



**HAL**  
open science

# Computation of Magnetic Exchange Couplings in Photoexcited Systems Based on KS-DFT

Grégoire David, Boris Le Guennic

► **To cite this version:**

Grégoire David, Boris Le Guennic. Computation of Magnetic Exchange Couplings in Photoexcited Systems Based on KS-DFT. *Journal of Physical Chemistry Letters*, 2024, 15 (39), pp.10026-10031. 10.1021/acs.jpcllett.4c02074 . hal-04718652

**HAL Id: hal-04718652**

**<https://hal.science/hal-04718652v1>**

Submitted on 13 Nov 2024

**HAL** is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

# Computation of magnetic exchange couplings in photoexcited systems based on KS-DFT

Grégoire David\* and Boris Le Guennic

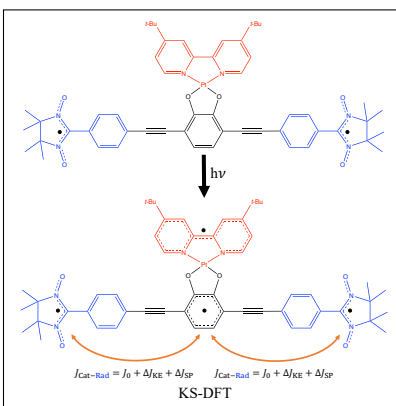
*Univ Rennes, CNRS, ISCR (Institut des Sciences Chimiques de Rennes)-UMR 6226,  
F-35000 Rennes, France*

E-mail: [gregoire.david@univ-rennes.fr](mailto:gregoire.david@univ-rennes.fr)

## Abstract

Many efforts have been made in the study of optically-excited spin-coupled molecules due to their appealing features for quantum information sciences. However, the characterisation of the magnetic exchange couplings occurring from the photoexcitation is challenging experimentally. In this context, theoretical determinations play a critical role and must provide evaluations with rigorous and cost-effective strategies. This work presents a new approach to compute magnetic exchange couplings in photo-excited systems based on the recently generalised Decomposition/Recomposition method (David et al., Phys. Chem. Chem. Phys., 2024, 6, 8952-8964). This corresponds to the first application of KS-DFT in this context and offers both a completely general method and a powerful rationalisation tool. This strategy is applied to mono- and biradical-based molecules recently synthesised by Kirk and coworkers.

## TOC Graphic



Magnetic exchange couplings in photogenerated excited states have attracted much attention over the last years for their possible applications in quantum information sciences.<sup>1-7</sup> They consist of a chromophore linked to a radical moiety. Once the chromophore is photoexcited, a coupling occurs between unpaired electrons of both open-shell moieties.<sup>8-13</sup> Important contributions have been made by Kirk et al. in the synthesis of such compounds.<sup>10-19</sup> Most of their works focused on complexes based on a (*t*-Bu<sub>2</sub>bpy)Pt(Cat-R) pattern with Cat = 3-*tert*-butyl-*o*-catecholate; bpy = bipyridine. Different radical ligands R have been investigated mainly based on nitronylnitroxide, resulting in a monoradical ground state.<sup>14</sup> More recently, they extended their investigation with a series of biradical ground state complexes, which lead once excited to four-spin-coupled systems.<sup>19</sup> Manipulating the coupling between the radical and the chromophore is of tremendous importance in modulating excited state spin dynamics,<sup>1</sup> and quantum chemistry may play a major role in the understanding of the underlying physical mechanisms as it is the case in the ground state context.<sup>20</sup>

Theoretical studies of photogenerated magnetic couplings turn out to be very challenging too and only a few works have been dedicated to them yet. Franz et al. recently used highly sophisticated wavefunction-based methods to study the coupling in organic molecules.<sup>21</sup> This strategy offers a quantitative evaluation of couplings with a correct description of the multiconfigurational nature of the wavefunction and much information may be extracted from this wavefunction to rationalise the underlying physical mechanisms.<sup>20</sup> However, these methods are not straightforward in their use and get a non-negligible computational cost. At the same time, Steenbock et al. used Spin-Flip Time-Dependent Density Functional Theory (SF-TD-DFT) calculations to compute exchange couplings in the above-mentioned monoradical-based series of bpy(Pt)-Cat-radical compounds synthesised by Kirk et al..<sup>22</sup> Whilst their calculations show excellent agreement with experiments, this computational procedure presents some important limitations. These calculations provide energy differences only and no information about the physical mechanisms is accessible. Another important limitation is intrinsic to the formalism of TD-DFT since being based on mono-excitations,

the application of this strategy beyond two- and three-unpaired electrons systems is not straightforward.<sup>23</sup> Another possibility to compute excited state is to exploit the principle of  $\Delta$ -SCF, sometimes called *orbital optimised* approaches, and which has regain much interest over the last ten years.<sup>24-30</sup> Whilst such a strategy is a well-known alternative to TD-DFT for modeling X-ray spectroscopy or charge transfer excitations,<sup>25</sup> from the best of our knowledge, it has never been applied to study of magnetic exchange couplings.

In this letter, we present a simple, cost-effective and general computational strategy to compute magnetic couplings  $J$  in photoexcited systems based on the *decomposition/recomposition* method.<sup>31-33</sup> Starting from the computation of the high spin (HS) state in the restricted open-shell (RO) formalism, successive non-optimised and constrained calculations of HS and broken symmetry (BS) determinants are performed to decompose  $J$  into its three main physical contributions i) the ferromagnetic direct exchange  $J_0$  between the magnetic centres, ii) the antiferromagnetic kinetic exchange contribution  $\Delta J_{\text{KE}}$  reflecting the relaxation of the magnetic centres in the low-spin state, and iii) the spin polarisation effect  $\Delta J_{\text{SP}}$  which corresponds to the differential response of the core (non-magnetic) orbitals in the HS and BS determinants and which may be ferro- or antiferromagnetic, depending on the system. This strategy has already shown its relevance to study either transition metal-based compounds<sup>34-39</sup> or radical systems.<sup>40-42</sup> In addition, this decomposition has been recently generalised to systems regardless of the number of magnetic centres and unpaired electrons, offering a spin-decontaminated evaluation of  $J$  by summing up the three contributions, the so-called *recomposition* method.<sup>32,33</sup>

This work focuses on the computation of chromophore-radical couplings and takes advantage of the use of non-optimised calculations and selective relaxations of orbitals to control the well-known variational collapse associated with the self-consistent optimisation of excited state determinants. To adapt the usual *decomposition* method to the present context, one starts the methodology with the computation of the excited HS state in the RO formalism (e.g. a quartet state for a radical ground state, a quintet state for a biradical ground state).

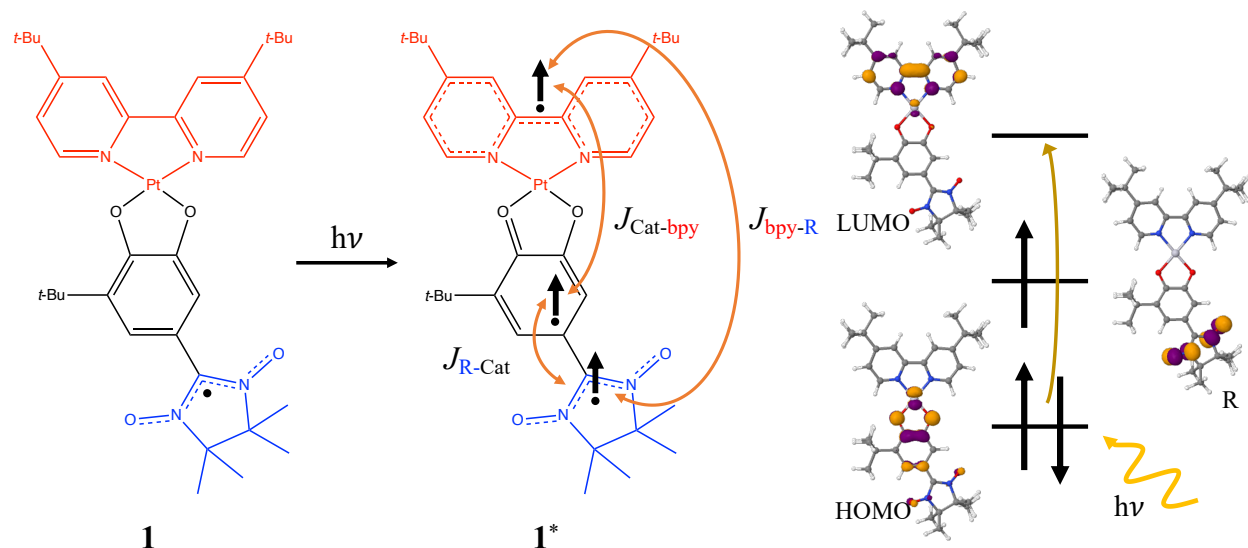


Figure 1: Schematic representation of the photoexcitation of compound **1** leading to **1\*** with the three couplings between the unpaired electrons (left) and of the molecular orbitals involved in the three couplings (right).

This state is the ground state of its given spin symmetry and presents then a clear definition, being readily accessible through a usual self-consistent field calculation. It defines a set of doubly occupied orbitals and the singly occupied molecular orbitals (SOMOs), constituted from the radical orbital(s) and the HOMO and LUMO located on the chromophore. The decomposition may then be performed without additional modifications according to Ref. 32 and the present work benefits from the recently developed input files generator introduced in Ref. 33. Computational details are presented in SI.

Let us start with the first series of compounds synthesised by Stein et al.<sup>14</sup> and studied by means of SF-TD-DFT by Steenbock et al..<sup>22</sup> They consist in three complexes based on a bpy(Pt)-Cat chromophore linked to a radical nitronylnitroxide, a thiophenyl nitronylnitroxide and a phenyl nitronylnitroxide and labelled **1**, **2** and **3**, respectively. Presented in Fig 1 (left), the photoexcitation of **1** results in complex **1\*** with three coupled unpaired electrons and in the same way for **2** and **3** with **2\*** and **3\*** presented in Fig 2 (the asterisk stands for the photoexcited complexes). This photoexcitation corresponds to promoting an electron from the HOMO, localised on the Cat moiety, to the LUMO, localised

**Table 1: Experimental ( $J_{\text{exp}}$ ),<sup>14</sup> TD-DFT ( $J_{\text{TD-DFT}}$ )<sup>22</sup> and DFT ( $J_{\Sigma}$ ) evaluations and decomposition ( $J_0$ ,  $\Delta J_{\text{KE}}$  and  $\Delta J_{\text{SP}}$ ) of the three couplings for **1\***, **2\*** and **3\*** in  $\text{cm}^{-1}$ . "/" corresponds to unexploitable values due to a variational collapse, "ND" to values not determined experimentally and "NC" to couplings not considered in the model.**

	<b>1*</b>			<b>2*</b>			<b>3*</b>		
	$J_{\text{Cat-R}}$	$J_{\text{Cat-bpy}}$	$J_{\text{bpy-R}}$	$J_{\text{Cat-R}}$	$J_{\text{Cat-bpy}}$	$J_{\text{bpy-R}}$	$J_{\text{Cat-R}}$	$J_{\text{Cat-bpy}}$	$J_{\text{Cat-R}}$
$J_{\text{exp}}$	550	1400	NC	220	ND	NC	100	ND	NC
$J_{\text{TD-DFT}}$	540	1463	NC	200	1200	NC	120	1183	NC
$J_{\Sigma}$	624	/	-153	458	/	-49	184	/	-109
$J_0$	535	306	18	368	256	94	149	297	17
$\Delta J_{\text{KE}}$	0	/	-171	-1	/	-147	-6	/	-127
$\Delta J_{\text{SP}}$	89	4	0	92	-2	4	40	4	1

on the bpy moiety, resulting in three unpaired electrons with the radical R, as depicted in Fig 1 (right). In the previously mentioned studies, two couplings, between the radical and the LUMO ( $J_{\text{R-Cat}}$ ) and between the electrons in the HOMO and LUMO ( $J_{\text{Cat-bpy}}$ ), have been considered and described by the Heisenberg-Dirac-van Vleck (HDvV) Hamiltonian  $\hat{H}^{\text{HDvV}} = -2J_{\text{R-Cat}}\hat{S}_{\text{R}} \cdot \hat{S}_{\text{Cat}} - 2J_{\text{Cat-bpy}}\hat{S}_{\text{Cat}} \cdot \hat{S}_{\text{bpy}}$ . As summarised in Table 1,  $J_{\text{R-Cat}}$  has been experimentally determined at 550, 220 and 100  $\text{cm}^{-1}$  for **1\***, **2\*** and **3\***, respectively.<sup>14</sup> For  $J_{\text{Cat-bpy}}$ , this coupling has been only determined for **1\*** with a very large ferromagnetic value of 1400  $\text{cm}^{-1}$  and the same values were considered for **2\*** and **3\***. SF-TD-DFT calculations showed excellent agreement with the experimental determination with values for  $J_{\text{R-Cat}}$  at 540, 200 and 120  $\text{cm}^{-1}$  and  $J_{\text{Cat-bpy}}$  at 1463, 1200 and 1183  $\text{cm}^{-1}$  for **1\***, **2\*** and **3\***, respectively.<sup>22</sup>

In order to set our methodology up, we first tested the importance of the  $J_{\text{bpy-R}}$  coupling and considered the more general HDvV Hamiltonian  $\hat{H}^{\text{HDvV}} = -2J_{\text{R-Cat}}\hat{S}_{\text{R}} \cdot \hat{S}_{\text{Cat}} - 2J_{\text{Cat-bpy}}\hat{S}_{\text{Cat}} \cdot \hat{S}_{\text{bpy}} - 2J_{\text{bpy-R}}\hat{S}_{\text{bpy}} \cdot \hat{S}_{\text{R}}$ . Table 1 presents the total magnetic exchange couplings  $J_{\Sigma}$  and their decomposition for the three couplings of each compound of the series. We here focus on **1\*** since similar conclusions may be drawn for **2\*** and **3\***. With a value of 624  $\text{cm}^{-1}$ ,  $J_{\Sigma}$  properly reproduces the ferromagnetic coupling and the experimental order of magnitude ( $J_{\text{exp}} = 550 \text{ cm}^{-1}$ ). This coupling results from a large direct exchange at 535  $\text{cm}^{-1}$ , which

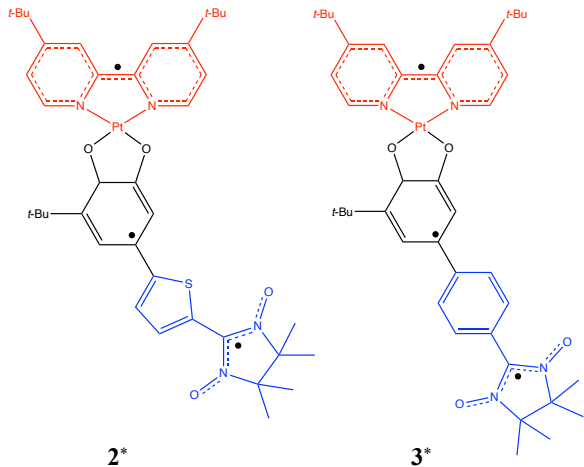


Figure 2: Schematic representation of the photoexcited compounds **2\*** (left) and **3\*** (right).

may be attributed to the close distance between the HOMO and R orbitals (Figs 1 and S1), and a non-negligible contribution from the spin polarisation effects ( $89 \text{ cm}^{-1}$ ). The kinetic exchange is null and reflects the fact that there are no relaxation effects between the HOMO and the radical orbital. Considering  $J_{\text{bpy-R}}$ , DFT calculations show a non-negligible coupling of an antiferromagnetic nature with a value of  $-153 \text{ cm}^{-1}$ . Despite the large distance between the bpy and radical moieties from which results the small  $J_0$  and  $\Delta J_{\text{SP}}$  contributions, the coupling is dominated by a relatively unexpected  $\Delta J_{\text{KE}}$  contribution of  $-171 \text{ cm}^{-1}$ . This may be attributed to the energy differences between the LUMO and the radical orbital since this effect only involved the LUMO to radical orbital relaxation. Finally, the evaluation of  $J_{\text{Cat-bpy}}$  is inaccessible through the proposed methodology. Indeed, while it is possible to evaluate  $J_0$  and  $\Delta J_{\text{SP}}$ , the determination of the kinetic exchange inevitably tends to describe the ground state solution, with the double occupation of the HOMO because of the variational collapse, and results in an unexploitable value. Interestingly, even though one may consider that this state could be a missed local minimum or saddle point (in the energy landscape) by neglecting  $\Delta J_{\text{KE}}$ , the sum of both ferromagnetic contributions ( $J_0$  and  $\Delta J_{\text{SP}}$ ) is far from the large ferromagnetic coupling at  $1400 \text{ cm}^{-1}$  determined experimentally and rules out this possibility. This last comment tends to indicate that the description of this state is beyond the present model which considers a three-unpaired-electrons-in-three-magnetic-centres sit-



uation, and of which the model space is spanned by eigenfunctions dominated by the neutral components, as a usual HDvV Hamiltonian. It may be worth mentioning that this point is not incompatible with the SF-TD-DFT calculations of Steenbock and coworkers<sup>22</sup> since their approach is not subject to the truncation and definition of a model space as the present work.

**Table 2: Experimental ( $J_{\text{exp}}$ ),<sup>14</sup> TD-DFT ( $J_{\text{TD-DFT}}$ )<sup>22</sup> and DFT ( $J_{\Sigma}$ ) evaluations and decomposition ( $J_0$ ,  $\Delta J_{\text{KE}}$  and  $\Delta J_{\text{SP}}$ ) of the three couplings for 1\*, 2\* and 3\* in  $\text{cm}^{-1}$ . Factor 4 in  $4J_{\{\text{bpyCat}\}\text{-R}}$  allows comparing with both coupling in  $\hat{H}^{\text{HDvV}} = -2J_{\text{R-Cat}}\hat{S}_{\text{R}} \cdot \hat{S}_{\text{Cat}} - 2J_{\text{Cat-bpy}}\hat{S}_{\text{Cat}} \cdot \hat{S}_{\text{bpy}}$ .**

	1*	2*	3*
$J_{\text{exp}}$	550	220	100
$J_{\text{TD-DFT}}$	540	200	120
$4J_{\Sigma}$	461	393	76
$J_{\Sigma}$	115	98	19
$J_0$	138	115	42
$\Delta J_{\text{KE}}$	-45	-41	-33
$\Delta J_{\text{SP}}$	22	24	10

The conclusions drawn on  $J_{\text{bpy-R}}$  and  $J_{\text{Cat-bpy}}$  encouraged us to envisage a different model. Hence, we proposed to consider the HOMO and LUMO spin centres as a local triplet spin state and to model the system as two interacting centres: the local triplet spin  $\{\text{bpyCat}\}$  centre and the radical centre coupled by the  $J_{\{\text{bpyCat}\}\text{-R}}$ . This amounts to considering the Hamiltonian  $\hat{H}^{\text{HDvV}} = -2J_{\{\text{bpyCat}\}\text{-R}}\hat{S}_{\{\text{bpyCat}\}} \cdot \hat{S}_{\text{R}}$ . This can be argued for several reasons, i) the HOMO-LUMO interaction is largely dominated by a ferromagnetic contribution, closer to the order of magnitude of the Hund’s rule than an exchange coupling, which allows then considering  $\{\text{bpyCat}\}$  as a local triplet, ii) this model permits to properly account for the contribution of the non-negligible  $J_{\text{bpy-R}}$ , and iii) it is closer to the experimental and the TD-DFT determinations since one may consider that the contribution of  $J_{\text{bpy-R}}$  is indirectly included in their evaluation of  $J_{\text{bpy-R}}$ . Table 2 presents the total  $J_{\{\text{bpyCat}\}\text{-R}}$  coupling and its decomposition for the three complexes. The fourth row presents the  $J_{\Sigma}$  with a factor 4, which allows direct comparison with  $J_{\text{exp}}$  and  $J_{\text{TD-DFT}}$ . Indeed, the interaction between

two doublets or a doublet and a triplet results in different factors in the definition of  $J$ .<sup>1</sup> Compounds **1\*** and **3\*** are fairly evaluated through  $J_{\Sigma}$  while **2\*** is overestimated compared to the experimental value. This may be attributed to the important tail of the HOMO over the radical moieties shown in Fig S2, which favours a large direct exchange. Comparing the decomposition of the three couplings, the direct exchange has a faster decrease with the {bpyCat}-R distance, going from 138 for **1\*** to 42  $\text{cm}^{-1}$  for **3\***, than the kinetic exchange, which stays of the same order of magnitude over the series.

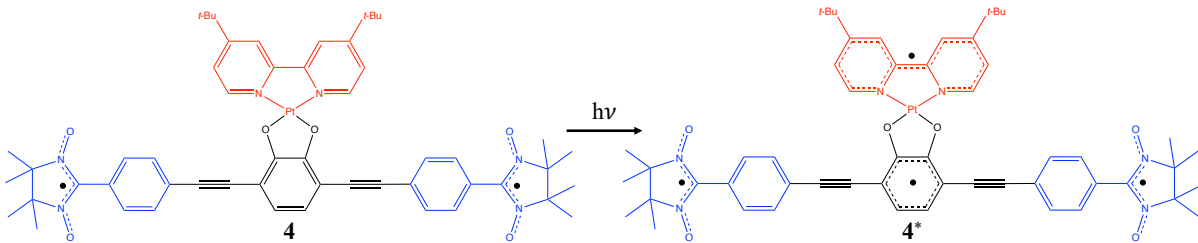


Figure 3: Schematic representation of compound **4** (left) and of its photoexcited version **4\*** (right).

We now turn to a diradical-based ground state constituted of the same donor-acceptor bpy(Pt)Cat moiety link to two nitronylnitroxide radicals through para-phenylethynyl bridges presented in Fig 3 and labelled **4**. Once photoexcited, it results in a tetra-radical system labelled **4\*** (Fig 3) while the SOMOs are presented in Fig S4. Whilst both radicals have been shown as weakly coupled ( $J_{\text{Rad-Rad}}$ ) in **4**, the Cat $\rightarrow$ bpy excitation results in a ferromagnetic coupling  $J_{\text{Cat-Rad}}$  at least three times larger.<sup>19</sup> Here again we applied the *decomposition/recomposition* method to study the couplings in both **4** and **4\*** systems presented in Table 3. Whilst for the former we used the following HDvV Hamiltonian  $\hat{H}^{\text{HDvV}} = -2J_{\text{R-R}}\hat{S}_{\text{R}} \cdot \hat{S}_{\text{R}}$ , for **4\*** the {bpyCat} has been considered as a local triplet state resulting in the HDvV Hamiltonian  $\hat{H}^{\text{HDvV}} = -2J_{\text{R-R}}\hat{S}_{\text{R}} \cdot \hat{S}_{\text{R}} - 2 \times 2J_{\{\text{bpyCat}\}-\text{R}}\hat{S}_{\{\text{bpyCat}\}} \cdot \hat{S}_{\text{R}}$ . In **4**, DFT calculations confirm the weak coupling between both nitronylnitroxide with an antiferromagnetic nature ( $J_{\Sigma} = -12 \text{ cm}^{-1}$ , Table 3). This coupling results only from the spin polarisation effects, which may be expected regarding the very long distance between

<sup>1</sup> $-2J_{\text{bpyCat-R}}\hat{S}_{\text{bpyCat}} \cdot \hat{S}_{\text{R}} = -2J_{\text{bpyCat-R}} \times \frac{1}{2} \times \frac{1}{2}$  and  $-2J_{\{\text{bpyCat}\}-\text{R}}\hat{S}_{\{\text{bpyCat}\}} \cdot \hat{S}_{\text{R}} = -2J_{\{\text{bpyCat}\}-\text{R}} \times 1 \times \frac{1}{2}$ .

both radicals, and the system may then be considered as a disjoint diradical system. Its anti-ferromagnetic nature of the spin polarisation can be anticipated according to Ovchinnikov’s rule<sup>43</sup> as shown in Fig S5. Once the system is photoexcited, the theoretical calculations confirm a more than three times (in magnitude) stronger ferromagnetic  $J_{\{\text{bpyCat}\}\text{-Rad}}$  with a value of  $49 \text{ cm}^{-1}$ . This value results from the direct exchange and a ferromagnetic spin polarisation contribution, both of the same order of magnitude, whilst there is no kinetic exchange mechanism. Interestingly, the presence of the unpaired electrons due to the photoexcitation does not affect the  $J_{\text{R-R}}$  coupling with an almost unchanged value of  $-13 \text{ cm}^{-1}$  in  $4^*$  compared to  $-12 \text{ cm}^{-1}$  in  $4$  (Table 3).

**Table 3: Total coupling ( $J_{\Sigma}$ ) and its decomposition ( $J_0$ ,  $\Delta J_{\text{KE}}$  and  $\Delta J_{\text{SP}}$ ) for  $J_{\text{Rad-Rad}}$  in the ground state  $4$  and for  $J_{\text{Rad-Rad}}$  and  $J_{\{\text{bpyCat}\}\text{-Rad}}$  in the photoexcited state  $4^*$  in  $\text{cm}^{-1}$ .**

	4	4*	
	$J_{\text{Rad-Rad}}$	$J_{\text{Rad-Rad}}$	$J_{\{\text{bpyCat}\}\text{-Rad}}$
$J_{\Sigma}$	-12	-13	49
$J_0$	0	0	29
$\Delta J_{\text{KE}}$	0	0	0
$\Delta J_{\text{SP}}$	-12	-13	20

This work presents the first application of KS-DFT to study magnetic exchange couplings in excited states. Based on non-self-consistent calculations and selective relaxations, the use of the recently generalised *decomposition/recomposition* method allows controlling the variational collapse to compute the main couplings of interest. This strategy properly reproduces the order of magnitude and the nature of the couplings experimentally determined in a series of chromophore-radical-based complexes. In addition, the decomposition of the couplings permits to rationalise the physical mechanisms governing the different couplings. However, the strategy proposed in the present work was enable to compute the  $J_{\text{Cat-bpy}}$  coupling and this represents a way of improvement which will be investigated in the future. In addition, future work will focus on the combination of the *decomposition/recomposition* method with  $\Delta$ -SCF-based algorithms as the maximum overlap method<sup>44</sup> to generalise the

study of excited states with this strategy.

In the series of complexes based on a monoradical ground state, we have highlighted the importance of the  $J_{\text{bpy-R}}$  coupling. To account for this contribution, we proposed to model the system as a radical interacting with a local triplet state, formed with both spins of the HOMO→LUMO excitation. Such a description is more in line with the physics of the interaction between the spin of the electrons of the photoexcited chromophore, largely ferromagnetic, as well as the experimental and previous theoretical determinations.

We also provided the first numerical determinations of the couplings for a diradical ground state-based system. We confirmed the experimental evidence of a weak coupling between both radical moieties and of a larger ferromagnetic coupling of them with the chromophore spins once the system is photoexcited. The *decomposition/recomposition* method offers a new strategy which is both more affordable than wavefunction-based methods and more general than SF-TD-DFT regarding the number of unpaired electrons. Hence, it opens up new possibilities to support the study of photoexcited magnetic exchange couplings in a context where the experimental determinations are particularly difficult.

## Acknowledgement

G.D. thanks Michael Franz (Institute of Physical Chemistry, University of Freiburg, Germany) for interesting discussions at the Jujols XI meeting and Dr. Torben Steenbock (Department of Chemistry, University of Hamburg, Germany) for providing geometries of the first series. The authors thank the French GENCI/IDRIS-CINES centres for high-performance computing resources. G.D. received research funding from the European Union’s 843 Horizon 2020 Research and Program under Marie Skłodowska-Curie Grant Agreement No. 899546.

## Supporting Information Available

Geometry of the four compounds. Computational details, figures of the singly occupied molecular orbitals for each system and schematic representation of Ovchinnikov's rule for compound **4**.

## References

- (1) Wasielewski, M. R.; Forbes, M. D. E.; Frank, N. L.; Kowalski, K.; Scholes, G. D.; Yuen-Zhou, J.; Baldo, M. A.; Freedman, D. E.; Goldsmith, R. H.; Goodson, T. et al. Exploiting chemistry and molecular systems for quantum information science. Nat. Rev. Chem. **2020**, 4, 490–504.
- (2) Wasielewski, M. R. Light-driven spin chemistry for quantum information science. Physics Today **2023**, 76, 28–34.
- (3) von Kugelgen, S.; Freedman, D. E. A chemical path to quantum information. Science **2019**, 366, 1070–1071.
- (4) Yu, C.-J.; von Kugelgen, S.; Laurenza, D. W.; Freedman, D. E. A Molecular Approach to Quantum Sensing. ACS Central Science **2021**, 7, 712–723.
- (5) Mani, T. Molecular qubits based on photogenerated spin-correlated radical pairs for quantum sensing. Chemical Physics Reviews **2022**, 3.
- (6) Quintes, T.; Mayländer, M.; Richert, S. Properties and applications of photoexcited chromophore–radical systems. Nature Reviews Chemistry **2023**, 7, 75–90.
- (7) Reid, O. G.; Johnson, J. C.; Eaves, J. D.; Damrauer, N. H.; Anthony, J. E. Molecular Control of Triplet-Pair Spin Polarization and Its Optoelectronic Magnetic Resonance Probes. Accounts of Chemical Research **2023**, 57, 59–69.

- (8) Mao, H.; Young, R. M.; Krzyaniak, M. D.; Wasielewski, M. R. Controlling the Dynamics of Three Electron Spin Qubits in a Donor–Acceptor–Radical Molecule Using Dielectric Environment Changes. The Journal of Physical Chemistry Letters **2021**, 12, 2213–2218.
- (9) Chernick, E. T.; Mi, Q.; Kelley, R. F.; Weiss, E. A.; Jones, B. A.; Marks, T. J.; Ratner, M. A.; Wasielewski, M. R. Electron Donor-Bridge-Acceptor Molecules with Bridging Nitronyl Nitroxide Radicals: Influence of a Third Spin on Charge- and Spin-Transfer Dynamics. Journal of the American Chemical Society **2006**, 128, 4356–4364.
- (10) Kirk, M. L.; Shultz, D. A.; Schmidt, R. D.; Habel-Rodriguez, D.; Lee, H.; Lee, J. Ferromagnetic Nanoscale Electron Correlation Promoted by Organic Spin-Dependent Delocalization. Journal of the American Chemical Society **2009**, 131, 18304–18313.
- (11) Rugg, B. K.; Krzyaniak, M. D.; Phelan, B. T.; Ratner, M. A.; Young, R. M.; Wasielewski, M. R. Photodriven quantum teleportation of an electron spin state in a covalent donor–acceptor–radical system. Nature Chemistry **2019**, 11, 981–986.
- (12) Kirk, M. L.; Shultz, D. A.; Habel-Rodriguez, D.; Schmidt, R. D.; Sullivan, U. Hyperfine Interaction, Spin Polarization, and Spin Delocalization as Probes of Donor-Bridge-Acceptor Interactions in Exchange-Coupled Biradicals. The Journal of Physical Chemistry B **2010**, 114, 14712–14716.
- (13) Kirk, M. L.; Shultz, D. A.; Depperman, E. C.; Habel-Rodriguez, D.; Schmidt, R. D. Spectroscopic Studies of Bridge Contributions to Electronic Coupling in a Donor-Bridge-Acceptor Biradical System. Journal of the American Chemical Society **2012**, 134, 7812–7819.
- (14) Stein, B. W.; Tichnell, C. R.; Chen, J.; Shultz, D. A.; Kirk, M. L. Excited State Magnetic Exchange Interactions Enable Large Spin Polarization Effects. Journal of the American Chemical Society **2018**, 140, 2221–2228.

- (15) Kirk, M. L.; Shultz, D. A.; Hewitt, P.; Stasiw, D. E.; Chen, J.; van der Est, A. Chromophore-radical excited state antiferromagnetic exchange controls the sign of photoinduced ground state spin polarization. Chemical Science **2021**, 12, 13704–13710.
- (16) Kirk, M. L.; Shultz, D. A.; Chen, J.; Hewitt, P.; Daley, D.; Paudel, S.; van der Est, A. Metal Ion Control of Photoinduced Electron Spin Polarization in Electronic Ground States. Journal of the American Chemical Society **2021**, 143, 10519–10523.
- (17) Kirk, M. L.; Shultz, D. A.; Hewitt, P.; van der Est, A. Excited State Exchange Control of Photoinduced Electron Spin Polarization in Electronic Ground States. The Journal of Physical Chemistry Letters **2022**, 13, 872–878.
- (18) Tichnell, C. R.; Daley, D. R.; Stein, B. W.; Shultz, D. A.; Kirk, M. L.; Danilov, E. O. Wave Function Control of Charge-Separated Excited-State Lifetimes. Journal of the American Chemical Society **2019**, 141, 3986–3992.
- (19) Kirk, M. L.; Shultz, D. A.; Marri, A. R.; van der Est, A. Photoinduced Magnetic Exchange-Jump Promotes Ground State Biradical Electron Spin Polarization. Journal of the American Chemical Society **2024**, 146, 9285–9292.
- (20) Malrieu, J. P.; Caballol, R.; Calzado, C. J.; de Graaf, C.; Guihéry, N. Magnetic Interactions in Molecules and Highly Correlated Materials: Physical Content, Analytical Derivation, and Rigorous Extraction of Magnetic Hamiltonians. Chemical Reviews **2013**, 114, 429–492.
- (21) Franz, M.; Neese, F.; Richert, S. Calculation of exchange couplings in the electronically excited state of molecular three-spin systems. Chemical Science **2022**, 13, 12358–12366.
- (22) Steenbock, T.; Rybakowski, L. L. M.; Benner, D.; Herrmann, C.; Bester, G. Exchange Spin Coupling in Optically Excited States. Journal of Chemical Theory and Computation **2022**, 18, 4708–4718.

- (23) Mayhall, N. J.; Head-Gordon, M. Computational Quantum Chemistry for Multiple-Site Heisenberg Spin Couplings Made Simple: Still Only One Spin–Flip Required. The Journal of Physical Chemistry Letters **2015**, 6, 1982–1988.
- (24) Evangelista, F. A.; Shushkov, P.; Tully, J. C. Orthogonality Constrained Density Functional Theory for Electronic Excited States. The Journal of Physical Chemistry A **2013**, 117, 7378–7392.
- (25) Hait, D.; Head-Gordon, M. Orbital Optimized Density Functional Theory for Electronic Excited States. The Journal of Physical Chemistry Letters **2021**, 12, 4517–4529, PMID: 33961437.
- (26) David, G.; Irons, T. J. P.; Fouda, A. E. A.; Furness, J. W.; Teale, A. M. Self-Consistent Field Methods for Excited States in Strong Magnetic Fields: a Comparison between Energy- and Variance-Based Approaches. Journal of Chemical Theory and Computation **2021**, 17, 5492–5508.
- (27) Shea, J. A. R.; Gwin, E.; Neuscammann, E. A Generalized Variational Principle with Applications to Excited State Mean Field Theory. Journal of Chemical Theory and Computation **2020**, 16, 1526–1540.
- (28) Levi, G.; Ivanov, A. V.; Jónsson, H. Variational Density Functional Calculations of Excited States via Direct Optimization. Journal of Chemical Theory and Computation **2020**, 16, 6968–6982, PMID: 33064484.
- (29) Carter-Fenk, K.; Herbert, J. M. State-Targeted Energy Projection: A Simple and Robust Approach to Orbital Relaxation of Non-Aufbau Self-Consistent Field Solutions. Journal of Chemical Theory and Computation **2020**, 16, 5067–5082.
- (30) Ziegler, T.; Krykunov, M.; Cullen, J. The implementation of a self-consistent constricted variational density functional theory for the description of excited states. The Journal of Chemical Physics **2012**, 136, 124107.



- (31) David, G.; Trinquier, G.; Malrieu, J.-P. Consistent spin decontamination of broken-symmetry calculations of diradicals. The Journal of Chemical Physics **2020**, 153, 194107.
- (32) David, G.; Ferré, N.; Le Guennic, B. Consistent Evaluation of Magnetic Exchange Couplings in Multicenter Compounds in KS-DFT: The Recomposition Method. Journal of Chemical Theory and Computation **2022**, 19, 157–173.
- (33) David, G.; Duplaix-Rata, G.; Le Guennic, B. What governs magnetic exchange couplings in radical-bridged dinuclear complexes? Physical Chemistry Chemical Physics **2024**, 26, 8952–8964.
- (34) David, G.; Wennmohs, F.; Neese, F.; Ferré, N. Chemical Tuning of Magnetic Exchange Couplings Using Broken-Symmetry Density Functional Theory. Inorganic Chemistry **2018**, 57, 12769–12776.
- (35) Coetzee, S.; Turnbull, M. M.; Landee, C. P.; Monroe, J. C.; Deumal, M.; Novoa, J. J.; Rademeyer, M. Satellite ligand effects on magnetic exchange in dimers. A structural, magnetic and theoretical investigation of  $\text{Cu}_2\text{L}_2\text{X}_4$  (L = methylisothiazolinone and X =  $\text{Cl}^-$ ,  $\text{Br}^-$ ). Physical Chemistry Chemical Physics **2023**, 25, 9176–9187.
- (36) Duplaix-Rata, G.; Le Guennic, B.; David, G. Revisiting magnetic exchange couplings in heterodinuclear complexes through the decomposition method in KS-DFT. Physical Chemistry Chemical Physics **2023**, 25, 14170–14178.
- (37) Le Guennic, B.; Ferré, N. Analysis of the Magnetic Exchange Interaction in Halide-Bridged Cu(II) Binuclear Complexes: Deciphering the Paths. Curr. Inorg. Chem. **2014**, 3, 235–241.
- (38) Goswami, D.; Patra, S. G.; Ray, D. Magneto-Structural Analysis of Hydroxido-Bridged  $\text{CuII}_2$  Complexes: Density Functional Theory and Other Treatments. Magnetochemistry **2023**, 9, 154.

- (39) Ziółkowska, A.; Witwicki, M. Understanding the Exchange Interaction between Paramagnetic Metal Ions and Radical Ligands: DFT and Ab Initio Study on Semiquinonato Cu(II) Complexes. International Journal of Molecular Sciences **2023**, 24, 4001.
- (40) Trinquier, G.; David, G.; Malrieu, J.-P. Qualitative Views on the Polyradical Character of Long Acenes. The Journal of Physical Chemistry A **2018**, 122, 6926–6933.
- (41) David, G.; Ferré, N.; Trinquier, G.; Malrieu, J.-P. Improved evaluation of spin-polarization energy contributions using broken-symmetry calculations. The Journal of Chemical Physics **2020**, 153, 054120.
- (42) Trinquier, G.; David, G.; Veillon, E.; Malrieu, J.-P. On Entangled Singlet Pure Diradicals. The Journal of Physical Chemistry A **2024**, 128, 4252–4267.
- (43) Ovchinnikov, A. A. Multiplicity of the ground state of large alternant organic molecules with conjugated bonds. Theoretica Chimica Acta **1978**, 47, 297–304.
- (44) Gilbert, A. T. B.; Besley, N. A.; Gill, P. M. W. Self-Consistent Field Calculations of Excited States Using the Maximum Overlap Method (MOM). J. Phys. Chem. A **2008**, 112, 13164–13171.