Molecular Spins:

a novel Frontier of Chemical Physics and Magnetic Resonance?

a conjecture by **Stan**islav **Sýkora**

Have you heard?

They completed water **D**ensity-**F**unction **T**heory of the whole Earth.

Really? Great!
Including the currents?

Eh!? What currents?

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Magnetic particles which we know *reasonably well* today

(*meaning that we know both the **spin** S and the **magnetic moment** μ*)

Leptons		Nucleons		Nuclides	
$e_{½}$	-28024.952	$^{1}p_{½} \equiv {}^{1}H_{½}$	42.57748 uud	$^{1}H_{½}$	42.57748
$\mu_{½}$	-135.539	$^{0}n_{½}$	-29.16469 udd	$^{2}H_{½}$	6.53590
$\tau_{½}$	too short-lived	**Hyperons**		$^{3}H_{½}$	45.41367
$\nu_{½}$	haha, catch me!			$^{3}He_{½}$	32.43410
Hadrons		**Λ, Σ, Χ, Ω**	too short-lived	$^{6}Li_{1}$	6.26587
$\eta_{½}$	too short-lived			etc.	≈ 81 of them

Can't we have more ???

Notes: lower-right index is the spin S, the value is the gyromagnetic ratio $\gamma = \mu / hS$ in MHz/T

What about magnetic properties of molecules?

Persistent magnetic properties conferred by incorporated magnetic particles:

* All practical magnetic *materials* are presently based on presence of unpaired electrons
* Some *devices* are based on persistent superconducting loops (BCS electron pairs)
* Only NMR exploits nuclear magnetism (detectable also without resonance)

But could molecules with no magnetic particles also have magnetic moments?

Property	Particles	Diamagnetic molecules
Electric dipole, induced	**Yes** (tiny)	**Always** (polarizability)
Electric dipole, permanent	**No** (?CP)	**Yes** (symmetry permitting)
Magnetic dipole, induced	undetectable	**Always** (susceptibility)
Magnetic dipole, permanent	**Yes** (S>0)	**??? What ???**

Permanent magnetic moments in diamagnetic molecules ???

Man, you must be CRAZY ?!?!?!

"There would have to exist persistent current loops inside the electron shells!"

The Postulate:

There may, and do, exist

persistent electron current loops

in molecular electronic shells, giving rise to

intrinsic molecular magnetism

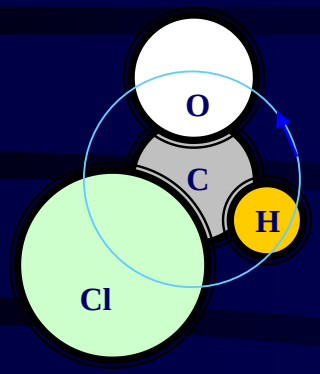
unrelated to incorporated magnetic particles

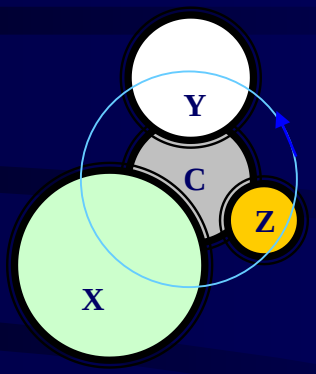
- *Question:* Why should such currents exist?
- *Answer:* Why not? Nothing forbids them!

But let me try and tackle also the *"why yes?"*

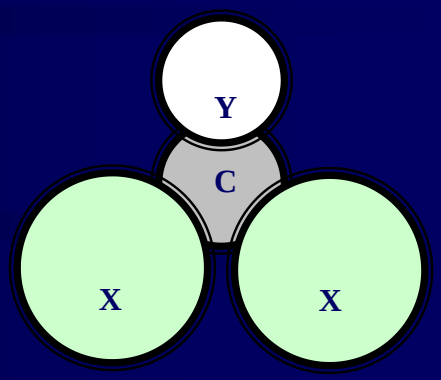
Molecular symmetry considerations

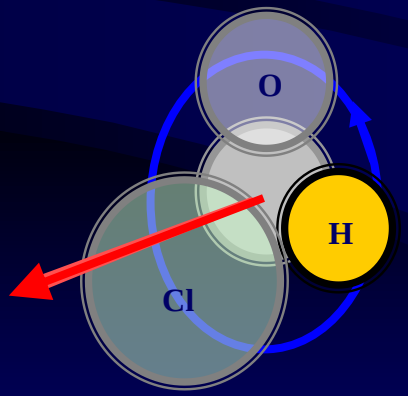
Circular asymmetry (axiality)





Circular symmetry (anaxiality)





Axiality & mirror reflections

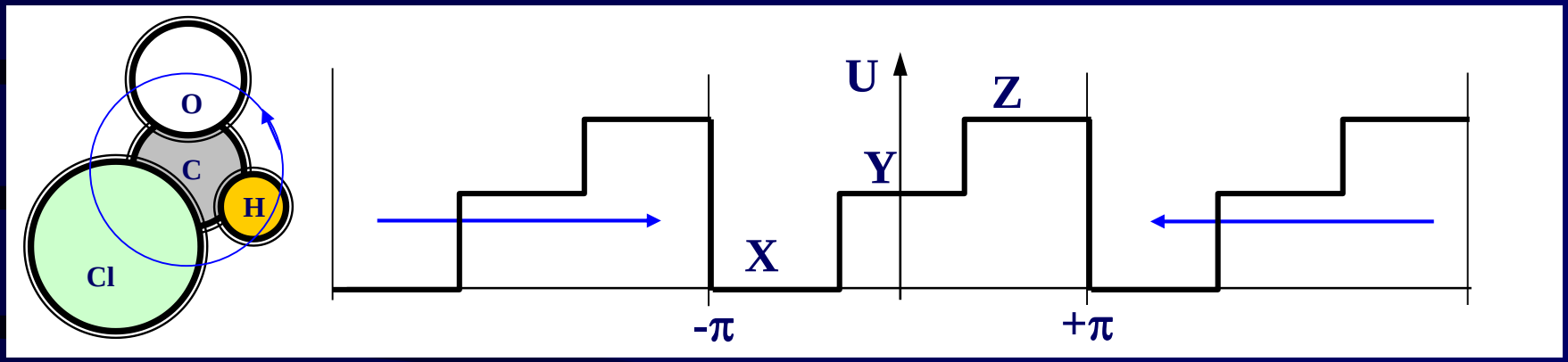
Notes:
axiality is **not** *chirality !!!*
It does not make the molecule optically active.
It does not lead to diastereomerism.

Why we never saw such magnetic moments so far?

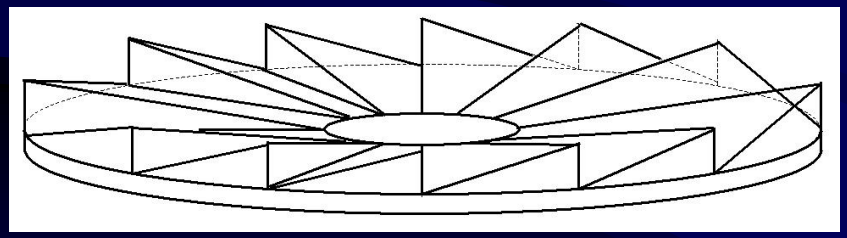
- Maybe it is simply the fact that we were not looking for them
- Most of their bulk effects average out due to molecular tumbling
- They are probably small compared to induced effects such as the bulk magnetic susceptibility μ
- In solids, deviations of the μ tensor from its liquid-state value are likely to be ascribed to packing, small structural deviations, etc
- *Last but not least:* nobody used the best tool to hunt for persistent magnetic dipoles which, of course, is Magnetic Resonance

More symmetry considerations

Running loops one way and the other



There are an infinity of examples of circularly polarized mechanical devices

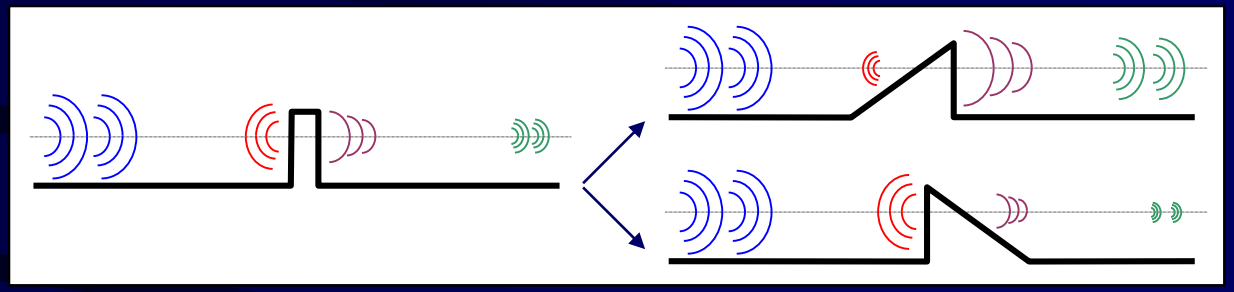


Fans, one-way clutches in all kinds of machinery, slipper clutches in motorbikes, etc, etc.

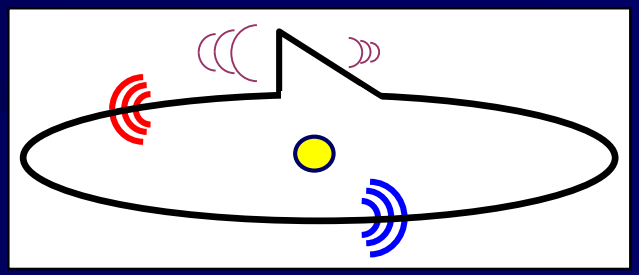
What about quantum analogies ?!?

Quantum Physics: traversing barriers (tunnelling)

- In these cases, the barrier asymmetry does matter (as it should)
- *Note: wavefunctions are* **pre-constructed** *from the incident wave, the reflected wave, the transmitted wave, and perhaps a near transient; only coefficients are adjusted to match the Schrödinger equation.*



- It is easy to close the linear path into an asymmetric circular loop:
- Shouldn't the asymmetry still matter !?



A fallacy in the standard handling of bound states

In molecules,
standing waves are **assumed before** facing the eigenvalue problem.
But in such multi-body systems, this may be too restrictive!

$$ih\frac{d}{dt}\Psi(s,t)=H\Psi(s,t) \rightarrow \Psi(s,t)=\exp\left(-i\frac{E}{h}t\right)\psi(s) \Longrightarrow H\psi(s)=E\psi(s)$$

For the ultra-simplified case of electron on a **loop orbital**, we might get:

$$ih\frac{d}{dt}\Psi(\varphi,t)=-\frac{h^2}{2G}\frac{\partial^2}{\partial\varphi^2}\Psi(\varphi,t)+U(\varphi)\Psi(\varphi,t)$$

$$\Psi(\varphi,t)=\exp\left(-i\frac{E}{h}t\right)\psi(\varphi) \Longrightarrow -\frac{h^2}{2G}\frac{\partial^2\psi(\varphi)}{\partial\varphi^2}+U(\varphi)\psi(\varphi)=E\psi(\varphi)$$

$$\Psi_{\pm}(\varphi,t)=\exp\left(-i\frac{E_{\pm}}{h}\left(t\pm\frac{\varphi}{v}\right)\right)\psi_{\pm}(\varphi) \Longrightarrow H(\varphi)\psi_{\pm}(\varphi)=E_{\pm}\,\psi_{\pm}(\varphi)$$

Notes: s … all the space-like generalized coordinates, φ … azimuth angle in a loop path

So what if, for example, $E_- < E_+$? Then E_- is the ground state, occupied by an electron pair, and the molecule hosts a persistent current.
This is necessarily the case when the molecule has no circular symmetry

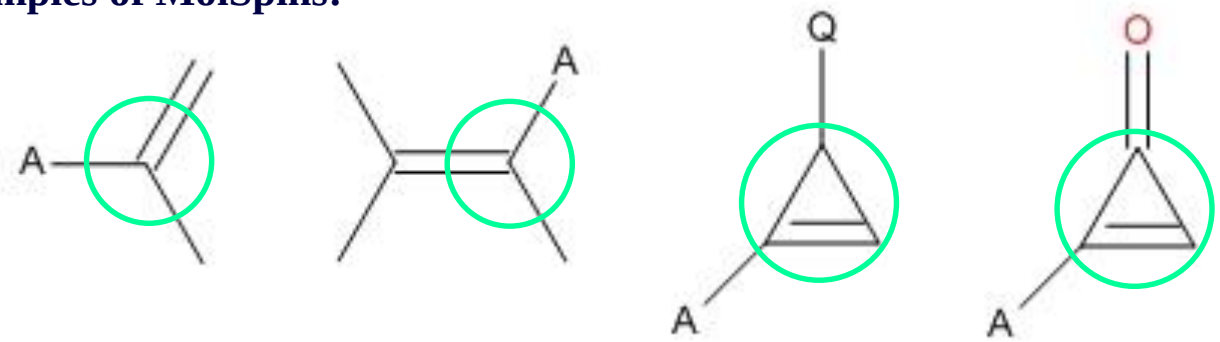
Loop orbitals and “classical” orbitals

- Classical (atomic, Slater) orbitals are legitimate solutions in simplified situations void of circularity (1 or 2 atoms)
- **Loop orbitals** are legitimate solutions in simplified situations with circular arrangements (minimum 3 atoms requited)
- Since atomic orbitals are combined in many ways to form various molecular shell approximations (LCAO, SCF-LCAO, …, DFT), these combinations should include also loop orbitals
- It is true that the manifold generated by all functions $\psi(s)$ is L_2-complete in the the space {s}, but it is NOT complete in {s,t}. The time-dependent Schrödinger equation has a broader set of solutions!

Consequences, *Part I*

In the case of small molecules, we might have new magnetic particles (molecular spins) with which to do Molecular Magnetic Resonance (**MMR**)

Examples of MolSpins:



Estimates of gyromagnetic ratios:

very uncertain, my early guesses indicate 0.1 – 2 MHz/Tesla

To search for the resonances,

highest possible fields should be used (1 GHz)

in combination with very broad-band front end (available)

Differences in the related Physics

MMR physics compared to that of NMR and EPR

Considerable, since some fortuitous particle properties are absent:

* Magnetic moment and spin do not need to be aligned (!)
* Interaction with molecular motions is not weak and therefore the
* abstracted Spin Hamiltonian (Wes Anderson) is not applicable.

Hence the resonances are likely to be very broad

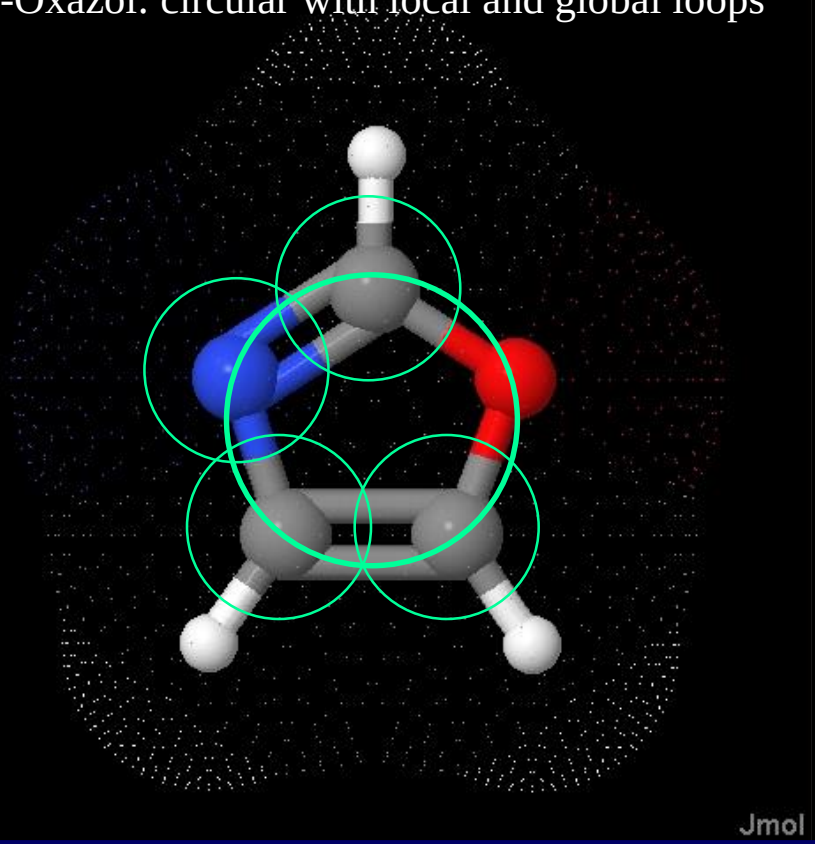
making MMR more a playground for chemical physicists.

But: one never knows !!!

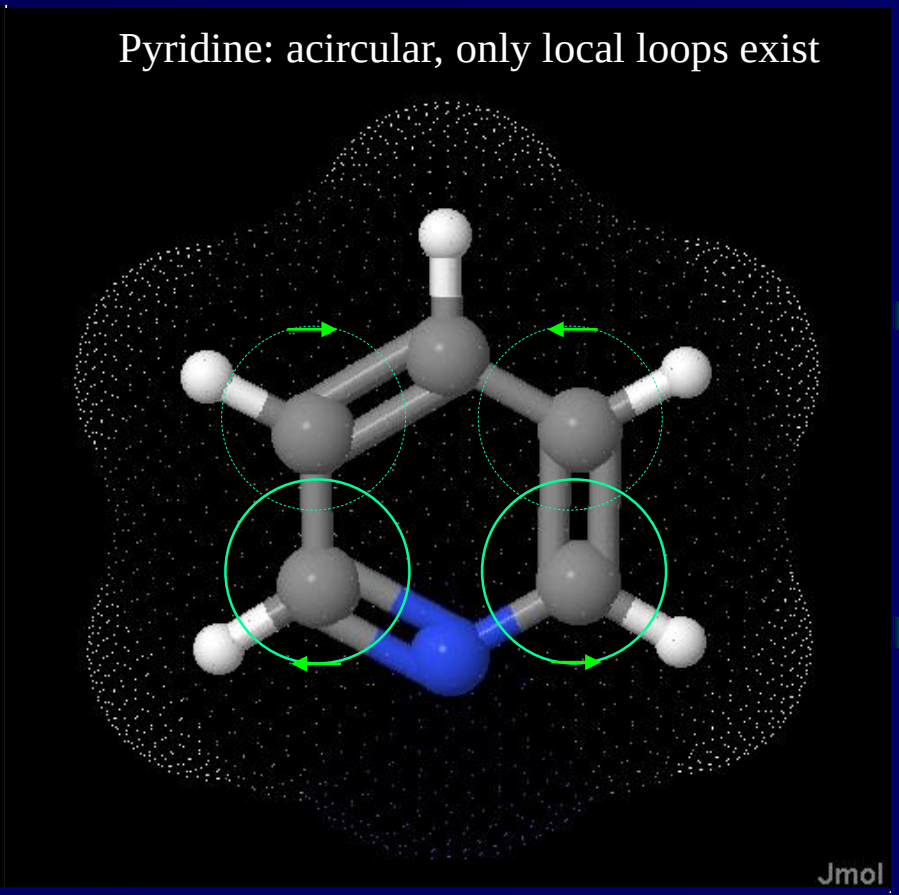
Global and Local circularity effects

Local current loops may exist even when, due to symmetry,
the whole molecule can not have a magnetic dipole moment

1,3-Oxazol: circular with local and global loops

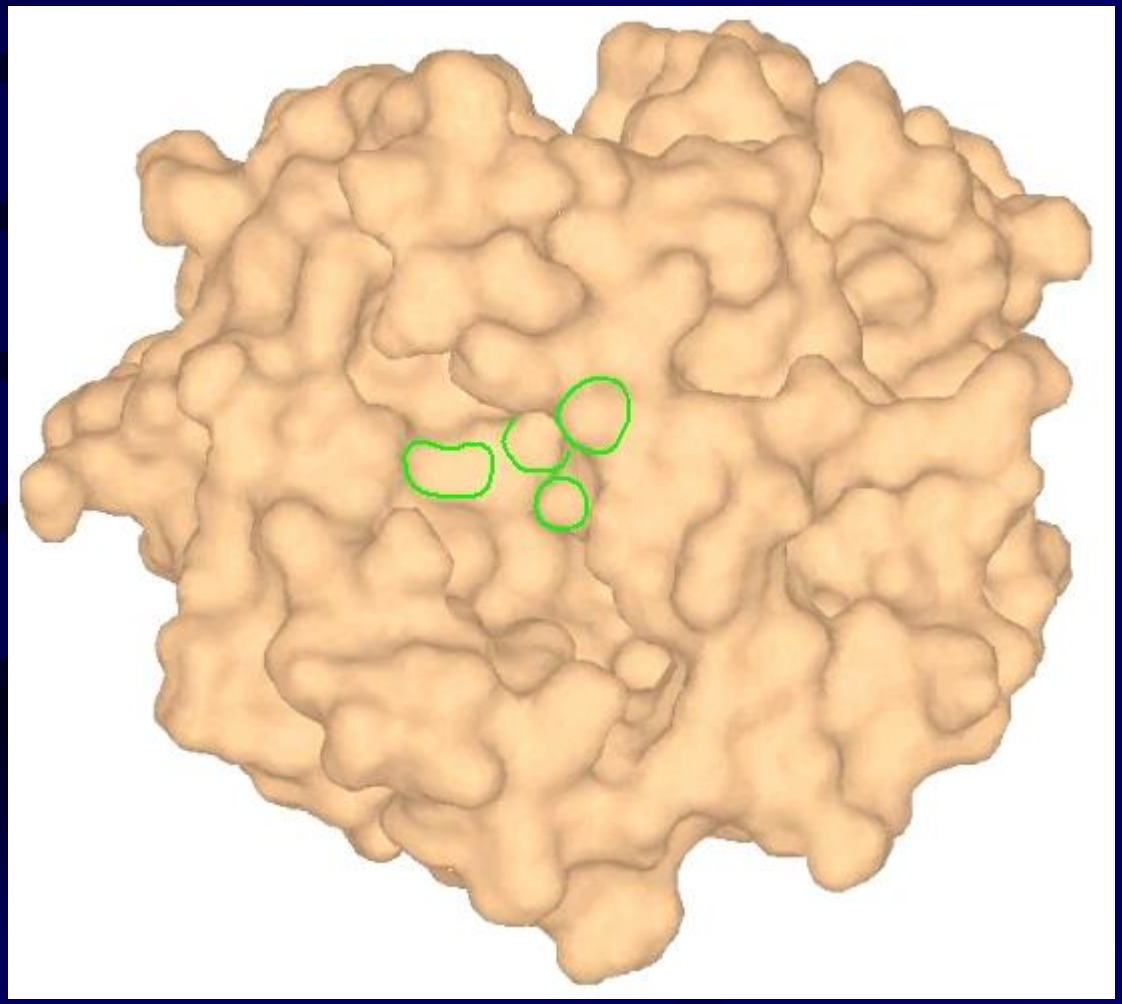


Pyridine: acircular, only local loops exist



Current loops distribution in large molecules

Only a few are drawn but they should constitute an intricate network



Consequences, *Part II*

In Quantum Chemistry, loop currents might remove a roadblock:

DFT (**Density-Function Theory**)

$\Rightarrow$

CCDFT (**Charge & Current Density-Function Theory**)

Potential benefits for NMR:

improved predictions of NMR parameters
(shifts and coupling constants)

which are stuck at about ±0.2 ppm since 20 years and improved only by a factor of 3 over more than 50 years, despite the enormous progress of computer technology.

Thank You for Your Attention

… and join the Quest …

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