic stress tensor,[21] to features of (time-dependent) density functionals.[22,23]

Switching to *non-collinear* states, the single-particle orbitals must be upgraded to two-component spinors — none of which may point just "up" or "down". The direction of the magnetization (defined more below) may change from point to point. *Locally* the magnetization provides us with a meaningful *collective* direction of spin, but may not represent the configuration of any of the underlying single-particle spinors. The restriction used in the construction of the ELF is eluded, which brings up the question whether it may be extended to work also for non-collinear states.

Solution. For tackling this problem, let us invoke the

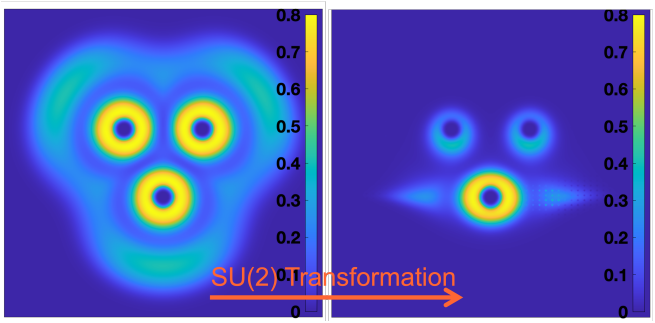

FIG. 1: Naïve ELF of Eq. (5) for the molecular plane of the Cr_3 non-collinear magnet obtained before (left) and after (right) an SU(2) gauge transformation (see main text for details). The curious reader can find the plot of the gauge-invariant ELF in Fig. 2.

expression *and* the interpretation of the ELF by Savin and collaborators[24]

$$\mathrm{ELF}(\mathbf{r}) \equiv \frac{1}{1+\left[D(\mathbf{r})/D^{\mathrm{unif}}(\mathbf{r})\right]^2} \tag{2}$$

Here, the spin-resolved quantity $D_\sigma(\mathbf{r})$ is replaced by the *spin-summed* quantity

$$D(\mathbf{r}) = \tau(\mathbf{r}) - \frac{\nabla n(\mathbf{r})\cdot\nabla n(\mathbf{r})}{8n(\mathbf{r})}\ , \tag{3}$$

which is thus normalized relative to the spin-unpolarized $D^{\mathrm{unif}}(\mathbf{r}) = \frac{3}{10}\left(3\pi^2\right)^{2/3} n^{5/3}(\mathbf{r})$. It can be readily shown that[25] $D(\mathbf{r})$ is a non-negative quantity $D(\mathbf{r}) \geq 0$. Thus, $D(\mathbf{r})$ can be regarded as the *excess* of the fermionic kinetic energy $\tau(\mathbf{r})$ as compared to the "bosonic kinetic energy" $\nabla n(\mathbf{r})\cdot\nabla n(\mathbf{r})/8n(\mathbf{r})$: small values of the electron localization correspond to large excess fermionic kinetic energy.[24]

Next, initiating the analysis that will bring us to the extension of the ELF, let us consider the gauge aspects involved in the electron localization function. In modern geometric parlance,[26,27] (local) gauge transformations can be understood in terms of the changes in the local frames used in the representation of the quantum states. This interpretation makes it apparent that gauge invariance must be a general and stringent condition for any quantity to hold an intrinsic physical meaning — i.e., expressing the independence of a physical property from the particular choices made for its representation (or computation).

As a well-known and enlightening example, consider states carrying a (paramagnetic) particle current, $\mathbf{j}(\mathbf{r}) = \sum_{k=1}^{N} \Im\left\{\varphi_k^*(\mathbf{r})\left[\nabla\varphi_k(\mathbf{r})\right]\right\}$, as for instance, a molecule in an external magnetic field. The necessary modification of the ELF, can be derived in several ways.[22,28,29] On parallel developments, the importance of the dependence of xc functionals on the particle current has been largely demonstrated[30–38] A unifying approach for adding particle currents to density functionals and the like is to consider the effect of a U(1) gauge transformations:[39] $\varphi'(\mathbf{r}) = \exp\left[\frac{i}{c}\chi(\mathbf{r})\right]\varphi(\mathbf{r})$. The particle density is obviously invariant but the kinetic energy density transforms as follows:

$$\tau'_{\mathrm{nc}}(\mathbf{r}) = \tau_{\mathrm{nc}}(\mathbf{r}) + \frac{1}{c}\mathbf{j}(\mathbf{r})\cdot\mathbf{A}_{\mathrm{G}}(\mathbf{r}) + \frac{n(\mathbf{r})}{2c^2}\mathbf{A}_{\mathrm{G}}(\mathbf{r})\cdot\mathbf{A}_{\mathrm{G}}(\mathbf{r}) \tag{4}$$

where $\mathbf{A}_{\mathrm{G}}(\mathbf{r}) = c\nabla\chi(\mathbf{r})$ is a pure gauge (Abelian) vector potential. Therefore, a current-dependent and gauge invariant ELF is readily recovered by replacing $\tau(\mathbf{r}) \to \widetilde{\tau}(\mathbf{r}) = \tau(\mathbf{r}) - \mathbf{j}(\mathbf{r})\cdot\mathbf{j}(\mathbf{r})/2n(\mathbf{r})$ in $D(\mathbf{r})$ in Eq. (3).

Keeping in mind the above observations, let us come back to consider non-collinear (nc) states, as for instance, the ground state of the planar Cr_3 molecular magnet. Ignoring for simplicity the U(1) aspects reviewed just above, it is tempting to extend the ELF by simply evaluating $\tau(\mathbf{r})$ on the two-component spinors $\Phi(\mathbf{r})$: i.e., $\tau(\mathbf{r}) \to \tau_{\mathrm{nc}}(\mathbf{r}) = \frac{1}{2}\Sigma_k\left[\nabla\Phi_k(\mathbf{r})\right]^\dagger\cdot\nabla\Phi_k(\mathbf{r})$. Performing such a replacement in $D(\mathbf{r})$, yields $D(\mathbf{r}) \to D_{\mathrm{nc}}(\mathbf{r}) \equiv \tau(\mathbf{r}) - \frac{1}{8}\nabla n(\mathbf{r})\cdot\nabla n(\mathbf{r})/n(\mathbf{r})$. Which, in turn, would suggest the following naïve expression

$$\mathrm{ELF}_{\mathrm{naïve}}(\mathbf{r}) = \frac{1}{1+\left[D_{\mathrm{nc}}(\mathbf{r})/D^{\mathrm{unif}}(\mathbf{r})\right]^2}\ . \tag{5}$$

Recall now that an SU(2) gauge transformation acts on the spinors by locally rotating them as follows $\Phi'(\mathbf{r}) = \exp\left[\frac{i}{c}\lambda^a(\mathbf{r})\sigma^a\right]\Phi(\mathbf{r})$, according to the spin-vector $\vec{\lambda}(\mathbf{r})$. It is straightforward to verify that under an SU(2) transformation, $\tau_{\mathrm{nc}}(\mathbf{r})$ transforms as follows:

$$\tau'_{\mathrm{nc}}(\mathbf{r}) = \tau_{\mathrm{nc}}(\mathbf{r}) + \frac{1}{c}\mathbf{J}^a(\mathbf{r})\cdot\mathbf{A}^a_{\mathrm{G}}(\mathbf{r}) + \frac{n(\mathbf{r})}{2c^2}\mathbf{A}^a_{\mathrm{G}}(\mathbf{r})\cdot\mathbf{A}^a_{\mathrm{G}}(\mathbf{r})\ , \tag{6}$$

where $\mathbf{J}^a(\mathbf{r}) = \sum_{k=1}^{N}\Im\left\{\Phi_k^\dagger(\mathbf{r})\sigma^a\left[\nabla\Phi_k(\mathbf{r})\right]\right\}$ are the (paramagnetic) spin currents and $\mathbf{A}^a_{\mathrm{G}}(\mathbf{r}) = -\frac{ic}{2}\mathrm{Tr}\left(\sigma^a U_{\mathrm{S}}^\dagger(\mathbf{r})\nabla U_{\mathrm{S}}(\mathbf{r})\right)$ are the component of a pure gauge (non-Abelian) vector potential.[40]

Let us visualize the effect of an SU(2) gauge transformation in the case of the aforementioned Cr_3 molecule. This is a planar molecule with C_{3v} symmetry. Consider the transformation where $\frac{1}{c}\lambda^a(\mathbf{r}) = r_a^2\delta_{a,z}$ and, thus, $A^a_\mu(\mathbf{r}) = c|r_a|\delta_{a,z}\delta_{\mu,z}$ applied to the Hartree-Fock spinorial wavefunction of the system. As a consequence of which, the transformed naïve ELF is dramatically different from the untransformed image: compare left and right panels of Figure 1.

But a physically meaningful ELF must not change under gauge transformations. In fact, a recent work on time reversal symmetric (TRS) states, has shown that the replacement $\tau_{\mathrm{nc}} \to \widetilde{\tau}_{\mathrm{nc}}(\mathbf{r}) = \tau_{\mathrm{nc}}(\mathbf{r}) - \mathbf{J}^a(\mathbf{r})\cdot\mathbf{J}^a(\mathbf{r})/2n(\mathbf{r})$ in $D_{\mathrm{nc}}(\mathbf{r})$, restores invariance under SU(2) transformations, and simultaneously adds a dependence on paramagnetic spin-currents.[41] Notice, however, that TRS states have vanishing magnetization. Cr_3, instead, exhibits a non-collinear magnetic structure. *Shouldn't such a magnetization play a role in deriving a gauge invariant ELF?*

This above question urges us to "mind our steps" and, thus, we also must examine the effect of *conjoined* U(1)×SU(2) transformations! In detail, such a transformation acts on a spinor as follows $\Phi'(\mathbf{r}) = \exp\left[\frac{i}{c}\chi(\mathbf{r})\mathrm{I} + \frac{i}{c}\lambda^a(\mathbf{r})\sigma^a\right]\Phi(\mathbf{r})$. As a result,

$$\begin{aligned}\tau'_{\rm nc}(\mathbf{r}) = \tau_{\rm nc}(\mathbf{r}) &+ \frac{n(\mathbf{r})}{2c^2}\left[\mathbf{A}_{\rm G}(\mathbf{r})\cdot\mathbf{A}_{\rm G}(\mathbf{r}) + \mathbf{A}^a_{\rm G}(\mathbf{r})\cdot\mathbf{A}^a_{\rm G}(\mathbf{r})\right] \\ &+ \frac{1}{c}\mathbf{j}(\mathbf{r})\cdot\mathbf{A}_{\rm G}(\mathbf{r}) + \frac{1}{c}\mathbf{J}^a(\mathbf{r})\cdot\mathbf{A}^a_{\rm G}(\mathbf{r}) \\ &+ \frac{1}{c^2}m^a(\mathbf{r})\mathbf{A}^a_{\rm G}(\mathbf{r})\cdot\mathbf{A}_{\rm G}(\mathbf{r})\,. \end{aligned} \tag{7}$$

Eq. (7) is lengthy but worth a careful consideration. Crucially, we notice that Eq. (7) does not reduce to the simple sum of terms due to *individual* U(1) and SU(2) gauge transformations. In fact, the expression also includes an additional term coming from the *coupling* of the U(1) and SU(2) gauge potentials $\mathbf{A}_{\rm G}(\mathbf{r})$ and $\mathbf{A}^a_{\rm G}(\mathbf{r})$ via the spin-magnetization $\vec{m}(\mathbf{r})$.

Direct cancellation of the transformation-induced terms in Eq. (7), leads to the gauge invariant quantity

$$\begin{aligned}\widetilde{\tau}_{\rm nc}(\mathbf{r}) = &\left(\tau_{\rm nc}(\mathbf{r}) - \frac{\mathbf{j}(\mathbf{r})\cdot\mathbf{j}(\mathbf{r})}{2n(\mathbf{r})} + \frac{\nabla m^a(\mathbf{r})\cdot\nabla m^a(\mathbf{r})}{8n(\mathbf{r})}\right) \\ &+ \left(\frac{m^a(\mathbf{r})\tau^a_{\rm nc}(\mathbf{r})}{n(\mathbf{r})} - \frac{\mathbf{J}^a(\mathbf{r})\cdot\mathbf{J}^a(\mathbf{r})}{2n(\mathbf{r})}\right)\,, \end{aligned} \tag{8}$$

with $\vec{\tau}_{\rm nc}(\mathbf{r}) = \frac{1}{2}\sum_{k=1}^{N}\sum_{\mu}\left[\partial_\mu\Phi^\dagger_k(\mathbf{r})\right]\vec{\sigma}\partial_\mu\Phi_k(\mathbf{r})$ being the *spin*-kinetic energy density. Eq. (8) implements the task of enforcing U(1)×SU(2) gauge invariance adding a *minimal* set of terms — only using quantities which involve first-order derivatives. The gauge invariance of Eq. (8) can be more easily verified by exploiting its connection to the curvature of the exchange hole,[42] as shown in Section 1 of the Supplementary Material.[43] Furthermore,

$$\widetilde{D}_{\rm nc}(\mathbf{r}) \equiv \widetilde{\tau}_{\rm nc}(\mathbf{r}) - \frac{1}{8}\frac{\nabla n(\mathbf{r})\cdot\nabla n(\mathbf{r})}{n(\mathbf{r})} \tag{9}$$

is, like $\widetilde{\tau}_{\rm nc}(\mathbf{r})$, gauge invariant and is, like $D(\mathbf{r})$, a non-negative quantity. Non-negativity is established by writing $\widetilde{D}_{\rm nc}(\mathbf{r})$ as the trace of a Hermitian positive semi-definite matrix in a reference frame in which the spin and particle currents vanish [see Section 2 of the Supplementary Material]. Therefore, an interpretation emerges naturally: $\widetilde{D}_{\rm nc}(\mathbf{r})$ captures the U(1)×SU(2) gauge-invariant *excess* of $\widetilde{\tau}_{\rm nc}(\mathbf{r})$ as relative to the reference $\frac{1}{8}\frac{\nabla n(\mathbf{r})\cdot\nabla n(\mathbf{r})}{n(\mathbf{r})}$. Finally, we write the U(1)×SU(2) gauge-invariant ELF

$$\widetilde{\rm ELF}(\mathbf{r}) \equiv \frac{1}{1+\left[\widetilde{D}_{\rm nc}(\mathbf{r})/D^{\rm unif}(\mathbf{r})\right]^2}\,. \tag{10}$$

Notice, Eq. (10) reduces to the SU(2) invariant ELF for TRS states,[41], it reduces to the U(1) invariant ELF for current-carrying closed shell states,[22,28,29] and it reduces to the original ELF for zero current closed shell states.[14,24] Strikingly, Eq. (10) does *not* reduce to $D(\mathbf{r})$ on globally collinear spin-polarized states — a surprising fact that we shall carefully consider more below.

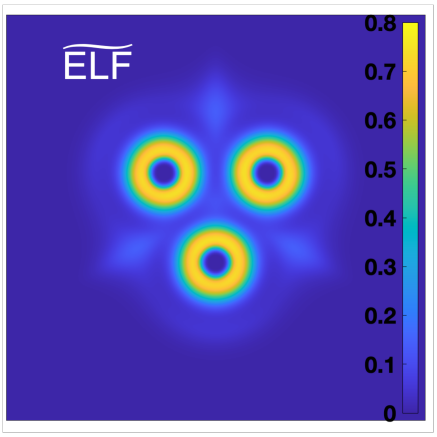

FIG. 2: U(1)×SU(2) gauge invariant $\widetilde{\rm ELF}$ [see Eq. (10)] in the Cr_3 plane.

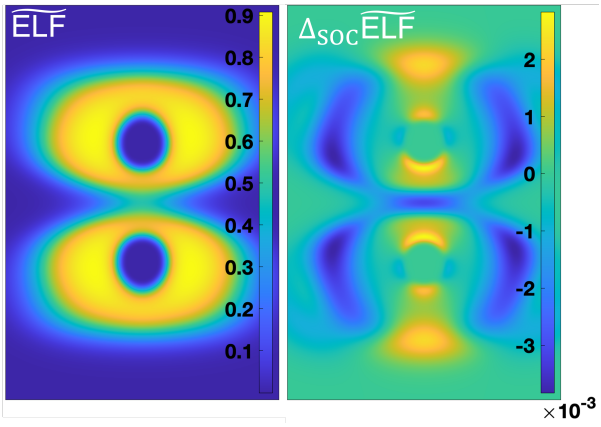

FIG. 3: (left) U(1)×SU(2) gauge invariant $\widetilde{\rm ELF}$ [see Eq. (10)] in the I_2^- molecule and (right) the difference due to SOC.

Applications and further analysis. Eq. (10) and, thus, Eq. (9) have been implemented in a developer's version of the CRYSTAL23 program.[44] Computational details are provided in the Supplementary Material. Further analyses are carried out below.

Let us first return to the example of Cr_3. The spin-magnetic moments are oriented within the plane of the molecule at angles of 120° in the triangular geometry, which breaks mirror symmetry and leads to a chiral electronic state. Here, the spin-current reaches a magnitude much larger than in any of the other cases discussed below. We also finds particle currents, which are however negligible.

In Fig. 2, we provide the plot of the U(1)×SU(2) gauge-invariant $\widetilde{\rm ELF}$ for Cr_3. The non-collinear spin structure increases the conditional pair-probability density at a given point in space, leading to a lower localization in the $\widetilde{\rm ELF}$, compared to the naïve (gauge-

dependent) ELF of Eq. (5). Differences are largest in the anti-bonding region, where the naïve ELF significantly overestimates electron localization. In the central bonding region, the largest contribution to the difference $\widetilde{\text{ELF}}$-ELF is provided by the $(\nabla m^a(\mathbf{r}))(\nabla m^a(\mathbf{r}))/8n$ term. The difference reaches a value as large as -0.4, or 40% of the total.

Let us now consider a globally collinear, yet spin-orbit coupled case: the I_2^- molecule. We provide the corresponding $\widetilde{\text{ELF}}$ in Figure 3. The plot nicely displays the bonding valence manifold of both σ and π character. The effect of spin-orbit coupling on the $\widetilde{\text{ELF}}$, reported in the right panel of Figure 3, is to increase electron localization along the molecular axis in the region of the singly-occupied σ^* anti-bonding orbital (i.e. both close to the atoms and, mainly, behind them) and decrease localization at the bond center and in directions orthogonal to the bond, in the region of the π bonding orbitals. The $\widetilde{\text{ELF}}$ thus provides us with a gauge-invariant description of bonding in spin-orbit-coupled orbital manifolds.

Next, let us look into the remarkable novelties that emerge even at the level of simple collinear states. Let us consider the simplest of molecules: H_2^+. The (eigen)states of this molecule are spin polarized single-particle ones. For this one-electron system, the $\text{ELF}(\mathbf{r}) = 1$ (see top left panel of Figure 4), everywhere. This is fixed by the $\widetilde{\text{ELF}}$ by accessing the extra information on the spin-polarization. Figure 4 (top right) reports the plot of $\widetilde{\text{ELF}}$, which reveals that the electron is shared by the two nuclei.

In the case of the Li atom (bottom panels of Figure 4), both the ELF and $\widetilde{\text{ELF}}$ display a shell structure (labels for the closed $1s$ and open $2s$ shells are provided to guide the eye). However the ELF (left bottom of Figure 4), predicts large values of the electron localization also in regions far away from the atomic center where the electrons is unlikely to be found. Again, the $\widetilde{\text{ELF}}$ (right bottom of Figure 4) fixes the issues by accessing extra information on the spin polarization.[45]

Finally, let us consider the H_2 molecule (not plotted). As a consequence of the Pauli principle, two electrons are in the same singlet spin configuration at each point in space. Moreover $\vec{m}(\mathbf{r}) = 0$, $\vec{\tau}(\mathbf{r}) = 0$, and $\vec{\mathbf{J}}(\mathbf{r}) = 0$ everywhere. Hence, $\widetilde{\text{ELF}}(\mathbf{r}) \equiv \text{ELF}(\mathbf{r}) = 1$. A resolution of the localization of the electron pair in H_2, would require to account for correlations beyond single Slater determinants[46–49] — a task that is beyond the scope of a "simple" ELF.

Conclusions. In solving the longstanding issue of extending the electron localization function (ELF) to general non-collinear states, we have discovered that a fundamental step had been so far missed. Namely, the key step is to enforce the *conjoint* U(1)×SU(2) gauge-invariance. This is necessary to ensure that the ELF will depend only on intrinsic physical features rather than on *any* particular gauge in which the Pauli equation is solved.

The U(1)×SU(2) gauge-invariance adds to an otherwise gauge dependent ELF — not only the already known quadratic terms in the particle and spin currents but also — a quadratic term in the gradient of the spin-magnetization *and* a term involving the contraction of the magnetization with the (non-collinear) spin-kinetic energy-density. These are quantities which, in general, have sizable magnitude that cannot be ignored. As illustrations, we have shown the cases of the Cr_3 and I_2^- molecules. Furthermore, we have shown that, the U(1)×SU(2) gauge-invariant ELF also improves the description of the localization of one-electron-like collinearly spin-polarized states.

In view of the impact of the original ELF on the analysis of bonds and on the construction of advanced density functional approximations, we believe that the extended ELF here presented will importantly support the analyses of a larger class of quantum materials as well as find use in the design of improved density functional approximations.

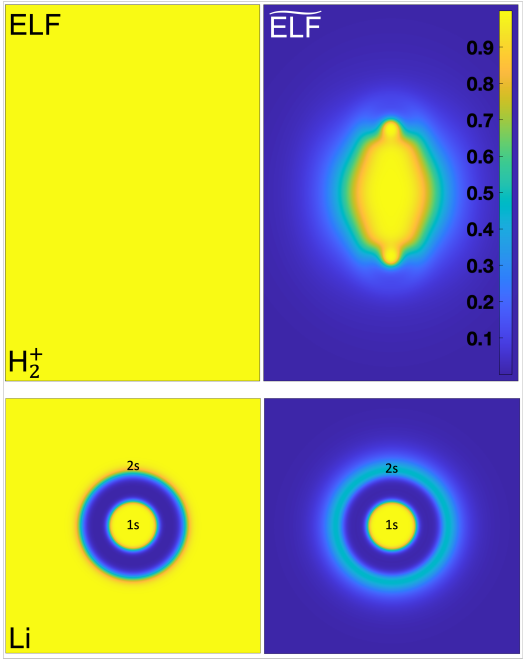

FIG. 4: (left) ELF and (right) $\widetilde{\text{ELF}}$ for (top) the numerically exact Hartree-Fock wavefunction of the H_2^+ molecule and (bottom) the Li atom. The H atoms are centered on each tip of the lemon-shaped region in the right panel, at a bond distance of 0.74 Å. The plot of the Li atom is in a 6×6 Å^2 square.

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