

Gauge-Invariant Calculation of Static and Dynamical Magnetic Properties from the Current Density

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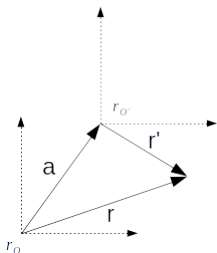
July, 10th 2015

Two magnetic properties will be discussed in this talk:

- 1 Magnetizability: paradigm of magnetic quantities.
- 2 Circular dichroism: dynamical quantity. A lot of experimental data are available for this property.

Before starting...

- \vec{r}_O : origin of the coordinate system



- \vec{r}_G : gauge-origin of the vector potential
 $\vec{A}(\vec{r}, \omega) = \frac{1}{2} \vec{B}(\omega) \times (\vec{r} - \vec{r}_G)$ ($\vec{B} = \nabla \times \vec{A}$)
- \vec{r}_C : reference point around which the multipole expansion is done

$$\delta \vec{m}(\omega) = \frac{1}{2} \int d\vec{r} (\vec{r} - \vec{r}_C) \times \delta \vec{j}(\vec{r}, \omega)$$

- Fundamental problem: Many current theories for the calculation of (dynamical) magnetic properties **depend on the origin of the coordinate system \vec{r}_O** . This dependence is unphysical.
- Numerical problem: Standard calculations show an **artificial dependence on the gauge-origin \vec{r}_G** when using finite basis sets, which is related to a **slow convergence** with basis set. Most famous method regarding this issue: GIAO \rightarrow Can solve the slow convergence problem, but is not gauge-invariant...

Magnetizability

Relation between the induced magnetic dipole moment $\delta\vec{m}$ and the **magnetizability** tensor ξ :

$$\delta m_i(\omega) = \sum_j \xi_{ij}(\omega) B_{\text{ext},j}(\omega)$$

Induced magnetic dipole moment:

$$\delta\vec{m}(\omega) = \frac{1}{2} \int d\vec{r} (\vec{r} - \vec{r}_C) \times \delta\vec{j}(\vec{r}, \omega)$$

\vec{r}_C : fixed reference point in the molecular frame. **Contamination** of δm by the induced electric dipole moment $\delta\mu$:

$$\int d\vec{r} \delta\vec{j}(\vec{r}, \omega) = -i\omega \int d\vec{r} \vec{r} \delta\rho(\vec{r}, \omega)$$

$$\xi_{ij}(\omega) = \frac{1}{2B_{\text{ext},j}(\omega)} \int d\vec{r} \left[(\vec{r} - \vec{r}_C) \times \delta\vec{j}(\vec{r}, \omega) \right]_i$$

Choice of the potentials

We have some gauge freedom.

We choose a vector potential of the following form:

$$\vec{A}_{\text{ext}}(\vec{r}, \omega) = \frac{1}{2} \vec{B}_{\text{ext}}(\omega) \times (\vec{r} - \vec{r}_G) .$$

The external electric field is then expressed as

$$\vec{E}_{\text{ext}}(\vec{r}, \omega) = \frac{-i\omega}{2} \vec{B}_{\text{ext}}(\omega) \times (\vec{r} - \vec{r}_G) .$$

$\forall \vec{r}_G$, we have the same \vec{B} but not the same \vec{E} !

This dependence on \vec{r}_G is physical.

Numerical problem: convergence of the current density

The current density can be split in 2 terms:

$$\vec{j}_p(\vec{r}, \omega) = \int d\vec{r}' \chi_{\vec{j}_p \vec{j}_p}(\vec{r}, \vec{r}', \omega) \cdot \vec{A}(\vec{r}', \omega)$$

$$\vec{j}_d(\vec{r}, \omega) = \rho_0(\vec{r}) \vec{A}(\vec{r}, \omega)$$

$$\chi_{\vec{j}_p \vec{j}_p}(\vec{r}, \vec{r}', \omega) = \lim_{\eta \rightarrow 0} \sum_n \langle \Psi_0 | \hat{j}_p(\vec{r}) | \Psi_n \rangle \langle \Psi_n | \hat{j}_p(\vec{r}') | \Psi_0 \rangle \left[\frac{1}{\omega - (E_n - E_0) + i\eta} - \frac{1}{\omega + (E_n - E_0) + i\eta} \right]$$

- \vec{j}_d : ground-state wavefunction, converges with a small basis.
- \vec{j}_p : excited states, needs a larger basis set to converge.

\vec{j}_d and \vec{j}_p are **not calculated on equal footing !**

Finite basis set: **artificial dependence on \vec{r}_G** , leading to a slow convergence of the total current

Link between $\chi^{\vec{j}_p, \vec{j}_p}$ and the ground-state density ρ_0 [1]:

$$\sum_j \partial'_j \chi^{\vec{j}_p, \vec{j}_p}_{ij}(\vec{r}, \vec{r}', \omega = 0) + \rho_0(\vec{r}) \partial'_i \delta(\vec{r} - \vec{r}') = 0$$

One can then **rewrite the diamagnetic component** [2]:

$$\vec{j}_d(\vec{r}, \omega) = \rho_0(\vec{r}) \vec{A}(\vec{r}, \omega) = - \left[\int d\vec{r}' \chi_{j_p j_p}(\vec{r}, \vec{r}', 0) \right] \cdot \vec{A}(\vec{r}, \omega)$$

The total current (at $\omega = 0$) is then expressed as

$$\delta \vec{j}(\vec{r}, \omega = 0) = \frac{1}{2} \int d\vec{r}' \chi^{\vec{j}\vec{j}}(\vec{r}, \vec{r}', 0) \cdot \vec{B}(0) \times (\vec{r}' - \vec{r}),$$

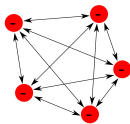
and doesn't show any dependence on \vec{r}_G anymore, even with a finite basis set.

¹G. Strinati, La Rivista Del Nuovo Cimento 11, 1 (1988)

²N. Raimbault, P. L. de Boeij, P. Romaniello, and J. A. Berger, Phys. Rev. Lett. 114, 066404 (2015)

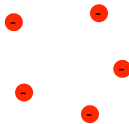
The Kohn-Sham system (TDCDFT)

Actual system



(v, \vec{A})

Kohn-Sham system



(v_s, \vec{A}_s)

\longrightarrow

$$\vec{j} = \vec{j}_s$$

$$\rho = \rho_s$$

$$i \frac{\partial}{\partial t} \phi_i = \left[\frac{1}{2} \left[-i \vec{\nabla} + \vec{A}_s \right]^2 + v_s \right] \phi_i$$

$$v_s[\vec{j}] = v_H + v_{xc}$$
$$\vec{A}_s[\vec{j}] = \vec{A}_{\text{ext}} + \vec{A}_{xc}$$

$$\vec{j} = \sum_{i=1}^N \left[\frac{1}{2i} \phi_i^* \vec{\nabla} \phi_i + c.c. \right] + \rho \vec{A}_s$$

$$\rho = \sum_{i=1}^N |\phi_i|^2$$

The equations need to be solved self-consistently.

Convergence with basis set

- Program: ADF (Amsterdam Density Functional)
- Molecule: C_2H_4
- Augmented Basis sets: 1 more diffuse basis function for s and p than the standard basis sets
- Functionals: LDA + ALDA

$\tilde{\xi}$: without sum rule / ξ : with sum rule

Basis set	$\tilde{\xi}(\omega = 0)$	$\xi(\omega = 0)$	$\tilde{\xi}(\omega \neq 0)$	$\xi(\omega \neq 0)$
ASZ	-6.57	-3.22	-6.29	-2.93
ADZ	-6.39	-3.47	-6.10	-3.19
ADZP	-5.37	-4.14	-5.07	-3.83
ATZP	-5.29	-4.16	-4.98	-3.85
ATZ2P	-5.23	-4.12	-4.93	-3.81
QZ4P	-4.20	-4.16	-3.90	-3.86

Basis set used: ADZP

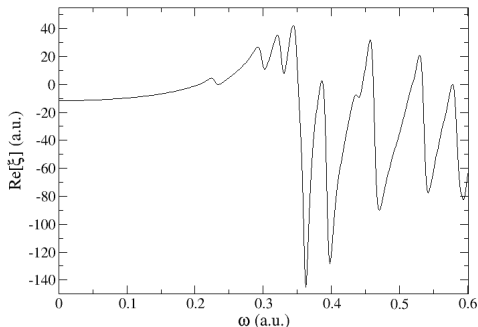
Molecules	This work	Experiment
H_2O	-3.01	-2.76
NH_3	-3.73	-3.68
C_2H_4	-4.14	-4.23
C_6H_6 (benzene)	-11.70	-11.53
$C_{22}H_{14}$ (pentacene)	-41.85	-40.56

Numerical verification of the origin independence

Basis set used: ADZP

Molecules	$\xi(\omega = 0)$	$\xi(\omega = 0)$ (shift)	$\xi(\omega = 4\text{eV})$	$\xi(\omega = 4\text{eV})$ (shift)
H_2O	-3.01	-3.01	-2.99	-2.99
NH_3	-3.73	-3.73	-3.68	-3.68
C_2H_4	-4.14	-4.14	-2.76	-2.76
Benzene	-11.70	-11.70	-6.89	-6.89
Pentacene	-41.85	-41.85	50.04	50.04

Real part of the magnetizability for the benzene molecule as a function of the frequency (in a.u.)



No experimental data was available to compare with.

Conclusions (1)

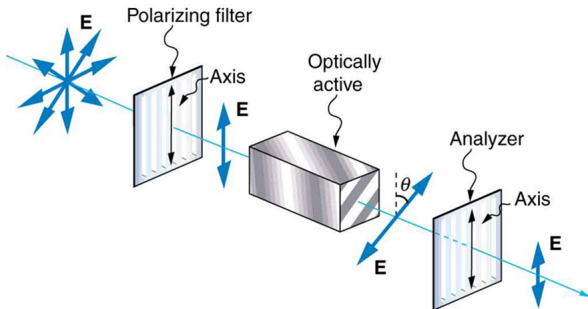
- The dynamical quantities depend on \vec{r}_G and \vec{r}_C , but are independent of \vec{r}_O . The choice for \vec{r}_G and \vec{r}_C depends on the experimental setup.
- For the static case, there is no dependence on \vec{r}_G anymore.
- We have derived a general framework allowing us to calculate magnetic properties. This framework could be used with any method that can calculate the current density.
- Magnetizabilities calculated with our approach rapidly converge with the size of the basis set.

For further explanations, see:

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Optical activity

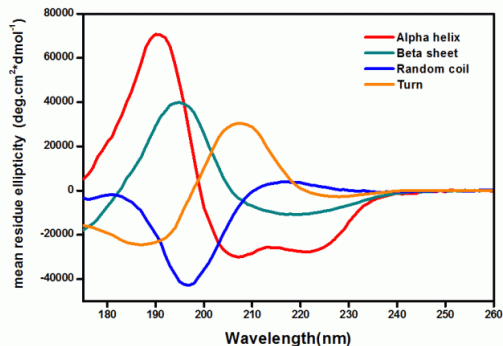
Optical activity: process of rotating polarized light in either clockwise or counterclockwise direction



Can be useful in various fields. For example in chemistry: allows to quantify the relative amount of enantiomers in a sample.

Circular Dichroism

- Circular Dichroism (CD) is the difference in absorption between a left-handed circularly polarized light and a right-handed circularly polarized light.
- Alpha helices in proteins and double helices in nucleic acids for example show **specific signatures** in CD spectra.



Optical Rotation Tensor

The optical rotation tensor can be defined as

$$\delta\vec{\mu} = G\vec{B} \Rightarrow G_{ij} = \frac{i}{\omega} \frac{1}{B_j} \int d\vec{r} \delta\vec{j}_i(\vec{r}, \omega)$$

or

$$\delta\vec{m} = \tilde{G}\vec{E} \Rightarrow \tilde{G}_{ij} = \frac{1}{2E_j} \int d\vec{r} \left[\vec{r} \times \delta\vec{j}(\vec{r}, \omega) \right]_i$$

with \vec{m} the magnetic dipole moment and $\vec{\mu}$ the electric dipole moment.

The optical rotation parameter β is then defined as:

$$\beta(\omega) = \frac{1}{\omega} \text{Tr}(G) = -\frac{1}{\omega} \text{Tr}(\tilde{G})$$

The trace of G and \tilde{G} is independent of both \vec{r}_G and \vec{r}_C !

\Rightarrow The comparison with experiments will be easier.

Note: Most calculations are done with randomly-oriented molecules, hence the necessity to take the trace.

Calculated specific rotations for C_4H_8O (DMO), with LDA+ALDA:

Table : Convergence behavior of the specific rotation (in $\text{deg cm}^3/(\text{dm g})$) of $C_4H_8O(\text{DMO})$ at the sodium D-line frequency ($\omega = 0.077318$ a.u.).

Basis set	$\alpha(\omega)$
ASZ	-25.55
ADZ	-59.54
ADZP	-68.34
ATZP	-60.98
ATZ2P	-60.74

$$[\alpha]_{\vec{v}} = 1.343 * 10^{-4} \frac{\beta(\omega) \vec{v}^2}{M}$$

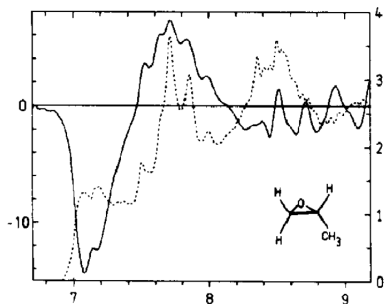
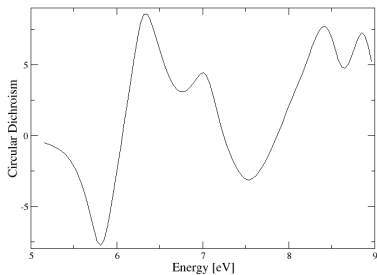
Note: diffuse functions are important for this property.

Table : Specific rotations at the sodium D-line frequency of various molecules, using the ATZP basis set.

Molecule	$\alpha(\omega = 0.077318 \text{ a.u.})$	
	this work	experiment
C ₃ H ₆ O	0.65	18.7
DMO (C ₄ H ₈ O)	-60.98	-58.8
C ₄ H ₈ S	136.73	129.0
C ₅ H ₈	122.86	81.0
C ₅ H ₁₀	52.93	42.0

Circular Dichroism Spectrum

Molecule studied: C_3H_6O



Conclusions and perspectives

- We have developed a fully gauge-invariant method.
- As our approach seems to be numerically efficient, we aim at calculating the circular dichroism spectrum of a biomolecule.

To be continued...

Thank you for your attention !