

Molecular Spins: a new Frontier of Chemical Physics and Magnetic Resonance !?!

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Introduction and Abstract:

The idea presented here falls between “*totally crazy*” and “*how comes we have overlooked it*”. I have already hinted at it at the last year’s meeting of the Italian GIDRM¹ and this presentation is the first one to expand on it in more detail.

Consider a planar *diamagnetic* molecule which has an axial sense, such as that of chloraldehyde or, in general C(XYZ), where C is a central atom and XYZ are three different atoms/groups arranged around it (see **Figure 1**):

Obviously, the “*axiality*” of the arrangement due to the conceptual difference between a clockwise and a counter-clockwise circumnavigation of the (XYZ) atoms can not lead to distinct molecular species (such as in chiral arrangements). But it does define an axial vector well oriented with respect to the common plane, a fact compatible with the existence of a preferential direction of motion and a **persistent electron current loop**. A bond electron partially shared by all three atoms can in fact circulate around the structure either in one sense (XYZ), or in the other sense (XZY) and, when XYZ are all different, these two types of “**loop orbits**” have distinct energies. In practice, such loop orbits will mix with the conventional electron orbitals and thus convey to them an **axial character** and contribute in part to the energy of the molecule. From the symmetry point of view, *the axiality needs to be accounted for in any math model of the molecule, lest an important feature of the latter is a-priori missed*.

As far as the author is aware, the present quantum theory of chemical bonding never considers *any* axial aspects. They are absent in models based on combinations of electron Slater-type orbitals, because the latter are inherited from two-particle models (electron and a nuclide), while axiality requires at least four bodies (electron and three nuclides). Nor are they accounted for in DFT² which considers only electron densities, but *no persistent electron current loops*. This **overlooked factor** might yet explain the scarce progress of quantum chemistry. For example, the errors in quantum predictions of chemical shifts are today only 2-3 times lower than 40 years ago, despite the huge progress in computing technology. This makes sense only if one admits that a cog is missing somewhere inside the quantum chemistry blueprints. Which might be the need to **complement electron charge density with an electron current density**.

Another telltale indication is that we all know about *electric dipoles* of molecules and their fragments, both *permanent* and *induced*, and we are also aware of *induced magnetic dipole moments* in molecules, such as those responsible for diamagnetic susceptibility, or for the induced ring currents evidenced by NMR chemical shifts. However, *permanent magnetic moments in diamagnetic molecules*³ have never been contemplated – without any apparent reason!

Why should the idea of *persistent electron current loops in diamagnetic molecules* and in their fragments be presented at this meeting? The answer is that if the insight is correct then some molecules, just like some elementary particles and some nuclides, should possess an *intrinsic spin* (an orbital one) and an associated *permanent magnetic moment*, thus giving rise to magnetic resonance phenomena similar to those we are used to (in particular a specific Larmor frequency). We are therefore talking about the possibility of extending radically the range of “*particles*” endowed with spin properties and gyromagnetic moments and giving birth to **Molecular Magnetic Resonance (MMR)**.

However, before starting the search for such *molecular spins*, one should try and estimate the energy difference between axially distinct electronic states, their lifetimes, inter-conversion rates, Larmor frequencies, and MMR relaxation times. Some of this physics, based on grossly simplified quantum models, has been done (though with some difficulty because *so much in Quantum Physics is based on mere assumptions*, and it indicates that the search might be anything but trivial because, with no firm advance knowledge of the Larmor frequencies, it should entail an extremely *broad-band hardware approach*.

Please, come and attend my presentation of the concept at the ENC meeting
And let the presentation be a call to arms to conquer this New World!

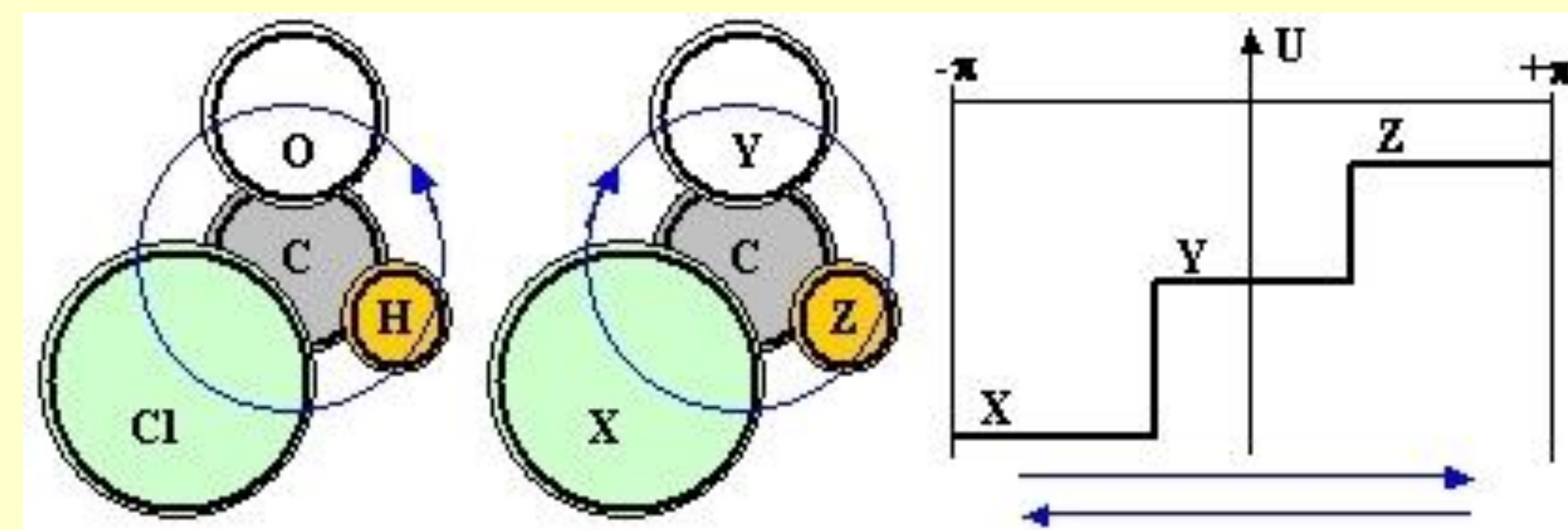


Figure 1: A bonding-shell electron shared by three different atoms XYZ is a bit like a particle constrained to a circular path and moving under the influence of a potential U (solid line in periodically repeating diagram on the right) with no circular symmetry. In this case it evidently matters whether its wavefunction propagates clockwise or counter-clockwise (indicated by blue arrows) and the energies of the corresponding (eigen)states should be different.

Presentation syllabus:

Review of magnetic particles which we know reasonably well today:

- Leptons (electrons, muons): excellent theoretical descriptions, lacking intuitive understanding
- Baryons (neutrons, protons, nuclides): lacking theoretical description, no intuitive understanding

What about molecular magnetism:

- Magnetic properties conferred by mutually uncompensated magnetic particles (unpaired electrons)
- Could genuine spin-less molecules have magnetic moments?
- We know well induced as well as intrinsic molecular electric dipole moments
- but we only know (so far) induced molecular magnetic moments !!!

Postulate:

There may (and do) exist persistent current loops in the outer electronic shells of molecules

Emergence of intrinsic molecular magnetism not related to incorporated particles

- **Question:** Why should such currents exist?
- **Answer:** Why should they NOT exist if there is nothing to forbid them?!

Why did we never saw them so far?

- Maybe because we were not looking for them
- They are probably not very prominent
- But maybe they explain why Quantum Chemistry seems to be stuck

Symmetry considerations:

- Circular and a-circular molecules
- There are many mechanic examples of circularly polarized device; what about quantum analogies?
- Axiality and mirror reflections (circularity has nothing to do with chirality)

Quantum Physics: Traversing barriers and handling of scattering processes

- Assumptions about wavefunctions are made BEFORE the “solutions” are constructed
- Anyway, the potential barrier asymmetry DOES matter in these cases
- Closing the linear-propagation case into a loop

continued in the right column ...

... continued from the left column:

Traditional treatment of the quantum states of molecules

- A fallacy: standing waves are ASSUMED even before attempting a solution to the eigenvalues problem

$$H\psi(\varphi) = -\frac{\hbar^2}{2G} \frac{\partial^2 \psi(\varphi)}{\partial \varphi^2} + U(\varphi)\psi(\varphi) = E\psi(\varphi)$$

$$\text{Usual assumption: } \Psi(\varphi, t) = \exp\left(-i \frac{E}{\hbar} t\right) \psi(\varphi)$$

$$\text{Amended assumption: } \Psi_{\pm}(\varphi, t) = \exp\left(-i \frac{E}{\hbar} \left(t \pm \frac{\varphi}{v}\right)\right) \psi_0(\varphi)$$

- Loop orbitals as legitimate solutions of the Schrödinger equation for the molecule
- Loop orbitals as admixtures in addition to traditional Slater-type orbitals

Global and Local circularity effects:

- Local current loops are possible even when, due to symmetry, the whole molecule has no moment

Consequences, Part I:

- We might have new magnetic particles (small molecules) with which to do Magnetic Resonance (MMR)
- Estimates of the gyromagnetic ratios: very uncertain, probably fractions of MHz/Tesla

Differences in the related Physics, compared to particles and nuclides:

- Considerable, because some fortuitous particle properties are absent:
- There is no reason why the spin (angular momentum) and the magnetic moment should be aligned
- Consequently, **MMR is likely to be quite different from NMR**

Consequences, Part II:

- In Quantum Chemistry, the incorporation of loop currents could remove a roadblock
- DFT \Rightarrow **CCDFT (Charge & Current Density - Function Theory)**
- Expectations regarding NMR: **Improved predictions of NMR parameters** (shifts & coupling constants)

References:

- [1] Stan Sykora, *The Gold Medal Talk “In Spin we Trust”* at the 40th Annual Meeting of GIDRM, September 26-28, 2011, Parma, Italy.
- [2] See *Density functional theory* in Wikipedia, and the many references therein
- [3] *Note:* The well known permanent magnetism due to unpaired electron spins is not discussed here at all.

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This poster was presented also as a Talk. All the materials, and any future developments

And discussions are available on the URL www.ebyte.it/stan/Talk_ENC_2012.html. This document’s DOI: [10.3247/SL4Nmr12.004](https://doi.org/10.3247/SL4Nmr12.004)

