On the quantum origin of few response properties

Leonardo A. Millán,[1,2] (iD) Claudia G. Giribet,[3,4] (iD) and Gustavo A. Aucar[1,2,a] (iD)

AFFILIATIONS

[1] Institute for Modeling and Innovative Technology, IMIT (CONICET-UNNE), Corrientes, Argentina
[2] Physics Department, Natural and Exact Science Faculty, Northeastern University, Corrientes, Argentina
[3] Physics Institute of Buenos Aires, IFIBA (CONICET-UBA), Buenos Aires, Argentina
[4] Physics Department, Natural and Exact Science Faculty, Buenos Aires University, Buenos Aires, Argentina

[a] Author to whom correspondence should be addressed: gaaucar@conicet.gov.ar

ABSTRACT

In modern physics, the entanglement between quantum states is a well-established phenomenon. Going one step forward, one can conjecture the likely existence of an entanglement between excitations of one-particle quantum states. Working with a density matrix that is well defined within the polarization propagator formalism, together with information theory, we found that the quantum origin of, at least, few molecular response properties can be described by the entanglement between two pairs of virtual excitations of molecular orbitals (MOs). With our model, we are able to bring new insights into the electronic mechanisms that are behind the transmission, and communication, of the effects of a given perturbation to the whole electronic system described by the Hamiltonian of an unperturbed quantum system. With our entanglement model, we analyzed the electronic origin of the Karplus rule of nuclear magnetic resonance spectroscopy, a well-known empirical phenomenon, and found that this rule is straightforwardly related to the behavior of entangled MO excitations. The model compound used to show it is the H_2O_2 molecule.

Published under license by AIP Publishing. https://doi.org/10.1063/5.0027545

I. INTRODUCTION

The importance of the applications of usual entanglement is hardly overestimated.[1–3] This feature of quantum physics is, at the moment, mostly considered in terms of multiparticle states or different particles or systems,[4,5] but never in terms of excitations between one-particle states located in different spatial places of the same quantum system. Some of its applications in chemical physics, among many others, are focused on complexity in excited states of atoms, quantum computing, and electron–electron correlation.[6–10]

In a recent experiment, whose setup is analogous to what we shall expose here for a molecular system, it was shown that one can transfer quantum bits of information from, let us say, node A to a distant node B, by sending a single photon across fiber links.[11] Remote entanglements are created between distant single-atom nodes based on the transmission of a single photon so that an elementary network is formed. The atom–photon entanglement is thus converted into entanglement between the two nodes. It is worth to highlight here that one of the most remarkable properties

of a quantum network is the existence of entangled quantum states shared among several network nodes.[11] Then, would it be possible to think about an equivalent network for which the nodes would be given by the nuclear dipole moments in a molecule and the interactions between their nuclear-spin states are transmitted through the electronic framework? One of the aims of this work is to show that this last network does exist and can be observed by using nuclear magnetic resonance (NMR) spectroscopy. Furthermore, the mechanism behind such electronic transmission may be the entangled excitations between occupied and virtual electronic states. In other words, we propose that the likely entanglement between every pair of nuclear dipole moments would occur by the entanglement between each of the nuclear-spin states and the excitations of electronic states, which, in turn, are also entangled between them.

Indirect NMR J-coupling is one of the best examples to test the conjecture mentioned above, with the quantum information being stored in this case in the nuclear-spin states of two coupled nuclei. Furthermore, the J-coupling does not depend on external magnetic fields; it is an intrinsic property of molecular systems that

depends on the magnetic fields arising from nuclear magnetic dipole moments.[12]

Polarization propagators or two-times Green functions are useful theoretical tools for describing the electronic mechanisms that are behind several atomic and molecular response properties.[13] Previous applications of those propagators to the analysis of the Karplus rule suggested that non-local interactions were involved.[14] One of the elements that belongs to those propagators (the principal propagator term that will be explained below) has matrix elements that are of Coulomb-type, G matrix, and exchange-type, H matrix, whose elements suggest non-locality when describing the behavior of electrons. Then, another aim of this work is to use some of the newest developments of the polarization propagator formalism[15] to give a deeper explanation about the physical origin of that empirical rule, which tells us about the dependence of vicinal (three-bond distant) J-couplings on the dihedral angle.[16] We shall show that Karplus-type behavior of those J-couplings has a direct relationship with two measures of the entanglement between two pairs of excitations of localized molecular orbitals (MOs), a fact that we have been unable to show in a previous work.[15]

In Sec. II, we start giving a short description of the formalism we use to analyze the physical insights that are behind NMR J-couplings. Then, we describe what our model of entanglement between excitations of localized molecular orbitals is about and two of its proper measures, which give, in our case, the same values. We

show that that entanglement is the mechanism that can naturally explain the well-known Karplus rule for the three-bond J-coupling, e.g., $^3J(H_1–H_2)$ in the $H_1O_1O_2H_2$ molecule. There are some technological advantages that our model introduces due to the fact that molecular systems with a number of J-coupled nuclei may be used as quantum computers.[17,18] We shall show that the network of normal excitations of one-particle states of the molecule is the channel through which the quantum information, stored in qubits (in our case, nuclear-spin states), is transmitted within the molecular quantum system. We shall also uncover another unexpected finding: the appearance of two different ways of understanding the interaction between two qubits through the electronic framework, i.e., by the quantum propagation of a disturbance or by its quantum communication [see Fig. 1(a)].

II. THEORETICAL MODELS FOR DESCRIBING MOLECULAR QUANTUM NETWORKS

As just mentioned, all quantum networks consider the transmission of quantum information through a quantum system. In all those cases, the quantum information is stored in particles or states. To explain the transmission of the effect of external perturbations within a quantum system, one can use different tools. Indirect J-couplings are pure quantum objects because they arise as an indirect coupling (meaning transmitted through electrons) of two nuclear spins. The theory of polarization propagators can be used to both reproduce and describe the physics underlying response properties. This is so due to the special formal expression one has at hand in actual calculations, which are the same in both regimes, relativistic and non-relativistic.[14,19] There are two objects, one known as the perturbator, **b** (one of them for each external perturbation), and another one known as the principal propagator, **P** (which describes the quantum behavior of the system as a whole), to calculate any second-order response property. This is explicitly given in the following equation for NMR J-couplings:

$$J_{N_1N_2}^X = \gamma_{N_1}\gamma_{N_2}\langle\langle V_{N_1}^X; V_{N_2}^X\rangle\rangle_{E=0}$$

$$= \sum J_{(N_1N_2);ia,jb}^X = \sum \left[\mathbf{b}_{N_1,ia}^X \mathbf{P}_{ia,jb} \mathbf{b}_{N_2,jb}^X\right], \quad (1)$$

with X being each of the four electronic mechanisms (X = FC, SD, PSO, DSO) involved in the non-relativistic theory of J-couplings, and the matrix elements of $\mathbf{b}_{N_1}^X$ and $\mathbf{b}_{N_2}^X$ are given by the integrals of the external perturbators with molecular orbitals, MOs, i, a and j, b. MOs i and j are occupied, and a and b are unoccupied. We will consider in this work only the Fermi contact, FC, mechanism on both nuclei N_1 and N_2 so that the perturbative Hamiltonians are given by $V_{N_1}^{FC}$ and $V_{N_2}^{FC}$.[14] At the RPA level of approach, the matrix **P** depends on matrices **A** (which contains Coulomb-type two-body matrix elements) and **B** (exchange-type two-body matrix elements) whose actual expressions are given in the supplementary material. The interaction among nuclear spins with electronic states together with their transmission through the electronic framework is related to each of the two perturbators and the principal propagator, respectively. All this is shown schematically in the lower part of Fig. 1(b). It is worth to mention that the principal propagator does not depend on which nuclei are being considered. So, the calculation of the FC contribution to J-couplings between nuclei separated by one, two, . . . bonds uses the same principal propagator, but they differ in their
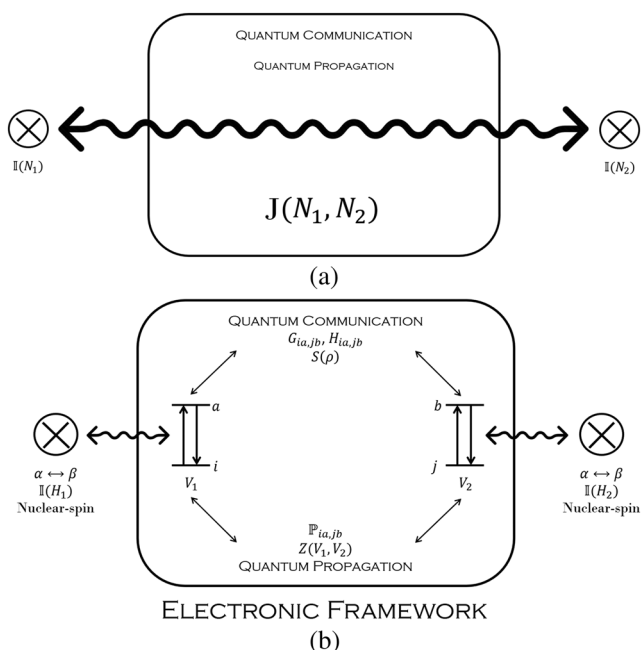

FIG. 1. The transmission of indirect interactions among two nuclear spins N_1 and N_2 (its nuclear-spin flip-flop) is carried out by the electronic framework. Different quantum tools can be used to describe two aspects of such transmission: quantum communication and quantum propagation of external perturbations. (a) Experiments measure J-couplings. (b) The formalism of the polarization propagator describes two different quantum phenomena: quantum communication and quantum propagation of external perturbations.

perturbators, which have the information about which nuclei are actually considered in calculations.

In what follows, we show that there is a relationship between the concept of normal modes and "coupling pathways," which are defined by each pair of MO excitations (ia, jb). It is worth to mention that both perturbator and principal propagator matrices are completely defined by the unperturbed system and also the fact that the four mechanisms of interaction between nuclear spins and the electronic framework become one within the relativistic regime.[14]

As shown in Fig. 1, there is an interaction between the nuclear-spin excitations and the electronic framework surrounding those nuclei. Such interactions produce single virtual excitations whose local contributions are quantified by the matrix elements of the perturbators; the effects of those excitations are transmitted through the electronic framework, with those effects being expressed by the matrix elements of the principal propagator. Furthermore, one may want to describe the way the magnetic disturbance is propagated from one nucleus to another [see the bottom of Fig. 1(b)], or learn about the way the excitations communicate with each other [see the top of Fig. 1(b)]. In the first case, one uses the principal propagator **P**, and in the second case (what is shown here), one uses information theory and calculations of von Neumann entropy of a selected reduced matrix of the inverse of the principal propagator.

A. Entanglement between two MO excitations

In order to analyze the entanglement among excitations of two given localized molecular orbitals, LMOs, we selected the HOOH molecule (see Fig. 2). This molecule has only two occupied O–H bonding orbitals and several vacant ones that can be related to each one of them (σ_i and σ_i^*, σ_i^{**}, ..., $i = 1, 2$, respectively). So, there are no other orbitals that may introduce any interference to the transmission of quantum communication between nuclear spins of hydrogen atoms, H_1 and H_2.
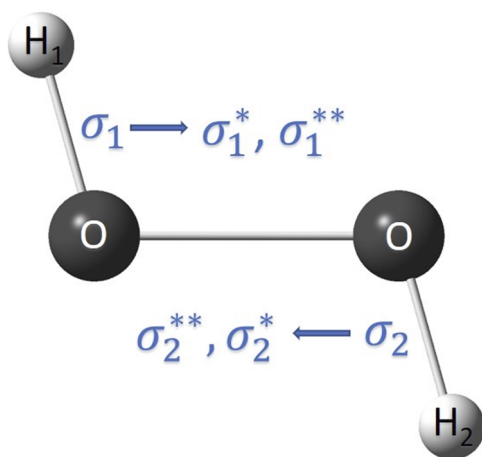

FIG. 2. In actual calculation of the contributions of all different coupling pathways, few LMO excitations contribute. We show here the principal coupling pathway for $^3J(H–H)$ in the HOOH molecule. Two excitations are considered, starting each one of them in each of two occupied LMOs that resemble ligand σ-type LMOs (σ_1 and σ_2) and ending in two anti-bonding LMOs of σ-type (σ_1^*, σ_1^{**} and σ_2^*, σ_2^{**}).

Actually, we restricted the number of unoccupied LMOs to two for each occupied one. In this way, the measurement of the entanglement given by both the mutual information $I_{i,j}$ and the function ζ_{vN} is calculated applying Eqs. (2) and (5),

$$I_{i,j} = 1/2\Big(S(1)_i + S(1)_j - S(2)_{i,j}\Big)(1 - \delta_{ij}) \geq 0, \quad (2)$$

where δ_{ij} is the Kronecker delta function and the factor $1/2$ prevents the same interactions to be counted twice. The single-orbital entropy, $S(1)_i$, and the two-orbital entropy, $S(2)_{i,j}$, are given by the following expressions:

$$S(1)_i = -\sum \lambda_{\alpha;i} \ln\lambda_{\alpha;i}, \quad (3)$$

$$S(2)_{i,j} = -\sum \lambda_{\alpha;i,j} \ln\lambda_{\alpha;i,j}. \quad (4)$$

Equations (3) and (4) give a measure of the entanglement between one and two excitations, respectively, with the set of all other excitations that can be constructed from LMOs different from the given i and j. The elements $\lambda_{\alpha;i}$ and $\lambda_{\alpha;i,j}$ are eigenvalues of the single-orbital reduced density matrix, RDM, and the two-orbital RDM, respectively. In our case, the equivalent RDMs are obtained by tracing out all degrees of freedom related to "orbital excitations" except those of the single-orbital excitation ($i \rightarrow a$) and the two-orbital excitations ($i \rightarrow a$, $j \rightarrow b$).[20]

Another well-known measure of entanglement is

$$\zeta_{vN} = S(1) - \ln N, \quad (5)$$

where N is the number of occupied excitations until unoccupied (2 in our case) and $\zeta_{vN} \geq 0$, being zero for non-entangled fermionic systems that are known as states with Slater rank one.[21] The matrix elements of the matrix **P** are obtained as the inverse of the matrix **M**, which, in turn, contains, at the RPA level of approach, two matrices: **A** and **B**,

$$\mathbf{M} = \begin{pmatrix} A & B^* \\ B & A^* \end{pmatrix}. \quad (6)$$

The matrix **A** has two contributing terms: **A**(0) and **A**(1). The first one includes the contribution of the one-particle part of the unperturbed Hamiltonian, and so, it introduces only the uncorrelated terms. The contribution of **A**(1) is due to singly excited CI elements, and the **B**(1) matrix elements are constructed between Hartree–Fock and doubly excited states. When the two terms of the matrix **A** are introduced, both kinds of correlations are being considered for the transmission; then, if only the quantum correlation is going to be considered, the matrix elements of **A**(0) must not be included in calculations. Matrix elements of **A** and **B** are given in the supplementary material as SI(1) and SI(2). Using the definition of the density matrix obtained from the generating functional of the polarization propagators,[19] it is possible to obtain the RDM of two excitations ia, jb. We use the CLOPPA (Contribution from Localized Orbitals within Polarization Propagator Approach) method[22] to obtain the elements of the matrix P that correspond to just those two excitations,

$$\rho_{ia,jb} = e^{M_{ia,jb}}/Z_{[0]}, \quad (7)$$

where $\mathbf{M}_{ia,jb} = (\mathbf{A} - \mathbf{B})_{ia,jb}$. Then, the entropy S(2) can be calculated from the eigenvalues $\lambda_{\alpha;i,j}$ as usual. The same methodology is applied to obtain the RDM of just one excitation, ia. If the dihedral angle dependence of J is similar to that of $I_{ia,jb}$, it would mean that J-coupling arises from the entanglement among MO excitations shown in Fig. 2.

III. ENTANGLEMENT AND THE KARPLUS RULE

We shall first highlight the fact that the NMR J-coupling parameter arises as a result of a non-local experiment and, then, how the Karplus rule is explained by applying our model.
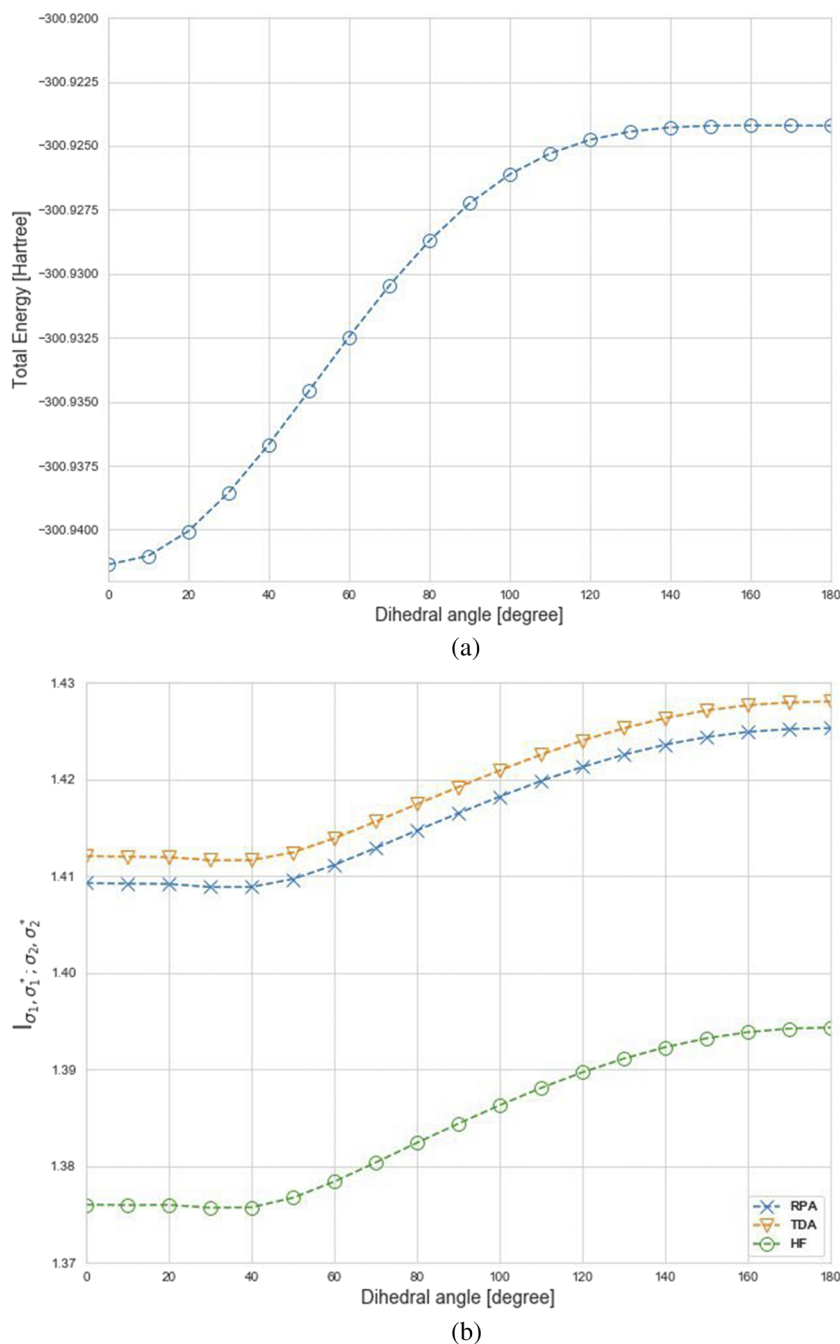

(a)

(b)

FIG. 3. Dependence of the (a) total electronic energy and (b) mutual information between two excitations of LMOs on the dihedral angle of H–O–O–H, ϕ, at different levels of theory.

A. The underlying physics of the NMR J-couplings

A set of non-zero nuclear spins embedded in an electronic framework can be considered a composite system. If each nuclear spin is considered a subsystem, it is not possible to get the J-coupling between two given nuclear spins using local measurements. In line with this knowledge and using the phenomenological second-order
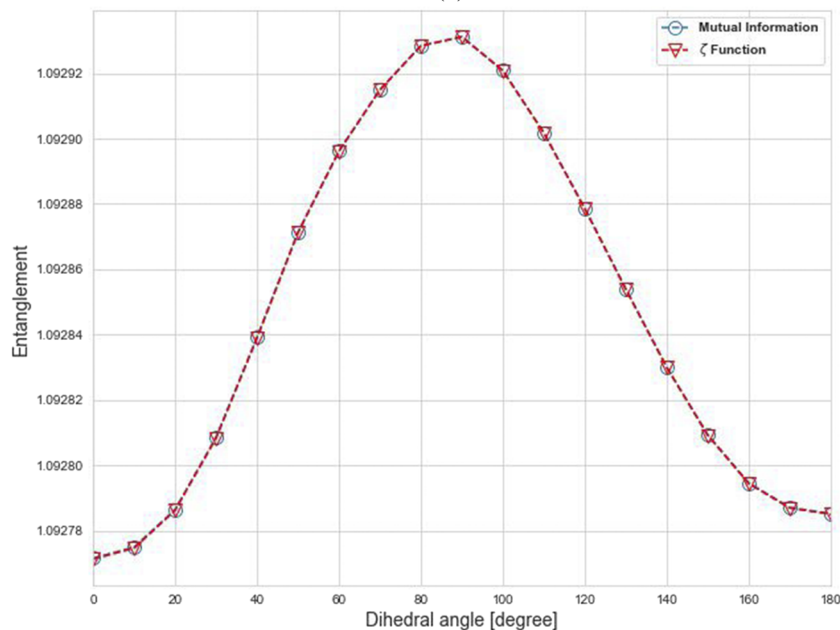
correction to the energy required to explain experimental spectra,

$$E_{N_1 N_2}^{(2)} = h\mathbf{I}_{N_1} \cdot \mathbf{J}_{N_1 N_2} \cdot \mathbf{I}_{N_2}, \tag{8}$$

one finds that J is a non-local observable, meaning that it cannot be obtained from local measurements; in other words, it cannot be obtained by measurements that are carried out only on one
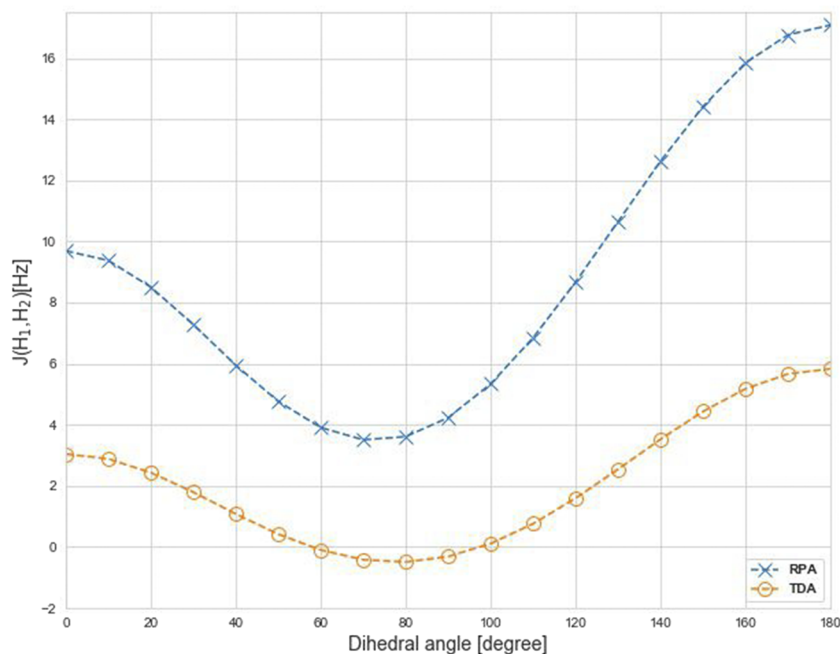
(a)

(b)

FIG. 4. Karplus-type dependence of vicinal J-couplings and entanglement of two excitations in the HOOH molecule: (a) dependence of the total indirect $^3J(H_1–H_2)$ at different levels of propagator theory and (b) dependence of measures of entanglement between the two principal excitations of LMOs, meaning $\sigma_1 \to (\sigma_1^*, \sigma_1^{**})$; $\sigma_2 \to (\sigma_2^*, \sigma_2^{**})$.

nuclear spin.[23] J-couplings can be observed only when two spatially separated quantum subsystems are simultaneously observed.

As mentioned above, the Karplus rule describes the dependence of vicinal J-couplings on the dihedral angle. We selected such a rule to learn about the way the "perturbations" originated in the nuclear magnetic dipole moments are transmitted through the electronic framework.

B. The origin of the Karplus rule

We first analyze the dependence of both the total electronic energy and the mutual information of the main coupling pathway of the principal propagator (meaning the coupling pathway $\sigma_1 \rightarrow \sigma_1^*$; $\sigma_2 \rightarrow \sigma_2^*$) on the dihedral angle of H–O–O–H. The mutual information was calculated, in this case, including $\mathbf{A}(0, 1)$ and $\mathbf{B}(1)$ matrix elements at different levels of theory. As observed in Fig. 3, we found a similar pattern in both cases. This similarity can be related to the fact that the values of mutual information contain classical and quantum correlations, given by the contributions from $\mathbf{A}(0)$ and $\mathbf{A}(1)$ and $\mathbf{B}(1)$, respectively [see Fig. 3(b)].

On the other hand, as observed in Fig. 4(a), there is a Karplus-type dependence of the total J-coupling, $^3J(H_1–H_2)$, at different levels of propagator theory, i.e., Tamm–Dancoff approximation, TDA, and random phase approximation, RPA.[14] A similar dependence on the dihedral angle ϕ is found for the principal coupling pathway. One

interesting behavior of this Karplus-type dependence is the fact that there are two maximum values of J at exactly 0° and 180°, but the minimum is shifted from 90°. This feature is also found in the behavior of both measurements of the entanglement of LMO excitations [Fig. 4(b)] when the calculations are performed with $\mathbf{A}(1) - \mathbf{B}(1)$ matrix elements. In such a case, one only considers the quantum correlation of the system. It is worth mentioning that both measures of entanglement [mutual information $I_{i,j}$ of Eq. (2) and ζ_{vN} of Eq. (5)] give exactly the same values. Some numerical values of calculations for a given dihedral angle are given as the supplementary material.

In a previous work, we have shown that the origin of the Karplus rule should be related to the entanglement we are considering here, but we could not find a clear functional dependence between them.[15] Further thinking suggested that this fact might be due to the symmetry of the selected molecule, ethane, for which there is no clear and unique principal coupling pathway as occurring for the HOOH molecule. Work is in progress to find the reason behind such behavior in the ethane molecule.

A small different functional dependence on ϕ is observed for both J-couplings and the measurement of entanglement in two different branches of the total dihedral angular spreading: one starts with 0° and ends in 90°; the other one starts at 90° and ends in 180°. In Fig. 5, we show the functional dependence between the J-coupling and the entanglement between the two principal LMO excitations: $\sigma_1 \rightarrow (\sigma_1^*, \sigma_1^{**})$ and $\sigma_2 \rightarrow (\sigma_2^*, \sigma_2^{**})$. This dependence is clear evidence that the Karplus-type dependence of vicinal J-couplings is
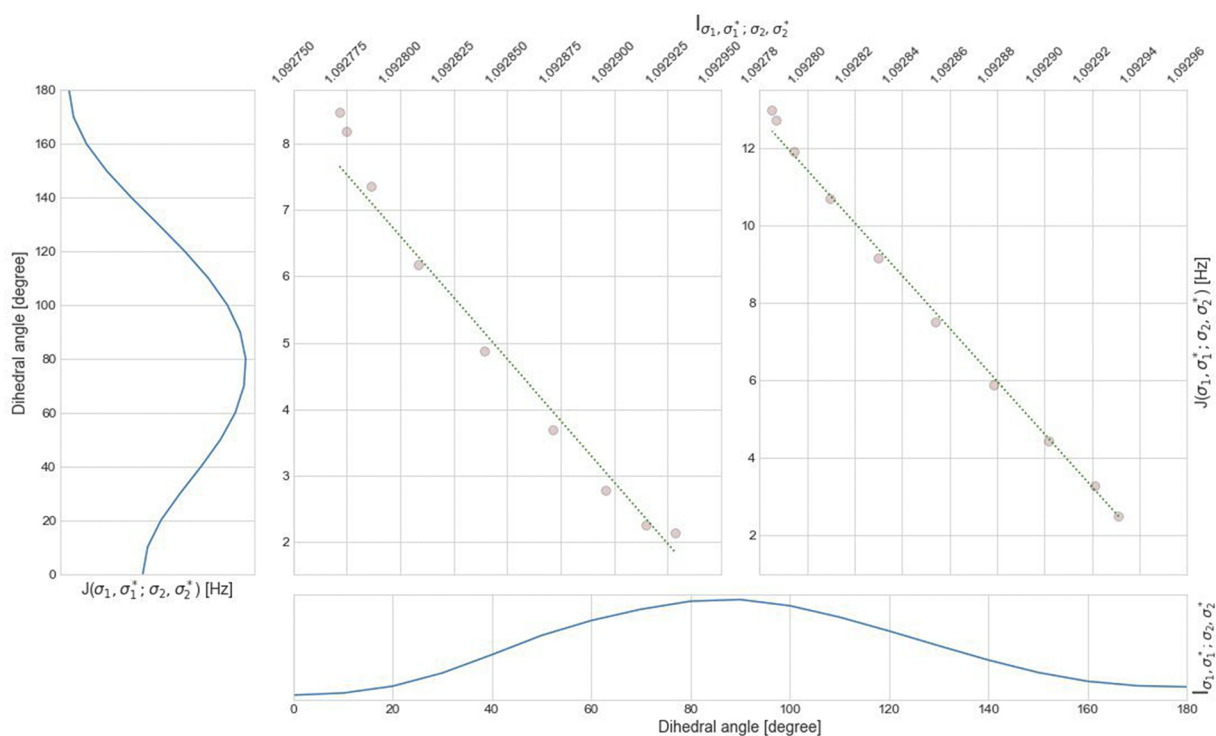

FIG. 5. Functional (linear) dependence among the principal coupling pathway of $^3J(H_1–H_2)$ in the HOOH molecule and the entanglement between the two principal LMO excitations: $\sigma_1 \rightarrow (\sigma_1^*, \sigma_1^{**})$ and $\sigma_2 \rightarrow (\sigma_2^*, \sigma_2^{**})$. The dihedral angle is taken as a parameter.

due to entanglement. The pattern of another important coupling pathway, the one that involves two equivalent lone-pairs, e.g., $LP_1 \rightarrow (\sigma_1^*, \sigma_1^{**})$ and $LP_2 \rightarrow (\sigma_2^*, \sigma_2^{**})$, follows quite a similar behavior as can be seen in the supplementary material.

IV. CONCLUSION

It is known that the principal propagator of the polarization propagator formalism gives the probability amplitude for the propagation of a unitary strength disturbance arising from "external" perturbations, meaning perturbations that are not included in the Hamiltonian used to describe the "unperturbed" quantum system. In our case, they are given by the magnetic fields due to the nuclear magnetic dipole moments. We assume that these nuclear moments are nodes of a molecular network and that they are connected by normal modes of one-particle excitations.

Working with that formalism, we developed an entanglement model that is consistent with the theoretical grounds of polarization propagators. Once a density matrix is well defined, the application of information theory leads to the finding of an entanglement between at least two pairs of excitations of localized molecular orbitals (two occupied and two unoccupied), with such entanglement being quantified with two usual measures of entanglement in many-particle systems.

One of our main findings is that the quantum communication between two virtual excitations of localized occupied MOs to localized unoccupied MOs, which arises from the interaction of the electronic framework with nuclear-spin dipole moments, is driven by the inverse of the principal propagator. Given that the matrix elements of the principal propagator are independent of the "external" perturbative fields, but only on the electron spin dependence of those perturbations, this kind of quantum communication should be common to all molecular systems and also to response properties that have the same electron spin dependence.

We applied our new entanglement model to the analysis of the quantum origin of the well-known Karplus rule, which describes the angular dependence of the vicinal NMR J-couplings on the dihedral angle. We found that the Karplus-type dependence of the principal coupling pathway of $^3J(H-H)$ in the HOOH molecule has almost the same behavior as any of both measures of entanglement, i.e., the mutual information and the zeta factor. Equivalent results are found for other coupling pathways. These results provide the first evidence of the appearance of the likely entangled nodes in a molecular network that underlies the NMR J-couplings.

SUPPLEMENTARY MATERIAL

See the supplementary material for an example of the actual calculation of mutual information and zeta measures of entanglement. There is also an example of the behavior of a coupling pathway different from the principal one.

ACKNOWLEDGMENTS

DATA AVAILABILITY

The data that support the findings of this study are available from the corresponding author upon reasonable request.

REFERENCES

[1]S. Wehner, D. Elkouss, and R. Hanson, "Quantum internet: A vision for the road ahead," Science **362**, eaam9288 (2018).

[2]Y. Yu, X.-Y. Luo, B. Jing, P.-F. Sun, R.-Z. Fang, C.-W. Yang, H. Liu, M.-Y. Zheng, X.-P. Xie, W.-J. Zhang, L.-X. You, Z. Wang, T.-Y. Chen, Q. Zhang, X.-H. Bao, and J.-W. Pan, "Entanglement of two quantum memories via fibres over dozens of kilometres," Nature **578**, 240–245 (2020).

[3]S. Ding and Z. Jin, "Review on the study of entanglement in quantum computation speedup," Chin. Sci. Bull. **52**, 2161–2166 (2007).

[4]L. Amico, R. Fazio, A. Osterloh, and V. Vedral, "Entanglement in many-body systems," Rev. Mod. Phys. **80**, 517–576 (2008).

[5]N. Friis, G. Vitagliano, M. Malik, and M. Huber, "Entanglement certification from theory to experiment," Nat. Rev. Phys. **1**, 72–87 (2019).

[6]J. P. Restrepo Cuartas and J. L. Sanz-Vicario, "Information and entanglement measures applied to the analysis of complexity in doubly excited states of helium," Phys. Rev. A **91**, 052301–052316 (2015).

[7]Y. Cao, J. P. Olson, M. Degroote, P. D. Johnson, M. Kieferová, I. D. Kivlichan, T. Menke, B. Peropadre, N. P. D. Sawaya, S. Sim, L. Veis, and A. Aspuru-Guzik, "Quantum chemistry in the age of quantum computing," Chem. Rev. **119**, 10856–10915 (2019).

[8]Z. Huang and S. Kais, "Entanglement as measure of electron–electron correlation in quantum chemistry calculations," Chem. Phys. Lett. **413**, 1–5 (2005).

[9]S. Kais, "Entanglement, electron correlation, and density matrices," Adv. Chem. Phys. **134**, 493–535 (2007).

[10]K. Boguslawski, P. Tecmer, Ö. Legeza, and M. Reiher, "Entanglement measures for single- and multireference correlation effects," J. Phys. Chem. Lett. **3**, 3129–3135 (2012).

[11]S. Ritter, C. Hahn, A. Reiserer, A. Neuzner, M. Uphoff, M. Mücke, E. Figueroa, J. Bochmann, and G. Rempe, "An elementary quantum network of single atoms in optical cavities," Nature **484**, 195–201 (2012).

[12]C. P. Slichter, *Principles of Magnetic Resonance*, 3rd ed. (Springer, New York, 1996).

[13]J. Oddershede, P. Jørgensen, and D. L. Yeager, "Polarization propagator method in atomic and molecular calculations," Comput. Phys. Rep. **2**, 33–92 (1984).

[14]G. A. Aucar, R. H. Romero, and A. F. Maldonado, "Polarization propagators: A powerful theoretical tool for a deeper understanding of NMR spectroscopic parameters," Int. Rev. Phys. Chem. **29**, 1–64 (2010).

[15]L. A. Millán, C. G. Giribet, and G. A. Aucar, "Polarization propagator theory and the entanglement between MO excitations," Phys. Chem. Chem. Phys. **20**, 24832–24842 (2018).

[16]M. Karplus, "Vicinal proton coupling in nuclear magnetic resonance," J. Chem. Phys. **85**, 2870–2871 (1963).

[17]D. G. Cory, E. Knill, L. Viola, T. F. Havel, N. Boulant, G. Boutis, E. Fortunato, S. Lloyd, R. Martinez, C. Negrevergne, M. Pravia, Y. Sharf, G. Teklemariam, Y. S. Weinstein, and W. H. Zurek, "NMR based quantum information processing: Achievements and prospects," Fortschr. Phys. **48**, 875–907 (2000).

[18]T. Xin, X.-Y. Kong, S.-J. Wei, T. Wang, D. Ruan, and G.-L. Long, "Nuclear magnetic resonance for quantum computing: Techniques and recent achievements," Chin. Phys. B **27**, 020308–020312 (2018).

[19]G. A. Aucar, "Toward a QFT-based theory of atomic and molecular properties," Phys. Chem. Chem. Phys. **16**, 4420–4438 (2014).

[20] Ö. Legeza and J. Sólyom, "Optimizing the density-matrix renormalization group method using quantum information entropy," Phys. Rev. B **68**, 195116–195119 (2003).

[21] A. R. Plastino, D. Manzano, and J. S. Dehesa, "Separability criteria and entanglement measures for pure states of N identical fermions," Europhys. Lett. **86**, 20005–20009 (2009).

[22] C. G. Giribet and M. C. Ruiz de Azúa, "CLOPPA–IPPP analysis of cooperative effects in hydrogen-bonded molecular complexes. Application to intermolecular ^{2h}J(N, C) spin–spin coupling constants in linear $(CNH)_n$ complexes," J. Phys. Chem. A **112**, 4386–4393 (2008).

[23] J. Audretsch, "Composite systems," in *Entangled Systems: New Directions in Quantum Physics* (Wiley-VCH, Weinheim, 2007), Chap. 7.