

Understanding NMR J-Couplings by the Theory of Polarization Propagators

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ABSTRACT: Propagators are powerful theoretical tools that were first developed within the nonrelativistic (NR) regime and were applied to calculate atomic and molecular properties more than 30 years ago. The recent relativistic generalization of polarization propagators has shown that these propagators play a special role in describing the quantum origin of any molecular property and the broad implication of their particular definition. In this article, we give a general overview on fundamentals and applications of polarization propagators to one of the most important NMR spectroscopic parameters, the nuclear spin coupling mediated by the electronic system within both regimes: relativistic and NR. This presentation is given in a level that can be followed with a basic knowledge of quantum mechanics. Our aim is to show what one can learn about molecular electronic configurations, and also the transmission and influence of magnetic perturbations on electronic systems from basic theoretical elements like molecular orbitals, electronic excitation energies, coupling pathways, entanglement, etc. by using propagators. We shall use i) semiempirical models and ii) *ab initio* calculations at different levels of approach. We give a deep insight on the electronic origin of the Karplus' rule, the sign of indirect nuclear spin couplings, unusually large long-range couplings, cooperativity effects, relativistic effects, and the origin of diamagnetism. Some of these analysis are based on previous publications, and some others are presented here for the first time. © 2008 Wiley Periodicals, Inc. Concepts Magn Reson Part A 32A: 88–116, 2008.

KEY WORDS: polarization propagators; NMR J-couplings; sign of J; Karplus' rule; cooperativity effects; Pople–Santry model; full relativistic; HF's stability; long-range couplings

INTRODUCTION

The history of NMR spectroscopy is full of new developments and theoretical understandings that improve its applications. Actually this technique has one of the largest fields of application in science, starting from basic physics more than 50 years ago (1, 2) to its applications in neuroscience (3), food science (4), material and nanoscience (5, 6), biochemistry (7), protein and biological cell structure determi-

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nation (8–11), etc. During the last decades experiments were carried on in all these fields, and many times it happened that they were far away ahead of theoretical understandings and formal developments. In the case of the most-used NMR spectroscopic parameters for structural and electronic molecular analysis, experimenters are starting to need and frequently use theoretical models to get rid of their measurements.

When we started to work with polarization propagators (in the late of '80s), well-established nonrelativistic (NR) formalisms were successfully applied to the calculation and analysis of electromagnetic properties in small molecules. There were very few codes that implemented the explicit expressions of that approach. It was the goal of Oddershede and co-authors (12–14) on *ab initio* schemes and Contreras and coworkers (15–17) on semiempirical schemes, promoting the intensive application of these new ideas on the vast field of quantum chemistry.

From the early '90s, polarization propagators were generalized to include properly relativistic effects by a fully relativistic theory (18) and later on we have extended it to a quantum electrodynamics (QED)-based formalism (19, 20). This was one of the long-term assessment that is almost finished: starting from semiempirical or *ab initio* NR models, these were extended to include relativistic effects in semiempirical pseudorelativistic schemes (21–24), then generalized to a full relativistic scheme and finally to a QED-based theory of electromagnetic molecular properties. It is worth to mention that polarization propagators and QED theories of molecular properties are related in a natural way, because they start from equivalent assumptions and definitions.

One of the goals of this article is to show in a possible, elementary manner the way by which one could get information of any electronic molecular system and the kind of information that is accessible from the theory of polarization propagators. The basic ideas that underlie propagator methodologies are quite simple and powerful: perturbing one localized region of the molecule (a perturbation that may also be applied to the whole molecule) by an external potential, the electronic surrounding of that region will be polarized, and the (polarization) propagators tell us about the magnitude and the electronic mechanisms that are involved in the modification of a given internal property compared with its value in the absence of that external perturbation. Polarization propagators are equivalent to double-time Green's functions.

The arrow line that both theoretical physicist and chemist gave to the development of the basic physi-

cal theory that explains NMR spectroscopic phenomena goes the other way around on what have happened with applications, which started working on quite small molecules and is now applied on very large molecules like proteins or fragments of DNA. From the early days, the theory formulated by Ramsey [chemical shift (25–28) and *J*-couplings (29)] was accepted and used every time when necessary to apply on calculations. But this theory was based on Schrödinger formulation of quantum mechanics, i.e. valid only within the NR domain. One can include relativistic effects by hand, i.e. adding perturbative terms to the Schrödinger's Hamiltonian or do better starting from a proper relativistic theory, i.e. a Dirac-like theory. Pionered work by Pyykkö (30, 31) and Pyper (32) extended Ramsey's theory to the relativistic domain. A fully relativistic polarization propagator theory (18) and then a QED-based theory (19, 20) appear afterwards, putting solid grounds on the way to include properly relativistic and QED effects on electric and magnetic molecular properties within a polarization propagator approach.

The relativistic polarization propagator approach is a natural extension of its NR counterpart, though it introduces completely new insights on the comprehension of the physical origin of magnetic properties. Even though Dirac theory seems to be more complicated than Schrödinger theory, there are at the moment a clear understanding on the way to treat and include relativity in molecular systems, the relatively new and very exciting field of research that is known as relativistic quantum chemistry.

When one tries to reproduce (or predict) molecular electromagnetic properties like the NMR spectroscopic parameters by applying modern theoretical methods, one has at hand several powerful alternatives that give results, specially for small molecules that are not far away from experimental error bars (33–35). In most cases, one needs to go quite ahead of including only leading order effects within the state-of-art methodologies.

Polarization propagators are between those theories that have

1. A simple and general definition that can be related in a proper way with the best theory of quantum physics that we have at hand, i.e. QED.
2. Few well-defined and coherent assumptions.
3. A formal definition that is the same for nonrelativistic and relativistic regimes, which means that it is based only on quantum mechanics assumptions. This fact gives to them a great advantage when one wants to move from one regime to the other.

4. Formal solutions of its basic equation of motions that can be expressed in a perturbational scheme so that they may be improved in a well-defined way.
5. Several implementations at different levels of approach that are well known at present.

From these characteristics and the large amount of results and experience acquired during the last 30 years, one can say that polarization propagators can give intuitive and simple ways to understand the physics that underlies most of the electric and magnetic molecular properties, static and time-dependent. When used properly, theoretical results obtained with polarization propagator schemes are theoretically convergent and in general close to experiments. For this last assessment being true, one should include in the calculations several small (sometimes not very small) effects like rovibrational effects or the effects of temperature. In this sense within the last decade, there appears several review articles concerning NMR spectroscopic parameters with comparative numbers between different approaches (35–37).

In this article, we will try to explain the main formal aspects of polarization propagator theory at both levels, relativistic and nonrelativistic. We will also discuss in detail few of their powerful and simple theoretical models together with applications on the analysis of NMR spectroscopic parameters. We start from the general theory at both levels, relativistic and nonrelativistic, and show that spin dependence can be generalized easily to time-reversal dependence. This gives new physical insights that only arise within a full relativistic regime. The section on applications will start with a detailed discussion of a semi-empirical model that was developed by Contreras and coworkers in the early '80s. This scheme is quite simple, though it gives a deep understanding on the physics underlying the NMR phenomena, like the origin of the sign of NMR J -coupling. Most of these applications are performed based on the experience of the present author.

In order to give a more comprehensive presentation, we choose the option of following the historical development of polarization propagators. This will be done for the first time here because of the inclusion of relativistic polarization propagators. It is clear that there would be some difficulties to present relativity at work for a general audience, mainly because it is a relatively new field for quantum chemists and molecular physics researchers. In any case, relativistic expressions are simpler than their NR counterparts, though less intuitive only because of our usual NR way of looking at the molecular world. Polariza-

tion propagators have the strong feature of being formally defined in exactly the same way in both domains. Starting from full relativistic expressions and numerical calculations, making $c \rightarrow \infty$ their NR analytical expressions, and numerical results are naturally obtained. There is no other current theory that has a similar behavior. Perhaps the deepest reason for this is the fact that polarization propagators are defined as a natural extension of the definition of two more basic propagators, i.e. the electronic and photonic propagators. They are the very basic blocks on which QED is built.

GENERAL THEORY

Propagators are theoretical devices that were first introduced by Feynman (38). He showed that it is possible to describe the time evolution of a quantum particle and its single interaction with other quantum particles through a new theoretical object different from the usual wave functions. This was coined as the path-integral formulation of quantum mechanics. Electrons and photons are elementary quantum objects. For an isolated electronic system interacting with low-energy electromagnetic fields, there are only two basic propagators that arise within a QED theory: electron- and photon-propagators (39). In an electron-electron Coulomb interaction or electron-electron scattering one can obtain, as an example, the scattering cross section to a first order of approach, considering only the interaction between those electrons through a “virtual” photon exchange. There are precise rules, namely the Feynman’s rules, from which one can describe and calculate measurable quantities that arise from this process. In the same way, when considering an interaction of electrons with two external fields, there is usually a virtual electron exchange between the external perturbative potentials in that two space-time points where the interactions occur (39). These ideas are in the core of the Feynman’s description of the quantum electrodynamic’s theory.

Given the success of propagators in the early '50s, their generalization for describing the dynamics of more complex systems was a natural challenge. Propagators were introduced in atomic and molecular physics by several authors (40–42). Considering bound-state electronic systems interacting with a given external electromagnetic field one may think about how to describe the propagation of this interaction within such a system. In this case, it would be quite difficult to consider explicitly the elementary interactions or the “virtual” particles that carry the

basic information of the electron-external field interaction from one place to another within the system. On the other side, one should be able to consider some kind of effective interactions that are transmitted through the system. One of the main comparative advantage of the use of propagators in the analysis of molecular properties is the fact that they give crucial information about the electronic mechanisms that are involved in the transmission of the effect of global or local external perturbations on the whole electronic molecular system. Indeed, their implementation in modern computational codes also gives accurate results that can reproduce accurately experimental measurements (33, 34).

One of the aim of this article is to show the powerful tool that propagators are, when used to analyse NMR *J*-couplings. We will sketch the main steps that one should do in order to get theoretical expressions for practical applications. The interested reader on mathematical aspects of these derivations should have a look on previous reviews and articles that are referenced whenever necessary. All aspects of theory are treated with some care, though only in a schematic way.

Double-time Green functions or propagators are objects that occupy the same place as wavefunctions in quantum mechanics. They give the probability amplitude that a polarized state arising from a perturbation $V^P(t)|0\rangle$ acting at a given time t on an unperturbed quantum state of a system would become in another polarized state $V^Q(t')|0\rangle$ at a different time t' :

$$V^P(t)|0\rangle \rightarrow V^Q(t')|0\rangle \quad [1]$$

This is equivalent to say that when an “external” perturbation is applied on a quantum state of a system, the average values of their physical observables will be modified. External perturbation could mean an external homogeneous magnetic field or the magnetic field due to the nuclear magnetic dipole moment.

There are three kinds of polarization propagators, all of them giving the same results for calculations of molecular magnetic properties. The most used causal polarization propagator is defined as

$$\langle\langle P(t); Q(t') \rangle\rangle = -i\hbar\theta(t-t')\langle 0|[P(t), Q(t')]|0\rangle \quad [2]$$

where P and Q are written instead of V^P and V^Q , respectively. The $\theta(t)$ function is the usual step function

$$\theta(t-t') = \begin{cases} 1 & \text{for } t \geq t' \\ 0 & \text{for } t < t' \end{cases} \quad [3]$$

The definition of Eq. [2] is completely independent on whether the underlying theoretical framework is relativistic or nonrelativistic (18), even though its first formulation was given within a NR regime (14).

Given that polarization propagators have the same basic nature as a wavefunction ψ , one may ask for its equation of motion, i.e. how the polarization propagates with time. One can write explicit expressions for the equation of motion that can be solved by formal procedures (14, 43). Furthermore, one can make a transformation from time-dependent to energy-dependent framework in order to make use of this tool in spectroscopic problems.

The equation of motion for propagators can be obtained first applying the Heisenberg equation of motion for the time-dependent operators, $P(t)$ and $Q(t')$ and then Fourier transforming the final expressions (43):

$$E\langle\langle P; Q \rangle\rangle_E = \langle 0|[P, Q]|0\rangle + \langle\langle [P, H]; Q \rangle\rangle_E \quad [4]$$

After the iteration of Eq. [4], one gets what is called the moment expansion of the polarization propagators. Solutions of this equation can be obtained by applying a well-defined technique first derived by Goscinski and Lukman (44): the superoperator technique. In Eq. [4] H is the unperturbed Hamiltonian describing the electronic system, and $|0\rangle$ represents the reference state that in our case will be a Hartree-Fock (HF) or Dirac-Hartree-Fock (DHF), i.e. one Determinantal state composed of one-electron wavefunctions, which are solutions of HF or DHF equations, respectively.

The final form of the equation of motion obtained with superoperator algebra and the inner projection technique is (45):

$$\langle\langle P; Q \rangle\rangle_E = (P^\dagger|h)(\tilde{h}|EI - H|h)^{-1}(\tilde{h}|Q) \quad [5]$$

h is a complete operator manifold of basic excitation operators, from which it is possible to describe the whole branch of excited states that may arise from a given reference state $|0\rangle$. The operators P and Q should also be described in terms of basic excitation operators that belongs to that excitation manifold. Furthermore, the basic excitation operators may be written with its explicit spin-dependence within the NR regime. In the case of the relativistic regime where the spin is no longer a good quantum number, the spin symmetry can be replaced by the more general time-reversal symmetry (46). This is a powerful way of obtaining excited states from the reference state and to solve the algebraic operations that are included in Eq. [5].

In this last equation, there are two different type of factors. We want to give their explicit form and meaning as a background of what follows.

The binary product ($P|Q$) is defined as

$$(P|Q) = \langle 0|[P^\dagger, Q]|0 \rangle \quad [6]$$

and the effect of the superoperator \hat{H} acting on the operator P is,

$$\hat{H}P = [H, P] \quad [7]$$

The operators P , Q , etc. that represent physical magnitudes or the Hamiltonian of the system can be expressed in terms of basic operators that are defined in an actual basis. This way of working out the equations is oriented to directly obtain explicit formulas which in turn are then codified in computational codes.

Any operator P can be written as

$$P = \sum_{p,q} P_{pq} a_p^\dagger a_q \quad [8]$$

where a_p^\dagger and a_q are creation and annihilation operators, respectively. Another way to get the same expansion is by using spin-adapted excitation operators (47):

$$P = \sum_{p,q} P_{pq} E_{pq} \quad [9]$$

or more generally by using time-reversal adapted excitation operators (46):

$$P = \sum_{p,q} P_{pq} X_{pq} \quad [10]$$

The complete excitation operator manifold, i.e. \mathbf{h} , may also be expanded in terms of the operators E or X . For polarization propagators, the operator manifold is chosen such that

$$\mathbf{h} = \{\mathbf{h}_2, \mathbf{h}_4, \dots\} \quad [11]$$

where

$$\mathbf{h}_2 = \{a_a^\dagger a_i, a_i^\dagger a_a\}; \quad \mathbf{h}_4 = \{a_a^\dagger a_b a_i a_j, a_j^\dagger a_i^\dagger a_b a_a\}; \text{ etc.} \quad [12]$$

and where a , b , ... refer to unoccupied HF or DHF orbitals and i , j , ... stand for occupied HF or DHF orbitals. Then by doing this, Eq. [5] is rewritten as

$$\langle\langle P; Q \rangle\rangle_E = (P_a^\dagger, P_b^\dagger, \dots) \begin{pmatrix} M_{aa} & M_{ab} & \dots \\ M_{ba} & M_{bb} & \dots \\ \dots & \dots & \dots \end{pmatrix}^{-1} \begin{pmatrix} Q_a \\ Q_b \\ \dots \end{pmatrix} \quad [13]$$

where

$$P_a = (P|h_a) \quad [14]$$

and

$$M_{ab} = (\tilde{h}_a | E\hat{I} - \hat{H} | h_b) \quad [15]$$

We can write Eq. [13] in a more compact way:

$$\langle\langle P; Q \rangle\rangle_E = \mathbf{b}^P \mathbf{M}^{-1} \mathbf{b}^Q \quad [16]$$

The term in the middle of the RHS of Eqs. [13] and [16] is known as the principal propagator. The other two are the property matrix elements or, as they were called within the semiempirical models, *perturbators*. The principal propagator depends only on both the electronic molecular system as a whole and the spin (time-reversal) dependence of the perturbators, i.e. it is independent of the particular molecular property. It gives the main streamlines of transmission of the interaction between the external perturbations related with the property matrix elements, through the unperturbed electronic system. It means that perturbation intervenes explicitly on the perturbators only.

All static second-order molecular properties, i.e. the properties that arise from the second-order correction to the energy depending on two external static fields, can be calculated by using polarization propagators. This is evident from the following equation:

$$E_{PQ}^2 = \frac{1}{2} \text{Real} \langle\langle H^P; H^Q \rangle\rangle_{E=0} \quad [17]$$

where H^P and H^Q are the external interaction Hamiltonians related with perturbations whose molecular response properties we are interested in.

In the case of NMR spectroscopic parameters, one should start with a phenomenological perturbed Hamiltonian that describe accurately the experimental NMR spectra (48). The complete Hamiltonian is then

$$H = H_0 + H_{\text{NMR}} \quad [18]$$

with H_0 being the unperturbed Hamiltonian and

$$H_{\text{NMR}} = \sum_{\text{MN}} \{\boldsymbol{\mu}_{\text{M}} \cdot \mathbf{D}_{\text{MN}} + \mathbf{J}_{\text{MN}}\} \cdot \boldsymbol{\mu}_{\text{N}} + \sum_{\text{M}} \{\boldsymbol{\mu}_{\text{M}} \cdot (\mathbf{1} - \boldsymbol{\sigma}_{\text{M}}) \cdot \mathbf{B}\} \quad [19]$$

where $\boldsymbol{\mu}_{\text{M}}$ is the nuclear dipole moment of nucleus M, \mathbf{D}_{MN} and \mathbf{J}_{MN} are the direct and indirect nuclear spin coupling tensors, $\boldsymbol{\sigma}_{\text{M}}$ is the nuclear magnetic shielding of nucleus M, and \mathbf{B} is the static external

magnetic field. From these last equations, it is clearly seen that when one wants to derive theoretical expressions for NMR spectroscopic parameters, one should propose bilinear perturbative Hamiltonians depending on two different nuclear dipole moments or one nuclear dipole moment and the external magnetic field. Then the interaction energy, linearly dependent on two nuclear spins, \mathbf{I}_M and \mathbf{I}_N , is expressed as

$$E_{MN}^{(2)} = h\mathbf{I}_M \cdot \mathbf{J}_{MN} \cdot \mathbf{I}_N \quad [20]$$

and the interaction energy between nuclear spin \mathbf{I}_M and the external static magnetic field \mathbf{B} is

$$E_M^{(2)} = -h\mathbf{I}_M \cdot \boldsymbol{\sigma}_M \cdot \mathbf{B} \quad [21]$$

When using perturbation theory to get theoretical expressions of both NMR parameters, the NR, paramagnetic-like terms arise from second-order corrections to the electronic energy, because each of the matrix elements depends on a linear perturbative Hamiltonian:

$$E_{PQ}^{(2)} = \sum_{n \neq 0} \left\{ \frac{\langle 0 | H^P | n \rangle \langle n | H^Q | 0 \rangle}{E_0 - E_n} \right\} \quad [22]$$

The perturbative Hamiltonians H^P and H^Q may be any of the linear Hamiltonians that will be given in the next section (see Eqs. [39], [41], [43], and [45]). Both should have the same time-reversal symmetry (49).

On the other side, the NR diamagnetic-like expressions are obtained from a first-order correction of the electronic energy:

$$E^{(1)} = \langle H^S \rangle \quad [23]$$

where H^S has a bilinear dependence with the external perturbative parameters and are given in the next section (see Eqs. [44] and [46]).

The First Three Basic Levels of Approach

Right now the expressions of polarization propagators are exact, since we considered the exact reference state $|0\rangle$ and a complete excitation manifold of operators, \mathbf{h} . In practice it is not possible to do exact calculations, because one does not know the exact reference state and cannot work with a complete \mathbf{h} . Then one should apply some approximations. One clever way to do it is to consider an expansion of both type of terms in Eq. [13] as a function of the

fluctuation potential, which is defined expressing the unperturbed Hamiltonian in terms of the HF or DHF term and the fluctuation potential

$$H_0 = F + V \quad [24]$$

with

$$F = \sum_p \varepsilon_p a_p^\dagger a_p \quad [25]$$

and

$$V = 1/2 \sum \langle pq | rs \rangle a_p^\dagger a_q^\dagger a_s a_r - \sum_{pr} u_{pr} a_p^\dagger a_r \quad [26]$$

The matrix elements of the SCF potential are determined as

$$u_{pr} = \sum_{\alpha}^{\text{occ}} \langle p\alpha || r\alpha \rangle \quad [27]$$

We use the conventional notation

$$\langle pq || rs \rangle = \langle pq | rs \rangle - \langle pq | sr \rangle \quad [28]$$

and

$$\langle pq | rs \rangle = \int \Psi_p^*(1) \Psi_q^*(2) r_{12}^{-1} \Psi_r(1) \Psi_s(2) d(1) d(2) \quad [29]$$

The random-phase approximation (RPA) level of approach, which is of first order in the fluctuation potential, is obtained when

$$|0\rangle = |\text{HF}(\text{DHF})\rangle \quad [30]$$

with HF or DHF ground states, respectively, and

$$|\mathbf{h}\rangle = |\mathbf{h}_2\rangle \quad [31]$$

All one-electron operators shall be expanded in normal ordered second-quantized form (see Eq. [8]) as

$$P = \sum_{ia} [\mathbf{P}_{ai} a_a^\dagger a_i + \mathbf{P}_{ai}^* a_i^\dagger a_a] \quad [32]$$

and

$$\mathbf{P}_{ai} = \langle a | P | i \rangle \quad [33]$$

Then applying Eqs. [13]–[15] and Eqs. [24] and [31] one obtains

$$\langle\langle P; Q \rangle\rangle_E = (\tilde{\mathbf{P}}, \tilde{\mathbf{P}}^*) \begin{pmatrix} \mathbf{A} & \mathbf{B}^* \\ \mathbf{B} & \mathbf{A}^* \end{pmatrix}^{-1} \begin{pmatrix} Q \\ Q^* \end{pmatrix} \quad [34]$$

where

$$\begin{aligned} A_{ia,jb} &= -\langle 0 | [a_i^\dagger a_a, [a_b^\dagger a_j, H_0]] | 0 \rangle \\ &= \delta_{ab} \delta_{ij} (\varepsilon_a - \varepsilon_i) + \langle aj || ib \rangle \end{aligned} \quad [35]$$

and

$$B_{ia,jb} = -\langle 0 | [a_i^\dagger a_a, [a_j^\dagger a_b, H_0]] | 0 \rangle = \langle ji || ab \rangle \quad [36]$$

Matrix **A** does contain the average value of the unperturbed Hamiltonian H_0 between two singly excited states with respect to the reference state, and matrix elements of **B** are the matrix elements of H_0 between the reference state and the doubly excited states. So matrix **A** has terms of order 0 and 1 in V , while matrix **B** has a term of order 1.

Following the same line of reasoning, one could go one step up or down in the order of the fluctuation potential considered for calculations. The pure-zeroth order approach (PZOA) is obtained when matrix **B** and all two-electron matrix elements of **A** are neglected. Then the principal propagator becomes the inverse of the first term in the last RHS of Eq. [35].

From RPA, the next step up in the inclusion of dynamic electronic correlation is the second-order polarization propagator approach (SOPPA) (14, 50). At this level one should consider

$$|0\rangle = |\text{HF(DHF)}\rangle + |0\rangle^{(1)} \quad [37]$$

where $|0\rangle^{(1)}$ are doubly excited states from a Rayleigh–Schrödinger expansion of the reference state. For this second-order propagator, the excitation manifold of operators should also be expanded to include \mathbf{h}_4 , i.e.

$$|\mathbf{h}\rangle = |\mathbf{h}_2, \mathbf{h}_4\rangle \quad [38]$$

Then the transition matrix elements and the principal propagator are modified in such a way that there appears new well-defined matrix elements that arise from two particle–two hole excitations, \mathbf{h}_4 . Another improvement is found when Moller-Plesset correlation coefficients are replaced by coupled cluster singles and doubles amplitudes in all matrix elements belonging to SOPPA matrices (51). A previous partial implementation of this last modification was published by Oddershede and coworkers (52).

Nonrelativistic and Spin-Restricted Polarization Propagator Theory

Historical theoretical explanation of NMR spectroscopic parameters is based on NR expressions and

understandings. The famous four papers by Ramsey (25–29) gave the first expressions and were based completely on NR assumptions. Within this domain, the external interaction Hamiltonians that should be used to get theoretical expressions for the NMR spectroscopic tensor parameters, \mathbf{J}_{MN} and $\boldsymbol{\sigma}_{\text{M}}$, are given as follows. We will give first that for NMR- J couplings:

$$\begin{aligned} H^{\text{FC}} &= \left(\frac{8}{3}\right) \pi \mu_{\text{B}} \hbar g_{\text{e}} \sum_{\text{N}} \gamma_{\text{N}} \sum_i \delta(r_{i\text{N}}) s_i \cdot \mathbf{I}_{\text{N}} \\ &= \sum_{\text{N}} \gamma_{\text{N}} \mathbf{I}_{\text{N}} \mathbf{V}_{\text{N}}^{\text{FC}} \end{aligned} \quad [39]$$

where μ_{B} is the nuclear magneton, γ_{N} is the gyro-magnetic constant of nucleus N, g_{e} is the electronic g -factor, and

$$\mathbf{V}_{\text{N}}^{\text{FC}} = \left(\frac{8}{3}\right) \pi \mu_{\text{B}} \hbar g_{\text{e}} \sum_i \delta(r_{i\text{N}}) s_i \quad [40]$$

The Fermi contact (FC) perturbative Hamiltonian of Eq. [39] depends on the electronic density at the site of the nuclei. One should include two of these Hamiltonians for calculating the NMR- J coupling. So this spectroscopic parameter is related directly to the electronic densities on the sites of two different nuclei, say M and N.

FC interaction is usually the most important, though there are several molecular systems where this is not a valid assumption and the other two “paramagnetic-like” perturbative Hamiltonians are more important than the FC one. They are the so-called spin-dipolar (SD) and paramagnetic spin-orbital (PSO):

$$H^{\text{SD}} = 2\mu_{\text{B}} \hbar \sum_{\text{N}} \gamma_{\text{N}} \sum_i \left(\frac{3(s_i \cdot \mathbf{r}_{i\text{N}})(\mathbf{I}_{\text{N}} \cdot \mathbf{r}_{i\text{N}})}{r_{i\text{N}}^5} - \frac{s_i \cdot \mathbf{I}_{\text{N}}}{r_{i\text{N}}^3} \right) \quad [41]$$

or

$$H^{\text{SD}} = \sum_{\text{N}} \gamma_{\text{N}} \mathbf{I}_{\text{N}} \cdot \mathbf{V}_{\text{N}}^{\text{SD}} \quad [42]$$

and

$$\begin{aligned} H^{\text{PSO}} &= -2i\mu_{\text{B}} \hbar \sum_{\text{N}} \gamma_{\text{N}} \frac{\mathbf{I}_{\text{N}} \cdot \sum_i \mathbf{r}_{i\text{N}} \times \nabla_i}{r_{i\text{N}}^3} \\ &= \sum_{\text{N}} \gamma_{\text{N}} \mathbf{I}_{\text{N}} \cdot \mathbf{V}_{\text{N}}^{\text{PSO}} \end{aligned} \quad [43]$$

As observed in Eqs. [39]–[43] the first two depends on the electron spin, and the last one is electron spin-independent.

Finally, the perturbative “diamagnetic-like” Hamiltonian does not depend explicitly on the electronic spin:

$$H^{\text{DSO}} = \frac{e}{c} \hbar \mu_B \sum_{MN} \gamma_M \gamma_N \times \frac{\sum_i (\mathbf{I}_M \cdot \mathbf{I}_N) (\mathbf{r}_{iM} \cdot \mathbf{r}_{iN}) - (\mathbf{I}_M \cdot \mathbf{r}_{iN}) (\mathbf{I}_N \cdot \mathbf{r}_{iM})}{r_{iM}^3 r_{iN}^3} \quad [44]$$

Theoretical expressions for nuclear magnetic shielding, σ , depend on two quite different perturbative Hamiltonians: one is clearly paramagnetic in its effects on the “shielded” nucleus,

$$H^{\text{P}} = \frac{4\pi}{h} \mu_B \sum_N \gamma_N \frac{\mathbf{I}_N \cdot \mathbf{I}_N}{r_N^3} \quad [45]$$

and the other has a diamagnetic effect, i.e. it reduces the magnetic field that effectively appears in the nucleus of interest,

$$H^{\text{d}} = \frac{e^2}{2m} \sum_N \gamma_N \frac{\sum_i (\mathbf{B} \cdot \mathbf{I}_N) (\mathbf{r} \cdot \mathbf{r}_{iN}) - (\mathbf{B} \cdot \mathbf{r}_{iN}) (\mathbf{I}_N \cdot \mathbf{r})}{r^3 r_{iN}^3} \quad [46]$$

As shown in Eqs. [17] and [22], paramagnetic contributions to both NMR spectroscopic parameters can be obtained within NR polarization propagator theory. One should be aware that it is not allowed to mix perturbations with different electron spin dependence (49). When considering electron spin-dependent Hamiltonians, the excitation energies of Eq. [22] shall be restricted to that of singlet or triplet type. In the same manner will the principal propagator of Eq. [15] be restricted (46, 49). Then, in the case of J -couplings there will be two kind of terms: i) electron spin-dependent terms which are related with triplet principal propagators: ${}^3\mathbf{M}^{-1}$ and ii) electron spin-independent terms which must be calculated with singlet principal propagators: ${}^1\mathbf{M}^{-1}$.

Then, the indirect nuclear spin coupling tensor is written as

$$\mathbf{J} = \mathbf{J}^{\text{FC}} + \mathbf{J}^{\text{SD}} + \mathbf{J}^{\text{PSO}} + \mathbf{J}^{\text{FC/SD}} + \mathbf{J}^{\text{DSO}} \quad [47]$$

When calculated by the NR polarization propagator theory, each of the first three terms of the RHS of Eq. [47] are written as

$$\mathbf{J}_{MN}^X = \gamma_M \gamma_N \langle \langle \mathbf{V}_M^X; \mathbf{V}_N^X \rangle \rangle_{E=0} \quad [48]$$

where $X = \text{FC, SD, or PSO}$. The first term of Eq. [47] is isotropic and the fourth term does not contribute for systems that are not in their solid state phase;

so it will not be considered here. All terms of Eq. [48] can be calculated at different levels of approach depending on the fluctuation potential, i.e. PZOA, consistent first-order or RPA, SOPPA, TOPPA, etc. (50). We will mainly be concerned with applications of propagators at RPA level of approach because of the fact that it is much easier to get the physical insights that underlie some important characteristic of NMR spectroscopic parameters at this level. Results from PZOA and SOPPA calculations will also be given.

At RPA level of approach, the explicit expression for the indirect NMR coupling constant between nuclei M and N corresponding to isotropic FC mechanism is

$$\begin{aligned} \mathbf{J}_{MN}^{\text{FC}} &= \gamma_M \gamma_N \langle \langle \mathbf{V}_M^{\text{FC}}; \mathbf{V}_N^{\text{FC}} \rangle \rangle_{E=0} \\ &= \sum_{ia,jb} [b_{M,ia}^{\text{FC}} \mathbf{P}_{ia,jb} b_{N,jb}^{\text{FC}}] \end{aligned} \quad [49]$$

The other two expressions for SD and PSO electronic mechanisms are

$$\begin{aligned} \mathbf{J}_{MN}^{\text{SD}} &= \gamma_M \gamma_N \langle \langle \mathbf{V}_M^{\text{SD}}; \mathbf{V}_N^{\text{SD}} \rangle \rangle_{E=0} \\ &= \sum_{ia,jb} [b_{M,ia}^{\text{SD}} \mathbf{P}_{ia,jb} b_{N,jb}^{\text{SD}}] \end{aligned} \quad [50]$$

and

$$\begin{aligned} \mathbf{J}_{MN}^{\text{PSO}} &= \gamma_M \gamma_N \langle \langle \mathbf{V}_M^{\text{PSO}}; \mathbf{V}_N^{\text{PSO}} \rangle \rangle_{E=0} \\ &= \sum_{ia,jb} [b_{M,ia}^{\text{PSO}} \mathbf{P}_{ia,jb} b_{N,jb}^{\text{PSO}}] \end{aligned} \quad [51]$$

The principal propagator can be factored out in such a way to put explicitly its electron spin dependence. Then, matrices \mathbf{A} and \mathbf{B} of Eqs. [35] and [36] can be rewritten in such a way that

$${}^m\mathbf{P}_{ia,jb} = {}^m\mathbf{M}_{ia,jb}^{-1} = ({}^m\mathbf{A} \pm {}^m\mathbf{B})_{ia,jb}^{-1} \quad [52]$$

where $m = 1$ (3) for singlet (triplet) type properties. When $m = 1$ (3) the $+$ ($-$) sign between ${}^1\mathbf{A}$ (${}^3\mathbf{A}$) and ${}^1\mathbf{B}$ (${}^3\mathbf{B}$) is applied. The matrix elements for these spin-dependent matrices are (50)

$$\begin{aligned} {}^1\mathbf{A}_{ia,jb} &= (\varepsilon_a - \varepsilon_i) \delta_{ab} \delta_{ij} + 2 \langle aj|ib \rangle - \langle aj|bi \rangle \\ {}^3\mathbf{A}_{ia,jb} &= (\varepsilon_a - \varepsilon_i) \delta_{ab} \delta_{ij} - \langle aj|bi \rangle \\ {}^1\mathbf{B}_{ia,jb} &= \langle ab|ji \rangle - 2 \langle ab|ij \rangle \\ {}^3\mathbf{B}_{ia,jb} &= \langle ab|ji \rangle \end{aligned} \quad [53]$$

In a completely similar manner, one can work out the NR nuclear magnetic shielding expressions.

Full Relativistic and Time-Reversal Restricted Polarization Propagator Theory

Few decades after the publication of the nonrelativistic Ramsey's expressions for hyperfine interactions, theoretical quantum physicists were motivated to derive the NMR perturbative Hamiltonians starting from Dirac theory. Once relativistic effects were shown to be very important in several properties of heavy-atom containing molecular systems, they realized that local magnetic molecular properties like the NMR spectroscopic parameters should need important relativistic corrections. As a matter of fact, a proper derivation of NMR spectroscopic parameters should start from the best theory we have at the moment, the QED: a theory of NMR spectroscopic parameters based on QED was published recently (19, 20). Any basic explanation of this theory is out of the scope of this article because one would need to start working with a quantized magnetic field instead of a classical magnetic field.

In the case of polarization propagators, their relativistic generalization appeared 20 years after the publication of their NR theory. The general theory was first published in 1993 (18), and after the discovery of the time-reversal restricted or X operators (published few years later (46) and mostly known as Kramers restricted operators) which in turn generalized the spin-dependence of any kind of operators, this theory was implemented in a computational code [named DIRAC (53)] that contains a module for calculation of response properties. First ab initio calculations of electric response properties appeared in 1997 (54) and calculations of magnetic response properties in 1999 (55–57). DIRAC code was implemented rewriting all equations within a quaternionic algebra (58, 59), which is completely equivalent to that of the X operators, though it seems to be more efficient.

Within the relativistic domain, the total Hamiltonian of an electronic system that consists of the sum of two terms, the unperturbed and the perturbed Hamiltonian (say H'), can be written as

$$H = H^D + V^C + H' \quad [54]$$

where H^D is the Dirac N -electron Hamiltonian and V^C is the Coulomb two-electron interaction operator:

$$H^D = \sum_i h^D(i) \quad [55]$$

with

$$h^D(i) = c\alpha_i \cdot p_i + (\beta_i - 1)mc^2 + \sum_M \frac{Z_M}{r_{iM}} \quad [56]$$

In Eq. [56] $\alpha = (\alpha_x, \alpha_y, \alpha_z)$ are the 4×4 Dirac matrices, which can be written in terms of the 2×2 Pauli matrices $\sigma = (\sigma_x, \sigma_y, \sigma_z)$ as

$$\alpha = \begin{pmatrix} 0 & \sigma \\ \sigma & 0 \end{pmatrix} \quad [57]$$

The interaction of an N -electron system with an external magnetic field is accounted for by the minimal coupling prescription (39), $p \rightarrow p + eA$ leading to the introduction of the following perturbative Hamiltonian

$$H' = ec \alpha \cdot A \quad [58]$$

where $A = A_M + A_B$ is the vector potential that involves the sum of the nuclear and external vector potentials

$$A_M = \frac{1}{c^2} \frac{\mu_M \times r_M}{r_M^3} \quad [59]$$

and

$$A_B = \frac{1}{2} B \times r_G = \frac{1}{2} B \times (r - R_G) \quad [60]$$

respectively. R_G is the gauge origin, $r_M = r - R_M$ and r and R_M are the coordinates of the electron and the nucleus M , respectively.

Considering both the nuclear and the external vector potential of Eqs. [59] and [60]

$$\begin{aligned} H' &= \sum_M H'_M = ec \alpha \cdot \sum_M \left\{ \frac{1}{c^2} \frac{\mu_M \times r_M}{r_M^3} + \frac{1}{2} B \times r_G \right\} \\ &= -\frac{e}{c} \hbar \sum_M \left\{ \gamma_M I_M \cdot \left(\frac{\alpha \times r_M}{r_M^3} \right) - ec B \cdot (\alpha \times r_G) \right\} \end{aligned} \quad [61]$$

Dirac's relativistic equation have solutions with both positive- and negative-energy states. Only for one-particle systems that solutions are bounded from below. When it contains more than one particle, there appears problems to get eigensolutions from a variational procedure. The way it was overcome was applying positive-energy projection operators. In the case of many-electron DHF calculations, Mittleman suggested to use projection operators that include the Hamiltonians H^D and H^C of Eq. [54] in such a way that the projection operators are continually updated during the iterative solution of the DHF equations (55, 60). This is then applicable to variational models like the single determinant DHF. It is worth to remark that from this procedure one gets both kind of solutions, i.e. positive-energy and negative-energy

one-electron states. Details are given elsewhere (55, 60, 61).

Once we are able to express the unperturbed Hamiltonian as

$$H_0 = H^{\text{DF}} + V \quad [62]$$

getting the reference state from a DHF calculation, all equations of The First Three Basic Levels of Approach Section are valid. One should always be aware that in this case all molecular orbitals have four-components (not scalar or Schrödinger's type) and all operators are written in a 4×4 matrix representation. There are also negative-energy electron states that should be included, otherwise the diamagnetic contributions to properties will not appear, as will be shown later.

From Eqs. [17], [58], and [61], the second-order perturbative correction to the energy is written as

$$\begin{aligned} E^{(2)} &= \frac{1}{2} \text{Real} \langle \langle H'; H' \rangle \rangle \\ &= \frac{1}{2} \frac{e^2 \hbar^2}{c^2} \sum_{\text{MN}} \gamma_{\text{M}} \gamma_{\text{N}} I_{\text{M}} \cdot \text{Real} \left\langle \left\langle \frac{\boldsymbol{\alpha} \times \mathbf{r}_{\text{M}}}{r_{\text{M}}^3}; \frac{\boldsymbol{\alpha} \times \mathbf{r}_{\text{N}}}{r_{\text{N}}^3} \right\rangle \right\rangle \\ &\quad \cdot I_{\text{N}} + \frac{e^2 \hbar}{2} \sum_{\text{M}} \gamma_{\text{M}} I_{\text{M}} \cdot \text{Real} \left\langle \left\langle \frac{\boldsymbol{\alpha} \times \mathbf{r}_{\text{M}}}{r_{\text{M}}^3}; \boldsymbol{\alpha} \times \mathbf{r}_{\text{G}} \right\rangle \right\rangle \cdot \mathbf{B} \end{aligned} \quad [63]$$

Finally, from Eqs. [20] and [21], full relativistic expressions of the NMR spectroscopic parameters are obtained as

$$J_{\text{MN}} = \frac{e^2 \hbar^2}{h} \gamma_{\text{M}} \gamma_{\text{N}} \text{Real} \left\langle \left\langle \frac{\boldsymbol{\alpha} \times \mathbf{r}_{\text{M}}}{r_{\text{M}}^3}; \frac{\boldsymbol{\alpha} \times \mathbf{r}_{\text{N}}}{r_{\text{N}}^3} \right\rangle \right\rangle \quad [64]$$

and

$$\sigma_{\text{M}} = e^2 \text{Real} \left\langle \left\langle \frac{\boldsymbol{\alpha} \times \mathbf{r}_{\text{M}}}{r_{\text{M}}^3}; \boldsymbol{\alpha} \times \mathbf{r}_{\text{G}} \right\rangle \right\rangle \quad [65]$$

From these equations it is observed that there is only one electronic mechanism involved in the indirect nuclear spin couplings instead of the four in the NR regime. There is also no distinction between dia- and para-magnetic terms. This fact is completely new and its explanation gave us the opportunity to get new insights on the electronic origin of molecular magnetic properties.

As in the NR response theory, it is possible to express the magnetic properties as a product of two perturbators times the principal propagator matrix. In 1993 (18) it was shown that, expressing the NMR J-coupling as

$$J_{\text{MN}} = \tilde{\mathbf{b}}_{\text{M}} \mathbf{P}(E=0) \mathbf{b}_{\text{N}} \quad [66]$$

its NR limit fulfil ($c \rightarrow \infty$),

$$\mathbf{b}_{\text{M}}^{\text{R}} \rightarrow \mathbf{b}_{\text{M}}^{\text{NR}} \quad [67]$$

and

$$\mathbf{P}^{\text{R}}(E=0) \rightarrow \mathbf{P}^{\text{NR}}(E=0) \quad [68]$$

It means that the relativistic perturbators \mathbf{b}^{R} and the relativistic principal propagators \mathbf{P}^{R} goes to their NR limit, each of them separately, when $c \rightarrow \infty$ (!). It was just clear at that time that if one considers only the positive energy branch of the Dirac's spectra, the diamagnetic terms do not appear (see Eq. [48] of Ref. (18)). Completely equivalent transformations to their NR limits for relativistic perturbators and principal propagators of the nuclear magnetic shielding are found.

It is worth to mention that this formal NR limit is obtained quite naturally and numerical examples will be given in sec III.

At RPA level of approach, the formal relativistic expressions are exactly the same as their NR counterparts. So the matrix elements of the principal propagator are now complex (because the four-component orbitals are complex), and they should include virtual orbitals that belong to the negative energy branch of the DHF energy spectra. Then considering explicitly the virtual orbitals that are contained in the \mathbf{A} and \mathbf{B} matrices of the principal propagator (see Eqs. [35] and [36]) as positive-energy (named e) and negative-energy (named p) one is able to write (55)

$$\mathbf{M}_{lm}^{-1} = \begin{bmatrix} \mathbf{A}_{lm} & \mathbf{B}_{lm}^* \\ \mathbf{B}_{lm} & \mathbf{A}_{lm}^* \end{bmatrix}^{-1} \quad [69]$$

being $(l, m) \equiv e$ or p . So the total principal propagator can be written as

$$\mathbf{P} \equiv \begin{bmatrix} \mathbf{M}_{ee} & \mathbf{M}_{ep} \\ \mathbf{M}_{pe} & \mathbf{M}_{pp} \end{bmatrix}^{-1} \quad [70]$$

Let's analyse now the order of magnitude of the different \mathbf{A} and \mathbf{B} block matrices contained in Eq. [70] using the explicit expressions of that matrices given in Eqs. [35] and [36] (55). There are four types of two-electron integrals. In the ep - and pe -blocks one of the virtual bi-spinors (4-component MOs) belongs to the negative-energy spectra (we will use overbar indices, like \bar{s} , for them) and the other virtual bi-spinors belongs to the positive-energy spectra. Then all integrals appearing in this block are of order $O(c^{-1})$. In the ee -block, all integrals are of order $O(c^0)$ and in

the pp -block there are integrals of order $O(c^0)$ and integrals of order $O(c^{-2})$. From this analysis, one may neglect the ep - and pe -block, such that the principal propagator can be divided in two blocks. Then

$$\begin{aligned} \langle\langle H'; H' \rangle\rangle &\approx \langle\langle H'; H' \rangle\rangle_{ee} + \langle\langle H'; H' \rangle\rangle_{pp} \\ &= \left(\sum_{is,jt} b_{is}^* (M_{ee}^{-1})_{is,jt} b_{jt} + cc \right) \\ &\quad + \left(\sum_{i\bar{s},j\bar{t}} b_{i\bar{s}}^* (M_{pp}^{-1})_{i\bar{s},j\bar{t}} b_{j\bar{t}} + cc \right) \quad [71] \end{aligned}$$

It is nicely seen that $\langle\langle \cdot \rangle\rangle_{ee}$ corresponds to the equivalent paramagnetic term of any of both NMR spectroscopic parameters within the relativistic domain, and $\langle\langle \cdot \rangle\rangle_{pp}$ corresponds to the diamagnetic-like term. We should stress here that within the relativistic domain there is no A^2 term in the perturbed Hamiltonian, so diamagnetic contributions do not appear in the same manner as in the NR regime. These considerations have new insights in the analysis of magnetic properties.

There is another point that one should mention: within the relativistic regime the spin is no longer a good quantum number. So it is not possible to consider singlet- or triplet- type principal propagators. Anyway, as was pointed out in the beginning of this section, the X operators are now of pseudo-singlet and pseudo-triplet type. Then it is possible to split the matrix M in two blocks depending on whether each term of the perturbed Hamiltonian of Eq. [61] is time-reversal symmetric or antisymmetric.

MODELS AND APPLICATIONS

Having developed the theory of polarization propagators as far as possible, it is time to show some numerical applications. We will start defining one of the most important semiempirical models, which was dubbed "contributions from localized orbitals within polarization propagator approach", (CLOPPA). This scheme was largely applied during the last decade by professor Contreras group on light-atom containing molecules, then extended by us and some collaborators together with professor Contreras to heavy-atom containing molecules; and then their main ideas were also extended to DFT and ab initio methods (62).

CLOPPA-X (X = INDO, MNDO, AM1, PM3, INDO/S) Models

The CLOPPA model was developed mainly to decompose the analysis of NMR- J couplings in term of "local" contributions, that means the contribution from individual coupling pathways which involves

two virtual excitations $i \rightarrow a$ and $j \rightarrow b$ with i, j (a, b) occupied (vacant) localized MOs that belongs to the local "L" fragment of interest:

$$J_{MN} = \sum_{ia,jb} J_{MN;ia,jb}^{L(X)} \quad [72]$$

In this way one is able to extract some crucial information on transmission mechanisms involved in the propagation of a given specific magnetic perturbation, say X ($X = \text{FC, SD, or PSO}$).

A given semiempirical ground state wavefunction can be used as the reference ground state for polarization propagator calculations (15–17). The CLOPPA scheme is based on this assumption, at RPA level of approach, together with the use of localized molecular orbitals (63). It was first implemented at the INDO level (64). With such an approach, indirect nuclear spin coupling constants can be calculated for molecules containing first and second row atoms as well as Se and Te. Some years later similar, schemes (21–24) were implemented at MNDO (65), AM1 (66), PM3 (67) and INDO/S (68) levels of approach.

There are several basic physical assumptions considered in the implementation of CLOPPA schemes: i) The transmission of the J -couplings involves largely molecular valence electrons; ii) relativistic effects modify (strongly for heavy atoms) the one-electron wavefunctions and therefore the electronic densities within the regions close to the heavy atomic nuclei, where the electronic mechanisms for J -couplings, are more important; iii) both the electronic density at the nuclear sites $S_M^2(0)$, and the $\langle r^{-3} \rangle$ average value corresponding to the p-type atomic orbitals can be considered as atomic parameters. Their values were taken from relativistic multiconfigurational Dirac-Fock ab initio theoretical calculations (69).

Each term of the sum in Eq. [72] can be written as (see Eqs. [49]–[51])

$$J_{MN;ia,jb}^X = \left(U_{M,ia}^X U_{N,jb}^X + U_{N,ia}^X U_{M,jb}^X \right)^m P_{ia,jb} \quad [73]$$

where $U_{M,ia}^X$ is a measure of the strength of the virtual excitation $i \rightarrow a$ due to the perturbation X , and $m = 3$ (1) for $X = \text{FC or SD (PSO)}$. The principal propagator ${}^m P_{ia,jb}$ gives the response of the molecular fragment connecting two virtual excitations $i \rightarrow a$ and $j \rightarrow b$. For a CLOPPA calculation the principal propagator matrix is evaluated in such a way that the whole molecule is described in terms of LMOs.

The perturbators within the CLOPPA method are implemented at the semiempirical level using a one-center approximation, and they have the form:

Table 1 Comparison of CLOPPA-X (X = AM1 and INDO/S) Numerical Results for Sn-Containing Molecules with Experiments and Some Other Ab Initio Calculations

Molecule	Coupling	X = AM1	X = INDO/S	Ab Initio	Exp
SnH ₄	¹ J(Sn—H)	–2500.00	–2164.00	–2616.84 ^a	–1930.00 ^b
SnMe ₄	¹ J(Sn—C)	–300.31	–378.03		–337.80 ^c
	² J(Sn—H)	150.00	36.22		+54 ^d
SnMeH ₃	¹ J(Sn—H)	–2310.00	–1862.00		–1852 ^e
					–1744 ^d
S(SnMe ₃) ₂	² J(Sn—Sn)		–237.04		218 ^f
Sn ₂ Me ₆	¹ J(Sn—Sn)	2640.00	4500.09		4460 ^f
	¹ J(Sn—C)	–295.00	–311.00		–240 ^f
	² J(Sn—H)	150.00	40.00		49 ^f

^a Taken from Ref. (52).^b Taken from Ref. (70).^c Taken from Ref. (71).^d Taken from Ref. (72).^e Taken from Ref. (73).^f Taken from Ref. (24, 74, 75).

$$\begin{aligned}
 U_{M,ia}^{\text{FC}} &= \langle i | \delta(\mathbf{R}_M) | a \rangle = C_{i,M}^s C_{a,M}^s S_M^2(0) \\
 U_{M,ia}^{\text{PSO},\alpha} &= i \langle r_M^{-3} \rangle \left(C_{i,M}^{\alpha} C_{a,M}^{\gamma} - C_{i,M}^{\gamma} C_{a,M}^{\alpha} \right) \epsilon_{\alpha\beta\gamma} \\
 U_{M,ia}^{\text{SD},\alpha\beta} &= \frac{1}{5} \langle r_M^{-3} \rangle f \left(C_p^{\alpha}, C_p^{\beta}, C_p^{\gamma} \right) \quad [74]
 \end{aligned}$$

where α , β , and γ refer to Cartesian coordinates, coefficients $C_{i(a)M}^s$ are those of “s” type belonging to atom M, $C_{i(a),M}^{\alpha}$ is the atomic coefficient np_{α} , $\epsilon_{\alpha\beta\gamma}$ is the antisymmetric tensor and “f” is a function of “np” type atomic coefficients of i and a LMOs.

Numerical Results. The main successful applications of the semiempirical CLOPPA model were on the understanding of electronic mechanisms that underlies NMR- J couplings in such cases where it was able to reproduce experimental tendency in a qualitative or semiquantitative manner. In particular, the application of CLOPPA-X (X = MNDO, AM1 and INDO/S) on heavy-atom containing molecules gave semiquantitative reproduction of experimental results in molecules where it was not possible to apply ab initio and full relativistic, semirelativistic or quasirelativistic theoretical calculations due to their large computational cost.

From Table 1 we can get an idea of what do we mean when we talk about qualitative description of experimental trends. Calculations of Sn—C and Sn—H do not reproduce in a quantitative way experiments, though they follow their tendencies. Then one can go one step further and analyse the electronic mechanism that underlies the total J value. There are several review articles (76, 77) where these criteria were applied. In the case of S(SnMe₃)₂, calculations with full relativistic methods are not avail-

able at the moment and CLOPPA-INDO/S gives quite approximate results. Some other calculations on medium-size tin-containing molecules (1,2,4,5-tetra stanna cyclohexanes with Me substitutes) are given in Ref. (22).

Zeroth-Order of the Principal Propagator Approach and the Pople–Santry Model. Within ab initio schemes to calculate response properties by polarization propagator methods, the calculation of the inverse of the principal propagator is never done 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 (50). The alternatives schemes developed to overcome these difficulties (47, 78) 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 uncontrollable way the individual elements which participate in the calculation.

A new procedure [a generalization of a previous one (76, 79)] to get the inverse of the principal propagator as a series was developed recently (80, 81). In this new scheme, the matrix elements of singlet and triplet principal propagators are written as power series

$$\begin{aligned}
 ({}^m P_S)_{ia,jb} &= \left[E^{-1} (I - {}^m N E^{-1})^{-1} \right]_{ia,jb} \\
 &= \left(E^{-1} \sum_{i=0}^{\infty} ({}^m N E^{-1})^i \right)_{ia,jb} \\
 ({}^m P_S)_{ia,jb} &\approx \left(E^{-1} \sum_{n=0}^p ({}^m N E^{-1})^n \right)_{ia,jb} \\
 &= ({}^m P_S)_{ia,jb} \quad [75]
 \end{aligned}$$

where p stands for the number of terms in each series corresponding to a given coupling pathway; \mathbf{E} is a diagonal matrix when canonical orbitals are used and is built from the difference of MO energies, and ${}^m\mathbf{N}$ represents the matrix of two-electron integrals of Eq. [53]. 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 in a power series each element of ${}^m\mathbf{P}$ (45, 82). When $p \rightarrow \infty$ the last term of Eq. [75] converges to ${}^m\mathbf{P}$.

The ${}^m\mathbf{P}_s$ matrix elements can be written in terms of localized or canonical MOs. When we use localized orbitals, ${}^m\mathbf{E}$ is nondiagonal. In such a case one can always use the same procedure as that used for calculation of ${}^m\mathbf{P}_s$ matrix elements.

From this development one can compare this way of expressing the principal propagator, and then the polarization propagators, with the Pople-Santry's model (83), which is still useful for understanding experimental results. This model relates the FC mechanism of indirect nuclear spin coupling between nuclei M and N with their mutual polarizability

$$\Pi_{MN} = -4 \sum_i^{\text{occ}} \sum_a^{\text{vac}} C_{iM} C_{aM} C_{iN} C_{aN} (\epsilon_a - \epsilon_i)^{-1} \quad [76]$$

in such a way that

$$J^{\text{FC}}(M, N) = -\left(\frac{44}{9}\right) \mu_B^2 h \gamma_M \gamma_N S_M^2(0) S_N^2(0) \Pi_{MN} \quad [77]$$

where μ_B represents the Bohr magneton. Each Π_{MN} term can be of either sign and refers to the contribution of each single excitation.

Within the CLOPPA approach, the FC term has the expression (see Eqs. [73] and [74]):

$$J^{\text{FC}}(M, N) = \Omega^{\text{FC}} S_M^2(0) S_N^2(0) \times \sum_{ia,jb} C_{iM}^s C_{aM}^s C_{jN}^s C_{bN}^s {}^3\mathbf{P}_{ia,jb} \quad [78]$$

From this equation, it is straightforward to relate the Pople-Santry model with the first term in the expansion by series of J^{FC} (80)

$$J_S^{\text{FC}}(M, N) \approx \Omega^{\text{FC}} S_M^2(0) S_N^2(0) \times \sum_{ia,jb} C_{iM}^s C_{aM}^s C_{jN}^s C_{bN}^s \left(\mathbf{E}^{-1} \sum_{n=0}^p ({}^3\mathbf{N}\mathbf{E}^{-1})^n \right)_{ia,jb} \quad [79]$$

Then each individual coupling pathway contribution is written as a series

$$J_{S,ia,jb}^{\text{FC}} = \Omega^{\text{FC}} S_M^2(0) S_N^2(0) \left[C_{iM}^s C_{aM}^s C_{jN}^s C_{bN}^s (\epsilon_a - \epsilon_i)^{-1} \delta_{ij} \delta_{ab} + C_{iM}^s C_{aM}^s C_{jN}^s C_{bN}^s \frac{(\langle ab|ji \rangle + \langle aj|bi \rangle)}{(\epsilon_a - \epsilon_i)(\epsilon_b - \epsilon_j)} + \text{higher order terms} \right] \quad [80]$$

Here the first term is the same as that of Eq. [77] representing the zeroth-order contribution within the polarization propagator at any level of approach. In the same manner, it is possible to obtain zeroth-order contributions when PSO or SD terms are calculated with response schemes.

The development of the principal propagator as a series, together with the analysis of how close to zero their eigenvalues can be in order to get the inversion of the corresponding matrix, was used to understand the old problem of instabilities and quasiinstabilities (QIs). We have found an alternative and efficient procedure to partially overcome this problem (81).

Relationship Between the Matrix Elements of the Principal Propagators and the HF's Stability Problem. Theoretical study of the NMR- J spectroscopic parameter in compounds which are of interest for organic and inorganic chemistry is many times plagued with problems of instabilities or QIs when

the calculations are done at RPA level of approach. In such a case, the restricted Hartree-Fock (RHF) electronic ground state of the given molecular system is not (quite close to) the lowest energy state, but a triplet state is (quite close to) the lowest. In this case at least one eigenvalue of the triplet-type principal propagator is negative (close to zero) and it is said that the whole system is nonsinglet unstable (quasi unstable). Then it is not possible to calculate the FC or SD contributions to J . In the case of QI problems one can get FC or SD contributions but overvalued. So when this happens one cannot make any theoretical analysis of calculated J s (84, 85).

If the molecular system has a π -electronic framework, it is very likely that it will produce at least QI problems for calculations at RPA level (36, 85–87). But also some saturated compounds could have that kind of problems (76). The usual way to overcome this problem by ab initio methods is to use post-RPA schemes (i.e. including more electron correlation),

Table 2 FC Contributions to *J* (in Hz) in H₂CCH₂ and H₂CNH for the Complete RPA Calculation and for Different Prescriptions Concerning the Removal of Two-Electron Contributions to the Principal Propagator Matrix

	${}^3P_{\pi\pi^*,\pi\pi^*}$	${}^1J_{C-X}$	${}^1J_{C-H}$	${}^2J_{C-H}$	${}^2J_{H-H}$	cis- ${}^3J_{H-H}$	trans- ${}^3J_{H-H}$
H ₂ CCH ₂							
a	146.19	226.04	321.43	−154.33	−131.43	120.29	142.66
b	6.53	34.30	178.05	−10.90	−24.13	13.00	35.36
c	3.73	30.46	175.18	−8.02	−21.98	10.85	33.98
d	2.42	28.65	173.82	−6.67	−20.97	9.83	32.19
SOPPA(CCSD) ^a		76.25	156.29	−1.49	0.40	12.17	18.51
H ₂ CNH							
a	19.75	1.16	192.96	−22.30	1.47	33.16	56.85
b	4.80	6.93	179.87	−12.42	11.24	26.05	49.47
c	3.04	7.60	178.33	−11.26	12.38	25.22	48.61
d	2.05	7.98	177.47	−10.60	13.03	24.75	48.12
SOPPA(CCSD) ^a		−10.14	160.72	−10.36	16.88	18.36	25.01

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(a) Every term is taken as such. (b) The $\langle ab|ji \rangle$ integral is removed from the problematic matrix element. (c) The $\langle aj|bi \rangle$ integral is removed from the problematic matrix element. (d) Both integrals are removed.

^a Taken from Ref. (88).

though this results in a restriction on reliable calculations only for small-size molecules. The other way to tackle that problem is to apply a more crude approximation which is used on semiempirical methods. A different alternative was developed in Ref. (81) to handle with nonsinglet QIs. It is worth to mention that semiempirical schemes were designed in such a way that they use some empirical parameters to fit theoretical results with experiments. This means that electron correlation is included in a suitable, though unsystematic way. This explain why semiempirical calculations of NMR-*J* parameters fit at least in a qualitative (sometimes semiquantitative) way with experimental results.

Several criteria were given in order to know whether a calculation could be affected by QI problems. Two of them are: i) the HOMO-LUMO difference and ii) the value of the smallest eigenvalue of the principal propagator matrix (76, 84). In Ref. (81) we proposed a new criterion that refers to the maximum value of the matrix element $v_{ia,jb}$ (see Eq. [79]), where

$$v_{ia,jb} = ({}^3NE^{-1})_{ia,jb} \quad [81]$$

We should expect a QI problem every time $v_{ia,jb}^{\max}$ is larger than 0.75. This is equivalent to have a lowest eigenvalue of the RPA principal propagator matrix lower than 0.11 (84).

It is known that $v_{ia,jb}^{\max}$ is close to 1 for some molecules with a π -electronic system like H₂CCH₂

($v_{\pi\pi^*,\pi\pi^*}^{\max} = 0.964$) and H₂CNH ($v_{\pi\pi^*,\pi\pi^*}^{\max} = 0.885$). In order to minimize QI problems one can implement the following procedure:

1. Evaluate $v_{ia,jb}^{\max}$.
2. If this value is larger than 0.75 remove the integrals $\langle ab|ji \rangle$ and/or $\langle aj|bi \rangle$ that corresponds to the (ia,jb) coupling pathway.
3. Calculate again all principal propagator matrix elements and check whether $v_{ia,jb}^{\max}$ is lower than 0.75.

In Table 2 we show how this procedure works for the model systems H₂CCH₂ and H₂CNH. In both systems $v_{ia,jb}^{\max}$ is larger than 0.75 and corresponds to the $\pi\pi^*, \pi\pi^*$ coupling pathway. All couplings are overvalued for the complete RPA calculations. The principal propagator matrix element for that coupling pathway diminishes drastically when any or both of the MO integrals, $\langle ab|ji \rangle$ and/or $\langle aj|bi \rangle$ are removed. It is observed that *J*-couplings become closer to SOPPA(CCSD) results when this procedure is applied. Some of these couplings are better reproduced, mainly couplings such as ${}^1J_{C-H}$, ${}^2J_{N-H}$ and both vicinal couplings. It is worth to mention that couplings for which the problematic coupling pathway is much involved cannot still be well reproduced, and that is something we should expect.

The Sign of *J*. Let's now analyse one of the most conspicuous physical properties of the NMR indirect nuclear spin couplings: its sign.

It is well known that not only the absolute value of J but also its sign is of great value when one tries to get structural and electronic information from NMR spectra (85). Nuclear spins can be coupled without electron transmission of their perturbation on the electronic molecular system. Direct coupling, D , as this last mechanism is called, may be used to obtain information about the absolute sign of J . Given that the sign of D can be obtained when the sample is subjected to an external electric field, and the fact that the relative signs of D and J can be derived from spectra of a partially oriented molecule, the absolute sign of J can be inferred from an electric-field experiment (89). One needs to know at least the absolute sign of only one coupling constant in order to get the sign of all others in a relative way (90).

One can ask oneself about the physical process that produce the sign of J , given that it does not arise from a convention. There are old and relative new models trying to explain this phenomenon. The oldest one is referred as Dirac-Peenev model (48) and is one of the most used by NMR spectroscopists. This model considers only the FC mechanism that is described by the Hamiltonian of Eq. [39]. If the gyromagnetic constant is positive, then from Eq. [39] the molecular system is more stable when the electron spin and the nuclear spin are antiparallel. In the same manner, considering the NMR phenomenological Hamiltonian of Eq. [19], the system is more stable when both nuclear spins are antiparallel assuming that J_{MN} is positive, because in this case the magnetic interaction energy of the two nuclei, M and N, will diminish the total energy of the molecular system. This vector model for J -couplings predict a positive J for the HD molecule as observed in Fig. 1. This would happen for every coupling of nuclei with positive gyromagnetic constants. In practice not all couplings of nuclei with positive gyromagnetic constants are positive. If the electron spin-nuclear spin interaction is transmitted through a third atom, the electrons that are close to the nucleus of this atom fulfil Hund's rule so that they are more likely parallel as shown in the Fig. 1. Then the coupled nuclear spins that are separated by two bonds will tend to be parallel and so the system will be more stable when J is negative. The extension of this model to coupled nuclei separated by any number of bonds shows that when the number of bonds in the middle are odd, the interaction energy will stabilize the system when J is positive, and negative when the number of intermediate bonds are even. This is not always the case as happens for the geminal coupling $^2J_{H-H}$ in formaldehyde. There is also another shortcoming because that model is valid for J -couplings transmitted only by

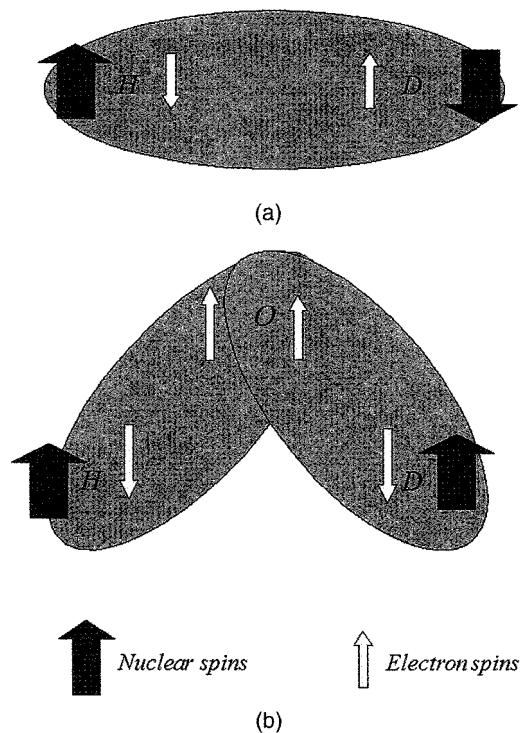


Figure 1 Schematic representation of the Dirac-Peenev vector model applied to (a) one-bond coupling for the HD molecule and (b) two-bond coupling for HDO molecule. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

σ -type molecular orbitals. It explains a large attenuation of the coupling for nuclei that are distant more than four bonds between them.

Recently Del Bene and Elguero (91) proposed another model, the nuclear magnetic resonance triplet wave-function model (NMRTWM) applied only to molecules that belongs to $D_{\infty h}$ point groups; specifically the linear systems of type $A_1-B_1 \dots B_2-A_2$. They assume that the orientation of the nuclear magnetic moment vector responds to the phase of the excited triplet state wavefunction, and arbitrarily assign nuclear spin up (\uparrow) when the wavefunction is positive and down (\downarrow) when it is negative. Then, from the analysis of the nodal pattern of each excited state one can infer the individual contribution to J . In the case of molecules of type $A_1-B_1 \dots B_2-A_2$ one can in principle consider only two patterns of excited triplet states $^3\Sigma_g^+$ and $^3\Sigma_g^-$ and obtain an arrangement of all nuclear spin vectors belonging to the molecule. Finally the sign of the total coupling constant is the result of competing positive and negative contributions from all excited triplet states. They were able to

Table 3 Contributions of the Main Coupling Pathway Terms (in Hz) and Their Perturbator and Principal Propagator Elements for the Geminal H—H Coupling in Formaldehyde

<i>i</i>	<i>a</i>	<i>j</i>	<i>b</i>	$J_{ia,jb}$	$P_{ia,jb}$	$U_{ia,H2}$	$U_{jb,H1}$	$U_{ia,H1}$	$U_{jb,H2}$
σ_1	σ_2^*	σ_2	σ_2^*	18.43	−0.81	0.028	−0.003	−0.028	0.266
σ_1	σ_1^*	σ_2	σ_1^*	18.43	−0.81	−0.003	0.028	0.266	−0.028
σ_1	σ_1^*	σ_2	σ_2^*	−7.04	−0.03	−0.003	−0.003	0.266	0.266
σ_1	σ_2^*	σ_1	σ_2^*	4.47	−1.85	−0.028	0.028	0.028	−0.028
σ_1	σ_1^*	σ_2	σ_1^*	4.47	−1.85	−0.028	0.028	0.028	−0.028
σ_1	σ_1^*	σ_1	σ_1^*	7.18	−2.97	0.266	0.266	−0.266	0.003
σ_2	σ_2^*	σ_2	σ_2^*	7.18	−2.97	−0.003	−0.003	−0.003	0.266

predict different signs of F—F couplings in both arrangements: H—F...F—H (which would be positive) and F—H...H—F (negative). This last case should be positive from Dirac-Peeney vector model. The NMRTWM model was also successfully applied to analyse the sign of the reduced ${}^{2h}K_{XY}$ couplings transmitted through A—H—D hydrogen bonds where A, D were atoms of O, N, C and F (92). A final remark is on the magnitude of the contribution to J for a given pair on nuclei from a particular excited state: it depends on the electron densities (mainly s-electron).

Let's have a look on what can we get from the CLOPPA model (93). For convenience let's write again Eqs. [72] and [73] for $X = FC$

$$J_{MN}^{FC} = \sum_{ia,jb} J_{MN,ia,jb}^{L(FC)} \\ = \sum_{ia,jb} \left(U_{M,ia}^{FC} U_{N,jb}^{FC} + U_{N,ia}^{FC} U_{M,jb}^{FC} \right)^3 P_{ia,jb} \quad [82]$$

In actual calculations, there are in general only one term of Eq. [82] that contribute much more than the other. This term is such that both *perturbators* are built from LMOs that have a larger slope in each nucleus of interest compared with the slope of the corresponding LMOs of the other two perturbators.

Within the CLOPPA model, the diagonal matrix elements of the principal propagator are negative. But this is not the case for its nondiagonal matrix elements. In such a case there is always the possibility for changing the sign of a pair (${}^3P_{ia,jb}$; $U_{M,ia}^{FC}$) without any change on the sign of J . So we will use that arbitrariness to consider principal propagator matrix as negative terms.

The sign of a perturbator $U_{M,ia}^{FC}$ has implicit relation between the phases of the LMOs that are involved in the virtual excitation $i \rightarrow a$ in the site of the nucleus M. Its sign is positive (+) when both LMOs have the same phase. Within the monocentric approximation, the sign of the phases is carried out by the coefficients of Eq. [78]. Then within our model

the sign of each coupling pathway, i.e. $J_{ia,jb}$ is completely defined through the sign of both perturbators U_M^{FC} and U_N^{FC} for that given coupling pathway (93).

A typical example is the geminal coupling ${}^2J_{H-H}$ in the formaldehyde. The Dirac-Peeney vector model predicts a negative J -coupling though it is known positive. Some of their most important coupling pathway contributions are given in Table 3. Both C—H bonds are involved in all the main coupling pathways. This means that the virtual excitations to be considered are those where the excitations arise from bonding and antibondings of both C—H bonds, i.e. the bonding and antibonding of C—H₁ bond: σ_1 and σ_1^* , and their equivalents for the bonding and antibonding of C—H₂ bond.

As observed in Table 3 there is only one negative term: $J_{\sigma_1\sigma_1^*,\sigma_2\sigma_2^*}$. This term corresponds to the Dirac-Peeney model, because it considers the excitation of both bonding \rightarrow antibonding belonging to each bond C—H separately. All other terms are positive (!). They arise from excitations that mix bondings and antibondings of both C—H or belongs to only one C—H bond. The main point here is the fact that the sign of each coupling pathway term is defined completely by the relative signs of the larger product of two perturbators belonging to that coupling pathway. For example the sign of the first term in Table 3 arises from the product between $U_{\sigma_1\sigma_2^*,1}$ and $U_{\sigma_2\sigma_2^*,2}$. The sign of these two perturbators is opposite, which means that the relative phases of both virtual excitations at the site of both nuclei is opposite: the phases of the bonding and antibonding LMOs of the virtual excitation $\sigma_1 \rightarrow \sigma_2^*$ at the site of the nucleus 1 are different, and the phases of the bonding and antibonding LMOs of the virtual excitation $\sigma_2 \rightarrow \sigma_2^*$ at the site of the nucleus 2 are similar. In summary, the sign of each coupling pathway term, $J_{ia,jb;MN}$, arises from the relative phases of the excitations $i \rightarrow a$ at the nucleus M and $j \rightarrow b$ at the nucleus N, or $i \rightarrow a$ at the nucleus N and $j \rightarrow b$ at the nucleus M, with independence on how far away are both coupled nuclei M and N (!).

Table 4 Contributions of the Main Coupling Pathway Terms (in Hz) and Their Perturbator and Principal Propagator Elements for the Geminal H—H Coupling of Methane and the One-Bond C—F Coupling in CH₃F

<i>i</i>	<i>a</i>	<i>j</i>	<i>b</i>	<i>J</i> _{<i>ia,jb</i>}	<i>P</i> _{<i>ia,jb</i>}	<i>U</i> _{<i>ia,H2</i>}	<i>U</i> _{<i>jb,H1</i>}	<i>U</i> _{<i>ia,H1</i>}	<i>U</i> _{<i>jb,H2</i>}
CH ₄									
σ ₁	σ ₁ [*]	σ ₂	σ ₂ [*]	−58.15	−0.26	0.000	0.001	−0.273	−0.273
σ ₁	σ ₂ [*]	σ ₂	σ ₂ [*]	4.88	−0.47	0.000	0.001	0.013	−0.273
<i>i</i>	<i>a</i>	<i>j</i>	<i>b</i>	<i>J</i> _{<i>ia,jb</i>}	<i>P</i> _{<i>ia,jb</i>}	<i>U</i> _{<i>ia,F</i>}	<i>U</i> _{<i>jb,C</i>}	<i>U</i> _{<i>ia,C</i>}	<i>U</i> _{<i>jb,F</i>}
CH ₃ F									
σ ₁	σ ₁ [*]	σ ₁	σ ₁ [*]	452.72	−2.40	−1.036	0.254	0.254	−1.036
LP	σ ₁ [*]	σ ₁	σ ₁ [*]	−538.84	−0.75	4.008	0.254	0.014	−1.036

As a second example we propose the geminal H—H coupling in methane. As observed in Table 4, the principal coupling pathway term is by far the diagonal, which is equivalent to that of the Dirac-Peeney model. All others are much smaller. This gives a natural explanation on why the sign of *J* is positive in this case. In the same Table we give the partial contributions of two coupling pathway terms for the one-bond coupling ¹*J*_{C—F} in CH₃F. We give only two terms which are by far the more important. One is the diagonal which is positive as should be, the other one is negative and more important than the diagonal. For the largest term, one of both excitations starts from the lone pair MO, LP. Its sign arises from the fact that the main perturbators have the same relative phases in their excitations.

This interpretation for the origin of the sign of *J* based only on the FC mechanism can be extended to the other two types of paramagnetic electronic mechanisms. It tells us that the origin of the sign of *J* arises from the “relative” phases of the LMOs that intervene in the given coupling pathways “at the site of the nuclei involved.” These relative phases are completely defined for any given molecular system. The results of previous models are contained within our model. We are now able to explain why the Dirac-Peeney rules for the sign of *J* are not fulfilled in all cases, as it happens with our model.

Electronic Origin of the Famous Karplus’ Rule.

From the early days of NMR spectroscopy, Karplus realized that vicinal couplings (couplings through three bonds) fulfil a rule which then was known as Karplus’ rule (94, 95): *J* has an harmonic dependence with the dihedral angle. This rule is independent of the nature of the coupled nuclei. Karplus’ rule is empirical, and is extremely useful to get structural information about any kind of molecular compounds.

There were several attempts to theoretically explain its electronic origin, from early days (96) to

recent years (97–101). In our case, when we developed the way to get the inverse of the principal propagator matrix (see Eq. [75]) we were able to add a new interpretation about this rule. Our CLOPPA model gives us two completely different elements that intervene in the calculation of *J*-couplings: perturbators which depends on two LMOs (one occupied and one unoccupied) and that may be close to the coupled nuclei: local perturbator or far away: nonlocal perturbator. The second element is the principal propagator matrix that depends on four LMOs, though in a way that the whole electronic structure of the molecule is involved. Given that Karplus’ rule is independent of the nature of the coupled nuclei and also of the nature of the other nuclei that are in the middle of the transmission pathway, one can think that this rule should arise from a subtle general mechanism.

We proposed few years ago that Karplus’ rule can be completely explained from an hyperconjugative mechanism (102). Our proposal differs from that of Weinhold and coauthors, mainly because we were able to have a different analysis of the electronic mechanisms involved. They suggested a hyperconjugative electron-transfer mechanism that involves only one partial electron transfer from a nearly doubly occupied (bonding) orbital to a nearly vacant (antibonding) orbital. We explicitly considered the fact that each coupling pathway term involves at least two simultaneous excitations, and then the hyperconjugative mechanism we are able to analyse, contains more details than the one-electron excitation mechanism proposed by Weinhold and collaborators and also by Contreras and collaborators. We also applied our procedure to get the principal propagator explicitly.

We had a look on whether one of the two different terms that define each coupling pathway may produce the dihedral angular dependence of vicinal *J*s. At this stage, we may have a guess: if only one term is responsible of that functional dependence it should be related with the principal propagator because it

and

$$H_{ia,jb} \equiv \langle ab|ji \rangle = \int \psi_a^*(1) \psi_j^*(1) r_{12}^{-1} \psi_b(2) \psi_i(2) dr_1 dr_2 \quad [85]$$

G is called Coulomb matrix because it represents a coulombic interaction between two electrons: an electron in a virtual state, when $a = b$, and the other electron in an occupied state, when $i = j$. In the same line of reasoning, H is called exchange integral matrix in our model.

Let's analyse a given molecular model: $H_3Sn-C_2H-SnH_3$ with few of the main excitations between occupied to vacant LMOs as shown in Fig. 2. It was shown in Ref. (102) that all coupling pathways follows a Karplus' curve. Then we investigated the most important terms. In Fig. 3 we show the dihedral angular dependence of some of them. We have introduced a particular nomenclature: a) local-with other-local hyperconjugative (LLH) means that both excitations are localized in the bonds of the coupled nuclei ($\sigma_1 \rightarrow \sigma_1^*$; $\sigma_2 \rightarrow \sigma_2^*$); b) double vicinal hyperconjugative (DVH) means two excitations of a vicinal type ($\sigma_1 \rightarrow \sigma_2^*$; $\sigma_1 \rightarrow \sigma_2^*$); etc.

When analysing the dihedral angular dependence of the matrix elements of perturbators and principal propagators belonging to that coupling pathways we found out that the principal propagator matrix elements and also nonlocal perturbators matrix elements follows a Karplus-type dependence. In the case of

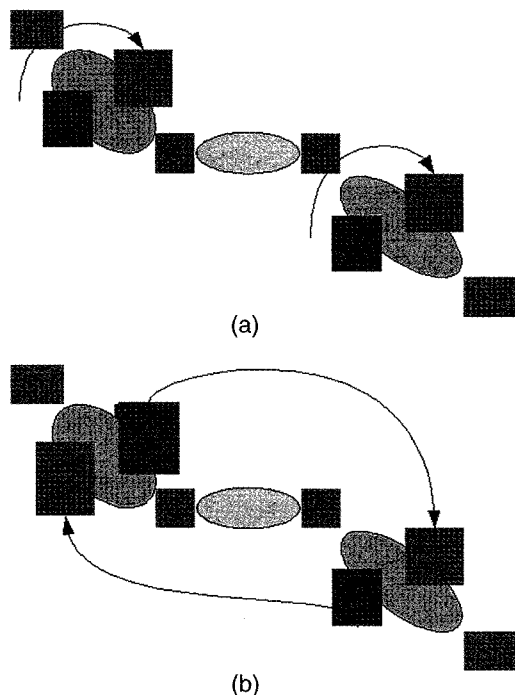


Figure 2 Some hyperconjugative mechanisms that involve two simultaneous excitations. (a) The main local-local hyperconjugative mechanism or LLH; (b) The double vicinal hyperconjugative mechanism or DVH. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

depends on the electronic behavior of the molecule as a whole. The matrix elements of the principal propagators should carry out the information from one part of the molecule to the other. The answer is affirmative. Not only that. Any coupling pathway term follows the Karplus' rule (!). Still there is a deeper insight on the physics that underlies this phenomenon. It is based on quantum physics and its discovery sheds new light on the NMR phenomenon.

Let's go back to Eq. [75]. There we developed each principal propagator matrix element as a series. The numerator of that series elements are the two-electron integrals of Eq. [53]. We will consider here only the FC coupling mechanism, so

$${}^3N_{ia,jb} = (G + H)_{ia,jb} \quad [83]$$

where

$$G_{ia,jb} \equiv \langle aj|bi \rangle = \int \psi_a^*(1) \psi_b^*(1) r_{12}^{-1} \psi_i(2) \psi_j(2) dr_1 dr_2 \quad [84]$$

Total FC values and some coupling pathway contributions

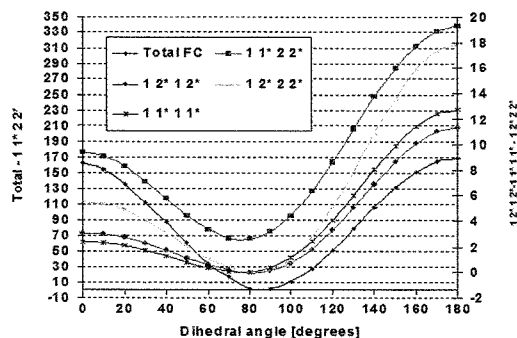


Figure 3 Coupling pathway contributions as a function of dihedral angle for vicinal ${}^3J(\text{Sn-Sn})$ couplings in the $H_3SnCH_2CH_2SnH_3$ molecule. The main bonding (anti-bonding) localized MOs for vicinal ${}^3J(\text{Sn-Sn})$ couplings are σ_1 and σ_2 (σ_1^* and σ_2^*). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

LLH coupling pathway mentioned earlier (and all others), both $P_{\sigma_1\sigma_1^*,\sigma_2\sigma_2^*}$ and $U_{\sigma_1\sigma_1^*,\text{Sn}_2} U_{\sigma_2\sigma_2^*,\text{Sn}_1}$ follow a Karplus-type curve, though the nonlocal perturber's contribution is quite small compared with their local counterpart. Then it does not intervene in the final contribution of the given coupling pathway, and so it is the principal propagator matrix element alone that one needs to analyze. This particular matrix element is a function of the following \mathbf{G} and \mathbf{H} matrix elements,

$$P_{\sigma_1\sigma_1^*,\sigma_2\sigma_2^*} \propto \mathbf{G}_{\sigma_1\sigma_1^*,\sigma_2\sigma_2^*} + \mathbf{H}_{\sigma_1\sigma_1^*,\sigma_2\sigma_2^*} \quad [86]$$

The dihedral angular dependence of \mathbf{G} and \mathbf{H} matrix elements is such that they follow a Karplus-type behavior only when at least one of the two electrons depends simultaneously on different LMOs describing fragments within which the coupled nuclei are included. In the case of the main coupling pathway LLH which we are analysing:

$$\mathbf{G}_{\sigma_1\sigma_1^*,\sigma_2\sigma_2^*} = \int \sigma_1^*(1)\sigma_2^*(1)r_{12}^{-1}\sigma_2(2)\sigma_1(2)d\mathbf{r}_1d\mathbf{r}_2 \quad [87]$$

and

$$\mathbf{H}_{\sigma_1\sigma_1^*,\sigma_2\sigma_2^*} = \int \sigma_1^*(1)\sigma_2(1)r_{12}^{-1}\sigma_2^*(2)\sigma_1(2)d\mathbf{r}_1d\mathbf{r}_2 \quad [88]$$

It is clear that in both matrix elements electron 1 depends on two different LMOs that are close to the coupled nuclei, i.e. $\psi_{\sigma_1^*}(1)$ and $\psi_{\sigma_2^*}(1)$ or $\psi_{\sigma_2}(1)$. A quite similar dependence is observed for electron 2.

There are terms for which their principal propagator matrix elements do not follow a Karplus' curve. They are such that neither electron 1 nor electron 2 does fulfil the restriction we mentioned earlier. As an example we analyze the $(\sigma_1 \rightarrow \sigma_1^*; \sigma_1 \rightarrow \sigma_1^*)$ coupling pathway which is called double-local hyperconjugative (DLH). Their Coulombic and exchange matrix elements of Eqs. [84] and [85] are

$$\mathbf{G}_{\sigma_1\sigma_1^*,\sigma_2\sigma_2^*} = \int |\sigma_1^*(1)|^2 r_{12}^{-1} |\sigma_1(2)|^2 d\mathbf{r}_1 d\mathbf{r}_2 \quad [89]$$

and

$$\mathbf{H}_{\sigma_1\sigma_1^*,\sigma_2\sigma_2^*} = \int \sigma_1^*(1)\sigma_1(1)r_{12}^{-1}\sigma_1^*(2)\sigma_1(2)d\mathbf{r}_1d\mathbf{r}_2 \quad [90]$$

The Coulombic matrix element gets its name from here. It expresses a Coulombic interaction between

electron 1 and electron 2 described by the electronic probability densities given by $|\psi_{\sigma_1^*}(1)|^2$ and $|\psi_{\sigma_1}(2)|^2$.

There are also intermediate situations where the restriction is fulfilled by only one of the two electrons, 1 or 2. In such a case, the principal propagator matrix elements follow a Karplus' curve, though their contributions are much smaller than that for the main coupling pathway terms. This is shown in Fig. 3.

Then Karplus' curve arise from a new type of entanglement, given that for second-order properties we must consider two simultaneous excitations, one for each of two "entangled" or "disentangled" electronic wavefunctions. Usual quantum entanglement means a nonlocal interaction of two different particles that may be photons, electrons, or whatever quantum particle may exist. In our case, if the description of at least one of the two excitations is entangled, then a Karplus' type behavior for the *coupling pathway* to which that excitation belongs to will be obtained. We assume here a nonlocal interaction of the same particle through occupied and vacant LMOs that describe its excitation. This conclusion have a lot of sense because we can realize now that when one of the excitations of the two electrons, say electron 1, which describe the propagation of the polarization produced by electron-spin nuclear-spin interaction, is given by LMOs that belongs to functions describing chemical bonds of *both* coupled nuclei, then that excitation is like an entangled excitation. So the description of that electronic excitation gives new insights on the particular physics of what is going on in both regions of the molecule to which coupled nuclei belongs. In a way this complements the finding of the physical origin of the sign of J : it depends on the simultaneous relative phases of LMOs describing excitations of two-electrons at the site of the coupled nuclei.

We can conclude this section on applications of the CLOPPA model saying that this model gives us a new and deeper understanding of the physics that underlies two of the most intriguing aspects of NMR J -couplings: its sign and the Karplus's rule. Furthermore in most cases, it reproduces experimental tendency and so one can apply this model to analyse the electronic mechanisms that are involved in the measured values of NMR J -couplings.

Nonrelativistic Ab Initio Schemes

The first implementation of SOPPA in a computational code was made by Oddershede and coauthors (103). Given that the implemented method did not introduce any external parameter different from the

basic electronic and mass charge, nuclear charges, etc. this was properly *ab initio*. As discussed in section II one needs to include the first-order correction to the reference state, $|0\rangle^{(1)}$, plus the h_4 manifold in order to get polarization propagators at second-order approach in the fluctuation potential. Any response molecular property can be expressed in a similar manner as was written at RPA level of approach (see Eq. [34]), but the property integrals (perturbators at RPA level) and the matrices that define the principal propagator contains more terms consistent with the order expansion mentioned earlier (50).

We want to give some applications of polarization propagators to calculate and analyse NMR spectroscopic parameters considering both domains, i.e. relativistic and nonrelativistic. NR examples will be given in this section and some full relativistic applications will be presented in the next section.

Large Long-Range Coupling Constants. Applying Dirac–Peeney vector model, one is forced to consider that indirect nuclear spin couplings should decrease quickly in magnitude when the number of intermediate bonds increases. We have shown in previous sections that this model is contained within the CLOPPA model, and so there are not only one but many alternative ways (coupling pathways) for the transmission of the indirect nuclear spin coupling through electrons. It may also be the case that Dirac–Peeney model is unable to predict correctly the transmission of nuclear-spin couplings in unsaturated molecular systems.

Several calculations were published (with results close to experimental findings) showing that when coupled nuclei are close in space, even though they may be separated by a long through-bond distance, their J -couplings are large (48, 104). This was explained considering a “through-space” mechanism, which means that indirect nuclear spin couplings could be transmitted by electrons even though there is no covalent bonds between them.

In the case of F–F couplings, several publications during the last few years reported unusually large long-range couplings; some of them explained by through-space mechanism (105, 106) but others due to conjugative effects or π -conjugation (77, 107). These last mechanisms are related with noncontact contributions (PSO and SD) as shown by recent calculations (108–110). Given also that unsaturated F-substituted carbon chains were used as quantum computers with five qubits (111), it is highly recommended to have a look on this kind of general systems. We investigated the magnitude and characteristics of long-range F–F couplings, ${}^{n+1}J_{F-F}$ in

1, n -difluoro-(alkanes, polyenes, cumulenes, and polyynes) (112). For J calculations in these kind of systems one should be very careful with the appearance of instabilities (or QIs). In the case of a largely conjugated system like (1, n) cumulenes, these problems will very likely appear even for calculations at SOPPA level of approach.

In Table 1 of Ref. (112) the behavior of the four coupling mechanisms in the four kinds of compounds mentioned earlier is shown. The most important for our purposes are the (1, n) difluoropolyenes. In these cases, the SD is the main F–F coupling mechanism which has a contribution of 9.46 Hz for a F–F bond distance of nine bonds (!). Its FC contribution is also not vanishingly small: 2.40 Hz. The total ${}^9J_{F-F}$ is 12.30 Hz. This means that it is highly probable that one can measure F–F indirect nuclear spin couplings in difluoro-polyenes where both F atoms are separated by distances of the order of 1–2 nm. There are still no experimental evidence that confirm or reject these theoretical findings.

Cooperativity Effects. Transmission of J -couplings through H-bonds were confirmed by experimental findings in proteins between a backbone amide proton and metal ions (113, 114); then extended to ${}^hJ_{N-H}$ in nucleic acid base pairs (115), ${}^{3h}J_{N-C}$ in proteins (116), and ${}^{2h}J_{N-N}$ and ${}^{1h}J_{N-H}$ in Watson–Crick base pairs in a DNA duplex (117). Precise experimental measurements together with quantum-chemical calculations of NMR spectroscopic parameters could give new insights on the physical nature of H-bonds, which is still a matter of discussion (118–122). H-bonds can be attributed to electrostatic plus polarization interactions or covalent interactions. They can also be considered partly due to both.

Cooperativity is a “global” electronic effect that may have an strong influence on “local” properties like the NMR spectroscopic parameters. We will be concerned with cooperativity effects that cannot be predicted by pairwise interactions. The meaning of this effect is such that when it appears on a system that is composed of, say $2n$ interacting monomers, the magnitude of its effect is larger than that arising from the sum of $(2n-1) + 1$ interacting monomers.

The analysis of the energetics for the linear chains $(HCN)_n$ and $(HNC)_n$ ($n = 1-6$) (123, 124) shows that these chains have important cooperativity effects. They are observed in the length of all hydrogen bonds which are shortened as the size of the cluster increases (125). Shall there be cooperativity effects on their NMR spectroscopic parameters? The analysis of inter- and intramolecular J -couplings shows that the answer is affirmative (123). One

should look for a new way to quantify cooperativity effects on local magnetic properties. Given a long chain of (HCN) monomers, the largest intramolecular $^1J_{C-N}$ is obtained within the second monomer mainly because of the FC mechanism. It is this mechanism that governs the behavior of most of the intra and intermolecular couplings. In the case of $^2J_{N-H}$, the PSO mechanism is as important as the FC. The general tendency is such that intramolecular couplings are larger for monomers in the middle of the chain.

We were interested in answering one of the main questions about the origin of cooperativity effects on J -couplings in that kind of linear chains: is the modification of the bonds length the main source of cooperativity effects on J -couplings? In the first place it was found that even when the C—H bond length is almost the same with independence of the number of monomers which form the chain, its $^1J_{C-H}$ coupling varies 8.3 Hz (3%) from monomer to pentamer. Furthermore C—N bonding distances are almost unchanged along the series of complexes, but their couplings varies from -12.9 Hz to -17 Hz. As a definitive explanation on the independence of the values of J -couplings with geometrical factors of bond length, we calculated all intramolecular J s for monomers with different geometries isolated or included in the chain. The answer was that even when the geometry considered was exactly the same, if the monomer is in the middle of the chain, all intramolecular J -couplings are quite more larger than equivalent J -couplings in those cases where the monomer is isolated.

Another interesting point related with intermolecular couplings in that linear chains is that of their sign. In most cases, the sign is opposite to the sign that one could infer from the Dirac–Peeney model. Del Bene and Elguero were able to explain the origin of these signs but in different H-bonded systems using their NMRTWM model. They found out that geminal J -couplings through H-bonding is almost always positive (92), as it happens in our case.

All J calculations for (HCN) $_n$ and (HNC) $_n$ linear chains were done at SOPPA level of approach. One needs to include as much correlation as possible due to QIs or instabilities that arise in unsaturated systems. In the case of H-bonded systems, this fact is less important than in unsaturated compounds.

Relativistic Regime

As mentioned earlier relativistic effects must be included in calculations of NMR spectroscopic parameters when considering heavy atom containing systems. Relativistic quantum mechanics is quite a different regime compared with the usual NR, and so

one should expect to get new physics or new understandings of the same phenomena only when staying working within the full relativistic theory. For example, spin-orbit terms arise from perturbative corrections to the pure NR Hamiltonian when one include the interaction between spin angular momentum and the orbital angular momentum; or when Dirac Hamiltonian is manipulated to get the Pauli's Hamiltonian. But one should always be aware that spin is no longer a good relativistic quantum number so that spin-orbit corrections arise only when one uses a "NR way of thinking."

It is interesting to note that pure relativistic effects appear in the case of paramagnetic contributions to NMR shielding, σ^p , of rare gases, where a nonzero value is obtained. This is a completely unexpected result from a NR point of view (126, 127). There are few recent review articles concerning the state of the art about relativistic effects on nuclear magnetic shieldings (127–130). This is a topic on which are working several research groups in the World and have some fundamental physical aspects to be clarified.

Another important difference comes from the analysis of the separation between para and diamagnetic terms. This is also a theoretical NR concept that cannot be confirmed by experiments. Within the relativistic polarization propagator approach (RPPA) there is only one term from which one obtains the whole contribution to both tensors: \mathbf{J} and $\boldsymbol{\sigma}$. Then the aforementioned separation arises from manipulation. If one goes up one step further in theory, i.e. within noncovariant QED theory, one can show that paramagnetic terms arise from virtual electron–electron excitations and diamagnetic terms arise from virtual electron–positron pair creation and annihilations.

Furthermore, within the NR regime there is a very important relationship between the nuclear magnetic shielding tensor and the spin-rotation tensor (131, 132). This is the basis for the establishment of the absolute shielding scale for nuclei of light elements that is no longer valid within the relativistic regime (!). One needs to generalize Flygare's derivation, but no one knows how to do it at the moment.

The Nonrelativistic Limit. As shown in Ref. (18), there is a natural way to get the NR limit of fully relativistic calculations of \mathbf{J} (and of course to other response properties like $\boldsymbol{\sigma}$) i.e. making $c \rightarrow \infty$ (see Eqs. [67] and [68]). As shown in Fig. 4 one gets (smoothly) accurate NR values of tensor \mathbf{J} when c arbitrarily goes to infinity. In actual calculations, it is enough to make $c = 10$ au. It is quite interesting to see this limit numerically. For $^1J_{H-Br}$ one can observe the way J changes its sign. It is worth to

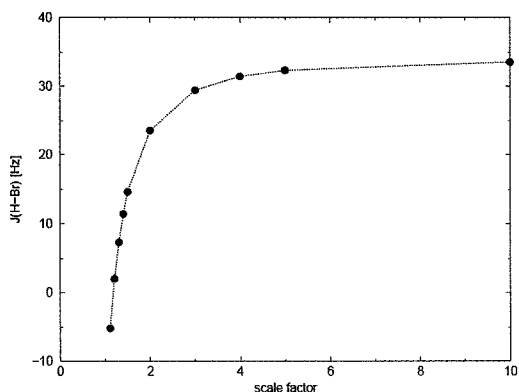


Figure 4 Indirect nuclear spin–spin coupling, $J(\text{HBr})$, in HBr molecule as a function of the speed of light.

emphasize that starting within the full relativistic expression of tensor J (see Eq. [64]) there appears all four Ramsey component when we make $c \rightarrow \infty$. There is a distinction between pseudosinglet and pseudotriplet components of J depending on time-reversal symmetry (46).

Fully Relativistic Calculations. In order to get indirect nuclear spin coupling results with independence of the gyromagnetic constant (that may be negative) one can use the reduced indirect nuclear spin coupling, K , which is defined as

$$K_{\text{MN}} = \frac{2\pi}{h} \frac{1}{\gamma_{\text{M}}\gamma_{\text{N}}} J_{\text{MN}} \quad [91]$$

Table 5 Fully Relativistic One- and Two-Bond Reduced Coupling Constants in XH_3 and XH_2 Molecular Systems^a

X	K(X–H)		K(H–H)	
	K^{iso}	ΔK	K^{iso}	ΔK
XH_3				
N	64.07 (63.94)	–17.59 (–15.49)	–2.04 (–2.05)	–2.94 (–2.99)
P	53.02 (52.73)	42.04 (43.67)	–2.04 (–2.09)	–0.98 (–1.05)
As	72.67 (84.18)	142.93 (121.75)	–2.43 (–2.51)	–0.78 (–0.95)
Sb	78.92 (143.56)	365.42 (217.97)	–2.68 (–2.65)	0.51 (–0.69)
Bi	–1367.83 (188.91)	1867.29 (468.40)	–7.29 (–3.40)	8.09 (–0.67)
XH_2				
O	63.14 (63.66)	10.70 (8.98)	–1.85 (–1.89)	–4.16 (–4.25)
S	45.14 (45.52)	43.10 (56.32)	–1.58 (–1.77)	–1.91 (–1.37)
Se	25.24 (46.15)	186.60 (165.23)	–2.04 (–2.13)	–0.97 (–1.15)
Te	–21.86 (86.01)	342.41 (343.67)	–1.90 (–1.95)	1.84 (–0.84)
Po	–1481.13 (73.70 ^b)	868.53 (330.59 ^b)	–2.67 (–1.61)	2.02 (1.90)

K is given in $10^{19} \text{ N A}^{-2} \text{ m}^{-3}$ units and nonrelativistic values are given in parenthesis.

^aTaken from Ref. (133).

^bCalculated with $c = 12$.

The first applications of the RPPA theory to calculate J (or K)-couplings with DIRAC code were done on XH_2 ($X = \text{O, S, Se, Te and Po}$) model compounds (55) and hydrogen halides (56); then extended to couplings in Sn-containing molecules (52).

One interesting relativistic effect on J -couplings is that which changes its sign in several one-bond couplings, like $^1J_{\text{X–H}}$ in XH_3 ($X = \text{N, P, As, Sb and Bi}$) and also in XH_2 ($X = \text{O, S, Se, Te and Po}$) model compounds. This effect was predicted by Pyykkö and Wiesenfeld (69), and Aucar and Contreras have completed the understanding of its origin applying the CLOPPA model (21).

As observed in Table 5 relativistic effects are important and their contributions are negative for K^{iso} . This is explicitly seen for molecules that contain atoms belonging to the 4th–6th rows of the periodic table (57). In the case of XH_3 systems, K change its sign for $X = \text{Bi}$. In the case of XH_2 systems the change of sign is explicitly seen for $X = \text{Te}$. As explained when applying semiempirical methods, the reason for the occurrence of that change of sign is the negative contribution of excitations that starts from lone pairs (21, 69). The absolute value of these LP contributions grows up when Z grows, becoming larger than the other contributions for BiH_3 and TeH_2 . NR results of Table 5 were taken using DALTON suite of programs (134) at RPA level of approach. The same basis set was used both in NR calculations and as the “large” component in relativistic calculations.

The anisotropic reduced nuclear spin couplings follows a similar behavior. Relativistic $\Delta K_{\text{H–H}}$ changes

its sign when $X = \text{Sb}$ in XH_3 and when $X = \text{Te}$ in XH_2 molecular systems. This is a relativistic effect that is larger in the case of XH_3 systems where there is no change of sign for their NR results of $\Delta K_{\text{H-H}}$.

DFT-Based Methods and Calculations

Even though this article is only based on development and applications of polarization propagator methodology within both regimes, nonrelativistic and relativistic, it deserves a short comment on the every time more popular basic scheme used to calculate J -couplings: density functional theory (DFT). Calculations within this methodology do not suffer of non-singlet instability problems (135), and given that DFT also includes electron correlation effects at a computational cost equivalent to that of HF methods, they can be applied to molecular systems of large size. There are several molecular systems for which there are still some difficulties to get reliable J -couplings, but there are continuous improvements in such a way that one could expect that these weaknesses will be diminished in the future.

The main drawback concerning DFT is the fact that there is no systematic way to improve the exchange-correlation functional which one shall apply on calculations. Several review articles appear recently, that contain evaluation and comparison of results based on OM methods and DFT calculations (35, 37, 77).

Until now there are no applications of polarization propagators with DFT approach. It would be interesting to start a program of research in this direction, given the performance of the DFT for calculating J -couplings.

SUMMARY

Propagators are very powerful tools not only to do reliable calculations on electric and magnetic molecular properties, but also to get insights on what are the electronic processes that underlie measurable spectroscopic quantities. Polarization propagators are defined in such a way that one can work with them within completely different frameworks i.e. relativistic and nonrelativistic. They are quantum-based theoretical objects that can naturally be obtained from the theory of QED. This fact gives solid grounds for the whole theoretical analysis that one can make with them.

In this article we have had the intention to show in an elementary and schematic way how one can obtain explicit expressions to calculate NMR J tensor

within both regimes: relativistic and nonrelativistic; and also the intrinsic relation that arise naturally between them. We have shown that we should be very careful when one wants to discuss electronic effects like relativistic effects by using theoretical tools based on NR theories. This is the case, for example, of the separation on para and diamagnetic effects. Dia- and para-magnetism arise only as an approximation of a unique full relativistic expression. Diamagnetic contributions to any magnetic response property is completely described by an interval of excitation energies: $2mc^2 \leq |\epsilon_i - \epsilon_s| < 4mc^2$ [see its analysis for the case of nuclear magnetic shielding (136)]. All these news and some others arise only within the full relativistic regime. Then when working within the proper relativistic regime one should avoid to think on magnetic properties in the same manner as in the usual NR regime. If we want to get new insights on the physics (purely relativistic) underlying heavy-atom containing molecules we should stay working within the full relativistic framework. Otherwise by making manipulations that guide us to get semi or quasirelativistic expressions, we always loose part of the physical content of the best predictive theory we have at the moment.

Another important issue we have addressed in this article refers to the development of theoretical models and their implementations, based on polarization propagators at different levels of approach. Starting from the semiempirical CLOPPA model we end up into ab initio schemes of calculations. Applying the CLOPPA model we were able to obtain new insights on the origin of some of the most conspicuous properties of NMR spectroscopic parameters, like the sign of NMR- J coupling and the electronic origin of the Karplus' rule. The development of the concept of coupling pathways defined by two excitations (from one occupied to one virtual MO) was crucial for our understanding on the underlying physics. From then we realized that the relative phases of the occupied and virtual MOs at the nuclear sites are the only important factors that one should consider in order to predict the sign of any indirect spin-spin coupling. Our model generalizes previous models as the Dirac-Peeney and also the Pople-Santry model.

When we want to understand the electronic origin of the famous Karplus' rule we found out that the matrix elements of the principal propagators are the main factors that explain it. We stressed that the hyperconjugation mechanism is responsible for this rule but considering two simultaneous excitations. In these excitations, one or two of the excited electron states may be entangled. If this happens, the corresponding matrix elements of the principal propagator

matrix follow a Karplus' type dependence with the dihedral angle. So this is a deep insight on the way a quantum information (the nuclear spin of a given nucleus) is transmitted from one to any other nucleus with nonvanishing nuclear spins.

As an important application of *ab initio* schemes for calculations of NMR spectroscopic parameters at second-order level of approach we showed the prediction of large long-range F—F coupling constants in conjugated systems. We predict measurable J_{F-F} for systems where both coupled nuclei are separated by a distance of the order of 1–2 nm. This means that these molecular systems can be good candidates for quantum computers containing more than seven qubits as suggested in Ref. (112).

At the same level of approach we investigated cooperativity effects on NMR coupling constants. We showed that by measuring coupling constants in a linear chain of H-bonded monomers containing C, N, and H one can infer from what element of the chain that coupling does arise.

Finally, we have shown some examples of relativistic effects on heavy atom containing molecules, and the way one finds their NR limit within the scheme of polarization propagators.

At first sight, polarization propagators may appear to a broad audience as quite complicated theoretical devices that only some experts on this field can understand and manipulate. We believe that our presentation showed that this is not the case. The beauty and simplicity of the equations involved when working within the full relativistic framework, their natural NR limit, the predictive power and reliability of proper calculations, and the number of new insights that one can grasp when applying simple models makes the polarization propagators as one of the most wonderful theoretical devices one has at hand to treat and learn on NMR spectroscopic parameters.

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BIOGRAPHY



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