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PCCP

Accepted Manuscript

Volume 18 | Number 1 | 7 January 2016 | Pages 1–636

PCCP

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www.rsc.org/pccp

ISSN 1463-9076

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Polarization propagator's theory and the entanglement between MO excitations

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Entanglement is at the core of quantum physics and so, one may conjecture that it should have some influence on atomic and molecular response properties. The usual way of treating entanglement is by applying information theory via the von Newman entropy. Being the principal propagator the operator that contain the physical information that arises due to the transmission of the effects of two external perturbations through the electronic framework of a quantum system, it should have in it the information necessary to quantify the likely entanglement among molecular orbital excitations. In this article we first propose a proper density matrix and from it, the way to quantify entangled excitations by using information theory. The NMR J-couplings are among the best candidates to learn about the potentialities of this formalism. We applied this new tool to analyze the famous Karplus rule and found a relationship among the dihedral angular dependence with the entanglement. We also found that the entangled excitations are related with electron correlation. The new formalism can be applied to all other response properties

Introduction

The transmission of quantum information consists in the propagation of quantum systems between two different apparatus, being the quantum information stored in quantum states.[1] According to Raimond and coauthors:[2] *when two systems are in an entangled state each one of them can reveal information about the other, behaving as a measuring device*. Thus, to perform several quantum information tasks such as quantum information transfer or quantum computation, entanglement can be used as one of its main resource. These concepts were recently applied to many-body quantum systems, showing that the interaction between orbitals or electrons can be calculated by employing concepts taken from the quantum information theory, like the von Neumann entropy or the mutual information.[3,4]

Response properties arises as a consequence of the application of external fields to the quantum system under study. Between them, the NMR spectroscopic parameters are highly used in quantum chemistry. Their understandings requires the full use of quantum methods, being the polarization propagator one of the most accurate.[5] It is also usually applied to the study of other response

properties.[6] The main aim of this article is then to show that the principal propagators of the polarization propagator formalism are related to one of the most intriguing aspects of quantum mechanics, the appearance of non-local interactions and more specifically to the entanglement between molecular orbital excitations.

Reiher and coauthors have proposed a new scheme to quantify electron correlation effects by using entanglement measures among molecular orbitals.[7] Their analysis is based on the assessment of the entanglement between any pair of orbitals and the entanglement of anyone of them with all others, as encoded in a full CI-type wave function. The single- and multireference nature of a quantum system, can be distinguished by examining the entanglement patterns of the orbitals. Its analysis is comprised by the measure of the single-orbital entropy, and the mutual information which measures the entanglement of orbitals i and j embedded in the environment of all other active-space orbitals.[4]. Reiher and collaborators' analysis of the bond-forming and bond-breaking processes showed how single-orbital entropy can be employed to monitor the cleavage of chemical bonds[8] and the estimation of bond orders of simple diatomic and polyatomic molecules.[7,9] Entanglement is also used to estimate entangled transition states[10] and dissociation process of diatomic molecules.[11]

If non-local quantum interactions are present in the electronic framework of molecules, we might assume that the response properties would depend on the information transfer carried out by the electronic framework. One of the best candidates for checking out such assumption, is the indirect J-couplings obtainable from NMR experiments. We should stress that the NMR spec-

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troscopy is one of the experimental resources applied to implement and verify quantum algorithms.[12] Furthermore it was recently shown that the NMR spectroscopy can be used to prepare and detect entangled states between an electron-spin 1/2 and a nuclear-spin 1/2 in a molecular single cristal.[13] By manipulating both spins through NMR and ESR pulses Mehring *et al* obtained entangled states from pure states. J-couplings arise as a result of a magnetic perturbation generated by the interaction of a given nuclear spin with its electronic environment, which is then transmitted to the whole molecule through electronic excitations. All other nuclear spins play the role of the "measurement" apparatus of such previous interaction.[14] We should be aware that such J-coupling does not depend on the external magnetic field. Thus, it is an internal property of the molecule that can be observed when the system is subject to a convenient experimental measuring device.

Within a theoretical framework a novel relationship among the behavior of the matrix elements of the principal propagator and the Karplus rule was published in 2004.[15] By applying the CLOPPA model[16–18] it was shown that most of the so called "coupling pathways" follow the Karplus rule, which relates the vicinal NMR-J coupling with the dihedral angle of the bondings' to which the coupled nuclei belong. Later on, an article shared some insights on the reasons behind such behavior.[19] The matrix elements of the principal propagator involved in the transmission of magnetic perturbations arises due to the introduction of electron correlation and have a non-local behavior. Given that the inverse of the principal propagator can be written as a series of its own matrices, it was shown that some of its matrix elements also follow the Karplus rule.

At that time, it was theorized that electron correlation in NMR J-couplings should be related with entanglement. This conjecture is partially related with the previous work of Wang and Kais, and Esquivel and coauthors, where they showed that entanglement is related to electron correlation in quantum chemistry calculations.[20,21] However, it could not be tested due to the absence of a proper definition of the von Newman entropy within the polarization propagator formalism.

In our pursuit to improve the applications of this formalism we were led to investigate the feasibility of using it to learn about one of the most intriguing facets of quantum theory: the entanglement. One of the aims of this work was to find out a way to relate each pair of excitations between localized molecular orbitals, LMO, to a non-local transmission of information. In this article we will show how the von Newman entropy can be expressed as a function of one density function that naturally arises from the polarization propagator formalism. To figure out what the form of such density function would be, it was of paramount importance the previous derivation of polarization propagators from the Feynman approach to quantum mechanics.[22]

Another aim of this work was to search about a likely relationship among the Karplus rule and the entangled transmission of those elementary MO excitations, when they are located close to the coupled nuclei.

Bellow, we include a Theory section to supply the basic concepts related with non-relativistic polarization propagators, some exchange operators and the CLOPPA model. We also give for the first time a definition of a polarization propagator density matrix which is afterwards used to define the mutual information among pairs of LMOs. In the following section we apply this general formalism to analyze the origin of the Karplus rule in the ethane molecule. There, we show that both elements of the main coupling pathways are entangled and have a dihedral angular dependence. The main conclusions are given in the last Section.

Theory

To the best of our knowledge, this is the first article in which the polarization propagator formalism is applied to analyze the entanglement that may appear in atomic or molecular electronic frameworks. We started this research program some years ago developing a formalism from which we could analyze the entangled MO excitations. The first step was to find a relationship between polarization propagators and electronic density functions, and only then could information theory be applied to quantify those likely entangled excitations.

In order to introduce this new formalism, we will overview the polarization propagator formalism at random phase level of approach, RPA, alongside with its application to the calculations of NMR J-couplings. We will then show that some of the two-electron matrices that belong to the principal propagator have a non-local character. Afterwards we will briefly sketch the usual way in which entanglement is quantified in a quantum system by using von Newman entropy, and then we will introduce some of the mathematical apparatus necessary to define the von Newman entropy within the polarization propagator theory. The definition of the density matrix and the way it shall be used to calculate the entangled MO excitations will also be given at the end of this Section.

The polarization propagator and the principal propagator

Propagators are formal objects well known in both, quantum physics[23] and quantum chemistry.[14,22,24] They are as fundamental objects as wave functions are. In principle, with them one can describe the whole behavior of a given quantum system.

According to information theory the quantum information is stored in quantum states which are carried out by quantum systems. The transmission is accomplished by the propagation of the carriers between one place where a perturbation occurs and the place where the perturbation is absorbed or measured. In addition, it is known that quantum information can also be stored in the correlation between subsystems, which in our case are the coupled nuclear spins or the perturbation related with the interaction between them and the surrounding electrons.

The propagation of a bosonic perturbation, from one space-time point to another one in a given electronic molecular framework, can be described by using polarization propagators which are double-time Green functions. Their explicit expressions are obtained as a solution of the propagator's equation of motion.[24] When applying both, the superoperator algebra and the inner projection technique,[25] their solutions are expressed as a product of two kind of terms that contain different information about the

physical process under investigation.[19] The actual polarization propagator that arises from the two perturbative operators, V^P and V^Q, is written as

$$\langle\langle V^P; V^Q \rangle\rangle_E = \left(V^{P\dagger}|\mathbf{h}\right)\left(\tilde{\mathbf{h}}|E\hat{I} - \hat{H}|\mathbf{h}\right)^{-1}\left(\tilde{\mathbf{h}}|V^Q\right)$$
$$= \left(V^{P\dagger}|\mathbf{h}\right)\mathbf{M}^{-1}\left(\tilde{\mathbf{h}}|V^Q\right) \tag{1}$$

where $\mathbf{M}^{-1} = \mathbf{P}$ is known as the *principal propagator* matrix and $\mathbf{h}$ is a complete operator manifold that contain basic excitation operators from which it is possible to obtain the whole branch of excited states that may be built from a reference state, $|0\rangle$. The perturbative operators V^P and V^Q should also be described in terms of basic excitation operators that belong to that excitation manifold, and from the binary product $(V^{P\dagger}|\mathbf{h})$ one obtains the *perturbators*. Each response property is related to some given perturbative operators. For example, the theoretical explanation of the NMR spectroscopic parameters hangs on a non relativistic, NR, theory proposed by Norman Ramsey.[26,27] Within this domain there are four electronic mechanisms that are involved in the indirect J-couplings. The response operators are known as: Fermi-contact, FC, Spin-dipolar, SD and Paramagnetic spin orbital, PSO.[14] The fourth contribution, known as Diamagnetic spin orbital, DSO, is calculated as a ground-state expectation value.

Approximate polarization propagators are obtained using perturbation theory. Its order depends on the number of times the fluctuational potential appears in each of the three terms of eqn.(1).[24] The consistent first order level of approach, known as random phase approximation or RPA, requires that the reference state be the Hartee-Fock, HF, state, and $\mathbf{h} = \{\mathbf{h}_2\} = \left\{\mathbf{q}_{ia}^\dagger, \mathbf{q}_{jb}\right\} = \left\{a_a^\dagger a_i, a_i^\dagger a_b\right\}$. Subindices a and b refer to unoccupied HF molecular orbitals and i and j to occupied MO ones.

The matrix of the principal propagator is

$$\mathbf{M} = \begin{pmatrix} \mathbf{M}_A & \mathbf{M}_B \\ \mathbf{M}_{B*} & \mathbf{M}_{A*} \end{pmatrix} \tag{2}$$

being

$$\mathbf{M}_{A;ia,jb} = \left(\mathbf{q}_{ia}^\dagger, |E\hat{I} - \hat{H}|\mathbf{q}_{jb}^\dagger\right) = -\left\langle 0\left|\left[a_i^\dagger a_a, \left[a_b^\dagger a_j, H\right]\right]\right|0\right\rangle$$
$$= \mathbf{A}_{ia,jb}^{(0,1)} = \delta_{ab}\delta_{ij}(\varepsilon_a - \varepsilon_i) + \langle aj||ib\rangle \tag{3}$$

and

$$\mathbf{M}_{B;ia,jb} = \left(\mathbf{q}_{ia}, |E\hat{I} - \hat{H}|\mathbf{q}_{jb}^\dagger\right) = -\left\langle 0\left|\left[a_a^\dagger a_i, \left[a_b^\dagger a_j, H\right]\right]\right|0\right\rangle$$
$$= \mathbf{B}_{ia,jb}^{(1)} = \langle ab||ij\rangle \tag{4}$$

One of the perturbators of Eq.(1) is defined as the following binary product, $(V^{P\dagger}|\mathbf{q}_{ia}^\dagger)$, which is explicitly given by

$$V_{ia}^{P\dagger} = \left\langle a\left|V^P\right|i\right\rangle \tag{5}$$

For convenience we rewrite equation (1) as

$$\langle\langle V^P; V^Q\rangle\rangle_{E;ia,jb} = \left[\mathbf{V}_{ia}^P, \mathbf{V}_{ia}^{P*}\right]\begin{pmatrix} \langle\langle\tilde{\mathbf{q}}_{ia}; \mathbf{q}_{jb}^\dagger\rangle\rangle_E & \langle\langle\tilde{\mathbf{q}}_{ia}; \mathbf{q}_{jb}\rangle\rangle_E \\ \langle\langle\tilde{\mathbf{q}}_{ia}^\dagger; \mathbf{q}_{jb}^\dagger\rangle\rangle_E & \langle\langle\tilde{\mathbf{q}}_{ia}^\dagger; \mathbf{q}_{jb}\rangle\rangle_E \end{pmatrix}^{-1}\begin{bmatrix} \mathbf{V}_{jb}^Q \\ \mathbf{V}_{jb}^{Q*} \end{bmatrix} \tag{6}$$

Replacing V^P by $\tilde{\mathbf{q}}_{ia}$ and V^Q by $\mathbf{q}_{jb}^\dagger$ we get

$$\langle\langle\tilde{\mathbf{q}}_{ia}; \mathbf{q}_{jb}^\dagger\rangle\rangle_E = [1, 0]\begin{pmatrix} \langle\langle\tilde{\mathbf{q}}_{ia}; \mathbf{q}_{jb}^\dagger\rangle\rangle_E & \langle\langle\tilde{\mathbf{q}}_{ia}; \mathbf{q}_{jb}\rangle\rangle_E \\ \langle\langle\tilde{\mathbf{q}}_{ia}^\dagger; \mathbf{q}_{jb}^\dagger\rangle\rangle_E & \langle\langle\tilde{\mathbf{q}}_{ia}^\dagger; \mathbf{q}_{jb}\rangle\rangle_E \end{pmatrix}^{-1}\begin{bmatrix} 1 \\ 0 \end{bmatrix} \tag{7}$$

and so

$$\langle\langle\tilde{\mathbf{q}}_{ia}; \mathbf{q}_{jb}^\dagger\rangle\rangle_{E=0} = (\mathbf{q}_{ia}^\dagger\,|\,\hat{H}\,|\,\mathbf{q}_{jb}^\dagger) = \left\langle 0\left|\left[q_{ia}, \left[H, q_{jb}^\dagger\right]\right]\right|0\right\rangle$$
$$= \delta_{ab}\delta_{ij}\langle 0|H|0\rangle + \langle 0|a_i^\dagger a_a H a_b^\dagger a_j|0\rangle \tag{8}$$
$$= \delta_{ab}\delta_{ij}(\varepsilon_a - \varepsilon_i) + \langle aj||ib\rangle$$

Then, each matrix element (ia, jb) of the principal propagator represent the response of the system to a given perturbative polarization (say V_{jb}^Q) of unitary intensity that becomes a different polarization (V_{ia}^P) whose intensity is also equal to one. This is the usual meaning of a Green function though in this case such a function correlates two basic excitations. Both perturbative polarizations, V_{ia}^P and V_{jb}^Q, are related with local perturbations as happens for the magnetic perturbations considered to get theoretically both NMR spectroscopic parameters.

Non relativistic polarization propagators at different levels of approach

The FC electronic mechanism is one of the most important for coupling among hydrogen nucleus. Its perturbative Hamiltonian is

$$H^{FC} = (8/3)\pi\mu_B\hbar g_e\sum_K \gamma_N\sum_i \delta(r_{iK})\,\mathbf{s}_i\cdot\mathbf{I}_K = \sum_K \gamma_K\mathbf{I}_k\cdot\mathbf{V}_K^{FC} \tag{9}$$

where μ_B is the nuclear magneton, γ_K is the gyromagnetic constant of nucleus K, g_e is the electronic g-factor, and

$$\mathbf{V}_K^{FC} = (8/3)\pi\mu_B\hbar g_e\sum_i \delta(\mathbf{r}_{iK})\,\mathbf{s}_i \tag{10}$$

The Fermi contact perturbative Hamiltonian of Eq.(9) depends on the electronic density at the site of the nuclei. One should include two of these Hamiltonians for calculating the FC contribution to the NMR-J coupling. So this spectroscopic parameter is straightly related to the electronic densities on the sites of two different nuclei, say K and L.

At RPA level of approach, the explicit expression for the FC contribution to the indirect NMR coupling constant between nuclei K and L is:

$$J_{KL}^{FC} = \gamma_K\gamma_L\,\langle\langle\mathbf{V}_K^{FC}; \mathbf{V}_L^{FC}\rangle\rangle_{E=0} = \sum_{ia,jb}\left[\mathbf{b}_{K,ia}^{FC}\,\mathbf{P}_{ia,jb}\,\mathbf{b}_{L,jb}^{FC}\right] \tag{11}$$

The principal propagator $\mathbf{P}$ can be factored out to make explicit its electron spin dependence. Then, the triplet-type princi-

pal propagator is written as

$$^3\mathbf{P}_{ia,jb} = \left(^3\mathbf{M}^{-1}\right)_{ia,jb} = \left(^3\mathbf{A} \pm ^3\mathbf{B}\right)^{-1}_{ia,jb} \qquad (12)$$

where the spin-dependent matrices are [24]

$$
\begin{aligned}
^3\mathbf{A}_{ia,jb} &= (\varepsilon_a - \varepsilon_i)\,\delta_{ab}\delta_{ij} - \langle aj|bi\rangle = \mathbf{E}_{ia,jb} - \mathbf{G}_{ia,jb} \\
^3\mathbf{B}_{ia,jb} &= \langle ab|ji\rangle = \mathbf{H}_{ia,jb}
\end{aligned}
\qquad (13)
$$

One may use another little less accurate level of approach known as Tamm-Dancoff or TDA, which is obtained making the matrix elements of $^3\mathbf{B}$ equal to zero.

The theoretical scheme represented by Eq.(11) was introduced more than 20 years ago by an Argentinian team lead by professor Rubén Contreras. It was coined as CLOPPA (contributions from localized orbitals within the polarization propagator approach).[16–18] It was later on implemented at *ab initio* level within a modified version of the SYSMO program,[28–30] for the theoretical analysis of NMR spin-spin couplings.[31–34]

The perturbators related with the FC mechanism accounts for a local perturbation arising from the interaction between the nuclear spin with the electronic spin at the site of the coupled nuclei. As mentioned above, the principal propagator at RPA level of approach arise from the inverse of a matrix whose elements are orbital energies and two-electron integrals. The development of a procedure to get this inversion as a series[15] gave new insights to understand the physical meaning of such a term. Several conspicuous aspects of the NMR spectroscopy can deeply be understood by using this formalism.[35]

Working with *ab initio* schemes, the inverse of the principal propagator is never calculated explicitly. This is due to the fact that when large basis set are considered it is not possible to get the inverse of its matrix representation by conventional methods[24]. The alternative schemes developed to overcome these dificulties[36,37] are such that the physical information contained within the principal propagator (which is related with the electronic molecular structure as a whole) is lost. This is because these procedures modify in an incontrollable manner the individual elements which participate in the calculation.

In order to maintain the advantages of getting the inverse explicitly, a new procedure which is a generalization of a previous one[31,38], was developed.[19,39] In this new scheme the matrix elements of triplet principal propagators are written as power series

$$\left(^3\mathbf{P}_S\right)_{ia,jb} \approx \left(\mathbf{E}^{-1}\sum_{n=0}^{p}\left(^3\mathbf{N}\mathbf{E}^{-1}\right)^n\right)_{ia,jb} \qquad (14)$$

where p stands for the number of terms in each series corresponding to a given coupling pathway; $\mathbf{E}$ is a diagonal matrix, built from the difference of MO energies when canonical orbitals are used, and $^3\mathbf{N}$ is the addition of the two matrices of two-electron integrals of Eq.(13). Given that each element of the $\mathbf{E}$ matrix is larger than any of the elements of the $^m\mathbf{N}$ matrix, one can expand each element of $^m\mathbf{P}$ in a power series.[25,40] When $p \to \infty$ the summation of Eq.(14) converge to $^3\mathbf{P}$.

The $^3\mathbf{P}_S$ matrix elements can be written in terms of localized or canonical MOs. When localized orbitals are used $^3\mathbf{E}$ is non-

diagonal. In such a case one can always use the same procedure as that used for calculation of $^3\mathbf{P}_S$ matrix elements.

Generalized exchange operators

Let's have a look on the meaning of both triplet-type matrices: $^3\mathbf{A}$ and $^3\mathbf{B}$. Each matrix element $\langle aj|bi\rangle$ of the matrix $\mathbf{A}$ is related with the following two-electron integral

$$\langle aj|bi\rangle = \int d\mathbf{r}_1\mathbf{r}_2\,\psi_a^*(1)\psi_j^*(2)r_{12}^{-1}\psi_b(1)\psi_i(2) \qquad (15)$$

Defining a new *exchange* operator as

$$K_{jb}(1)\psi_i(1) = \left[\int d\mathbf{r}_2\,\psi_j^*(2)r_{12}^{-1}\psi_i(2)\right]\psi_b(1) \qquad (16)$$

then

$$\langle\psi_a(1)|K_{jb}(1)|\psi_i(1)\rangle = \int d\mathbf{r}_1\mathbf{r}_2\,\psi_a^*(1)\psi_j^*(2)r_{12}^{-1}\psi_i(2)\psi_b(1) \equiv G_{ia,jb} \qquad (17)$$

For subindice j = i and b = a we find that $\langle aj|bi\rangle \to \langle ai|ai\rangle$. Then

$$
\begin{aligned}
\langle ai|ai\rangle &= \langle\psi_a(1)|K_{ia}(1)|\psi_i(1)\rangle \\
&= \int d\mathbf{r}_1 d\mathbf{r}_2\,\psi_a^*(1)\psi_a(1)r_{12}^{-1}\psi_i^*(2)\psi_i(2) \\
&= \int d\mathbf{r}_1 d\mathbf{r}_2\,|\psi_a(1)|^2 r_{12}^{-1}|\psi_i(2)|^2
\end{aligned}
\qquad (18)
$$

which shows explicitly that the interaction it refers to is Coulombic.

We should also remember that the triplet excitation energy that arise from the MO expression of indirect J-coupling is:

$$\Delta^3 E_{i\to a} = (\varepsilon_i - \varepsilon_a) = \varepsilon_i - \varepsilon_a - J_{ai} \qquad (19)$$

with

$$J_{ai} = \int d\mathbf{r}_1 d\mathbf{r}_2\,\psi_a^*(1)\psi_a(1)r_{12}^{-1}\psi_i^*(2)\psi_i(2) \qquad (20)$$

which is equal to Eq.(18).

The triplet-type B matrix is

$$^3B_{ia,jb} = \langle ab|ji\rangle = \int d\mathbf{r}_1 d\mathbf{r}_2\,\psi_a^*(1)\psi_b^*(2)r_{12}^{-1}\psi_j(1)\psi_i(2) \qquad (21)$$

so that we can define another *exchange* operator as

$$K_{bj}(1)\psi_i(1) = \left[\int d\mathbf{r}_2\,\psi_b^*(2)r_{12}^{-1}\psi_i(2)\right]\psi_j(1) \qquad (22)$$

and then

$$\langle\psi_a(1)|K_{bj}(1)|\psi_i(1)\rangle = \int d\mathbf{r}_1\mathbf{r}_2\,\psi_a^*(1)\psi_b^*(2)r_{12}^{-1}\psi_j(1)\psi_i(2) \equiv H_{ia,jb} \qquad (23)$$

We find two generalized non-local or exchange operators arising from the matrices $^3A_{ia,jb}$ and $^3B_{ia,jb}$, meaning that one cannot obtain a simple potential, be it $K_{jb}(\mathbf{x}_1)$ or $K_{bj}(\mathbf{x}_1)$ for which one needs to consider only a local point in space, $\mathbf{x}_1$. In other words, the result of operating with $K_{jb}(\mathbf{x}_1)$ or $K_{bj}(\mathbf{x}_1)$ on $\psi_i(\mathbf{x}_1)$ depends on the value of ψ_i in the whole space through the integral on electron 2, and so, not just at $\mathbf{x}_1$.

CLOPPA model and Karplus rule

The CLOPPA model was developed as a tool to decompose the analysis of NMR-J couplings in term of "local" contributions, meaning the contribution from individual *coupling pathways* which involves two virtual excitations $i \to a$ and $j \to b$ with i, j (a, b) occupied (vacant) MOs that belongs to the local fragment "L" of interest:

$$J_{MN} = \sum_{ia,jb} J_{MN;ia,jb}^{L(X)} \qquad (24)$$

being X the specific magnetic perturbation (X = FC, SD or PSO).

The CLOPPA model was at the beginning written at the RPA level of approach but recently it was extended to include second-order or SOPPA.[24,37] Localized MOs are mostly used because one wants to analyze the influence of local regions or given coupling pathways on the total J couplings.[17–19]

Each term of the sum in eqn.(24) can be written as (see Eq. (11))

$$J_{MN;ia,jb}^{X} = \left(U_{M,ia}^{X} U_{N,jb}^{X} + U_{N,ia}^{X} U_{M,jb}^{X} \right) {}^{m}P_{ia,jb} \qquad (25)$$

where the perturbator $U_{M,ia}^{X}$ is a measure of the strength of the virtual excitation $i \to a$ that arises due to the perturbation X, and m=3 (1) for X = FC or SD (PSO). The principal propagator ${}^{m}P_{ia,jb}$ gives the response of the molecule that connects the two virtual excitations: $i \to a$ and $j \to b$.

In the case of the vicinal couplings, which means the coupling through three bonds, there is a well-known empirical rule, the Karplus rule,[41,42] that relate the total value of J with the dihedral angle among the bonds of the coupled nuclei. In Fig. 1 we show the H-H coupling and the dihedral angle for the ethane molecule.
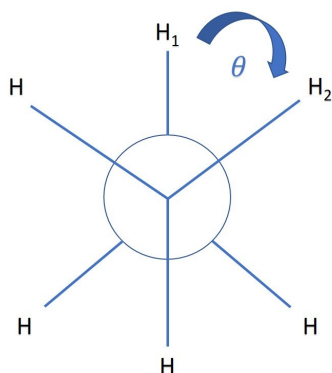

Fig. 1 Scheme of the ethane molecule

The vicinal J coupling has an harmonic dependence with the dihedral angle ϕ, being such a dependence independent of the nature of the coupled nuclei. The Karplus rule can be written as

$$^{3}J = a\cos 2\phi + b\cos \phi + c \qquad (26)$$

where a, b and c are empirical parameters whose values depend on the coupled nuclei and the substituents involved.

In previous works[19] we found that the Karplus rule is reproduced at RPA level of approach. We also found that each coupling

pathway of Eq.(24) follow the same pattern. The main coupling pathways together with the corresponding principal propagator matrix elements follow the same pattern, as the total coupling pathway do. In those cases the matrix elements $G_{ia,jb}$ and $H_{ia,jb}$ have a Karplus-type dependence with the dihedral angle. For the main coupling path they are written as

$$G_{ia,jb} \longrightarrow G_{\sigma_1 \sigma_1^*, \sigma_2 \sigma_2^*} = \int \sigma_1^*(1)\sigma_2^*(1) r_{12}^{-1} \sigma_2(2)\sigma_1(2) d\mathbf{r}_1 d\mathbf{r}_2 \quad (27)$$

and

$$H_{ia,jb} \longrightarrow H_{\sigma_1 \sigma_1^*, \sigma_2 \sigma_2^*} = \int \sigma_1^*(1)\sigma_2(1) r_{12}^{-1} \sigma_2^*(2)\sigma_1(2) d\mathbf{r}_1 d\mathbf{r}_2 \quad (28)$$

We can see that in both matrix elements, electron 1 is described by two different LMOs being one and the other close to the two different coupled nuclei, *i.e.* $\psi_{\sigma_1}^*(1)$ and $\psi_{\sigma_2}^*(1)$ or $\psi_{\sigma_1}^*(1)$ and $\psi_{\sigma_2}(1)$. Quite a similar dependence is observed for electron 2. The non-local dependence of both electrons is then apparent.

There are terms for which their principal propagator matrix elements do not follows a Karplus curve. They are such that neither electron 1 nor electron 2 do has a non-local dependence with the LMOs. We show it from an example. Their Coulombic and Exchange matrix elements of the ($\sigma_1 \to \sigma_1^*$; $\sigma_1 \to \sigma_1^*$) *coupling pathway* are

$$G_{\sigma_1 \sigma_1^*, \sigma_1 \sigma_1^*} = \int |\sigma_1^*(1)|^2 r_{12}^{-1} |\sigma_1(2)|^2 d\mathbf{r}_1 d\mathbf{r}_2 \qquad (29)$$

and

$$H_{\sigma_1 \sigma_1^*, \sigma_1 \sigma_1^*} = \int \sigma_1^*(1)\sigma_1(1) r_{12}^{-1} \sigma_1^*(2)\sigma_1(2) d\mathbf{r}_1 d\mathbf{r}_2 \qquad (30)$$

The Coulombic matrix element gets from here its name. It express a Coulombic interaction between electron 1 and electron 2 described by the electronic probability densities given by $\left|\psi_{\sigma_1}^*(1)\right|^2$ and $\left|\psi_{\sigma_1}(2)\right|^2$.

The polarization propagator density matrix

To our knowledge nobody has proposed till now a density operator which is valid within the polarization propagator formalism. In order to quantify the quantum entanglement that likely appears in an electronic molecular system, we need to find out an expression for the density operator that fulfill the requirements of such operators.

Since we know that all the information of the system is carried out by the principal propagator **P**, and that the integrals **G** and **H** are the ones that present a non-local behaviour, we assume that this new definition of the density operator must be expressed as a function of the principal propagator matrices.

The Feynman propagator and so, the 2-point Green function, can be also obtained from the path integral formalism. It can be proven that (see chap 14 of Ref.[43])

$$\langle 0, t_f \mid T[q(t_A)q(t_B)] \mid 0, t_i \rangle = N \int Dq \, q(t_A) q(t_B) e^{\frac{i}{\hbar} \int_{t_i}^{t_f} L dt} \qquad (31)$$

when $t_i \to -\infty$ and $t_f \to \infty$ the last equation becomes the defini-

tion of the path integral of the Feynman propagator.

From the last fundamental identity one can obtain a relation between the generating functional and the Feynman propagator.

$$Z_0[J] = \int D\phi\, e^{\frac{i}{\hbar}\int d^4x(L+J\phi)} \tag{32}$$

where J is a perturbation over the ground state of the system and $Z_0[J]$ is the generating functional of the Green function that include all connected and disconnected Feynman diagrams.

Then it is sound to define, using the superoperator formalism, a generating functional for the polarization propagator formalism. In the case of the FC mechanism of J-couplings this generating functional can be written as [22]

$$Z_{[V_K^{FC},V_L^{FC}]} = \int D\,|\,\tilde{\mathbf{h}})D(\mathbf{h}\,|\,e^{|\tilde{\mathbf{h}})(\mathbf{h}|E\hat{I}-\hat{H}_0|\tilde{\mathbf{h}})(\mathbf{h}|+(V_K^{FC}|\tilde{\mathbf{h}})(\mathbf{h}|+(V_L^{FC}|\tilde{\mathbf{h}})(\mathbf{h}|}$$

$$= Z_{[V_K^{FC}=0,V_L^{FC}=0]}e^{W_{[V_K^{FC},V_L^{FC}]}} \tag{33}$$

where

$$W_{[V_K^{FC},V_L^{FC}]} = (V_K^{FC}|\tilde{\mathbf{h}})(\mathbf{h}|E\hat{I}-\hat{H}_0^{Sch}|\tilde{\mathbf{h}})^{-1}(\mathbf{h}|V_L^{FC}) \tag{34}$$

is the generating functional of the polarization propagator that has no disconnected part. The Hamiltonian $\hat{H}_0^{Sch}$ is the NR Schrödinger Hamiltonian for the unperturbed atomic or molecular system.

The generating functional of Eq.(33) is analogue to the partition function of the statistical thermodynamics.[44] Using such partition function (meaning $Z = Tr(e^{-\beta\hat{H}})$), the density operator of the system can be written as

$$\hat{\rho} = \frac{e^{-\beta\hat{H}}}{Z} \tag{35}$$

Our ansatz for a polarization propagator density matrix follows the same physical grounds. So

$$\rho = \frac{e^{|\tilde{\mathbf{h}})(\mathbf{h}|E\hat{I}-\hat{H}_0|\tilde{\mathbf{h}})(\mathbf{h}|}}{Z_{[V_K^{FC}=0,V_L^{FC}=0]}} = \frac{e^{|\tilde{\mathbf{h}})(\mathbf{h}|E\hat{I}-\hat{H}_0|\tilde{\mathbf{h}})(\mathbf{h}|}}{Z_{[0]}} \tag{36}$$

where $Z_{[0]}$ is the partition function for the unperturbed system. This new density function is written in terms of the inverse of the principal propagator $\mathbf{P} = \mathbf{M}^{-1}$, being $\mathbf{M} = (\mathbf{h}|E\hat{I}-\hat{H}_0^{Sch}|\tilde{\mathbf{h}})$, and carry all the information about the excitations of the system. When calculations are performed at RPA level of approach (see Eqs. (12) and (13)), each matrix element of $\mathbf{M}$ is

$$\mathbf{M}_{ia,jb} = (\mathbf{E} - \mathbf{G} - \mathbf{H})_{ia,jb} \tag{37}$$

The polarization propagator density matrix of Eq. (36) fulfill the properties of a density matrix:

1. $Tr\, \rho = 1$ and

2. $\rho \geq 0$ or $(\mathbf{h}|\rho|\mathbf{h}) \geq 0$.

It is straightforward to show that both properties are fulfilled. In the case of the first one it is clear that

$$Tr\rho = \frac{\sum_k(\mathbf{h}_k|e^{|\tilde{\mathbf{h}})(\mathbf{h}|E\hat{I}-\hat{H}_0|\tilde{\mathbf{h}})(\mathbf{h}|}|\mathbf{h}_k)}{Z_{[0]}} = 1 \tag{38}$$

In the case of the second property it is enough to be aware that the polarization propagator density matrix arises as the quotient of two positive definite magnitudes, and the exponents are all real numbers. Given that the exponential of a real variable is always positive, and since Z[0] is, in our case, the sum of exponentials, it is straightforward to show that $\rho > 0$.

Matrix ρ of Eq.(36) is also non-idempotent.

$$\begin{aligned}
\rho^2 &= (\frac{e^{|\tilde{\mathbf{h}})(\mathbf{h}|E\hat{I}-\hat{H}_0|\tilde{\mathbf{h}})(\mathbf{h}|}}{Z_{[0]}})(\frac{e^{|\tilde{\mathbf{h}})(\mathbf{h}|E\hat{I}-\hat{H}_0|\tilde{\mathbf{h}})(\mathbf{h}|}}{Z_{[0]}}) \\
&= \frac{1}{Z_{[0]}^2}[\sum_k \frac{(|\tilde{\mathbf{h}})(\mathbf{h}|E\hat{I}-\hat{H}_0|\tilde{\mathbf{h}})(\mathbf{h}|)^k}{k!}][\sum_l \frac{(|\tilde{\mathbf{h}})(\mathbf{h}|E\hat{I}-\hat{H}_0|\tilde{\mathbf{h}})(\mathbf{h}|)^l}{l!}] \\
&= \frac{1}{Z_{[0]}^2}(\tilde{\mathbf{h}}|\sum_k \frac{|\tilde{\mathbf{h}})(\mathbf{h}|E\hat{I}-\hat{H}_0|\tilde{\mathbf{h}})^k}{k!}(\mathbf{h}|](\tilde{\mathbf{h}})\sum_l \frac{|\tilde{\mathbf{h}})(\mathbf{h}|E\hat{I}-\hat{H}_0|\tilde{\mathbf{h}})^l}{l!}(\mathbf{h}|] \\
&= \frac{1}{Z_{[0]}^2}\tilde{\mathbf{h}})e^{(\mathbf{h}|E\hat{I}-\hat{H}_0|\tilde{\mathbf{h}})}\overbrace{(\mathbf{h}|\tilde{\mathbf{h}})}^{1}e^{(\mathbf{h}|E\hat{I}-\hat{H}_0|\tilde{\mathbf{h}})}(\mathbf{h}| \\
&= \frac{1}{Z_{[0]}^2}\tilde{\mathbf{h}})e^{2(\mathbf{h}|E\hat{I}-\hat{H}_0|\tilde{\mathbf{h}})}(\mathbf{h}| \neq \rho \tag{39}
\end{aligned}$$

Quantification of entangled states and entangled LMO excitations

The influence of the measurement of the state of a qubit that affect the state of another, as happens in an entangled state, may have a *non-local* character.[45].

In a many-particle system the von Newman entropy can be used as a measure of the correlation strength,[46,47] and also as a quantitative measure of the entanglement.[48] As mentioned above the entanglement is a quantum mechanical property that describes a correlation between quantum mechanical systems that has no classical analog. So it was suggested more than one decade ago that it might be useful as an alternative measure of electron-electron correlation in quantum chemistry calculations.[48]

The Von Newman entropy is defined as

$$S = -Tr(\rho\, ln\rho) \tag{40}$$

being ρ the density matrix of the whole quantum system.

Dividing the system in two parts, say A and B, one can find the entanglement between them in terms of the density matrices of each subsystem. The interaction between those two parts can be quantified by using the entanglement entropy $S_{A|B}$ which uses a reduced density matrix, RDM, of each part.

When looking for quantifying the interaction among two orbitals, say, orbitals i and j, one must define the single-orbital entropy, $S(1)_i$ and the two-orbital entropy, $S(2)_{i,j}$. They are given in terms of the elements $\lambda_{\alpha;i}$ and $\lambda_{\alpha;i,j}$ which are the eigenvalues of the single-orbital RDM and the two-orbital RDM, respectively. Those RDM are obtained by tracing out all other orbitals degree of freedom except those of the orbitals i, and orbitals i and j.[49]

Then,

$$S(1)_i = -\sum_\alpha \lambda_{\alpha;i} \, ln\lambda_{\alpha;i} \tag{41}$$

and

$$S(2)_{i,j} = -\sum_\alpha \lambda_{\alpha;i,j} \, ln\lambda_{\alpha;i,j} \tag{42}$$

The total amount of electron correlation, meaning classical and quantum, can be evaluated by using the orbital-pair mutual information. Given that any entanglement between the orbitals i and j reduces $S(2)_{i,j}$ with respect to the sum of $S(1)_i$ and $S(1)_j$, Rissler and collaborators defined it by[4]

$$I_{i,j} = \frac{1}{2} \left(S(1)_i + S(1)_j - S(2)_{i,j} \right) (1 - \delta_{ij}) \, 0 \tag{43}$$

where δ_{ij} is the Kronecker delta and the factor $1/2$ prevents interactions from being counted twice.

In previous studies, Rissler *et al* identified entanglement with orbital interactions,[4] and Reiher and collaborators used orbital entanglement as a measure to evaluate the single- and multireference- character of any molecular structure in a given orbital basis set.[50] They also used it as a measure of the entanglement between orbitals i and j embedded in the environment of all other active-space orbitals.[50,51] In other words, they used $I_{i,j}$ as a measure of how much more information is stored in the composite system than in the subsystems.

There is another way of measuring the electronic entanglement of N-electron systems. This is given by the measure,[11]

$$\zeta_{vN} = S(\rho_r) - lnN \tag{44}$$

where ρ_r is the single-particle reduced density matrix associated with N-fermion pure state, and $S(\rho_r)$ is the von Newman entropy of ρ_r. $\zeta_{vN} \geq 0$, being zero for non-entangled fermionic systems (states with Slater rank one).[10]

We are now able to extend the applications of the quantum information theory to quantify the likely entanglement between pairs of LMO excitations using polarization propagators. As mentioned in previous sections they were also expressed applying perturbation theory in such a way that we can include different levels of correlation for the interaction among orbital excitations.

Quantum information can be stored in the correlation between subsystems.[1] In our case the subsystems are the nuclear spins or the excitations between electronic states that arise from the interaction of electron spins or its orbital angular momentum with the nuclear spins. In short, our subsystems A and B are built from a set of excitations between LMOs.

In line with this reasoning we should be aware that, in the NMR experiment, one is performing *non-local* measurements because one use an apparatus that carry on instantaneous measurements on two or more subsystems altogether (being them nuclear spins or electronic excitations). The result of the NMR experiment cannot be obtained by carrying out measurements separately on each individual subsystem.

So, we search for the correlation between two MO excitations that occur simultaneously in two different regions of the molecule, being them of the kind $i \to a$, $j \to b$. The localized

molecular orbitals i and j are occupied states and a and b are unoccupied states. In Fig. 2 we have shown the ethane molecule and also highlighted only two excitations, $\sigma_1 \to \sigma_1^*$, and $\sigma_2 \to \sigma_2^*$, that are likely entangled.
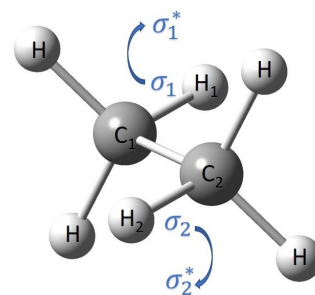
Fig. 2 Two local excitations that are considered in our treatment of the mutual information

From the definition of the polarization propagator density matrix of Eq. (36), the reduced density matrix of two given excitations, lets say, $i \to a$ and $j \to b$, will be given by

$$\rho_{ia,jb} = \frac{e^{M_{ia,jb}}}{Z_{[0]}} \tag{45}$$

Given that we will use the same formal expression of the mutual information of Eq. (43) to calculate the entanglement among those two excitations, we shall also need to define the following single excitation reduced polarization propagator density matrix

$$\rho_{ia} = \frac{e^{M_{ia}}}{Z_{[0]}} \tag{46}$$

The next step is to define the appropriate single-excitation entropy, $S(1)_{i \to a}$ and the two-excitation entropy, $S(2)_{i \to a, j \to b}$. So,

$$S(1)_{i \to a} = -\sum_\alpha \lambda_{\alpha;(i,a)} \, ln\lambda_{\alpha;(i,a)} \tag{47}$$

and

$$S(2)_{i \to a, j \to b} = -\sum_\alpha \lambda_{\alpha;(i,a),(j,b)} \, ln\lambda_{\alpha;(i,a),(j,b)} \tag{48}$$

The elements $\lambda_{\alpha;(i,a),(j,b)}$ and $\lambda_{\alpha;(i,a)}$ are the eigenvalues of the reduced density matrices of Eqs (45) and (46), respectively.

It should also be mentioned that the entropy of the molecular system at RPA level of approach is written in terms of the integrals **G** and **H**.

Results and discussion

In this section we shall show the first results of the theory shown above. We do it applying it to the study of vicinal ^3J(H-H) coupling in the ethane molecule. We shall evaluate it as a function of the dihedral angle ϕ (See Fig. 1), and then quantify the mutual information and the one-excitation entropy, that give new insights about the origin of the Karplus rule.

Karplus rule and main coupling pathways

At the beginning we show the dependence of the vicinal H-H J-coupling with the dihedral angle at three levels of approach, RPA, TDA and HF. Each one of them is related with the principal propagator. At RPA level we use the whole matrix elements of Eqs (12) and (13). The other two approximations arises when the matrix $\mathbf{B} = 0$ (TDA) and the HF approximation requires that matrix $\mathbf{G} = 0$ and matrix $\mathbf{H} = 0$ (see Eq. (13)).

In Fig. 3 we show the dependence of $^3J(\mathrm{H_1\text{-}H_2})$ with ϕ. It follows the Karplus rule at all three levels of approach. The TDA values are almost half of the RPA ones, and the HF values are different from zero. It is worth to highlight that the value of $^3J(\mathrm{H_1\text{-}H_2})$ for $\phi = 90$ is zero in the last two levels of approach. Furthermore, as previously shown working with semiempirical methods in Refs.[15,19,35] such a dependence is followed by most of the coupling pathways.
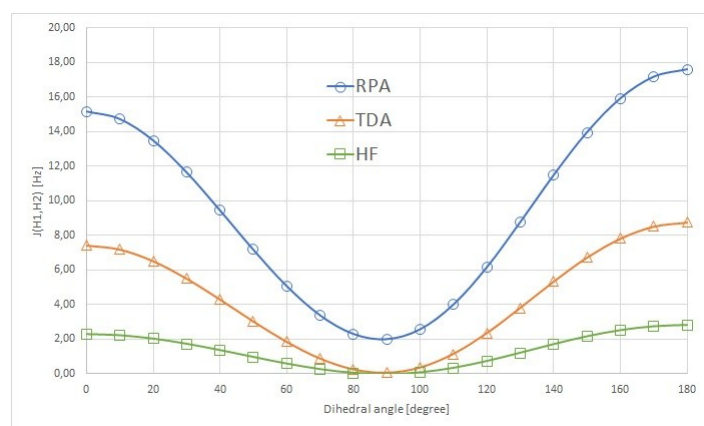
Fig. 3 Total $^3J(\mathrm{H_1\text{-}H_2})$ dependence with the dihedral angle at RPA, TDA and HF level of approach

Then it follows that there must be a Karplus-type dependence with the principal propagator. We calculated the matrix elements corresponding to the coupling pathway $\sigma_1 \rightarrow \sigma_1^*$; $\sigma_2 \rightarrow \sigma_2^*$ for the principal propagator and its inverse. They both follow a Karplus-type dependence with ϕ, which is shown in Fig. 4. This indicates that non-local interactions occur.
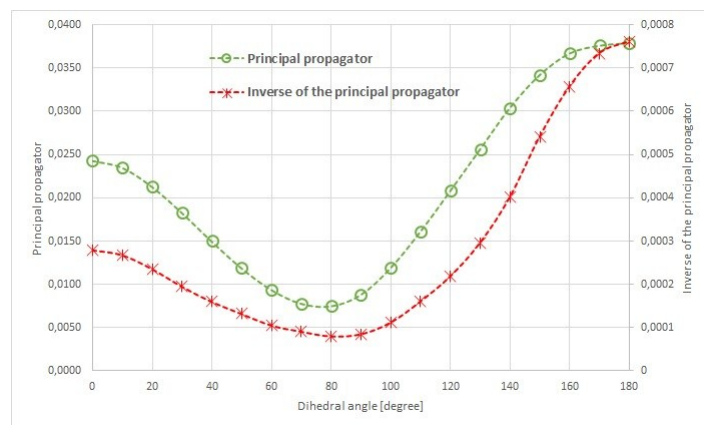
Fig. 4 Dependence of the main coupling pathway of the principal propagator and its inverse with the dihedral angle

The dependence with ϕ of the matrix elements of matrices $\mathbf{G}$ and $\mathbf{H}$, shown in Fig. 4, arises from eight excitations of LMO. In that figure we show that the sum of them follows the Karplus rule. This is due the fact that, using the basis set we selected four unoccupied LMOs for each occupied LMO. They are included in each LMO named as σ^* in Fig. 1.

Entangled LMO excitations in ethane

The next step is to apply our theory to the analysis of the likely entanglement between those excitations.

In order to do that we calculated the matrix elements of both, the density matrix of Eq. (45) and the reduced density matrix of Eq. (46). Since the inverse of the propagator, $\mathbf{M}$, can be diagonalized, we can easily obtain the eigenvalues of ρ from the eigenvalues of $\mathbf{M}$. All those eigenvalues are given as Additional Information.

Once the density matrix elements are obtained, the quantum entanglement between the excitations $\sigma_1 \rightarrow \sigma_1$, $\sigma_2 \rightarrow \sigma_2$ are quantified by using the definition of mutual information of Eq. (43).

| $i \rightarrow a$ \ $j \rightarrow b$	$\sigma_1 \rightarrow \sigma_1^*$	$\sigma_2 \rightarrow \sigma_2^*$
$\sigma_1 \rightarrow \sigma_1^*$	$E - (G + H)$	$-(G + H)$
$\sigma_2 \rightarrow \sigma_2^*$	$-(G + H)$	$E - (G + H)$

Fig. 5 Scheme of the reduced matrix density used to calculate the mutual information

In our case we consider only the matrices $\mathbf{G}$ and $\mathbf{H}$ because they have an explicit non-local character. Then, given that at RPA level of approach one include also the $\mathbf{E}$ matrix, what we did was to take out the contribution of this last matrix of Eq. (13). The scheme used to calculate the eigenvalues of the reduced density matrix is shown in Fig. 5.

Results of calculation of the corresponding mutual information are shown in Fig. 6. We observe that the excitations show a quantum entanglement between them, and that the dependence with the dihedral angle is related with the symmetry of the molecule. The highest value of entanglement appears when the molecule is in its eclipsed symmetry and the minimum, when it is staggered.

The entanglement between the excitations of the studied LMOs is larger when more correlation is included, meaning that $I_{\sigma_1,\sigma_1^*;\sigma_2,\sigma_2^*}(\mathrm{RPA}) > I_{\sigma_1,\sigma_1^*;\sigma_2,\sigma_2^*}(\mathrm{TDA})$.

Rissler *et al* have given an interpretation for one-orbital entropies: each S_i describes the entanglement of the orbital i with the rest of the environment.[4] In our case the one-orbital excitation entropy, $S(1)_{i \rightarrow a}$, is related with the entanglement of each LMO excitation with the whole set of excitations in the molecule.
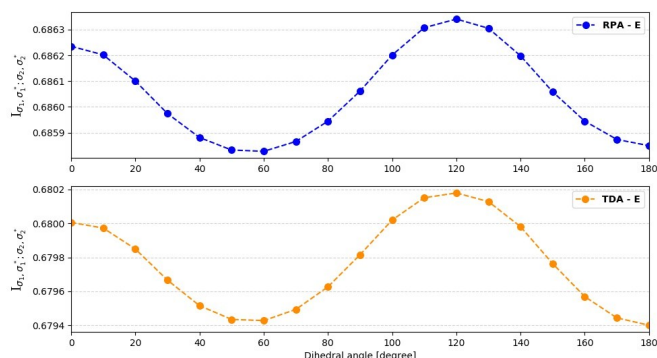
Fig. 6 Mutual information as a function of the dihedral angle for the ethane molecule

One way to check the measurement of entanglement by mutual information is through the calculation of ζ_{vN} of Eq.(44). In Fig.7 we show the dependence of ζ_{vN} with the dihedral angle, and also its relationship with $I_{\sigma_1,\sigma_1^*;\sigma_2,\sigma_2^*}$ at RPA level. We observe that both descriptors have the same pattern, and so, it confirms our proposal.
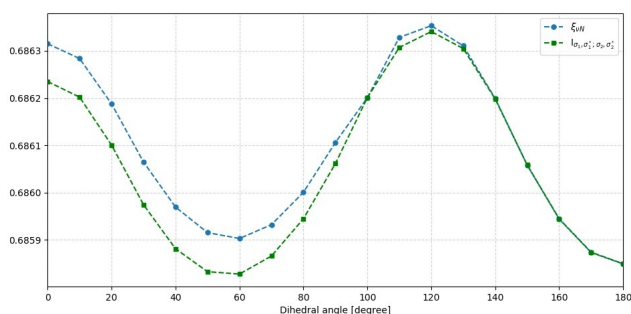
Fig. 7 Measurement of entanglement as a function of the dihedral angle for the ethane molecule

We were also interested to see whether the $S(1)_{i\to a}$ entropy shows a ϕ-dependence. As shown in Fig. 8, the one-orbital excitation entropy of one of the main excited LMOs that contribute to the main coupling pathway in the vicinal J-coupling we are working on, has a ϕ-dependence that is similar to the mutual information function of Fig. 6.
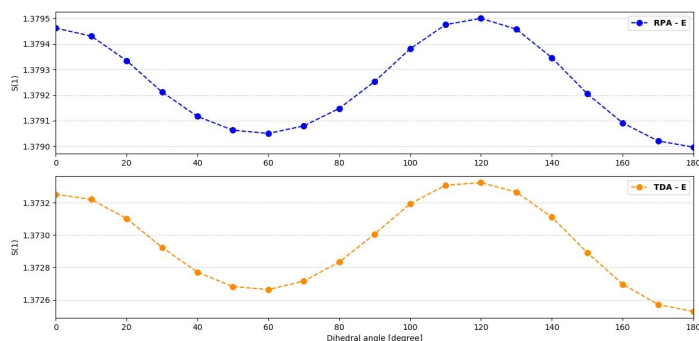
Fig. 8 One-orbital excitation entropy for the excitation $\sigma_1 \to \sigma_1^*$

Concluding remarks

As was previously shown in recent literature, the picture of interacting orbitals give new insights about the mechanisms of chemical reactions and chemical bonding. Besides, an entanglement analysis requires the use from the outset of correlated wavefunctions. That means that the orbital entanglement does not provide bonding information from one-determinant wavefunctions, like Hartree – Fock and Kohn – Sham density functional theory. From this basis we wanted to go one step further and apply similar concepts for describing the interaction between two molecular orbital excitations.

We show in this article a new theory that introduce information theory to the analysis of the electronic origin of response properties. We have used the fact that the principal propagator of the polarization propagators is a basic element of the quantum system that has the same nature as the wavefunction. Then, given that polarization propagators can be derived from the path integral formalism, we were able to define a density matrix that depends on the inverse of the principal propagator.

Once this density matrix is found, one-excitation orbital and two-excitation orbitals are easily derived. So, the mutual information between pair of orbital excitations is then straightly defined. Mutual information is also related with another descriptor of entanglement known as ζ_{vN}.

This theory is concerned about the quantum transmission of MO excitations (we considered localized MOs, LMO). They belong to the set of all "coupling pathways" that are the natural excitations of the unperturbed quantum system. Once the external perturbations are applied to the system, their effects are transmitted by those "coupling pathways" to the whole quantum system.

As a first example we applied this theory to the analysis of the origin of the famous and empirical Karplus rule of the NMR spectroscopy. This rule regards about a dihedral-angular dependence of the vicinal J-coupling, which does not depend on the molecular system under study. We have chosen in this study the ethane molecule.

We analyzed the vicinal H-H coupling in terms of the entanglement among the main LMO excitations that are involved in such J-coupling. They were written as $\sigma_1 \to \sigma_1^*$, and $\sigma_2 \to \sigma_2^*$. We found that they are entangled, and it grows as more electron correlation is included. In other words, the entanglement is larger at RPA than at TDA level of approach.

We summarize our findings as:
i) The principal propagator matrix describe the transmission of the interaction between nuclear spins. Some of its elements reflect non-local interactions.
ii) A density matrix can be properly defined from the theory of polarization propagators. This matrix can be used to apply the quantum information tools to explain the electronic origin of atomic and molecular response properties.
iii) The Karplus rule, which express a dihedral-angular dependence of the vicinal J-couplings, arises as a consequence of the entanglement of pairs of LMOs excitations.

Acknowledgments

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The likely quantum entanglement among excitations of MOs are described by using the polarization propagator formalism. Its first application to NMR-J couplings give new understandings about the way external perturbations are transmitted within molecular systems.

Physical Chemistry Chemical Physics Accepted Manuscript