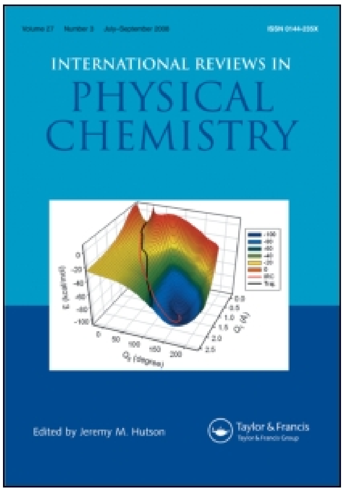

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Polarization propagators: A powerful theoretical tool for a deeper understanding of NMR spectroscopic parameters

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Polarization propagators: A powerful theoretical tool for a deeper understanding of NMR spectroscopic parameters

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Magnetic molecular spectroscopic properties, like NMR **J**-coupling and magnetic shielding σ, have been studied by non-relativistic quantum methods since their discovery. When they were found to depend strongly on relativistic effects in molecules containing heavy atoms, this started a new area of intensive research into the development of methods that include such effects. In most cases non-relativistic concepts were extended to the new field though keeping the previous non-relativistic point of view. Quantum mechanics can be formulated by two different formal approaches. Molecular physics and quantum chemistry were developed mostly within the Schrödinger or Heisenberg approaches. The path integral formalism of Feynman is less well known. This may be the reason why propagators are not broadly known in this field of research. Polarization propagators were developed in the early 1970s. Since that time they have been successfully applied to calculate NMR spectroscopic parameters. They are special theoretical devices from which one can do a deep analysis of the electronic mechanisms that underly any molecular response property from basic theoretical elements, like molecular orbitals, electronic excitation energies, *coupling pathways*, *entanglement*, contributions within different levels of theory, etc. All this is obtained in a natural way in both regimes: relativistic and non-relativistic. Its relativistic generalization in the early 1990s and the finding of a quantum electrodynamic (QED)-based theory for them, has given us the opportunity to improve our understanding of the physics behind such parameters. In this paper we give a presentation of polarization propagators that start in non-relativistic quantum physics and end up with the introduction of QED effects. The same and powerful basic quantum ideas are applied throughout this review, so that coherence and beauty arise in a natural way. We will give a new understanding that comes from the three levels of theory: non-relativistic, relativistic and QED. We will be cautious to highlight what one can learn when working in any of these regimes, being aware that the same concepts may have different meanings. Starting with a general overview of polarization propagators we develop both the theory and applications in each of the three levels mentioned above. We show how some of the most subtle properties of the NMR spectroscopic parameters can be explained in a simple and beautiful way: the sign of **J**, the Karplus rule, cooperative effects, diamagnetic and paramagnetic contributions; we also show

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new rules that appear within the relativistic regime and the way previously valid rules within the non-relativistic theory are broken. We highlight the fact that within the relativistic theory of polarization propagators the whole set of electronic mechanisms that appears within the NR regime and within its quasi-relativistic extension is unified. Furthermore the usual notion of diamagnetism and paramagnetism are now nonsense as such because they arise only after as an approximation from expressions which include a unique type of electronic (electron–positron) mechanism.

Keywords: polarization propagators; NMR spectroscopic parameters; electron correlation; Karplus rule; relativistic effects; diamagnetism; QED effects; gauge invariance

Contents

1. Introduction

Propagators are mathematical tools introduced in physics in the early 1940s, mainly by Richard Feynman [1], in order to develop a quantum theory equivalent to that of Heisenberg and Schrödinger, although from a different perspective. The main driving force was perhaps the explanation of quantum effects or quantum phenomena from theoretical ideas that may have a similar flavour to those of classical physics or the physics behind the least action principle. Within the path integral formalism infinitely many pathways contribute with a definite probability amplitude to the final calculated results which correspond to the measured property. That formalism can straightforwardly be written in terms of the usual molecular orbital language of molecular physics and quantum chemistry, so that the powerful physical and chemical ideas behind what was later called propagators can be applied to phenomena that are studied within this field of science. The Feynman propagator is a particular Green's function properly defined within the framework of quantum theory.

Propagators were introduced into molecular physics and quantum chemistry 30 years after their discovery, i.e. in the early 1970s [2]. Oddershede and Jorgensen were the main contributors to the development of polarization propagators from the beginning [3–5]. The application of such propagators to *ab initio* calculation of NMR spectroscopic parameters [6,7] was at that time exclusively based on the non-relativistic (NR) theory of Ramsey [8–12]. A *semi-empirical* scheme for calculating NMR **J**-couplings was developed by Contreras and coauthors in the 1980s [13–15].

In the early 1990s a generalization of such polarization propagators for including relativistic effects was presented [16]. It resorts to the same formal definition but its application within the Dirac formalism led to a new and interesting interpretation (or its complete modification) of previous well-established NR physical concepts, like the diamagnetic contribution to magnetic properties. It was quite remarkable that NR limits were obtained from the relativistic expressions, making c go to infinity. This is in line with the relationship between relativistic and non-relativistic classical expressions. They can be obtained taking the limit $c \rightarrow \infty$, though within the relativistic regime completely new concepts appear that modify our perspective of the world around us. Another fundamental aspect discovered when working within the relativistic regime is the fact that a single electronic mechanism arise as the source for each of both NMR spectroscopic parameters. The unification of the four NR traditional mechanisms – Fermi-contact (FC), spin-dipole (SD), paramagnetic spin-orbital (PSO), and diamagnetic spin-orbital (DSO) – for **J**-couplings, in a single mechanism can be considered an important step forward. Indeed, the inclusion of the leading relativistic corrections to these NR terms gives rise to some further terms which are related to different kinds of interplay between spin-independent and spin-dependent perturbed operators. This unification is of great help and shows that one can expect some more news on the physics described with such relativistic polarization propagators.

During the last few years, a quantum electrodynamic (QED)-based version of polarization propagators was developed [17,18]. This is another step upward in the theory from their relativistic formulation. It makes it possible to analyse the physics including radiative phenomena and also provides a deeper understanding of the electronic and nuclear origin of NMR spectroscopic parameters. Application of such a formalism allows us to explain what seems to happen within the region close to the magnetic nucleus, when they interact with the electron's charge, its spin and external magnetic fields. From a covariant approach of the formalism it is meaningless to talk about diamagnetic and paramagnetic contributions. They appear as NR artefacts, though such a splitting can be obtained when the polarization propagators are expressed in a non-covariant formulation. This is a nice finding: diamagnetic and paramagnetic terms of both NMR spectroscopic parameters, i.e. the nuclear magnetic shielding tensor, σ, and the indirect nuclear spin coupling tensor, $\mathbf{J}$, can be understood as related to the two non-covariant types of Feynman diagram corresponding to an electronic system interacting with two external magnetic fields. This explains, on different theoretical grounds, why they are not gauge-invariant when treated separately or, in other words, why the gauge-invariance is only fulfilled for calculations involving both terms.

The beauty and predictive power of propagators is not exclusive to the relativistic regime and QED theory. It was already appreciated within the NR regime where the subtle quantum behaviour of σ and $\mathbf{J}$ was easily explained, such as the origin of the sign of $\mathbf{J}$ which can be related to the relative phases between occupied and virtual molecular orbitals (MOs), as well as the origin of the Karplus rule. Aside from such physical insight calculation of molecular properties with polarization propagators, are between the most reliable ones.

The main purpose of this review article is to give a brief (though as complete as possible) introduction to polarization propagators independently of the regime where they are applied, whether non-relativistic or relativistic. We will give some fundamentals of the general theory and models that were developed within the last 20 years to calculate and analyse some of the most important electronic effects on NMR σ and $\mathbf{J}$. We will emphasize the ideas behind propagators and try to exploit them to get a global understanding on what one can grasp from the application of this theoretical tool.

We start with the basic definition of polarization propagators and their formal development to calculate and analyse molecular response properties. Non-relativistic theory and models are then revisited. We show several specific applications with *ab initio* and *semi-empirical* models. The next step is to introduce the relativistic theory and finally the QED-based theory. We describe the relatively new field of relativistic quantum chemistry (applied to molecular magnetic properties) in a manner that should be accessible to non-experts in this field. We introduce some new concepts that are needed to follow the formal development, and give more details in what we believe are new understandings arising from our formulation. As an example, we shall give some new insights into what are the negative-energy states that appear when solving the Dirac or fully-relativistic equations. The appearance of *virtual* negative-energy states or equivalently *virtual* electron–positron pair creation and annihilation is a new concept that goes further than the previous *virtual* orbitals, but is needed to describe magnetic molecular properties in a complete way.

2. Propagators: what are they and how do we apply them in theoretical molecular physics?

Quantum mechanics can be formulated in two different ways. In the usual approach the quantities $\mathbf{r}$ and $\mathbf{p}$ or the magnitudes of position and linear momentum are replaced by operators which obey Heisenberg commutation relations. Such operators act on functions which belong to a given Hilbert space. On the other hand, the path integral formulation of QM is less well known though it is completely equivalent to the previously mentioned approach. In this second form one needs to define a quantity, the *propagator* $K(t_f, \mathbf{r}_f; t_i, \mathbf{r}_i)$, which relates the wavefunction values at two different times and positions, $(t_i, \mathbf{r}_i)$ and $(t_f, \mathbf{r}_f)$, through the equation

$$\psi(t_f, \mathbf{r}_f) = \int K(t_f, \mathbf{r}_f; t_i, \mathbf{r}_i)\psi(t_i, \mathbf{r}_i)\mathrm{d}\mathbf{r}_i. \tag{1}$$

The propagator is related to the probability amplitude that a particle described by a wavefunction ψ at position $\mathbf{r}_i$ at time t_i is described by another wavefunction ψ at position $\mathbf{r}_f$ at time t_f. The main point to stress here is that such a probability involves the whole set of intermediate positions through which the particle may reach the point $(t_f, \mathbf{r}_f)$ having started at $(t_i, \mathbf{r}_i)$. One may say that the particle, in the path integral formulation, follows all possible paths connecting the initial and final points.

The propagator can be strictly defined in the non-relativistic domain for systems whose Hamiltonian is [19]

$$H = T + V = \frac{p^2}{2m} + V \tag{2}$$

through

$$K(t_f, \mathbf{r}_f; t_i, \mathbf{r}_i) = \Omega \int \mathcal{D}\mathbf{r} \exp\left[-\frac{i}{\hbar}\int_{t_i}^{t_f} L(\mathbf{r}, \dot{\mathbf{r}})\mathrm{d}t\right] \tag{3}$$

were Ω is a constant and $L = T - V$ is the Lagrangian of the system from which all equations of motion can be derived. Feynman started from this identity and then derived from it the corresponding Schrödinger equation.

The path integral formulation stresses a completely different perspective on the fundamental principle of linear superposition of quantum mechanics. This principle asserts that given n different wavefunctions that fulfil the Schrödinger equation corresponding to a given Hamiltonian of a system, their linear combination will give the general solution of that Schrödinger equation, the complex coefficients being the corresponding probability amplitudes. In the Feynman formulation such a linear combination is replaced by a superposition of all alternative pathways that are represented by all possible pathways that the system can follow from a given initial space-time point to the final space-time point. This is one of the main concepts from which one can grasp the interpretation that follows from a special type of propagator, the polarization propagator. When they are expressed in a MO basis they will be constructed as a summation over all possible electronic pathways that a perturbed density will follow from one point to another of the molecule. In a more general perspective, for quantum chemistry methods applied to calculate molecular properties, this will mean that the system will follow all possible excitations that contribute to the studied property.

The formal definition of propagators is the same whatever be the regime on which it is applied; they strive only on fundamental rules of quantum mechanics. Hence it is reasonable to expect them to be valid both in the relativistic and non-relativistic realms. In line with this, also the interpretation of propagators should have an equivalent flavour for every physical property to which it can be applied.

In linear response theory one describe how the average value of an arbitrary operator P develops when the external perturbation described by the operator Q is switched on. In the very special case of an electron propagator and within the NR regime, the corresponding Green's function may be considered to describe three successive steps: (i) the appearance of an electron at $(t_i, \mathbf{r}_i)$, (ii) the propagation of the electron from $(t_i, \mathbf{r}_i)$ to $(t_f, \mathbf{r}_f)$, and (iii) the disappearance of the electron at $(t_f, \mathbf{r}_f)$. Within this regime, the electron has only positive energies, so this process is physically acceptable for $t_f > t_i$. This will be modified when working within the relativistic regime.

Propagators are the Green's functions of the Schrödinger (Dirac) equation in the NR (R) regime. To describe processes that generate linear response properties of the electronic system, two-particle propagators are needed. Polarization propagators lend themselves to this because they are equivalent to two-particle double-time Green's functions.

2.1. *Response properties and polarization propagators*

The polarization propagator is defined as

$$i\langle\langle P(x); Q(y)\rangle\rangle = \hbar\theta\big(t_x - t_y\big)\langle 0|P(\mathbf{r}_x)Q(\mathbf{r}_y)|0\rangle + \hbar\theta\big(t_y - t_x\big)\langle 0|Q(\mathbf{r}_y)P(\mathbf{r}_x)|0\rangle, \tag{4}$$

where x and y stand for the space-time points $x = (t_x, \mathbf{r}_x)$ and $y = (t_y, \mathbf{r}_y)$, respectively. This definition is independent of whether the underlying theoretical framework is relativistic or non-relativistic [16], even though its first formulation was given within a non-relativistic regime [5]. This fact will be exploited widely in this article. The reference state $|0\rangle$ will be properly chosen according to the regime considered.

Since the polarization propagator has the same basic quantum nature as a wavefunction ψ one may ask for its equation of motion, i.e. how the polarization evolves with time. One can write explicit expressions for that equation of motion which can be solved by formal procedures [5,20]. Furthermore one can transform time-dependent expressions to their corresponding energy-dependent framework in order to make use of this tool in spectroscopic problems.

The equation of motion for propagators can be obtained by first applying the Heisenberg equation of motion for the time-dependent operators, $P(t)$ and $Q(t')$, and then Fourier transforming the final expressions [20]:

$$E\langle\langle P; Q\rangle\rangle_E = \langle 0|[P, Q]|0\rangle + \langle\langle [P, H_0]; Q\rangle\rangle_E. \tag{5}$$

Solving Equation (5) iteratively one gets 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 [21]: the superoperator technique. In Equation (5) H_0 is the unperturbed Hamiltonian describing the electronic system, and $|0\rangle$ represents the reference state that in our case will be a single-determinant state composed of one-electron wavefunctions which are solutions of the Hartree–Fock (HF; NR) or Dirac–Hartree–Fock equations (DHF; R), respectively.

The final form of the equation of motion obtained with superoperator algebra and the inner projection technique is [22]

$$\langle\langle P; Q\rangle\rangle_E = \left(P^\dagger|\mathbf{h}\right)\left(\tilde{\mathbf{h}}|E\hat{I} - \hat{H}_0|\mathbf{h}\right)^{-1}\left(\tilde{\mathbf{h}}|Q\right), \tag{6}$$

$\mathbf{h}$ being a complete operator manifold of basic excitation operators from which it is possible to describe the whole branch of excited states arising from a given reference state $|0\rangle$. The operators P and Q should also be described in terms of basic excitation operators belonging to $\mathbf{h}$. Furthermore, the basic excitation operators can be written with their explicit spin-dependence within the non-relativistic 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 [23]. This is a powerful way of obtaining excited states from the reference state and to solve the algebraic operations that are included in Equation (6). In this last equation there are two different type of factors: *perturbators* and *principal propagators*. We want to give their explicit form and meaning as a background of what follows.

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

$$(P|Q) = \langle 0|[P^\dagger, Q]|0\rangle, \tag{7}$$

while the effect of the superoperator $\hat{H}$ acting on the operator P is

$$\hat{H}P = [H, P]. \tag{8}$$

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 writing the equations is oriented to obtaining explicit formulas to be implemented in computational codes.

Any operator P can be written as

$$P = \sum_{p,q} P_{pq} a_p^\dagger a_q, \tag{9}$$

$a_p^\dagger$ and a_q being creation and annihilation operators, respectively. Another way to get the same expansion is by using spin-adapted excitation operators [24], that is,

$$P = \sum_{p,q} P_{pq} E_{pq}. \tag{10}$$

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

$$\mathbf{h} = \{\mathbf{h}_2, \mathbf{h}_4, \ldots, \}, \tag{11}$$

where

$$\begin{aligned} \mathbf{h}_2 &= \left\{a_a^\dagger a_i, a_i^\dagger a_a\right\}; \\ \mathbf{h}_4 &= \left\{a_a^\dagger a_b^\dagger a_i a_j, a_j^\dagger a_i^\dagger a_b a_a\right\}; \quad \text{etc.} \end{aligned} \tag{12}$$

and where $a, b, \ldots,$ refer to unoccupied HF or DHF orbitals, and $i, j, \ldots$ stand for occupied HF or DHF orbitals. Then, using this manifold decomposition, Equation (6) can be written in matrix form as

$$\langle\langle P; Q\rangle\rangle_E = \left(\mathbf{P}_a^\dagger, \mathbf{P}_b^\dagger, \ldots,\right)\begin{pmatrix} \mathbf{M}_{aa} & \mathbf{M}_{ab} & \ldots, \\ \mathbf{M}_{ba} & \mathbf{M}_{bb} & \ldots, \\ \ldots, & \ldots, & \ldots, \end{pmatrix}^{-1}\begin{pmatrix} \mathbf{Q}_a \\ \mathbf{Q}_b \\ \ldots, \end{pmatrix}, \tag{13}$$

where

$$\mathbf{P}_a = (P|\mathbf{h}_a), \tag{14}$$

and

$$\mathbf{M}_{ab} = \left(\mathbf{h}_a|E\hat{I} - \hat{H}_0|\tilde{\mathbf{h}}_b\right). \tag{15}$$

We can write Equation (13) in the more compact way

$$\langle\langle P; Q\rangle\rangle_E = \mathbf{b}^P\mathbf{M}^{-1}\mathbf{b}^Q. \tag{16}$$

The factor $\mathbf{M}^{-1}$ on the right-hand side of Equation (13) is known as the *principal* propagator, while $\mathbf{b}^P$ and $\mathbf{b}^Q$ are the property matrix elements or, as they were called within semi-empirical models, the *perturbators*. The principal propagator depends only on both the electronic molecular system as a whole and the spin (time-reversal) dependence of the perturbators, but it is independent of the particular molecular property. It gives the main streamlines of transmission of the interaction between the external perturbations related to the property matrix elements, through the unperturbed electronic system. This means that perturbations intervene explicitly only on the perturbators though indirectly on the principal propagator through its spin-dependence.

Every static second-order molecular property, i.e., those arising from a second-order correction to the energy and depending on two external static fields, can be calculated by using polarization propagators. This is apparent from the following equation

$$E^2_{PQ} = \frac{1}{2}\ \mathrm{Re}\langle\langle H^P; H^Q\rangle\rangle_{E=0} \tag{17}$$

where H^P and H^Q are the interaction Hamiltonians related to the external perturbations whose molecular response properties are of interest.

In the case of NMR spectroscopic parameters the starting point is a phenomenological perturbing Hamiltonian that describe accurately the experimental NMR spectra [25]. The complete Hamiltonian is then

$$H = H_0 + H_{1,NMR} \tag{18}$$

where

$$H_{1,NMR} = \sum_{MN}\left\{\boldsymbol{\mu}_M \cdot (\mathbf{D}_{MN} + \mathbf{J}_{MN}) \cdot \boldsymbol{\mu}_N\right\} + \sum_M\left\{\boldsymbol{\mu}_M \cdot (\mathbf{1} - \boldsymbol{\sigma}_\mathrm{M}) \cdot \mathbf{B}\right\} \tag{19}$$

and where $\boldsymbol{\mu}_M$ is the nuclear dipole moment of nucleus M, $\mathbf{D}_{MN}$ and $\mathbf{J}_{MN}$ are the direct and indirect nuclear spin coupling tensors, $\boldsymbol{\sigma}_M$ the nuclear magnetic shielding of nucleus M, and **B** is the static external magnetic field. From these last equations it is clear that to derive theoretical expressions for NMR spectroscopic parameters one should propose bilinear perturbative Hamiltonians depending on two different nuclear dipole moments (for **J**), and on a nuclear dipole moment and the external magnetic field (for $\boldsymbol{\sigma}$). Since the nuclear magnetic moments $\boldsymbol{\mu}_N$ are proportional to the nuclear spins $\mathbf{I}_N$, the magnetic interaction energy between the coupled nuclei depend on $\mathbf{I}_M$ and $\mathbf{I}_N$, and are expressed as

$$E^{(2)}_{MN} = h\mathbf{I}_M \cdot \mathbf{J}_{MN} \cdot \mathbf{I}_N \tag{20}$$

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

$$E^{(2)}_{M} = -h\mathbf{I}_M \cdot \sigma_M \cdot \mathbf{B}. \tag{21}$$

Using perturbation theory, the non-relativistic paramagnetic-like terms of **J** and $\boldsymbol{\sigma}$ arise from second-order corrections to the electronic energy.

$$E^{(2)}_{PQ} = \sum_{n\neq 0}\left\{\frac{\langle 0|H^P|n\rangle\langle n|H^Q|0\rangle}{E_0 - E_n}\right\}. \tag{22}$$

The perturbation Hamiltonians H^P and H^Q can be any of the Hamiltonians proportional to the nuclear spin $\mathbf{I}_M$ or the external static magnetic field **B**; their explicit forms will be given in the next section (see Equations 40, 42 and 44) for **J**-couplings and Equations (44) and (46) for $\boldsymbol{\sigma}$). It is worth to mentioning that in order to have a non-vanishing result, both Hamiltonians must have the same time-reversal symmetry [26].

On the other hand, the NR diamagnetic-like expressions are obtained as a first-order correction to the electronic energy

$$E^{(1)} = \langle H^S \rangle, \tag{23}$$

where H^S has a bilinear dependence with the external perturbation parameters and is also given in the next section (see Equations 45 and 47).

Formally, Equations (17) and (22) are equivalent for calculating second-order corrections to the energy. Nevertheless, in practical computations different strategies are followed for evaluating them through approximate methods. In any case, we shall emphasize here that propagators offer a powerful tool for the understanding of the electronic mechanisms involved in the phenomena studied, rather than the numerical identity of Equations (17) and (22) in approximate calculations. There is a connection between polarization propagators and the widely used response theory formalism; the interested reader can find it in [24,27–29].

2.2. *Including electron correlation: first three levels or PZOA, RPA and SOPPA*

So far the expressions for the polarization propagators are exact since we considered the exact reference state $|0\rangle$ and a complete manifold of excitation operators, **h**. In practice this is not the case because one does not know the exact reference state and cannot work with a complete **h**. Therefore, some approximations have to be applied. One clever way to do this is by expanding Equation (13) in terms of the fluctuation potential, which is defined by

$$V = H_0 - F, \tag{24}$$

where H_0 is the unperturbed Hamiltonian and F is the Fock operator written, in second quantization, as

$$F = \sum_p \varepsilon_p a_p^\dagger a_p. \tag{25}$$

The potential V represents the difference between the Coulomb and the self-consistent field (SCF) potential; its second-quantized form is

$$V = \frac{1}{2}\sum \langle pq|rs\rangle a_p^\dagger a_q^\dagger a_s a_r - \sum_{\alpha pr} u_{pr} a_p^\dagger a_r. \tag{26}$$

The matrix elements of the SCF potential are given by

$$u_{pr} = \sum_i^{occ} \langle pi||ir\rangle, \tag{27}$$

while the conventional notation for two-electron integrals has been used:

$$\langle pq||rs\rangle = \langle pq|rs\rangle - \langle pq|sr\rangle \tag{28}$$

and

$$\langle pq|rs\rangle = \int \Psi_p^*(\mathbf{r}_1)\Psi_q^*(\mathbf{r}_2) r_{12}^{-1} \Psi_r(\mathbf{r}_1)\Psi_s(\mathbf{r}_2) \mathrm{d}\mathbf{r}_1 \mathrm{d}\mathbf{r}_2. \tag{29}$$

The random phase approximation (RPA) level of approach, which is first-order in the fluctuation potential, is obtained when the reference state is obtained from a self-consistent field calculation, namely,

$$|0\rangle = |\mathrm{SCF}\rangle, \tag{30}$$

$|\mathrm{SCF}\rangle$ being the HF or DHF ground state for the non-relativistic and relativistic RPA, respectively, and the operator manifold is truncated up to single-excitation operators, i.e.

$$\{\mathbf{h}\} = \{\mathbf{h}_2\}. \tag{31}$$

All one-electron operators can be expanded in normal ordered second-quantized form (see Equation 9) in terms of the manifold $\{\mathbf{h}_2\}$ as

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

where

$$\mathbf{P}_{ai} = \langle a|P|i\rangle. \tag{33}$$

Then applying Equations (13)–(15) and Equations (24) and (31) one obtains

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

where

$$\mathbf{A}_{ia,jb} = -\langle 0|\left[a_i^\dagger a_a, \left[a_b^\dagger a_j, H_0\right]\right]|0\rangle = \delta_{ab}\delta_{ij}(\varepsilon_a - \varepsilon_i) + \langle aj||ib\rangle \tag{35}$$

and

$$\mathbf{B}_{ia,jb} = -\langle 0|\left[a_i^\dagger a_a, \left[a_j^\dagger a_b, H_0\right]\right]|0\rangle = \langle ji||ab\rangle. \tag{36}$$

Matrix **A** contains the average value of the unperturbed Hamiltonian H_0 between two singly excited states with respect to the reference state, and the 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 $\mathcal{O}(V^0)$ and $\mathcal{O}(V^1)$, while matrix **B** has a term of order $\mathcal{O}(V^1)$.

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 right-hand side of Equation (35).

From the RPA the next step upward in the inclusion of dynamic electronic correlation is the second-order polarization propagator approach (SOPPA) [5,28]. At this level one should consider

$$|0\rangle = |\mathrm{SCF}\rangle + |0^{(1)}\rangle, \tag{37}$$

where $|0^{(1)}\rangle$ 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.

$$\{\mathbf{h}\} = \{\mathbf{h}_2, \mathbf{h}_4\}. \tag{38}$$

Then the transition matrix elements and the principal propagator are modified in such a way that there appear new well-defined matrix elements which arise from two-particle–two-hole excitations, $\mathbf{h}_4$. Another improvement is found when Moller–Plesset correlation coefficients are replaced by coupled cluster single and double amplitudes in all matrix elements belonging to SOPPA matrices [30]. A previous partial implementation of this last modification was published by Oddershede and coworkers [31].

So far, SOPPA has only been derived for linear response functions and has therefore only been used to calculate second-order molecular properties.The SOPPA linear response function has been obtained by expressing the response function of the exact state within the superoperator inner-projection formalism [21,22], truncating the response function such that the response function and the poles are both correct to second order in perturbation theory. Recently the SOPPA approach was derived from time-dependent perturbation theory by parametrizing the time evolution of the exact state in terms of exponential operators for orbital rotations and for higher-order excitations [32]. This approach may straightforwardly be extended to quadratic and higher-order response functions.

As we shall show in the next section any given linear response property can be expressed as a product of two types of factors: the property matrix or perturbators **b** and the principal propagators $\mathbf{M}^{-1} = \mathbf{P}$:

$$R = \mathbf{b}^P \mathbf{M}^{-1} \mathbf{b}^Q. \tag{39}$$

At any level of approach, perturbators are mainly concerned with the outcome of the local interaction through a given external perturbation between one occupied and one virtual MO. The principal propagator describes how the interaction that occurs in one part of the molecule is transmitted to any other part of the molecule. This description has similar mathematical expressions to that of perturbation theory at an equivalent level of approach.

3. NR theory and models

Historically, the theoretical explanation of NMR spectroscopic parameters relied on non-relativistic expressions and concepts. The five famous papers by Ramsey [8–12] gave the first expressions and were based completely on non-relativistic assumptions. The non-relativistic external interaction Hamiltonians providing theoretical expressions for the NMR spectroscopic tensor parameters, $\mathbf{J}_{MN}$ and $\boldsymbol{\sigma}_M$, are given below. We will give first that for NMR-**J** couplings:

$$H^{FC} = \frac{8}{3}\pi\mu_B\hbar g_e \sum_N \gamma_N \sum_i \delta(r_{iN})\mathbf{s}_i \cdot \mathbf{I}_N = \sum_N \gamma_N \mathbf{I}_N \cdot \mathbf{V}_N^{FC} \tag{40}$$

where μ_B is the nuclear magneton, γ_N is the magnetogyric ratio of nucleus N, g_e is the electronic g-factor, and

$$\mathbf{V}_N^{FC} = \frac{8}{3}\pi\mu_B\hbar g_e \sum_i \delta(\mathbf{r}_{iN})\mathbf{s}_i \tag{41}$$

is the corresponding Fermi contact perturbator. The Fermi contact perturbation Hamiltonian of Equation (40) 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 directly related to the electronic densities on the sites of the coupled nuclei, say M and N. The Fermi contact 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-dipole (SD) and paramagnetic spin-orbital (PSO):

$$H^{SD} = 2\mu_B\hbar \sum_N \gamma_N \sum_i \left(\frac{3(\mathbf{s}_i \cdot \mathbf{r}_{iN})(\mathbf{I}_N \cdot \mathbf{r}_{iN})}{r_{iN}^5} - \frac{\mathbf{s}_i \cdot \mathbf{I}_N}{r_{iN}^3} \right), \tag{42}$$

or

$$H^{SD} = \sum_N \gamma_N \mathbf{I}_N \cdot \mathbf{V}_N^{SD}, \tag{43}$$

and

$$H^{PSO} = -2i\mu_B\hbar \sum_N \gamma_N \mathbf{I}_N \cdot \sum_i \frac{\mathbf{r}_{iN} \times \nabla_\mathbf{i}}{r_{iN}^3} = \sum_N \gamma_N \mathbf{I}_N \cdot \mathbf{V}_N^{PSO}. \tag{44}$$

As observed in Equations (40), (42) and (44) the first two depend 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:

$$H^{DSO} = \frac{e\hbar\mu_B}{c}\sum_{MN}\gamma_M\gamma_N\sum_i\frac{(\mathbf{I}_M\cdot\mathbf{I}_N)(\mathbf{r}_{iM}\cdot\mathbf{r}_{iN}) - (\mathbf{I}_M\cdot\mathbf{r}_{iN})(\mathbf{I}_N\cdot\mathbf{r}_{iM})}{r_{iM}^3 r_{iN}^3}. \tag{45}$$

Theoretical expressions for nuclear magnetic shielding, σ, depend on two quite different kinds of perturbative Hamiltonians: (i) There are two paramagnetic Hamiltonians, which means that their effects are such that they 'shield' the nucleus; that of Equation (44) and another that arises from the external static magnetic field **B**:

$$H^B = \frac{\mu_B}{2}(\mathbf{r}_G\times\mathbf{p})\cdot\mathbf{B} = \frac{\mu_B}{2}\mathbf{l}_G\cdot\mathbf{B} \tag{46}$$

where $\mathbf{r}_G$ refers to the electron position with respect to the gauge origin. (ii) The other perturbative Hamiltonian has a diamagnetic effect, i.e. it reduces the magnetic field that effectively appears in the nucleus of interest:

$$H^d = \frac{e^2}{2m}\sum_N\gamma_N\sum_i\frac{(\mathbf{B}\cdot\mathbf{I}_N)(\mathbf{r}\cdot\mathbf{r}_{iN}) - (\mathbf{B}\cdot\mathbf{r}_{iN})(\mathbf{I}_N\cdot\mathbf{r})}{r^3 r_{iN}^3}. \tag{47}$$

As shown in Equations (17) and (22) paramagnetic contributions to both NMR spectroscopic parameters can be obtained within non-relativistic polarization propagator theory. Its diamagnetic contribution, however, is obtained as a ground-state expectation value. Still Sauer has shown, through a transformation, that the diamagnetic contributions can also be calculated with polarization propagators [30]. It should be noted that mixing perturbations with different electron spin dependence gives vanishing results [26]. When considering electron-spin-dependent Hamiltonians, the excitation energies of Equation (22) should be restricted to that of singlet or triplet type. In the same manner, the principal propagator of Equation (15) will be restricted [23,26]. Then, in the case of **J**-couplings there will be two kinds of terms: (i) electron-spin-dependent terms which are related to the 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, there are five contributions to the indirect nuclear spin coupling tensor,

$$\mathbf{J} = \mathbf{J}^{FC} + \mathbf{J}^{SD} + \mathbf{J}^{PSO} + \mathbf{J}^{FC/SD} + \mathbf{J}^{DSO}. \tag{48}$$

When calculated by the non-relativistic polarization propagator theory each one of the first three terms is written as

$$\mathbf{J}^X_{MN} = \gamma_M\gamma_N\langle\langle\mathbf{V}^X_M;\mathbf{V}^X_N\rangle\rangle_{E=0} \tag{49}$$

where $X=$ FC, SD or PSO. In Equation (48) $\mathbf{J}^{FC/SD}$ only contributes for systems in the solid state phase, so it will not be considered here, while $\mathbf{J}^{DSO}$ is isotropic. All terms of Equation (49) can be calculated at different levels of approach depending on the fluctuation potential, i.e. pure zeroth-order (PZOA), consistent first-order or random-phase approximation (RPA), second-order level of approach (SOPPA), third-order level of approach (TOPPA), etc. [28]. We will mainly be concerned with applications of propagators at the RPA level of approach due to the fact that it is much easier to get physical insights that underly some important characteristic of NMR spectroscopic parameters at this level. Results from PZOA and SOPPA calculations will also be given.

Even though PZOA and RPA are equivalent to uncoupled and coupled Hartree–Fock respectively, we use this nomenclature in order to make explicit the different order in both expressions and the fact that they arise from polarization propagators. This becomes clearer when the SOPPA approximation is considered because in this case there is no other approach which gives the same expressions.

Within the RPA level of approach, explicit expressions for the indirect NMR coupling constant between nuclei M and N are

$$J^X_{MN} = \gamma_M \gamma_N \langle\langle \mathbf{V}^X_M; \mathbf{V}^X_N \rangle\rangle_{E=0} = \sum_{ia,jb} \mathbf{b}^X_{M,ia} \mathbf{P}_{ia,jb} \mathbf{b}^X_{N,jb} \tag{50}$$

with $X =$ FC, PSO or SD.

The principal propagator can be factored out to make explicit its electron spin dependence. Then, matrices **A** and **B** of Equations (35) and (36) can be rewritten in such a way that

$${}^m\mathbf{P}_{ia,jb} = {}^m\mathbf{M}^{-1}_{ia,jb} = ({}^m\mathbf{A} \pm {}^m\mathbf{B})^{-1}_{ia,jb} \tag{51}$$

where the superscripts $m = 1$ and $m = 3$ refers to singlet- and triplet-type properties and ${}^m\boldsymbol{M}$ is the sum or the difference of ${}^m\mathbf{A}$ and ${}^m\mathbf{B}$, respectively. The matrix elements for these spin-dependent matrices are given elsewhere [28].

In a completely similar manner one can work out the paramagnetic non-relativistic nuclear magnetic shielding expressions

$$\sigma^p_M = \gamma_M \langle\langle \mathbf{V}^{PSO}_M; \mathbf{l}_G \rangle\rangle_{E=0}. \tag{52}$$

Both perturbations here are electron-spin independent. So the principal propagator is of singlet-type.

In the next two subsections we give some comments and details about how each term of the response expressions, Equations (49) and (52), have been calculated. In the so-called *ab initio* schemes, every magnitude is calculated from the first principles of the theory, within a given approximation, in contrast to semi-empirical methods where some magnitudes are introduced as empirical parameters.

In what follows we will be concerned only with the 1/3 of the trace of both tensors **J** and **σ**, the magnitudes that are measured by experiments. We will not analyse the anisotropy of such spectroscopic parameters.

3.1. Ab initio *schemes and a few recent results at the SOPPA level of approach*

There is a large number of studies on NMR spectroscopic parameters applying *ab initio* SOPPA schemes [33]. During the last few years some new phenomena were also tackled with propagators at the SOPPA level: isotope effects [34,35], the intramolecular proton transfer mechanism in Schiff bases [36] and comparative results with state-of-the-art methods were reviewed [37].

Ab initio schemes were the first to be implemented and applied to calculate NMR spectroscopic parameters [3–5]. We want to stress here the fact that calculations at the SOPPA or SOPPA(CCSD) level of approach are among the most reliable ones [37,38]. Another important point is that, in actual calculations at the SOPPA or SOPPA(CCSD) level with very large basis sets of size N, one cannot calculate each term of Equation (39) separately. The CCSD amplitude calculation needed at SOPPA(CCSD) scales as N^6, while property calculations scale as N^5. This implies that the principal propagator matrix cannot be stored due to its size and one must calculate the product between the principal propagator matrix with one of the two perturbators (or property matrices). Hence, some important information contained within that matrix is lost.

Given that the computational cost of calculations at the SOPPA level is strongly dependent on the number of Gaussian functions used as basis set, a scheme for including an optimized number of functions within the basis set was developed and dubbed a *local-dense basis set* (LDBS) [39–43]. It depends on the studied property and also on the main pathways which describe the interaction and the local influence of different portions of the molecule. The development of LDBS applied to molecules with more than two non-hydrogen atoms was based on propagators. The larger the relative weight of the contributions of a given atom or molecular fragment to $\mathbf{J}$ or $\boldsymbol{\sigma}$, the more accurately it can be described.

The experimental discovery of **J**-couplings transmitted through H-bonding stimulated the study of such bonds by NMR spectroscopy [44–47]. New insights into the electronic mechanisms involved and the chemical nature of H-bonds can be obtained by applying theoretical models. The transmission of large enough **J**-couplings through n-monomers bonded by H-bonds can be regarded as a cooperative effect. This is a 'global' electronic effect though **J**-couplings are mainly built from local interactions. In a recent article [48] we analysed the influence of cooperative effects on **J**-couplings for the linear chains $(HCN)_n$ and $(HNC)_n$ $(n = 1, \ldots, 6)$. The FC is the most important intramolecular mechanism for $^1J(CN)$ though the PSO is as important as the FC for $^2J(NH)$. Looking for the origin of cooperative effects on such magnetic properties, we were able to show that they are purely electronic. They do not depend on the geometry of each monomer and there is a relationship between the number of monomers involved and the values of intra- and intermolecular **J**-couplings.

Given that a π-electronic framework is involved SOPPA calculations are essential to obtain reliable results due to instability problems. The RPA approximation of the principal propagator **P** is closely related to the stability condition of the restricted Hartree–Fock (RHF) ground state of the molecular system studied [28]. The RHF is not the most general independent particle state. In order to guarantee that the energy remains at a minimum, even when the imposed closed-shell restrictions were relaxed, the $({}^n\mathbf{A} \pm {}^n\mathbf{B})$ matrices must be positive definite. When a non-singlet (or triplet) instability situation arises [49,50], at least one eigenvalue of the triplet $({}^3\mathbf{A}-{}^3\mathbf{B})$ matrix is negative [51,52] or very close to zero (a non-singlet HF quasi-instability – QI) [53]. This is one of the most frequent problems encountered in calculations of some molecular properties like the NMR-**J** couplings. It usually originates in the π-electronic framework [40,54,55]. In such cases, both the FC and SD components of **J** could be exaggerated. A useful alternative solution to overcome this non-singlet QI problems was given in [52].

Large long-range through-bond **J**-couplings were postulated and measured for H–H couplings of unsaturated compounds [25]. What is the magnitude and the distance between

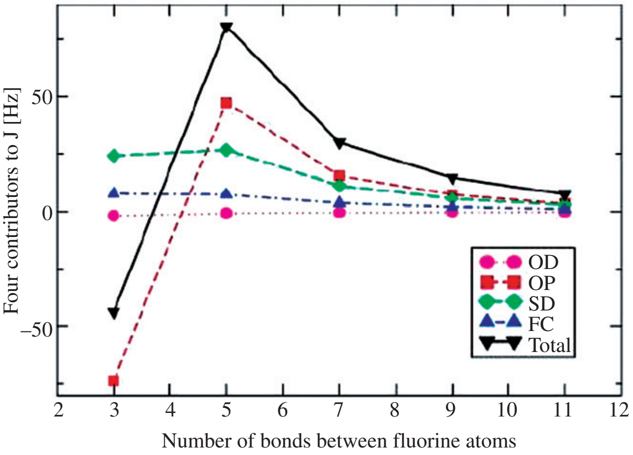

Figure 1. [Colour online] Contributions to ^{n}J(F–F) in Di-F-polyenes.

the coupled nuclei that one could expect for such couplings? Only a few Hz and also a few bonds away. If the FC mechanism is the main one, as happens for H–H couplings, its **J**-value would fall to zero quite rapidly as more bonds separate both coupled nuclei. Studies of **J**(F–F) on π-conjugated systems have shown that the PSO and SD mechanism becomes as important as FC [56–59]. All these studies considered short-range couplings. The behaviour of **J**(F–F) for several saturated and unsaturated compounds (1,*n*-difluoro-alkanes, polyenes, cumulenes and polyynes) was studied with the SOPPA and LDBS schemes [60]. In Figure 1 we show the behaviour of all four Ramsey mechanisms contributing to **J**(F–F) with the F–F bond distance in Di-F polyenes. The main conclusions of such studies were: (i) The couplings decays very quickly with the number of bonds in the saturated 1,*n*-difluoroalkanes. In the conjugated polyenes and polyynes, the F–F couplings can be transmitted over much longer distances. For difluorodecapentayne an F–F coupling of ~7 Hz over a distance of 1.4 nm or 11 bonds was predicted. (ii) The F–F couplings in molecules with conjugated π-systems are dominated by the non-contact PSO and SD contributions. In both cases, the overall behaviour of the PSO and SD contributions is similar, though they have different relative values. In the polyynes, the PSO term is always larger but also decreases faster than the SD term. In the conjugated polyenes, on the other hand, the spin-dipole term is the dominating contribution. This feature is completely unusual for other types of couplings. In 1,4-difluorobuta-1,3-diene the PSO term is still larger than the FC term, whereas in the longer molecules of this series the FC term is more important than the PSO term. In general, also the Fermi-contact term is still important for couplings over a nanometre or 11 bonds. The most important conclusion was that there should be measurable couplings between fluorine nuclear spins separated by distances of a few nanometres. These results suggest that one could find F–F coupling constants of a few hertz in 1,*n*-difluoropolyens or 1,*n*-difluoropolyynes over even longer distances. From the asymptotic behaviour of the calculated couplings in the 1,*n*-difluoropolyynes, they estimated couplings of **J**(F–F) $\approx$ 3.6 Hz over 13 bonds or a distance of ~1.6 nm and of **J**(F–F) $\approx$ 1.8 Hz over 15 bonds or a distance of ~2 nm. New studies have confirmed these findings [61].

A recent study of the intramolecular proton transfer mechanism in ortho-hydroxyaryl substituted Schiff bases with the B3LYP-DFT and SOPPA schemes shows that one can predict the dependence of both parameters, $^1J(^{15}N^1H)$ and $\sigma(^{15}N)$, with the distance d(NH) on OH and NH tautomers [36]. An inflection point is found when each NMR spectroscopic parameter is expressed as a function of d(N–H). The same happens when the correlation between both parameters, **J** and σ, is depicted. The analysis of these (cubic) functions shows whether the proton is bound to the oxygen or to the nitrogen atom, or it is shared by both atoms. In line with these findings, it is possible to predict the position of the proton in the bridge, which is supported by previous experimental measurements.

3.2. *Semi-empirical models: CLOPPA*

The CLOPPA model was developed mainly to analyse NMR-**J** couplings in term of 'local' contributions. The corresponding shielding analysis was not implemented. It is based on a decomposition of **J** as a summation of contributions from individual *coupling pathways* involving two virtual excitations $i \rightarrow a$ and $j \rightarrow b$ with i, j (a, b) occupied (vacant) localized MOs (LMOs) that belong to the local 'L' fragment of interest:

$$J_{MN} = \sum_{ia,jb} J^{\mathrm{L}(X)}_{MN;ia,jb}. \tag{53}$$

This allows one to extract some crucial information on transmission mechanisms involved in the propagation of a given specific magnetic perturbation, say X ($X =$ FC, SD or PSO).

A given semi-empirical ground state wavefunction can be used as the reference state of polarization propagator calculations [13–15]. The CLOPPA scheme is based on this assumption, at the RPA level of approach, together with the use of localized molecular orbitals [62]. It was first implemented at the INDO level [63]. 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 [71–73,117] were implemented at the MNDO [64], AM1 [65], PM3 [66] and INDO/S [67] levels of approach.

There are several basic physical assumptions considered in the implementation of CLOPPA schemes: (i) the transmission of **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 ($S^2_M(0)$), 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 multi-configurational Dirac–Fock *ab initio* theoretical calculations [68].

Each term of the sum in Equation (53) can be written as (see Equation 50)

$$J^X_{MN;ia,jb} = \left(U^X_{M,ia}U^X_{N,jb} + U^X_{N,ia}U^X_{M,jb}\right)^m P_{ia,jb} \tag{54}$$

where $U^X_{M,ia}$ is a measure of the strength of the virtual excitation $i \rightarrow a$ due to the perturbation X; $m = 3$ for $X =$ FC or SD, and $m = 1$ for $X =$ PSO. The principal propagator $^mP_{ia,jb}$ gives the response of the molecular fragment connecting the 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 *semi-empirical* level using a one-centre approximation, and for the FC mechanism they have the form:

$$U^{FC}_{M,ia} = \langle i|\delta(\mathbf{r}_M)|a\rangle = C^s_{i,M} C^s_{a,M} S^2_M(0) \tag{55}$$

where the coefficients $C^s_{i(a),M}$ are those of s-type orbitals belonging to atom M.

The main successful applications of the semi-empirical CLOPPA model were on the understanding of electronic mechanisms that underly NMR-**J** couplings in cases where it was able to reproduce experimental trends qualitatively or semi-quantitatively. In particular the application of CLOPPA-X ($X =$ MNDO, AM1 and INDO/S) on molecules containing heavy atoms gave semi-quantitative reproduction of experimental results in molecules where it was not possible (until the late 1990s) to apply *ab initio* and fully relativistic, semi-relativistic or quasi-relativistic theoretical methods due to their large computational cost. We should mention that currently one still cannot calculate NMR-**J** couplings for medium-size molecules containing more than three heavy atoms with *fully* and *ab initio* relativistic methods at second-order correlated levels, though DFT and *ab initio* RPA are available.

Calculations that reproduce experimental results in a qualitative or semi-quantitative manner were performed with AM1 and INDO/S semi-empirical wavefunctions for SnH_4, $SnMe_4$, $S(SnMe_3)_2$, and X_2Me_6 ($X =$ Si, Sn and Pb). From these results one can go one step further and analyse the electronic mechanism that underlies the total **J** value. There are several review articles [69,70] where these criteria were applied. It is worth mentioning that, for instance, there are no calculations of **J** with fully relativistic methods for $S(SnMe_3)_2$ where the CLOPPA-INDO/S method gives quite approximate results. Some other calculations on medium-size tin-containing molecules (1,2,4,5-tetrastannacyclohexanes with Me substituents) are given in [71].

We want to comment here on two of the most important insights that arise when applying the CLOPPA model: the electronic origin of both the sign of **J**-couplings and the Karplus rule.

The absolute sign of **J** can be experimentally measured [74,75], so it deserves a search for its physical origin. There is an old model that was used for decades by experimentalists [76], the Dirac–Peeney model. It is known that it fails to explain the sign of several couplings, e.g. one-bond and two-bond couplings of special systems like formaldehyde and F-methane. The Dirac–Peeney model is based on the FC mechanism; from Equation (40) and assuming that γ_M is positive, the model predicts that the magnetic energy becomes stabilized when the electron spin is antiparallel to the nuclear spin. As a consequence, the molecular system is more stable when all coupled nuclear spins are antiparallel (see Equation 19). This model predicts positive one-bond **J**-couplings and negative two-bond **J**-couplings. Nevertheless, it is known that the geminal ^2J(H–H) is positive in formaldehyde.

In calculations performed with the CLOPPA model one observes that only one of the two terms that contain perturbators in Equation (54) contributes significantly, while the other is vanishingly small. Another important point is the fact that all diagonal matrix elements of the principal propagator, i.e. $P_{ia,ia}$, are negative. This is not the case for non-diagonal elements but then it is always allowed to change the sign of the pair of

Table 1. Contributions of the main *coupling pathway* terms (in Hz) and their *perturbator* and principal propagator elements for ^2J(H–H) in formaldehyde and ^1J(C–F) in CH_3F.

CH_2O

i	a	j	b	$J_{ia,jb}$	$P_{ia,jb}$	U_{ia,H_2}	U_{jb,H_1}	U_{ia,H_1}	U_{jb,H_2}
σ_1[a]	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_1	σ_1^*	7.18	−2.97	0.003	0.266	−0.266	0.003

CH_3F

i	a	j	b	$J_{ia,jb}$	$P_{ia,jb}$	$U_{ia,F}$	$U_{jb,C}$	$U_{ia,C}$	$U_{jb,F}$
σ_b[b]	σ_b^*	σ_b	σ_b^*	452.72	−2.40	−1.036	0.254	0.254	−1.036
LP	σ_b^*	σ_b	σ_b^*	−538.84	−0.75	4.008	0.254	0.014	−1.036

[a] σ_i and σ_i^* are the bonding and antibonding LMOs corresponding to each of two C–H_i bonds ($i = 1, 2$).

[b] σ_b and σ_b^* are the bonding and antibonding LMOs corresponding to the C–F bond. LP means lone-pair.

elements $^3P_{ia,jb}$ and U_{ia}^{FC} without any change of the sign of **J**. Then we see that when different *coupling pathways* $J_{ia,jb}$ have different relative signs it should be related to the relative signs of equivalent perturbators. As shown in Table 1 there is only one pathway $(\sigma_1\sigma_1^*, \sigma_2\sigma_2^*)$ giving a negative contribution to geminal coupling H–H in formaldehyde, while the rest are positive. This negative term corresponds to the Dirac–Peeney vector model prediction. Nevertheless, since the positive contributing coupling pathways are larger in absolute value, the total **J**-coupling is positive, in agreement with the experimental evidence. Then, we can analyse the reason for the opposite sign for those coupling pathways. The sign of a perturbator $U_{M,ia}^{FC}$ has an implicit relation between the phases of the LMOs involved in the virtual excitation $i \to a$ at the site of the nucleus M. Its sign is positive when both LMOs have the same phase. Within the CLOPPA model the sign of each coupling pathway is defined by the sign of the two main perturbators U_M^{FC} and U_N^{FC} for the given coupling pathway [77]. As observed in Table 1 the sign of the first term arises from the product between $U_{\sigma_1\sigma_1^*;H_1}$ and $U_{\sigma_2\sigma_1^*;H_2}$. The sign of these two perturbators is opposite, thus meaning that the relative phases of both virtual excitations at the site of both nuclei are opposite; that is, the phases of the bonding and antibonding LMOs of the virtual excitation $\sigma_1 \to \sigma_1^*$ at the site of the nucleus H_1 are similar but the phases of the bonding and antibonding LMOs of the virtual excitation $\sigma_2 \to \sigma_1^*$ at the site of the nucleus H_2 are different. Another example is also given in the same Table 1 for the one-bond coupling C–F in CH_3F. We show only two terms which are by far the most important. One is diagonal and positive as it should be, the other is non-diagonal, negative and larger in absolute value than the first one. For the largest coupling pathway one of the two excitations starts from the LP. The relative phases of both perturbators are similar and so the contribution of the coupling pathway is negative. Then we can conclude that the origin of the sign of **J** due the FC mechanism arises from the relative phases of the

LMOs intervening in the given coupling pathways at the site of the nuclei involved [76]. The CLOPPA model generalizes the previous Dirac–Peeney model in a natural manner.

In NMR spectroscopy there is a rule that is widely used for interpreting or predicting NMR spectra: the Karplus rule [78,79]. It is concerned with the vicinal indirect coupling of two magnetically coupled nuclei. It is independent on the type of coupled nuclei and shows the harmonic dependence of **J** on the dihedral angle between both coupled nuclei. Several authors have given different explanations [80–85]. We will concentrate on ours that arises by applying the CLOPPA model. The origin of this rule is more related to the description of the molecule as a whole than on the precise local interactions like those defining the sign of **J**. Since an extensive explanation was given elsewhere [76,86] we shall give only a sketchy presentation of the CLOPPA model explanation of the Karplus rule.

From Equation (39) and expressing the principal propagator matrix as a series for the FC mechanism [52,87]

$$\left(\mathbf{M}^{-1}\right)_{ia,jb} \propto (\mathbf{G}+\mathbf{H})_{ia,jb}, \tag{56}$$

where

$$\mathbf{G}_{ia,jb} \equiv \langle aj|bi\rangle = \int \psi_a^*(1)\psi_b^*(1)r_{12}^{-1}\psi_j(2)\psi_i(2)\mathrm{d}\mathbf{r}_1\mathrm{d}\mathbf{r}_2, \tag{57}$$

and

$$\mathbf{H}_{ia,jb} \equiv \langle ab|ji\rangle = \int \psi_a^*(1)\psi_j^*(1)r_{12}^{-1}\psi_b(2)\psi_i(2)\mathrm{d}\mathbf{r}_1\mathrm{d}\mathbf{r}_2. \tag{58}$$

The matrix **G** is called the Coulomb matrix because its diagonal terms represents a Coulomb interaction between two electrons: one in a virtual state, $a=b$, and the other in an occupied state, $i=j$. The matrix **H** for the same orbitals is then an exchange integral matrix. Let us analyse again the nuclear spin indirect couplings in terms of pathways. It has been observed that all pathway contributions for vicinal couplings follow the Karplus rule [86]. Furthermore, for the most important terms the principal propagator is found to satisfy a Karplus-like dependence too. In general, the coupling pathway term that gives the main contribution is of the form $J_{\sigma_1\sigma_1^*,\sigma_2\sigma_2^*}$, where the two excitations refer to the two bonding–antibonding LMOs which contain the coupled atoms and the closest atom bonded to them; for them, the Coulomb and exchange interactions are

$$\mathbf{G}_{\sigma_1\sigma_1^*,\sigma_2\sigma_2^*} = \int \sigma_1^*(1)\sigma_2^*(1)r_{12}^{-1}\sigma_2(2)\sigma_1(2)\mathrm{d}\mathbf{r}_1\,\mathrm{d}\mathbf{r}_2 \tag{59}$$

and

$$\mathbf{H}_{\sigma_1\sigma_1^*,\sigma_2\sigma_2^*} = \int \sigma_1^*(1)\sigma_2(1)r_{12}^{-1}\sigma_2^*(2)\sigma_1(2)\mathrm{d}\mathbf{r}_1\,\mathrm{d}\mathbf{r}_2. \tag{60}$$

It is seen that in both cases electron 1 belongs to two different LMOs that are close to the coupled nuclei, e.g. $\psi_{\sigma_1^*}(1)$ and $\psi_{\sigma_2^*}(1)$ or $\psi_{\sigma_2}(1)$. Then, we can say that a Karplus curve arises from a new type of *entanglement*, since for second-order properties we must consider two simultaneous excitations, one for each of two 'entangled' or 'disentangled' electronic wavefunctions. If and only if at least one of the two excitations is entangled, the corresponding principal propagator matrix element will follow a Karplus-type behaviour with the dihedral angle. In other words, the Karplus rule arises as a non-local electron interaction that connects instantaneously the two coupled nuclear spins.

4. Relativistic polarization propagator

The relativistic generalization of polarization propagators was introduced by one of us together with Oddershede 20 years after the formulation of its NR theory [16]. Its time-reversal restricted formulation opened the door to Kramer restricted operators [23] and its implementation in a computational code (named DIRAC [88]) for calculation of response properties. We shall give here a brief introduction to the Dirac formalism, the formal extension of polarization propagators to the relativistic regime, the new insights that one obtains when the time-reversal symmetry is applied to it, and some specific applications on usual test systems. Then we shall go one step further in order to be able to apply the full machinery of the QED formalism to the understanding of magnetic molecular properties.

The free-particle Dirac equation is written in non-covariant form as

$$h^D \psi(\mathbf{x}) = \left(c\boldsymbol{\alpha} \cdot \mathbf{p} + \beta mc^2\right)\psi(\mathbf{x}) = E\psi(\mathbf{x}). \tag{61}$$

Multiplying by β/c one obtains a covariant (i.e. Lorentz invariant) form of the equation

$$(\gamma^\mu p_\mu - mc)\psi(x) = 0 \tag{62}$$

where $\gamma^0 \equiv \beta$, $\gamma^i \equiv \beta\alpha^i$, $\gamma^\mu = (\gamma^0, \boldsymbol{\gamma})$ and $p_\mu = (E/c, -\mathbf{p})$, so that $\gamma^\mu p_\mu = \gamma^0 p_0 - \gamma \cdot \mathbf{p}$. In these equations $\alpha = (\alpha_x, \alpha_y, \alpha_z)$ are the 4×4 Dirac matrices, which are written in the standard representation in terms of the 2×2 Pauli matrices $\boldsymbol{\sigma} = (\sigma_x, \sigma_y, \sigma_z)$ as

$$\boldsymbol{\alpha} = \begin{pmatrix} \mathbf{0} & \boldsymbol{\sigma} \\ \boldsymbol{\sigma} & \mathbf{0} \end{pmatrix}, \tag{63}$$

and

$$\gamma^0 = \begin{pmatrix} \mathbf{1} & \mathbf{0} \\ \mathbf{0} & -\mathbf{1} \end{pmatrix}, \ \gamma^i = \begin{pmatrix} \mathbf{0} & \boldsymbol{\sigma} \\ \boldsymbol{\sigma} & \mathbf{0} \end{pmatrix}. \tag{64}$$

If an equation is covariant it means that it will have the same form when written in any reference frame. The left-hand side of Equation (62) is invariant under a Lorentz transformation because it is a scalar. Written in this form it is easier to get its energy spectra. So for one Dirac particle at rest ($\mathbf{p} = \mathbf{0}$) Equation (62) is written as

$$\gamma^0 p_0 \psi = mc\psi \quad \text{or} \quad p_0 \psi = mc\gamma^0 \psi. \tag{65}$$

Given that the operator γ^0 has doubly degenerate eigenvalues ± 1, one obtains two positive-energy solutions and two negative-energy solutions. When $\mathbf{p} \neq \mathbf{0}$ there are doubly degenerate eigenvalues of $E = \pm(m^2c^4 + p^2c^2)^{1/2}$. There are two branches of continuum energies that must be considered. The lower branch is related to antiparticles (we shall give more details in Section 5.3), though their states are not antiparticle states, but negative-energy electron states. The corresponding antiparticle states can be obtained by charge-transforming them ($\psi \rightarrow \psi_C$) and then considering the 'absence' of electrons occupying negative-energy states [89]. Negative-energy electronic states should not be identified as positron states.

In what follows we shall consider the interaction of such a system with an applied external static field. Such an interaction is introduced by the minimal-coupling replacement [90]

$$\gamma^{\mu}\left(p_{\mu}-\frac{Q}{c}A_{\mu}\right)+mc\psi(x)=0 \tag{66}$$

where the 4-vector $A_{\mu}=(A_0,\ -\mathbf{A})$ includes both the external field and that originating in charged spin-$\frac{1}{2}$ particles, and Q is the electric charge of the particle ($Q=-e$ for electrons and $+e$ for positrons).

Under NMR experimental conditions the molecular system is perturbed by a relatively weak external field. So, within the relativistic domain (similarly as the NR description) the total electronic Hamiltonian can be written as the sum of the unperturbed H_0 and the perturbation Hamiltonian H_1:

$$H=H_0+H_1=H^D+V^C+H_1, \tag{67}$$

where H^D is the N-electron Dirac Hamiltonian,

$$H^D=\sum_i h^D(i) \tag{68}$$

and V^C is the two-electron Coulomb interaction operator. The interaction of an N-electron system with an external magnetic field is also accounted for by the minimal coupling prescription used in Equation (66) for a one-particle system, whose spatial expression is $\mathbf{p}\rightarrow\mathbf{p}-\frac{e}{c}\mathbf{A}$, leading to the introduction of the perturbation Hamiltonian

$$H_1=ec\boldsymbol{\alpha}\cdot\mathbf{A} \tag{69}$$

where $\mathbf{A}=\mathbf{A_M}+\mathbf{A_B}$ is the sum of the nuclear and the external vector potentials

$$\mathbf{A}_M=\frac{1}{c^2}\frac{\boldsymbol{\mu}_M\times\mathbf{r}_M}{r_M^3} \tag{70}$$

and

$$\mathbf{A}_B=\frac{1}{2}\mathbf{B}\times\mathbf{r}_G=\frac{1}{2}\mathbf{B}\times(\mathbf{r}-\mathbf{R}_\mathrm{G}) \tag{71}$$

where $\mathbf{R}_G$ is the gauge origin, $\mathbf{r}_M=\mathbf{r}-\mathbf{R}_\mathrm{M}$ and $\mathbf{r}$ and $\mathbf{R}_M$ are the coordinates of the electron and the nucleus M, respectively.

Considering both the nuclear and the external vector potentials of Equations (70) and (71), we have

$$\begin{aligned} H_{1,M}&=ec\boldsymbol{\alpha}\cdot\left(\frac{1}{c^2}\frac{\boldsymbol{\mu}_M\times\mathbf{r}_M}{r_M^3}+\frac{1}{2}\mathbf{B}\times\mathbf{r}_G\right)\\ &=-\frac{e}{c}\hbar\gamma_M\mathbf{I}_M\cdot\left(\frac{\alpha\times\mathbf{r}_M}{r_M^3}\right)-ec\mathbf{B}\cdot(\boldsymbol{\alpha}\times\mathbf{r}_G). \end{aligned} \tag{72}$$

Solutions of the Dirac equation for one-electron systems are bounded from below. When the number of particles is greater than one there appear severe problems in getting eigen solutions variationally. The way it was overcome was applying positive-energy projection operators. In the case of many-electron Dirac–Hartree–Fock calculations, Mittleman suggested the use of projection operators that included the Hamiltonians H^D and H^C of Equation (67) in such a way that projection operators are continually updated during the iterative solution of the DHF equations [91]. This is then applicable to variational models like the single-determinant DHF. It is worth remarking that from this procedure one gets both kinds of solutions, i.e. positive-energy and negative-energy one-electron states. Details are given elsewhere [29,91,92].

Once we express the unperturbed Hamiltonian as (see Equation 24)

$$H_0 = H^{DF} + V, \tag{73}$$

and use the DHF ground state as the reference state, all the equations of Section 2 are valid. It must be recalled that the molecular orbitals have four components (as opposed to one-component or Schrödinger type) and all operators are written as 4 × 4 matrices.

From Equations (17), (69) and (72), the second-order perturbative correction to the energy is written as

$$\begin{aligned} E^{(2)} &= \frac{1}{2}\mathrm{Re}\langle\langle H_1; H_1\rangle\rangle \\ &= \frac{1}{2}\frac{e\hbar^2}{c}\sum_{MN}\gamma_M\gamma_N\mathbf{I}_M\cdot\mathrm{Re}\left\langle\left\langle\frac{\alpha\times\mathbf{r}_M}{r_M^3};\frac{\alpha\times\mathbf{r}_N}{r_N^3}\right\rangle\right\rangle\cdot\mathbf{I}_N \\ &\quad+\frac{e^2\hbar}{2}\sum_M\gamma_M\mathbf{I}_M\cdot\mathrm{Re}\left\langle\left\langle\frac{\boldsymbol{\alpha}\times\mathbf{r}_M}{r_M^3};\boldsymbol{\alpha}\times\mathbf{r}_G\right\rangle\right\rangle\cdot\mathbf{B}. \end{aligned} \tag{74}$$

Finally, from Equations (20) and (21) the fully relativistic expressions of the NMR spectroscopic parameters are obtained as

$$\mathbf{J}_{MN} = \frac{e^2\hbar^2}{h}\gamma_M\gamma_N\left\langle\left\langle\frac{\boldsymbol{\alpha}\times\mathbf{r}_M}{r_M^3};\frac{\boldsymbol{\alpha}\times\mathbf{r}_N}{r_N^3}\right\rangle\right\rangle, \tag{75}$$

and

$$\boldsymbol{\sigma}_M = e^2\left\langle\left\langle\frac{\boldsymbol{\alpha}\times\mathbf{r}_M}{r_M^3};\boldsymbol{\alpha}\times\mathbf{r}_G\right\rangle\right\rangle. \tag{76}$$

From these equations it is observed that there is a single electronic mechanism involved in both NMR spectroscopic parameters. Furthermore, there is no distinction between diamagnetic and paramagnetic terms. This fact is something completely new and the search for its explanation gave us the opportunity to gain new insights into the electronic origin of molecular magnetic properties.

4.1. *Second-quantized operators, field operators and time-ordering*

The Dirac equation is not, as a matter of fact, a one-body equation but a many-body one due to the whole negative-energy branch of the spectra. One may consider this branch from different points of view depending on the definition of the vacuum state, what gives way to different pictures, namely, the hole, empty-Dirac and QED pictures. In the hole picture one considers that the whole negative-energy branch is occupied by electrons forming the Dirac sea; both in the empty-Dirac picture and in the QED-picture the negative branch is empty. Then Dirac solutions naturally introduce new particle states different from the usual positive-energy electron states. In a fully relativistic formalism, sooner or later one is forced to consider (it may be neglecting) them.

One way to introduce such states into consideration is through the application of the second-quantized formalism, largely used within the NR domain. As a prelude to the QED section we introduce here Dirac wavefunctions as (field) operators. This fact will enable us to work with (particle) states that can be created or annihilated. A given (field) operator can be decomposed in terms of a basis analogously to a Fourier decomposition of function.

For free particles the general solution of the Dirac equation is a linear combination of plane-wave solutions of Equation (61):

$$\begin{aligned}\psi^{+}(x) &= \exp(-ik\cdot x)u(k),\\ \psi^{-}(x) &= \exp(ik\cdot x)v(k)\end{aligned} \tag{77}$$

being the upper, two-component positive-energy solutions, and the lower, two-component negative-energy solutions. There are also the position 4-vector $x\equiv(x^0,\mathbf{r})$ and the 4-momentum $k\equiv(k^0,\mathbf{k})=(E/c,\mathbf{k})$. In this case a wave packet is written as

$$\psi(t,\mathbf{r}) = \int \frac{d^3k}{(2\pi)^3}\frac{m}{E}\sum_{\alpha=1,2}[a_k^{(\alpha)}u_k^{(\alpha)}\exp(-ik\cdot x)+\tilde{a}_k^{*(\alpha)}v_k^{(\alpha)}\exp(ik\cdot x)]. \tag{78}$$

The factor $[m/(2\pi)^3/E]$ is chosen for convenience in the normalization. This wave packet can be written in a completely similar fashion for bound-state systems, and the coefficients a and $\tilde{a}^*$ are transformed into annihilation and creation operators, when the wavefunction $\psi(t,\mathbf{x})$ is written as a wave operator $\hat{\psi}(t,\mathbf{x})$ as required in QED.

The notion of propagators is naturally extended to the relativistic regime. When considering free propagation, given that the Dirac equation is a first-order equation, it is possible to obtain, as in the NR case,

$$\psi(t_f,\mathbf{r}_f) = \int K(t_f,\mathbf{r}_f;\, t_i,\mathbf{r}_i)\gamma^0\psi(t_i,\mathbf{r}_i)\mathrm{d}\mathbf{r}_i. \tag{79}$$

After some manipulation and the introduction of the coefficients $a_k^{(\alpha)}$ and $\tilde{a}_k^{*(\alpha)}$ as a function of $\psi(t=0,\,\mathbf{r})$ one ends up with [93]

$$\begin{aligned}K(x_f,x_i) = \theta(t_f-t_i)\int \frac{d^3k}{2E(2\pi)^3}\big\{&(\gamma^\mu k_\mu+m)\exp\left[-ik\cdot(x_f-x_i)\right]\\ &+(\gamma^\mu k_\mu-m)\exp\left[ik\cdot(x_f-x_i)\right]\big\}.\end{aligned} \tag{80}$$

This kernel K is the retarded propagator K_{ret}. Now, based on the electron–hole theory we introduce a different Green's function which is called the Feynman propagator for the electron–hole system. When considering only electrons occupying positive-energy electron states, creation, propagation and annihilation processes are acceptable for $t_f > t_i$.

On the other hand, if we deal with a negative-energy electron, we would interpret its annihilation as the appearance of a hole (positron), and vice versa. The propagation should then be considered as the propagation of the positron from x_f to x_i which make sense only for $t_f < t_i$. Therefore in the electron–hole theory we would construct a Green's function that propagates the positive-energy solutions only for $t_f > t_i$ and the negative-energy ones only for $t_i > t_f$:

$$\begin{aligned} S_F(x_f, x_i) = -i \int \frac{d^3k}{2E(2\pi)^3} \big\{ &\theta(t_f - t_i)(\gamma^\mu k_\mu + m) \exp\big(-ik \cdot (x_f - x_i)\big) \\ &- \theta(t_i - t_f)(\gamma^\mu k_\mu - m) \exp\big(ik \cdot (x_f - x_i)\big) \big\}. \end{aligned} \tag{81}$$

By using the integral representation of $\theta(t)$ and changing variables, $p^0 = \pm(E - \omega)$ and $\mathbf{p} = \pm\mathbf{k}$, one gets the usual integral form of the Feynman propagator

$$\begin{aligned} S_F(x) &= \int \frac{d^4p}{(2\pi)^4} \exp(-ip \cdot x) \frac{\gamma^\mu p_\mu + m}{p^2 - m^2 + i\epsilon} \\ &= \int \frac{d^4p}{(2\pi)^4} \exp(-ip \cdot x) S_F(p). \end{aligned} \tag{82}$$

The Feynman propagator can be understood as follows: it propagates the positive-frequency particles (positive-energy electronic wavefunctions) forward in time and negative-frequency (negative-energy electronic wavefunctions) backward in time.

Can we express the Feynman propagator of Equation (82) as a time-ordered product of operators? We want to stress the relationship of such Feynman propagators (see Eq. (95)) with the definition of polarization propagators within NR domain (see Eq. (4)). We shall consider now the particle–hole wavefunction $\psi(x)$ of Equation (78) as a field operator $\hat{\psi}(x)$

$$\hat{\psi}(x) = \int \frac{d^3k}{(2\pi)^3} \frac{m}{k_0} \sum_{\alpha=1,2} [\hat{a}_\alpha(k) u^\alpha(k) \exp(-ik \cdot x) + \tilde{a}_\alpha(k) v^\alpha(k) \exp(ik \cdot x)]. \tag{83}$$

Its complex conjugate is

$$\hat{\bar{\psi}}(x) = \int \frac{d^3k}{(2\pi)^3} \frac{m}{k_0} \sum_{\alpha=1,2} [\hat{a}^\dagger_\alpha(k) \bar{u}^\alpha(k) \exp(ik \cdot x) + \tilde{a}^\dagger_\alpha(k) \bar{v}^\alpha(k) \exp(-ik \cdot x)]. \tag{84}$$

The time-ordered product of two Dirac field operators is defined as

$$T\hat{\psi}_\xi(x)\hat{\bar{\psi}}_{\xi'}(y) = \theta(t_x - t_y)\hat{\psi}_\xi(x)\hat{\bar{\psi}}_{\xi'}(y) - \theta(t_y - t_x)\hat{\bar{\psi}}_{\xi'}(y)\hat{\psi}_\xi(x), \tag{85}$$

where the subscripts ξ and ξ' label the components. Then,

$$T\hat{\psi}_\xi(x)\hat{\bar{\psi}}_{\xi'}(y) = \langle 0|T\hat{\psi}_\xi(x)\hat{\bar{\psi}}_{\xi'}(y)|0\rangle + :\hat{\psi}_\xi(x)\hat{\bar{\psi}}_{\xi'}(y): , \tag{86}$$

where the symbol : : stands for a normal-ordered product where every creation operator is written to the left of every annihilation operator. From this definition,

$$\langle 0||T\hat{\psi}_\xi(x)\hat{\bar{\psi}}_{\xi'}(y)|0\rangle = iS_F(x - y)_{\xi\xi'}. \tag{87}$$

For bound-state electronic systems, the plane-wave expansion is no longer adequate and a proper expansion should be given in terms of stationary solutions of the Dirac equation which can be written as

$$\psi_n(\mathbf{r}) = \begin{cases} u_n^{\alpha}(\mathbf{x}), & \text{for } E_n \geq 0 \\ v_n^{\alpha}(\mathbf{x}), & \text{for } E_n < 0 \end{cases} \tag{88}$$

with the corresponding time-dependent solutions given by

$$\psi_n(x) = \begin{cases} u_n^{\alpha}(\mathbf{x}) \exp\left(-\frac{i}{\hbar} E_n t\right), & \text{for } E_n \geq 0 \\ v_n^{\alpha}(\mathbf{x}) \exp\left(\frac{i}{\hbar} E_n t\right), & \text{for } E_n < 0. \end{cases} \tag{89}$$

Then the electron–hole field operator is expanded now in terms of electron–hole annihilation operators as

$$\hat{\psi}(x) = \sum_{E_n > 0} a_n \psi_n(x) + \sum_{E_m < 0} \tilde{a}_m \psi_m(x) \tag{90}$$

with a_n being the electron annihilation operator for an electron in a state n ($E_n > 0$) and $\tilde{a}_m$ is the electron annihilation operator for an electron in a state m ($E_m < 0$). Given that we will be concerned with the empty-Dirac picture (see [94] and Section 5.1) where the negative-energy branch of the electronic spectra is unoccupied, we will continue to consider that $\tilde{a}_m^{\dagger}$ ($\tilde{a}_m$) is the electron creation (annihilation) operator in a negative-energy state. In Section 5 the relation of negative-energy electronic states with positronic states will be given in more detail. Creation and annihilation operators fulfil the conventional anticonmutation relations

$$\{a_n, a_m^{\dagger}\} = \delta_{nm}; \{b_n, b_m^{\dagger}\} = \delta_{nm} \tag{91}$$

and all other anticonmutators are zero. The corresponding propagator S_F for bound-state QED is

$$\begin{aligned} iS_F(x - y) &= \langle 0 | T\{\hat{\psi}(x)\hat{\bar{\psi}}(y)\} | 0 \rangle \\ &= \sum_{E_n > 0, t_x > t_y} \hat{\psi}_n(x)\hat{\bar{\psi}}_n(y) - \sum_{E_n < 0, t_x < t_y} \hat{\psi}_n(x)\hat{\bar{\psi}}_n(y) \\ &= \theta(t_x - t_y) \sum_{E_n > 0} \hat{\psi}_n(x)\hat{\bar{\psi}}_n(y) - \theta(t_y - t_x) \sum_{E_n < 0} \hat{\psi}_n(x)\hat{\bar{\psi}}_n(y). \end{aligned} \tag{92}$$

In general, we can state that for two fermion or boson field operators the Feynman propagators are defined as a *contraction* of both fields. They are defined as the difference between time-ordering and normal-ordering of the operators involved:

$$\langle 0 | \hat{P}\hat{Q} | 0 \rangle = T(\hat{P}\hat{Q}) - N(\hat{P}\hat{Q}), \tag{93}$$

and because of the Lorentz-invariance of this operation, it becomes very useful when working within the relativistic domain. If the product $\hat{P}\hat{Q}$ is written in normal-ordering the last term does not contribute to the propagator given that propagators are defined as the expectation value of the time-ordering product of operators P and Q in a given reference state. The result of a contraction is a complex number. The time-ordering is defined for fermion or boson fields as

$$T\hat{P}(x)\hat{Q}(y) = \theta(t_x - t_y)\hat{P}(x)\hat{Q}(y) \pm \theta(t_y - t_x)\hat{Q}(y)\hat{P}(x) \tag{94}$$

where the plus (minus) sign is applied for bosons (fermions). For the polarization propagators both operators P and Q are bosons. Then their generalization to the relativistic regime is natural:

$$i\langle\langle \hat{P}(x); \hat{Q}(y)\rangle\rangle = \hbar\theta\big(t_x - t_y\big)\langle 0|\hat{P}(\mathbf{x})\hat{Q}(\mathbf{y})|0\rangle + \hbar\theta\big(t_y - t_x\big)\langle 0|\hat{Q}(\mathbf{y})\hat{P}(\mathbf{x})|0\rangle. \tag{95}$$

From this definition polarization propagators are covariant and it will be used in the QED section to discuss the gauge invariance of the sum of diamagnetic and paramagnetic terms.

4.2. *Kinetic balance*

There are some subtleties that arise only within the relativistic domain. One of them is the so-called *kinetic balance* condition which states a constraint on the relationship between the large (upper two) and small (lower two) components of each Dirac one-electron wavefunction. This is a necessary condition which ensures the correct NR behaviour of a Dirac wavefunction. The Dirac equation is not bounded from below for an N-electron system because it admits an infinite number of negative-energy states and no minimum-energy principle can be used to obtain a variational approximation to the ground state. This was dubbed *variational collapse*. The solution to this problem was suggested 25 years ago [91,95]. Each small component function must be *kinetically balanced* by a large component function to ensure that the kinetic energy will be correctly calculated, even in the non-relativistic limit.

The relativistic wavefunction solution of the time-independent one-electron Dirac equation in a static potential V (see Equation 66) provided by the nuclei in the Born–Oppenheimer frame can be written as

$$\psi(\mathbf{r}, t) = \begin{pmatrix} \psi^L(\mathbf{r}, t) \\ \psi^S(\mathbf{r}, t) \end{pmatrix}. \tag{96}$$

With this consideration, the Dirac equation can be written as a pair of coupled equations

$$(V - E)\psi^L + c(\sigma \cdot \mathbf{p})\psi^S = 0, \tag{97}$$

$$c(\sigma \cdot \mathbf{p}) + \psi^L + (V - E - 2mc^2)\psi^S = 0, \tag{98}$$

and so the small component can be written as

$$\psi^S = \frac{1}{2mc}\left[1 + \frac{E - V}{2mc^2}\right]^{-1} c(\sigma \cdot \mathbf{p})\psi^L. \tag{99}$$

In the limit $c \to \infty$ the squared bracket tends towards unity in such a way that one obtains the *kinetic balance* prescription

$$\lim_{c\to\infty} c\psi^S = \frac{(\sigma \cdot \mathbf{p})}{2m}\psi^L. \tag{100}$$

Given that in actual calculations the kinetic balance prescription can be fulfilled in two general forms we give a brief description of the way one applies kinetic balance in a restricted or unrestricted way.

In our calculations, a Gaussian basis set is used because it allows us to evaluate multi-centre integrals in a straightforward manner. The Cartesian Gaussian functions can be written as

$$G^{\alpha}_{ijk} = Nx^i y^j z^k e^{-\alpha r_A^2}, \tag{101}$$

where N is a normalization constant, A the nuclear centre, and the scripts i, j, k define the quantum angular number ℓ:

$$G^{\alpha}_{\ell} = \left\{ G^{\alpha}_{ijk} | \forall \, (i + j + k) = \ell \right\}. \tag{102}$$

It is possible to transform them to a set of two-spinor spherical Gaussian functions of the form

$$G^{\alpha}_{nkm_j} = N r_A^{n-1} e^{-\alpha r_A^2} \chi_{km_j}(\theta, \phi) \tag{103}$$

where χ_{km_j} is the angular part of the hydrogenic solution of the Dirac equation. Therefore this corresponds to the large component of the Dirac wavefunction. From Equation (100), for each large component function with angular quantum number ℓ, we get two small component functions with $\ell + 1$ and $\ell - 1$ angular quantum numbers:

$$\Psi^L \propto \chi^L \propto \eta^L(r) = \left\{ G^{\alpha}_{\ell} \right\} \Rightarrow \Psi^S \propto \chi^S \propto \eta^S(r) = \left\{ c_{\ell-1} G^{\alpha}_{\ell-1} + c_{\ell+1} G^{\alpha}_{\ell+1} \right\} \tag{104}$$

where $c_{\ell-1}$ and $c_{\ell+1}$ are constants. This is the *restricted kinetic balance*, RKB. It is also possible to keep both types of small basis functions as separate functions, i.e.

$$\Psi^L \propto \chi^L \propto \eta^L_{\mu}(r) = \left\{ G^{\alpha}_{\ell} \right\} \Rightarrow \Psi^S \propto \chi^S \propto \eta^S_{\mu}(r) = \left\{ c_{\ell-1} G^{\alpha}_{\ell-1} \right\} \cup \left\{ c_{\ell+1} G^{\alpha}_{\ell+1} \right\} \tag{105}$$

in which case we obtain the *unrestricted kinetic balance*, UKB. In the RKB prescription there is approximately a 1 : 1 ratio between the large and the small component basis set. On the other hand, in the UKB prescription each generated Gaussian function is independently used as a basis function and then it produces a 1 : 2 ratio between the size of the large and small component basis approximately. This increases the size of the small component basis set and so improves the description of the continuous negative-energy space.

The basis set used in actual calculations is, of course, not complete. One should be aware that getting an equivalent basis-set convergence with either prescription may require equivalent total basis sets. What about the computational time required? As shown in [96] the CPU time savings are larger when calculations are performed with the UKB prescription.

There is another implementation of kinetic balance. This takes into account the external fields and uses a magnetically balanced small component basis set which may help in practice to achieve converged results [29,97]. However, within the polarization propagator formalism this is not formally necessary because the molecular wavefunctions used in the response calculations are the zeroth-order solution of the Dirac equations.

4.3. *Symmetries that can explain relativistic molecular magnetism*

Any operator can be written in terms of time-reversal restricted basic excitation operators, the X operators, known as Kramers single replacement operators [23,94]. There are two types of X operators, depending on both the symmetry under time-reversal and the hermitian conjugation of the operators, say Ô, being represented as an expansion on the X operator basis:

$$\begin{aligned} \hat{X}^s_{pq} &= a^\dagger_p a_q + s a^\dagger_{\bar{q}} a_{\bar{p}}, \\ \hat{X}^s_{\bar{p}q} &= a^\dagger_{\bar{p}} a_q - s a^\dagger_{\bar{q}} a_p, \\ \hat{X}^s_{p\bar{q}} &= a^\dagger_p a_{\bar{q}} - s a^\dagger_q a_{\bar{p}}, \end{aligned} \tag{106}$$

where $s = \pm$ depending on whether the operator $\hat{O}$ is time-reversal symmetric (TRS) and hermitian (+) or not (−). In such an X-basis any one-particle hermitian and TRS operator, like the Hamiltonian, is written as

$$\hat{O} = \sum_{pq} \left[O_{pq} \hat{X}^+_{pq} + \frac{1}{2} \left(O_{\bar{p}q} \hat{X}^+_{\bar{p}q} + O_{p\bar{q}} \hat{X}^+_{p\bar{q}} \right) \right]. \tag{107}$$

If the operator $\hat{O}$ is time-reversal antisymmetric or antihermitian, it should be expanded in terms of X^-. This is the case for the binary products involving *perturbators* (see Equation 14) because they are time-reversal antisymmetric.

The binary products, i.e. the property matrix elements, will contain two type of elements in two different sub-blocks. We mean elements which contain virtual positive-energy states and elements which contain virtual negative-energy states. Considering the elements with excitations to positive-energy MOs one can find an equivalent expression to Equation (14):

$$\begin{aligned} \tilde{\mathbf{P}}_e = \left(\hat{P}^\dagger | \hat{\mathbf{X}}^+_{ia} \right) &= \sum_{pq} P_{pq} \langle 0 | \left[\hat{X}^-_{pq}, \hat{X}^+_{ia} \right] | 0 \rangle + \cdots, \\ &= \sum_{pq} P_{pq} \{ \delta_{qi} \langle 0 | \hat{X}^+_{pa} | 0 \rangle - \delta_{ap} \langle 0 | \hat{X}^+_{iq} | 0 \rangle \} = -2 P_{ai}. \end{aligned} \tag{108}$$

On the other hand, elements with excitations to negative-energy states will give only the $P_{\tilde{a}i}$ elements for the property matrix.

Calculation of Equation (6) in the Kramers basis means

$$\langle\langle \hat{P}; \hat{Q} \rangle\rangle_E = \left(\hat{P}^\dagger | \hat{\mathbf{X}}^+ \right) \left(\tilde{\hat{\mathbf{X}}}^+ | \mathbf{E}\hat{\mathbf{I}} - \hat{\mathbf{H}}_0 | \hat{\mathbf{X}}^+ \right)^{-1} \left(\tilde{\hat{\mathbf{X}}}^+ | \hat{\mathrm{Q}} \right). \tag{109}$$

At the RPA level of approach the new matrices A written in the X-basis are

$$\begin{aligned} \mathbf{A}_{ia,jb} &= -\langle 0 | \left[\hat{X}_{ia} \left[\hat{X}_{bj}, \hat{H}_0 \right] \right] | 0 \rangle \\ \mathbf{A}_{i\tilde{a},j\tilde{b}} &= -\langle 0 | \left[\hat{X}_{i\tilde{a}} \left[\hat{X}_{j\tilde{b}}, \hat{H}_0 \right] \right] | 0 \rangle. \end{aligned} \tag{110}$$

When considering both excitations from an occupied MO to positive- and to negative-energy MOs one can get an equivalent expression to that of Equation (34):

$$\langle\langle \hat{P}; \hat{Q} \rangle\rangle^R_E = \left(\tilde{\mathbf{P}}_e, \tilde{\mathbf{P}}_p, \right) \begin{pmatrix} \mathbf{A}_{ee} & \mathbf{A}_{ep} \\ \mathbf{A}_{pe} & \mathbf{A}_{pp} \end{pmatrix}^{-1} \begin{pmatrix} \mathbf{Q}_e \\ \mathbf{Q}_p \end{pmatrix}. \tag{111}$$

The NR limit of each block gives the spin-restricted expressions. Then the principal propagator can be split up in four blocks: the diagonal blocks belong to excitations to only positive- or only negative-energy MOs. The off-diagonal parts contain a mix of excitations. These last parts are a factor of $1/c$ smaller than the diagonal [29]. We will use this fact when we look for recovering the NR diamagnetic and paramagnetic terms.

The particular blocking of Equation (111) is quite similar to the original interpretation of the electron's motion given recently by Roger Penrose [98]. He considered the electron's motion as consisting of two kinds of particles: the zag and the zig particles. The first one is a right-handed particle and its counterpart, the zig particle, is of left-handed type. Each particle is the source of the other. Then the electron's motion is composed of a zig-zag process, where a zig particle is continually being converted into a zag particle and back again.

On the other hand, each zig-zag process contributes to an infinite quantum superposition, to the total propagator in the manner of a Feynman graph as observed in Figure 2. There are all kinds of zig-zag processes where one has one, two, . . . , such basic processes. The propagator can be constructed as a combination of all of them. In the diagonal part one gets the principal processes, i.e. the zig or the zag ones including then an odd number of other zag or zig processes; the off-diagonal elements are composed of mixtures of zig-zag or zag-zig processes from the very beginning.

One can associate each zag contribution with excitations to positive-energy MOs (the *ee* part of Equation 111) and each zig contribution with the excitation to any negative-energy MO (the *pp* part). The off-diagonal elements of the principal propagators are equivalent to a mix of zig-zag (the *pe* part) and zag-zig (the *ep* part) processes.

There is an interesting point that we want to highlight here. Within the four-component formulation one has only one electronic mechanism that is responsible for each of both NMR spectroscopic parameters; and also if one considers the whole principal propagator matrix one cannot distinguish the paramagnetic from the diamagnetic terms. On the other hand, as will be shown in Section 4.4, one can obtain

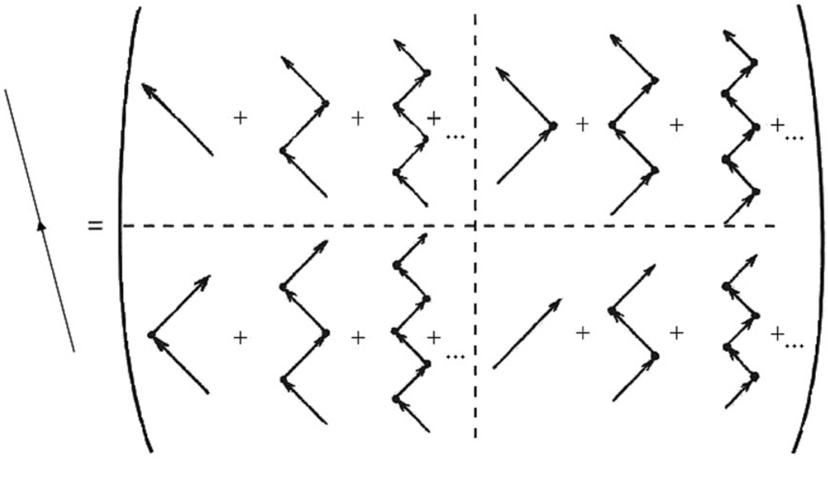

Figure 2. Zig-zag interpretation of electron propagator given by Penrose in [98].

the NR limit only making c go to infinity. When expressed in terms of the X operators we have shown that there is only one of them that can be used and they are of a pseudo-singlet type [23]. This is a clear advantage for both calculation and interpretation when comparing the full relativistic formulation of polarization propagators with its NR counterpart. In the last case there are several mechanisms (FC, SD, PSO and DSO for **J**-couplings), two of them of a triplet type (FC and SD) and the other two of a singlet type. The NR limit is reached with only one condition. In case of including relativistic corrections perturbatively, one should do it in an *ad hoc* manner, or through some transformation scheme from four-component to two-component formulations. Then what we have obtained is a formulation that is much simpler and introduces only one mechanism for explaining each molecular magnetic property.

In the same manner, two concepts that are considered as completely different in an NR formulation, i.e. paramagnetism and diamagnetism, do arise from the same scheme of interactions (the same electronic mechanism) though there is still one that involves only virtual electronic states and there is another that involves only *virtual* electron–positron pair creations and annihilations. This will be treated in more detail in Section 4.4 and also in Section 5.

4.4. *Relativistic vs. NR understanding of electronic mechanisms*

One should be very careful when trying to extend NR concepts to the relativistic domain. It is healthy to highlight the fact that Ramsey's formulation introduced perturbative Hamiltonians as *ad hoc* Hamiltonians. He considered all interactions that must appear and contribute to NMR spectroscopic parameters from a phenomenological NR point of view [8–12]. Within the relativistic domain they do not appear as such though we get them (and some others) starting from the proper perturbative Hamiltonian of Equation (72) and making c go to infinity.

Diamagnetic terms arise by excitations from occupied MOs to virtual negative-energy MOs as will be shown below. When the limit $c \to \infty$ is taken, the negative-energy spectra fall down to $-\infty$, which could appear as an inconsistency. We shall show in the following that this is not the case even though there is a subtlety. It is convenient to discuss separately each spectroscopic parameter. Let us first analyse magnetic shieldings. As shown in [29] the total relativistic propagator can be approximated by the sum of two terms

$$\begin{aligned}\langle\langle H_1; H_1\rangle\rangle &\approx \langle\langle H_1; H_1\rangle\rangle_{ee} + \langle\langle H_1; H_1\rangle\rangle_{pp}\\ &= \left(\sum\nolimits_{ia,jb} \mathbf{b}^*_{ia}(\mathbf{M}^{-1}_{ee})_{ia,jb}\mathbf{b}_{jb} + \text{c.c.}\right) + \left(\sum\nolimits_{i\tilde{a},j\tilde{b}} \mathbf{b}^*_{i\tilde{a}}(\mathbf{M}^{-1}_{pp})_{i\tilde{a},j\tilde{b}}\mathbf{b}_{j\tilde{b}} + \text{c.c.}\right) \qquad (112)\end{aligned}$$

where *ee* and *pp* mean that only excitations to positive-energy and negative-energy electronic orbitals are allowed, respectively. It is nicely seen that the $\langle\langle\ ;\ \rangle\rangle_{ee}$ corresponds to the equivalent paramagnetic term of either NMR spectroscopic parameters within the relativistic domain, and $\langle\langle\ ;\ \rangle\rangle_{pp}$ corresponds to the diamagnetic-like term.

In the negative-energy P_{pp} part of P we neglect $O(c^{-2})$ terms and we neglect the contribution of the $O(c^0)$ integrals $\langle \tilde{a}j \mid \tilde{b}i\rangle$ compared with the energy difference $(\varepsilon_{\tilde{a}} - \varepsilon_i)$, which is of the order of $-2mc^2$. We thus approximate $\mathbf{A}_{pp}$ by a diagonal matrix $\mathbf{A}^{pp}_{\tilde{a}i,\tilde{a}i}$. The negative-energy response function can thereby be written as

$$\langle\langle H_1; H_1\rangle\rangle_{pp} \approx \sum_{i,\tilde{a}} \frac{\langle i|H_1|\tilde{a}\rangle\langle\tilde{a}|H_1|i\rangle}{\varepsilon_i - \varepsilon_{\tilde{a}}}. \tag{113}$$

Given that the excitations $\varepsilon_i - \varepsilon_{\tilde{a}}$ are such that [99]

$$2mc^2 \leqslant \varepsilon_i - \varepsilon_{\tilde{a}} < 4mc^2 \tag{114}$$

and using the resolution of the identity for Dirac's one-electron states

$$\begin{aligned}\langle\langle H_1; H_1\rangle\rangle_{pp} \approx \frac{e^2}{2m}\sum\nolimits_i \{\langle i|A^2|i\rangle - \sum\nolimits_j \langle i|\alpha\cdot\mathbf{A}|j\rangle\langle j|\alpha\cdot\mathbf{A}|i\rangle\}\\ - \frac{e^2}{2m}\sum\nolimits_{i,a}\langle i|\alpha\cdot\mathbf{A}|a\rangle\langle a|\alpha\cdot\mathbf{A}|i\rangle.\end{aligned} \tag{115}$$

When c goes to infinity the last two terms go to zero. This would increase the values of σ^d when passing from the R to NR domains.

Another interesting feature is related to the paramagnetic-like terms. In this case we should consider the property matrix elements. As shown in Equation (76) there are two such matrix elements. We first show that both relativistic property matrix elements go to their Ramsey NR expressions. The explicit NR expressions for $\mathbf{b}_{ia}$ and $\mathbf{b}_{jb}$ are given, within the RPA level of approach and the RKB condition being imposed, as

$$\left\langle i\left|\frac{e}{c}\alpha\cdot\frac{\mu_M\times\mathbf{r}_M}{r_M^3}\right|a\right\rangle = \frac{e}{c}\mu_M\cdot\left\langle i\left|\frac{\mathbf{r}_M\times\alpha}{r_M^3}\right|a\right\rangle \to \frac{e}{2mc^2}\left\langle i^L\left|\left\{\sigma\cdot\frac{\mu_M\times\mathbf{r}_M}{r_M^3},\sigma\cdot\mathbf{p}\right\}_+\right|a^L\right\rangle. \tag{116}$$

Then after solving the anticommutator one obtains the NR $\mathbf{b}_{is}$. The NR expressions of $\mathbf{b}_{jt}$ are obtained in the same manner

$$\langle j|\frac{ec}{2}\alpha\cdot(\mathbf{B}\times\mathbf{r}_G)|b\rangle \longrightarrow \langle j^L|\frac{ec}{2}\{\sigma\cdot(\mathbf{B}\times\mathbf{r}_G),\sigma\cdot\mathbf{p}\}_+|b^L\rangle. \tag{117}$$

Here there is also an interesting subtlety. The Dirac position operator is not equivalent to the Schrödinger position operator. Given that the Dirac operators α can be related to the velocity operator, in both Equations (116) and (117) one has angular-momentum-like operators. They are expressed as four-component matrix elements. Following the development shown on pp. 65–66 of [89] there is a useful identity

$$mc\langle\psi|\vec{\mathbf{r}}\times\vec{\alpha}|\psi\rangle = \hbar\langle\psi|\beta(\boldsymbol{\Sigma} + (\mathbf{r}\times\mathbf{p}))|\psi\rangle \tag{118}$$

which is not an operator identity though a matrix identity. In this case matrix elements are obtained between the same states. The left-hand side refers to the instantaneous angular momentum and the second term of the right-hand side the average angular momentum. The factor β is the usual $1/(1-v^2/c^2)^{1/2}$. In the limit of $c\to\infty$ the right-hand side of this equality goes to

$$\langle\psi(\mathbf{L}+2\mathbf{S})\rangle\psi. \tag{119}$$

Given that the factor β depends on the electron velocities, or in other words, will be larger than 1 when $c \rightarrow 1$ starting from $c = \infty$, one can expect that both terms of Equations (116) and (117) will be larger when calculated within the relativistic domain as compared with their equivalent NR terms.

4.5. *Application to model compounds*

In this section we will focus on what the actual application of propagators can bring us concerning relativistic effects on NMR spectroscopic parameters. We will concentrate on two widely used molecules, HX and CH_3X ($X = Br$, I) for this kind of analysis. In the next subsection we will treat some novelties concerning **J**-couplings and in the next we will concentrate on shieldings.

The first calculations applying full relativistic propagators of electric response properties appeared in 1997 [100] and calculations of magnetic response properties in 1999 [29,101,102]. They were obtained using DIRAC code that was written re-expressing all equations within a quaternion algebra [103,104] which is completely equivalent to that of the X operators, though they have several practical advantages.

4.5.1. *New insights on NMR J-couplings from relativistic propagators*

Electron correlation effects are in general important for **J**-couplings in saturated molecules. What about relativistic effects? The dependence of ${}^1J$(C-X) for $X = \mathrm{F}$ with electron correlation in molecules like CH_3X is more pronounced than in all other cases: $X = \mathrm{Cl}$ and Br as observed in Table 2. Still NR SOPPA results are more negative than NR RPA for $X = \mathrm{F}$; for $X = \mathrm{Cl}$ they are close to each other and correlation effects are positive for $X = \mathrm{Br}$. In this last case relativistic effects have an opposite sign. If J^R(SOPPA–RPA) $\approx J^{NR}$(SOPPA–RPA) we would obtain ${}^1J^R$(C–Br) ≈ -50 Hz. On the other hand, for the CH_3Br molecule relativistic and correlation effects on ${}^1J$(C–H) and ${}^2J$(H–Br) are also opposite though also opposite to what we observe for ${}^1J$(C–Br) (see Figures 3 and 4). Relativistic effects on ${}^2J$(H–Br) are positive, though correlation effects are negative. We can predict that ${}^2J$(H–Br) ≈ 15.50 Hz. RPA or first-order correlation effects modify **J**-couplings such that they become more negative ($\simeq$30%) for ${}^1J$(C–Br) and more positive ($\simeq$20%) for ${}^2J$(H–Br). More pronounced behaviour is observed for ${}^1J$(HI) in the HI molecule. Figure 5 shows the importance of including correlation effects. At the RPA level of approach relativistic effects reinforce ${}^1J$(HI) by one order of magnitude. If the percentage of the contribution of electron correlation is the same at both limits, R and NR, the relativistic SOPPA would give ${}^1J$(HI) $\simeq -150$ Hz. What one can predict is that ${}^1J$(HI) $\ll 0$. We can compare the behaviour of this **J**-coupling with that of ${}^1J$(H–Br) (see Figure 6). In this last case when including relativistic effects one could get a theoretical coupling close to the experimental value: 62 Hz [75].

4.5.2. *New insights on magnetic shielding from relativistic propagators*

For σ(I; HI) the behaviour of σ^p and σ^d is opposite when c goes from 1 to ∞: σ^p becomes more positive (it changes its ‘nature’) and σ^d more negative (see Figure 7). The overall effect follows the behaviour of σ^p. The fact that σ^p changes its sign is further evidence of the relative meaning of both terms which is based on gauge-invariant conditions at the

Table 2. Comparative R and NR polarization propagator calculations of ${}^{n}J$ ($n = 1, 2$) on CH_3X molecules ($X = F, Cl, Br, I$) at different levels of approach.

Couplings	R-PZOA[a]	R-RPA[b]	lim NR-PZOA[c]	lim NR-RPA[d]	NR-RPA[e]	NR-SOPPA[f]
C–F	−56.27	−133.14	−55.70	−131.87	−131.33	−173.79
H–C	51.26	191.02	51.09	190.34	190.55	153.18
H–F	13.44	62.07	13.41	62.63	61.18	49.27
H–H	0.66	−22.95	0.64	−22.98	−23.06	−11.56
C–Cl	−4.06	−11.27	−3.97	−10.74	−10.45	−11.82
H–C	51.25	193.26	51.07	192.66	192.95	154.29
H–Cl	1.70	3.40	1.69	3.37	3.33	3.28
H–H	0.37	−25.42	0.35	−25.64	−25.90	−14.29
Br–C	−14.11	−62.42	−13.81	−48.17	−49.32	−36.97
H–C	52.24	196.96	51.98	195.96	196.34	156.28
H–Br	7.81	17.59	7.65	14.67	15.59	13.76
H–H	0.83	−24.10	0.77	−24.39	−24.50	−12.99
I–C	−12.15	−119.52	−11.28	−48.77	−51.20	−53.75
H–C	51.95	199.20	51.54	196.30	196.68	157.01
H–I	8.56	23.45	8.01	9.25	11.86	11.95
H–H	0.79	−24.60	0.67	−25.08	−25.35	−14.63

[a] Relativistic four-component calculation at PZOA level using the DIRAC program.
[b] Idem at RPA level.
[c] Non-relativistic limit calculation ($c = 10$) at PZOA level using the DIRAC program.
[d] Idem at RPA level.
[e] Non-relativistic calculation at RPA level using the DALTON program.
[f] Idem at SOPPA level.

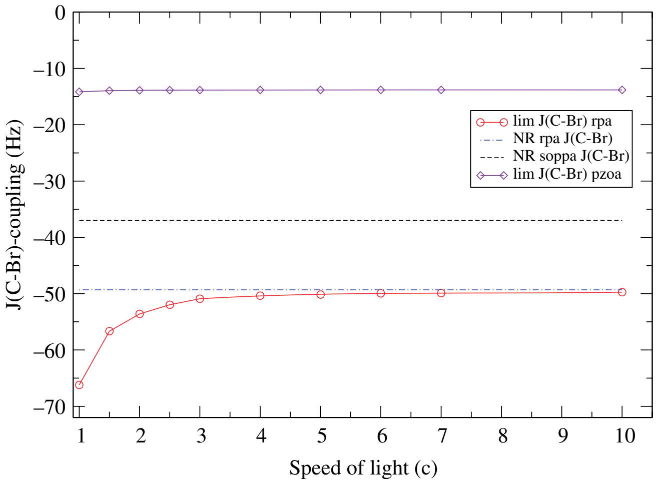

Figure 3. [Colour online] Relativistic and NR values of ${}^{1}J$(C–Br; $CBrH_3$) at the PZOA, RPA and SOPPA levels of approach.

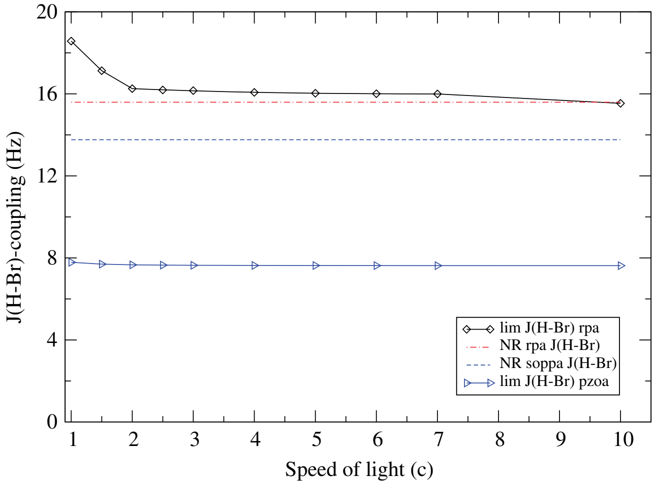

Figure 4. [Colour online] Relativistic and NR ^2J(H–Br; $CBrH_3$) at the PZOA, RPA and SOPPA levels of approach.

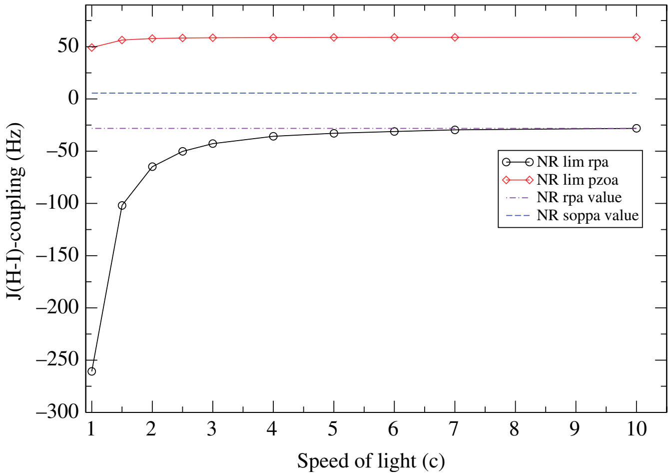

Figure 5. [Colour online] Correlation effects on J(H–I; HI) at the PZOA, RPA and SOPPA levels of approach.

NR limit [75]. In Section 5 we will give a new insight into why this may happen. We show that they arise only within a non-covariant QED formulation. Within a covariant formulation (the only one that is valid) one is not allowed to distinguish between them. Even within the proper relativistic formulation one should avoid expressing the shielding as

$$\sigma \neq \sigma^p + \sigma^d. \tag{120}$$

The equality in this equation arises only as an approximation as shown in Equation (112).

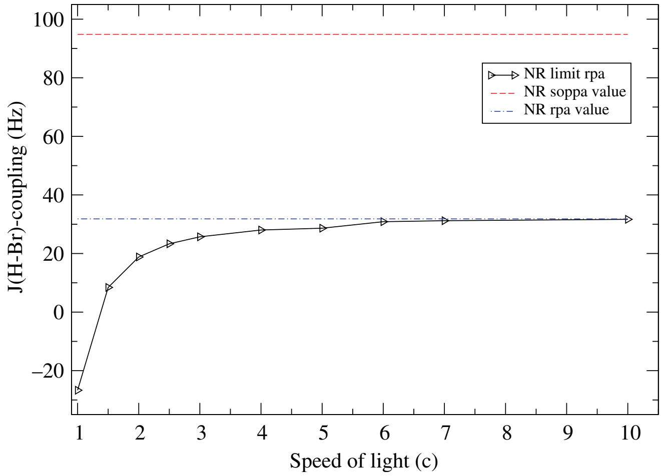

Figure 6. [Colour online] Correlation effects on J(H–Br; HBr) at the RPA and SOPPA levels of approach.

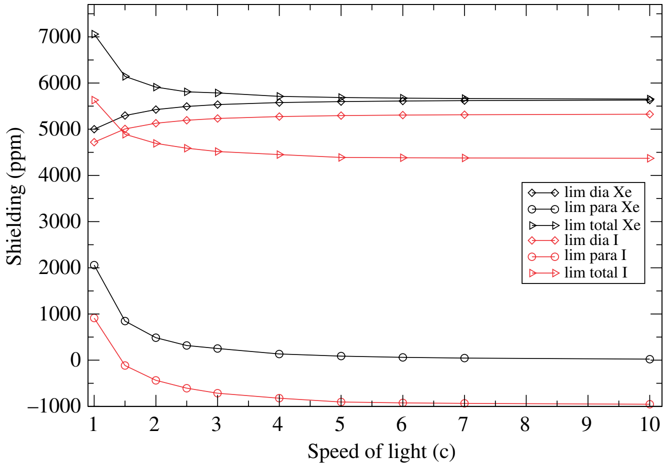

Figure 7. [Colour online] Relativistic and NR diamagnetic and paramagnetic contributions to σ(Xe and I; HI) at the RPA level of approach.

Another important finding just obtained when considering $c = 1$, is the appearance of paramagnetic-type contributions for closed shell atoms [105]. In Figure 7 we show the behaviour of the paramagnetic-type and diamagnetic-type contributions when $c = 1, 2, \ldots, \infty$. There is a smooth and quantitative convergence to its NR values, where $\sigma^p \equiv 0$. Relativistic effects are so dramatic that $\sigma^R(\mathrm{Rn}) \simeq 2\sigma^{NR}(\mathrm{Rn})$. From Equation (117) one can see that the operator in the up right part does not have the same symmetry of an angular momentum when acting on the small component of virtual MOs. This symmetry is recovered at the NR limit.

As shown in Figure 7, differences between $\sigma^{\text{p-like}}$(I; HI) and $\sigma^{\text{p-like}}$(Xe) are such that for iodine, in its NR limit, there is a negative contribution ($\simeq -10^3$) that becomes positive

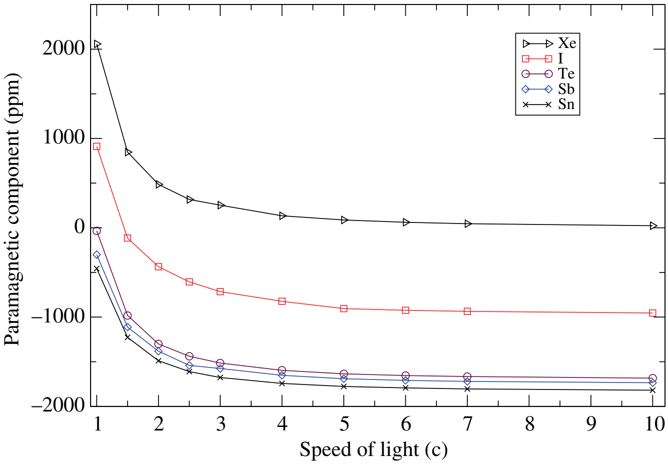

Figure 8. [Colour online] Paramagnetic behaviour of σ (X; X = Xe, I, Te, Sb and Sn) depending on the value of the velocity of light at the RPA level of approach.

when $c=1$ ($\simeq +10^3$); in the case of σ(Xe) this behaviour is similar though shifted to more positive values such that the total value coincides with $\sigma^{\text{d-like}}$(Xe) at the NR limit. This pattern is similar for Rn though much more pronounced.

Then we can try to figure out what kind of mechanism would be involved in the new relativistic behaviour of $\sigma^{\text{p-like}}$. We have studied the tendency for the shielding of all atoms belonging to the same row as Xe and being the heavy atoms of the following molecules: XH_n(X = Xe, I, Te, Sb and Sn; and $n=0$–4). In Figure 8 we show their paramagnetic behaviour. It is nice to see that a new and the same mechanism appears. What one observes, for rare gas atoms, is a particular value that produces its vanishing value for $c \to \infty$. But the physics involved seems to be the same in all cases. In the case of TeH_2 $\sigma^{\text{p-like;R(NR)}}(\text{Te}) = -7.78$ (-1696.03) ppm and for SbH_3 $\sigma^{\text{p-like;R(NR)}}(\text{Sb}) = -306.25$ (-1722.65) ppm [106]. This means that relativistic effects on the paramagnetic-type contribution of NMR shieldings is becoming more negative starting from noble gas atoms to the left on the periodic table, as shown in Figure 8. The fact that paramagnetic-type contributions becomes larger for $c \to 1$ can be explained from Equations (116) and (115) given above. It is also found that the behaviour of $\sigma^{\text{p-like}}$(X) when $n \geqq 2$ is almost the same. This would mean that only linear molecules and systems with strict spherical symmetry would have different numerical contributions.

Another interesting finding that is shown in Figure 7 is related to the growing value of σ^d when c goes from 1 to infinity. This is explained from Equation (113) where we can see that the positronic contribution to σ is approximated by Equation (115). Then, the last two terms are different from zero when $c=1$ but become zero when c goes to infinity.

4.6. *Comparison with other methods*

In this section we will include some brief comments on different methods that were developed to consider relativistic effects on magnetic molecular properties. There are a few recent review articles that focus on both methodologies and new results which the interested reader should have a look at [107–111].

MO-based *full* relativistic formulations for chemical shifts were first published in 1983 [112–115]. Previously Pyykkö proposed a relativistic theory for NMR **J**-couplings in 1977 [116]. Calculation of **J**-couplings for molecules containing heavy atoms were performed with a semi-empirical relativistic code named REX early in the 1980s [68], and later with CLOPPA-MNDO [117].

There are several two-component methods based on transformed Dirac–Coulomb Hamiltonians: (a) the zero-order regular approximation, ZORA; (b) the Douglas–Kroll–Hess method, DKH; (c) the infinite-order regular approximation with modified metric, IORAmm; (d) the infinite-order two-component theory, IOTC; and (e) the field-dependent unitary transformation to the Dirac operator.

(a) The ZORA approach [118] is the most widely used. It may underestimate [119] relativistic effects on shielding of heavy atoms as compared with four-component relativistic theory. ZORA only takes zeroth-order effects into account [120]. Fukui and coauthors extended the normalized ESC theory to include magnetic interactions. They applied it to calculate $\sigma(\mathrm{H})$ and $\sigma(\mathrm{X})$ in HX ($\mathrm{X} = \mathrm{F}$, Cl, Br and I) systems at the levels of ZORA or NESC-ZORA and second-order regular approximation or NESC-SORA [121].

(b) The DKH approach arises from a transformation proposed to uncouple the large to the small components, to some order n ($n = 1, 2$) in c^{-2}. This method does not suffer from gauge invariant problems. When including more accuracy the formalism becomes more and more complicated [122]. Recently Nakatsuji and coauthors improved previous methods along the lines of DKH theory by including the relativistic magnetic interaction operator into the generalized UHF scheme [123,124].

(c) Its Hamiltonians involve all relativistic terms of order c^{-2} correctly [126]. It was applied to calculate $^{1}J(\mathrm{Pb{-}H})$ in $\mathrm{PbH_4}$ and $\mathrm{PbHMe_3}$ molecules with BLYP and B3LYP functionals [127].

(d) Fukui and coauthors have extended the IOTC theory to include calculations of shielding tensors [128–130].

(e) The transformation can be obtained at the operator level, at the matrix level or as a mix of both methodologies [131–133]. Liu and coauthors prefer the external field-dependent unitary transformation at the operator level, EFUT, due to its explicit operator form. They have shown results of shielding for Rn and Rn^{85+}.

Relativistic effects have also been included as a perturbation to NR quantum mechanical calculations: (i) from response theory and applying the elimination of the small component, ESC, transformation: LR-ESC [134,135], and (ii) from the Breit–Pauli Hamiltonian [136–138]. Both schemes are completely equivalent in their numerical results though they involve different operators. Both give closest results compared with the four-component polarization propagator approach, and in some cases with experimental results [139,140]. Their shortcomings lie in the fact that they can quantitatively reproduce only the leading relativistic effects until elements of the fifth-row [99], though their advantages are on interpretations which in most cases are related with a mix of NR mechanisms [141]. The elimination of the small component reduction is applied directly to a four-component Rayleigh–Schrödinger perturbation theory expression of the magnetic properties. In this sense, it is wholly consistent with the most direct relativistic theory of magnetic properties. An alternative approach for the calculation of the negative-energy state contributions to magnetic properties within the LR-ESC approach has been presented with numerical results for Xe and I atoms [142].

Similar previous attempts were made by methods which include FC or SD plus one-electron SO corrections using finite-perturbation UHF [143–145] and DFT [146,147] methods.

Relativistic configuration interaction (CI) and coupled cluster (CC) methods using four-component spinors were developed by Nakatsuji and coauthors [148]. They start with the no-pair Dirac–Coulomb–Breit (DCB) Hamiltonian and include in it the magnetic vector potential. Molecular DF spinors are obtained considering the nuclear magnetic moment term explicitly. This is an important point because calculations are done in the post-SCF level of single and double CI (SDCI) and the relativistic CCSD method, where the Hellmann–Feymann theorem is not satisfied. The zero-order wavefunction in the electron-correlation calculations is approximated by a single Slater determinant of the positive-energy molecular DF spinors. Its application to the HX series shows excellent agreement with experimental values, though for larger systems results are not as good due to basis set requirements.

A four-component DFT theory for calculating nuclear magnetic shieldings [97] and **J**-couplings [149] was developed by Malkin and coworkers. This scheme is based on the restricted magnetic balance basis (RMB) and implemented at the level of Dirac–Khon–Sham. The method was dubbed mDKS-RMB. In this method the unperturbed equations are solved with the use of an RKB basis set for the small components, and the coupled-perturbed DKS equations were solved with the RMB prescription for the construction of the small component basis set. It does not have any problems of picture change effects, which may arise when transformation from four-component operators to two-component operators is applied. Calculations of $\sigma(\mathrm{H})$ and $\sigma(\mathrm{X})$ for XH ($\mathrm{X}=\mathrm{F}$, Cl, Br, I) systems with the coupled-perturbed mDKS-RMB scheme gives close results compared with experiments, though such experimental results are based on Flygare's approach. Benchmark calculations of ${}^{1}J(\mathrm{XH})$ and ${}^{2}J(\mathrm{H{-}H})$ for compounds XH_4 ($\mathrm{X}=\mathrm{C}$, Si, Ge, Sn and Pb) show that the BP86 correlation functional gives better results compared with experiments.

5. QED

The description of electrons in terms of the relativistic Dirac equation was a remarkable step forward in the search of a rigorous theoretical foundation for the physics of atoms and molecules. Nevertheless, the electromagnetic field remained as a 'scenery' for the electron motions. In the formal framework it was considered as an external source acting on the matter (particles) but without its own degrees of freedom and hence lacking a dynamics. There were at least two important conceptual problems with Dirac's theory. On the one hand, from the very beginning of quantum theory it was known that the electromagnetic field behaves, under some circumstances, as particles with quantized energies and momentum; this fact is not present in Dirac's equation. On the other hand, the infinitely many negative-energy solutions of Dirac's equation did not have consequences on the experiments, so they were thought to represent unavailable states. Dirac solved this problem by proposing that those states are occupied. Such a proposal required an infinite number of unobservable electrons forming a negative-energy many-particle 'sea'. Firstly, we shall address the introduction of a dynamics for the electromagnetic field, and later on we will discuss the effects introduced by the negative-energy sea or, equivalently, the treatment of positrons as virtual antiparticles.

Even though our applications are mainly oriented to bound-state systems, we can derive the relevant techniques for weakly interacting particles, where the formal calculations are easier, and afterwards extend the results by means of the Gell-Mann and Low theorem to bound-state systems. Then, the level-shift formula can be applied to the interaction with an external classical field, which is the case of the NMR parameters.

In order to treat the degrees of freedom of both matter and radiation on an equal footing, the electromagnetic field must be decomposed into its normal modes, within a box of volume V,

$$A^{\mu}(x) = A^{\mu+}(x) + A^{\mu-}(x), \tag{121}$$

where

$$A^{\mu+}(x) = \sum_{\boldsymbol{k}\lambda} \left(\frac{\hbar}{2\epsilon_0 ckV} \right)^{1/2} e^{\mu}_{\boldsymbol{k}\lambda} c_{\boldsymbol{k}\lambda} e^{-ik\cdot x} \tag{122}$$

$$A^{\mu-}(x) = \sum_{\boldsymbol{k}\lambda} \left(\frac{\hbar}{2\epsilon_0 ckV} \right)^{1/2} e^{\mu}_{\boldsymbol{k}\lambda} c^{*}_{\boldsymbol{k}\lambda} e^{ik\cdot x}, \tag{123}$$

and the coefficients have to be promoted to Fock operators satisfying proper commutation relations, i.e.

$$[c_{\boldsymbol{k}\lambda}, c_{\boldsymbol{k}'\lambda'}] = \left[c^{\dagger}_{\boldsymbol{k}\lambda}, c^{\dagger}_{\boldsymbol{k}'\lambda'} \right] = 0, \tag{124}$$

$$\left[c_{\boldsymbol{k}\lambda}, c^{\dagger}_{\boldsymbol{k}'\lambda'} \right] = \zeta_{\lambda} \delta_{\lambda\lambda'} \delta_{\boldsymbol{k}\boldsymbol{k}'}\ \zeta_0 = -1, \zeta_i = 1 (i = 1, 2, 3). \tag{125}$$

This is the basis of the *canonical quantization* method. The fields at each point of space are considered as the dynamical variables and the position coordinates as a continuous subscript labelling a given component of a field $\phi_r(x)$, $(r = 1, 2, \ldots, N)$. The electric and magnetic fields $\boldsymbol{E}$ and $\boldsymbol{B}$ are then derived from the 4-potential $A^{\mu} = (\phi, \boldsymbol{A})$. Therefore, the following covariant commutation relations are obtained

$$[A^{\mu}(x), A^{\nu}(x')] = i\hbar c D_F^{\mu\nu}(x - x'), \tag{126}$$

where $D_F^{\mu\nu}(x - x')$ is the *Feynman photon propagator* defined by

$$i\hbar c D_F^{\mu\nu}(x - x') = \langle vac | T\{A^{\mu}(x) A^{\nu}(x')\} | vac \rangle \tag{127}$$

and explicitly given by

$$D_F^{\mu\nu}(x) = -g^{\mu\nu} \int \frac{d^4k}{(2\pi)^4} \frac{e^{-ikx}}{k^2 + i\epsilon}. \tag{128}$$

We are interested in atoms and molecules under external magnetic fields. The choice of the Coulomb gauge allows us to separate the longitudinal and transverse fields in such a way that the scalar potential resembles the instantaneous Coulomb interaction, while the vector potential satisfies a wave equation. On the other hand, as an approximation a part of the vector potential can be considered as classical, while the rest has a quantum nature. This description is more intuitive on a physical basis because the scalar potential becomes included as the electrostatic potential of nuclei in the Dirac equation. Nevertheless, from a formal point of view it is less satisfactory because the covariance of the theory becomes broken. As discussed later on, another effect of the breaking of the symmetry is that the electron propagation forward and backward in time has to be considered separately, thus giving a different interpretation for either processes.

Now we change our picture for the electrons. Proceeding as before, the field ψ can be expanded in terms of a complete set of solutions to the Dirac equation (within a box of volume V) ψ_n. Since the time dependence of the negative-energy solutions is equivalent to the time dependence of positive-energy particles, we change from negative-energy electron states $a_{r\mathbf{p}}$ to positive-energy positron states $b^\dagger_{r\mathbf{p}}$

$$\begin{aligned}\psi(x) &= \psi^+(x) + \psi^-(x)\\ &= \sum_{r\mathbf{p}} \left(\frac{mc^2}{VE_p}\right)^{1/2} \left[a_{r\mathbf{p}} u_{r\mathbf{p}} e^{-ipx/\hbar} + b^\dagger_{r\mathbf{p}} v_{r\mathbf{p}} e^{ipx/\hbar}\right], \end{aligned} \tag{129}$$

and the corresponding expression for $\bar{\psi}(x)$. Henceforth, the anticommutation relations for the Fock operators a and $b^\dagger$ are

$$\left\{a_{r\mathbf{p}}, a^\dagger_{s\mathbf{p}'}\right\} = \left\{b_{r\mathbf{p}}, b^\dagger_{s\mathbf{p}'}\right\} = \delta_{rs}\delta_{\mathbf{p}\mathbf{p}'}, \tag{130}$$

and zero otherwise.

From them, a covariant anticommutation relation

$$\left\{\psi(x), \bar{\psi}(y)\right\} = iS(x-y) = i\left(i\gamma^\mu \partial_\mu + \frac{mc}{\hbar}\right)\Delta(x-y) \tag{131}$$

can be derived, where the *Feynman fermion propagator* $S_F(x-y)$ is defined by

$$\langle vac|T\{\psi(x)\bar{\psi}(y)\}|vac\rangle = iS_F(x-y), \tag{132}$$

having the representation

$$S_F(x) = \frac{\hbar}{(2\pi\hbar)^4}\int d^4p \frac{\gamma^\mu p_\mu + mc}{p^2 - m^2c^2 + i0} e^{-ipx/\hbar}. \tag{133}$$

Finally, in order to allow the electrons to interact with an external field, we invoke the *minimal coupling prescription* consisting in the replacement $\partial_\mu \to D_\mu = \partial_\mu + \frac{iQ}{\hbar c}A_\mu(x)$. Then, the Dirac equation for electrons ($Q = -e$) becomes

$$(i\hbar\gamma^\mu\partial_\mu - mc)\psi(x) = -\frac{e}{c}\gamma^\mu A_\mu(x)\psi(x), \tag{134}$$

which is equivalent to introducing a mutual interaction Hamiltonian density

$$\mathcal{H}_I = -e\bar{\psi}(x)\gamma^\mu\psi(x)A_\mu(x) = (1/c)j^\mu(x)A_\mu(x) \tag{135}$$

between the conserved 4-current $j^{\mu}(x) = -ec\bar{\psi}(x)\gamma^{\mu}\psi(x)$ and the electromagnetic field. It should be noted that we focus on the effect of the quantization of the electromagnetic field on the interaction between the electrons of a molecule with the spins of the nuclei. The NMR spectroscopic parameters $\mathbf{J}$ and σ are defined from their phenomenological energy expressions which are bilinear in the nuclear spins, and the external magnetic field and the spin of the nucleus considered, respectively. Two alternative formalisms can be used for defining them when a quantized electromagnetic field is present. One of them makes use of the Gell-Mann and Low energy expression for a given interaction Hamiltonian; the other one considers that the magnetic dipole moments associated with the nuclear spins interact with the magnetic field resulting from the quantized vector potential.

In the next subsection we shall be concerned with the interpretation of virtual excitations from occupied electronic states to negative-energy electronic states for the contributions to magnetic property calculations. This drives us to consider different pictures for getting matrix elements looking for their equivalence. The two formalisms named *S*-matrix and multi-polar (in particular, dipolar) QED, will then be presented in Sections 5.2 and 5.4 were we show two successful attempts to obtain NMR spectroscopic parameters from the QED theory. The appearance and treatment of 'virtual' antiparticles will be considered after Section 5.2.

5.1. *Empty Dirac vs. QED picture*

We need to introduce here two equivalent pictures for the second quantized form of any relativistic operator $\hat{O}$ [94]: (a) the 'empty Dirac' approach where the negative-energy states are empty, and are not reinterpreted as positron states, and (b) the QED approach. In the first approach

$$\hat{O} = \sum_{pq} \hat{O}_{pq} a_p^{\dagger} a_q + \hat{O}_{p\tilde{q}} a_p^{\dagger} a_{\tilde{q}} + \hat{O}_{\tilde{p}q} a_{\tilde{p}}^{\dagger} a_q + \hat{O}_{\tilde{p}\tilde{q}} a_{\tilde{p}}^{\dagger} a_{\tilde{q}} \tag{136}$$

where the tilde on Roman indices means orbitals which belongs to the negative-energy branch of Dirac's energy spectra. The unoccupied spinors consist of the unoccupied electron spinors and the negative-energy spinors. On the other hand, in the QED picture the negative-energy states are reinterpreted according to the QED approach as positive-energy positrons, and the operators are presented in normal-ordered form

$$: \hat{O} := \sum_{pq} \hat{O}_{pq} a_p^{\dagger} a_q + \hat{O}_{p\tilde{q}} a_p^{\dagger} \tilde{a}_q^{\dagger} + \hat{O}_{\tilde{p}q} \tilde{a}_p a_q - \hat{O}_{\tilde{p}\tilde{q}} \tilde{a}_q^{\dagger} \tilde{a}_p. \tag{137}$$

The unoccupied spinors consist of the unoccupied electron spinors and the negative-energy spinors, just as in the empty Dirac approach.

When calculating the property matrix elements of Equation (14) with operators expanded in both pictures one gets the same *c*-numbers.

Within the empty Dirac picture

$$\langle 0|\left[\hat{P}, \hat{a}_a^{\dagger}\hat{a}_i\right]|0\rangle = \sum_{pq} P_{pa}\left\{\delta_{qa}\langle 0|\hat{a}_p^{\dagger}\hat{a}_i|0\rangle - \delta_{pi}\langle 0|\hat{a}_a^{\dagger}\hat{a}_q|0\rangle\right\} \tag{138}$$

$$- \sum_{p\tilde{q}} P_{p\tilde{q}}\delta_{pi}\langle 0|\hat{a}_a^{\dagger}\hat{a}_{\tilde{q}}|0\rangle + \sum_{\tilde{p}q} \delta_{qa}\langle 0|\hat{a}_{\tilde{p}}^{\dagger}\hat{a}_i|0\rangle \tag{139}$$

$$= P_{ia}. \tag{140}$$

The contributions of the last three terms are zero because in the reference state there are no unoccupied spinors, so only the first one survives. A similar expression is found for the excitation $\hat{a}_{\tilde{a}}\ a_i$ though the property matrix element will be $\mathrm{P}_{i\tilde{a}}$

Working within the QED picture one gets the same results for both property matrix elements. Then one can say that all matrix elements of polarization propagators will be the same in both pictures.

5.2. *S-matrix formalism for bound state QED*

For convenience, we change now to the *interaction picture*

$$O_I(t) = e^{iH_0t/\hbar} O_S e^{-iH_0t/\hbar}. \tag{141}$$

where both the state vectors and the operators evolve with time:

$$i\hbar \frac{\mathrm{d}O_I(t)}{\mathrm{d}t} = [O_I(t), H_0], \tag{142}$$

$$i\hbar \frac{\mathrm{d}}{\mathrm{d}t} |\Phi_I(t)\rangle = H_I(t)|\Phi_I(t)\rangle \tag{143}$$

with the time-dependent Hamiltonian $H_I(t)$.

Consider an initial state $|i\rangle$ of a system of non-interacting particles having well-defined properties (such as particle number, energy, momentum, etc.). Let them collide, interacting during a short time, and fly apart from each other again. The evolution of the state of the system $|\Phi(t)\rangle$ is given by Equation (143) under the initial condition $|\Phi(-\infty)\rangle = |i\rangle$. The state long after the scattering will be $|\Phi(\infty)\rangle$ also having well-defined properties.

The *S-matrix* is defined as the operator performing the evolution of the system between both non-interacting states

$$|\Phi(\infty)\rangle = S\,|\Phi(-\infty)\rangle = S|i\rangle. \tag{144}$$

Together with the initial condition $|\Phi(-\infty)\rangle = |i\rangle$, this gives

$$S = \sum_{n=0}^{\infty} \frac{1}{n!} \left(-\frac{i}{\hbar}\right)^n \int_{-\infty}^{\infty} \mathrm{d}^4x_1 \int_{-\infty}^{\infty} \mathrm{d}^4x_2 \ldots \int_{-\infty}^{\infty} \mathrm{d}^4x_n T\{\mathcal{H}_I(x_1)\mathcal{H}_I(x_2)\ldots\mathcal{H}_I(x_n)\} \tag{145}$$

as a formal solution in terms of the time ordering operator.

Wick's theorem [150] allows us to express a T-product of any set of Fock operators $A, B, C, \ldots, X, Y, Z$ in terms of their *normal ordered* product and one, two, etc. *contractions*:

$$\begin{aligned} T\{ABC\cdots XYZ\} &= :ABC\cdots XYZ: + :\underbrace{AB}\,C\cdots XYZ: + :\underbrace{ABC}\ldots XYZ: + \cdots \\ &\quad + :\underbrace{ABC\ldots XYZ}: + \cdots \end{aligned} \tag{146}$$

i.e. a product of Fock operators with the creation operators placed to the left of the annihilation operators times photon and fermion propagators (represented by the underbrackets) defined as

$$S_F(x, y) = \langle T\{\psi(x)\bar{\psi}(y)\}\rangle, \tag{147}$$

$$D_{F\mu\nu}(x, y) = \langle T\{A_\mu(x)A_\nu(y)\}\rangle, \tag{148}$$

while for equal-time operators,

$$T\{A(t)B(t)\} = \frac{1}{2}A(t)B(t) - \frac{1}{2}B(t)A(t). \tag{149}$$

The time dependence of the propagators can be made explicit if we write them as follows

$$S_F(x, y) = \int \frac{\mathrm{d}E}{2\pi i} S_F(\boldsymbol{x}, \boldsymbol{y};\, E)e^{-iE(x^0-y^0)}, \tag{150}$$

$$D_{F\mu\nu}(x, y) = g_{\mu\nu} \int \frac{\mathrm{d}k_0}{2\pi i} D_F(\boldsymbol{x}, \boldsymbol{y};\, k_0)e^{-ik_0(x^0-y^0)}. \tag{151}$$

The fermion propagator $S_F(\boldsymbol{x}, \boldsymbol{y};\, E)$ has the following spectral representation [151]

$$S_F(\boldsymbol{x}, \boldsymbol{y};\, E) = \sum_n \frac{\phi_n(\boldsymbol{x})\bar{\phi}_n(\boldsymbol{y})}{E - \varepsilon_n(1 - i\delta)}, \tag{152}$$

where δ is an infinitesimal positive quantity and n runs over the complete spectrum of eigenfunctions.

The Dirac equation takes into account the electron–nucleus and electron–electron interaction by means of electrostatic fields; that description turns out to be enough to provide, to a large extent, agreement with experimental data. However, as already pointed out, some small discrepancies are measurable. The smallness of the corrections required to fit the theoretical predictions to the experimental measurements indicates that the quantum effects of the electromagnetic field can be treated as perturbations to the solutions of the Dirac equation with classical fields. This is the basis of the *bound state QED*. Within this formalism the total electromagnetic field is separated into two parts: a classical field $a^\mu(x)$ describing the gross electronic spectrum, and a perturbation $A^\mu(x)$ describing small corrections to it (such as processes of creation and annihilation of virtual particles).

Quantum electrodynamics of bound state systems is best formulated in the so-called *Furry bound interaction picture* [152]. In this picture, one starts from the solutions $\phi_i(x)$ to the Dirac equation in the potential $a^\mu(x)$ (such as the nuclear potential, for instance) described by the Hamiltonian H_0

$$H_0\phi(x) = \left(i\hbar\gamma^\mu\partial_\mu + \frac{e}{c}\gamma^\mu a_\mu - mc\right)\phi(x) = 0, \tag{153}$$

while the interaction between the quantized electromagnetic and Dirac fields is given by

$$H_I = -\frac{e}{c}\gamma^\mu A_\mu(x). \tag{154}$$

Expansion of the Dirac field in terms of a complete set of zeroth-order solutions $\phi_n(x) = \phi_n(\mathbf{x})e^{-iE_nt/\hbar}$ of the Dirac equation in the potential $a^{\mu}(x)$, and promotion of the coefficients of the expansion to creation and annihilation operators, allows us to hold the particle interpretation. Hence, the operator a_n ($b_m^{\dagger}$) annihilates (creates) electrons (positrons) in the bound state ϕ_n (ϕ_m) with $E_n > 0$ ($E_m < 0$).

Then the electron–positron field reads

$$\psi(x) = \sum_{E_n>0} a_n\phi_n(x) + \sum_{E_m<0} b_m^{\dagger}\phi_m(x), \tag{155}$$

and the Fock operators satisfy the usual anticommutator relations

$$\{a_n, a_m^{\dagger}\} = \{b_n, b_m^{\dagger}\} = \delta_{nm}, \tag{156}$$

and zero in every other case. The main interest in the bound state problem is the calculation of level shifts. In the approach by Gell-Mann and Low [153] and Sucher [154] the interaction Hamiltonian $H_I(t)$ is replaced by an adiabatically damped one

$$H_I^{\epsilon}(x) = \int d^3x e^{-\epsilon|x^0|} j^{\mu}(x)A_{\mu}(x). \tag{157}$$

so that the energy shift of an unperturbed state $|0\rangle$ is given by the *level shift formula*

$$\Delta E_0 = \lim_{\epsilon\to 0,\, \lambda\to 1} \frac{i\epsilon\lambda}{2} \frac{\frac{\partial}{\partial\lambda}\langle 0|S_{\epsilon,\lambda}|0\rangle_c}{\langle 0|S_{\epsilon,\lambda}|0\rangle_c} + \text{const.} \tag{158}$$

where $S_{\varepsilon,\lambda}$ is the S-matrix defined as

$$S_{\epsilon,\lambda} = 1 + \sum_{k=1}^{\infty} \frac{(-i\lambda)^k}{k!} \int d^4x_1 \cdots \int d^4x_k T\{H_I^{\epsilon}(x_1)\ldots H_I^{\epsilon}(x_k)\}. \tag{159}$$

where $T\{H_I^{\epsilon}(x_1)\ldots H_I^{\epsilon}(x_k)\}$ is the *time-ordered product* (i.e. $x_1^0 < x_2^0 < \cdots < x_k^0$) of the operators $H_I^{\epsilon}(x_1)\cdots H_I^{\epsilon}(x_k)$.

Expanding ΔE_0 in powers of λ, the energy formula can be written from first to fourth-order in the S-matrix as

$$\Delta E_0^{(1)} = \frac{i\epsilon}{2}\langle S^{(1)}\rangle, \tag{160}$$

$$\Delta E_0^{(2)} = \frac{i\epsilon}{2}\left(2\langle S^{(2)}\rangle - \langle S^{(1)}\rangle^2\right), \tag{161}$$

$$\Delta E_0^{(3)} = \frac{i\epsilon}{2}\left(3\langle S^{(3)}\rangle - 3\langle S^{(1)}\rangle\langle S^{(2)}\rangle + \langle S^{(1)}\rangle^3\right), \tag{162}$$

$$\Delta E_0^{(4)} = \frac{i\epsilon}{2}\left(4\langle S^{(4)}\rangle - 4\langle S^{(1)}\rangle\langle S^{(3)}\rangle - 2\langle S^{(2)}\rangle^2 + 4\langle S^{(1)}\rangle^2\langle S^{(2)}\rangle - \langle S^{(1)}\rangle^4\right). \tag{163}$$

It has been shown [151] that, for classical external potentials V and one-electron atoms in the state a, the first- and second-order level shift formula reduces to the well-known expressions from standard perturbation theory

$$\Delta E_a^{(1)} = V_{aa} \tag{164}$$

$$\Delta E_a^{(2)} = \sum_{E_n \neq E_a} V_{an}\frac{1}{E_a - E_n}V_{na}. \tag{165}$$

It would be instructive to analyse the second-order level shift from yet another point of view. Since for NMR applications we are interested in the effect of two external magnetic fields (from the nuclear spins or the aligning field from the spectrometer), the relevant term is

$$S_{\varepsilon\lambda}^{(2)} = \frac{(-i\lambda)^2}{2!} \int d^4x_1 d^4x_2 T\{\mathcal{H}_I(x_1)\mathcal{H}_I(x_2)\}. \tag{166}$$

Applying Wick's theorem, the time ordered product is decomposed in terms having zero, one and two contractions between the fermion operators. In order to give non-vanishing contributions they require two, one and none electrons, respectively, in both the initial and final states. The last possibility is ruled out as a purely vacuum process. The two-electron state refers to a process in which each electron interacts with one external field but not between them. Finally, the situation with one-electron states corresponds to a single electron interacting twice with the external fields. We shall focus on this process, which is equivalent to the PZOA level of approach. Note that in every case there is no contraction between photon operators, and hence no photon propagator, since the electromagnetic field is a classical one.

Writing the electron propagator in terms of the wavefunctions $\psi(x)$ and $\bar{\psi}(x)$, and using its representation in the frequency (or energy) domain, Equations (150) and (152), the second-order correction to the energy is given by

$$\Delta E_0^{(2)} = \langle \phi^0 | S_{\varepsilon\lambda}^{(2)} | \phi^0 \rangle \approx \int d^3x \bar{\Psi}_0(x) S_{\varepsilon\lambda}^{(2)} \Psi_0(x) \approx \int d^3x \bar{\Psi}_0(x) iS(x_1 - x_2) \Psi_0(x). \tag{167}$$

Then,

$$\Delta E_0^{(2)} = \iint dx_1 dx_2 \bar{\psi}_0(x_2) e^{-\varepsilon|t_2|} \gamma_\nu A_\nu(x_2) S(\mathbf{x_1}, \mathbf{x_2}, E) \gamma_\mu A_\mu(x_1) \psi_0(x_1) e^{-\varepsilon|t_1|} + \text{c.c.} \tag{168}$$

In this equation $\bar{\psi}_0(x_2)$ and $\psi_0(x_1)$ represent occupied estates $\psi_i(x)$. On the other hand, the photon fields can be expressed in terms of the vector potentials of the magnetic fields, that is, $A_\mu \cong e^{\pm i\omega t}\mathbf{A}(x)$. Hence, the second-order expression for the energy becomes

$$\Delta E_0^{(2)} \approx \int d^3x_1 \int d^3x_2 \int_{-\infty}^{\infty} dt_1 \int_{-\infty}^{\infty} dt_2 \int \mathrm{d}\omega e^{i(E_0+\omega)t_2 - \varepsilon|t_2|} e^{-i(E_0+\omega)t_1 - \varepsilon|t_1|} \tag{169}$$

$$\times \bar{\psi}_0(\mathbf{x_2}) \gamma \cdot \mathbf{A}^N(\mathbf{x_2}) \sum_s \frac{\psi_s(\mathbf{x_2}) \bar{\psi}_s(\mathbf{x_1})}{E_s(1 - i\eta) + \omega} \gamma \cdot \mathbf{A}^B(\mathbf{x_1}) \psi_0(\mathbf{x_1}). \tag{170}$$

Integrating over t_1, t_2, and ω, and taking the limit for $\varepsilon \to 0$ we get

$$\Delta E_0^{(2)} \approx \int d^3x_1 d^3x_2 \bar{\psi}_0(\mathbf{x_2}) \gamma \cdot \mathbf{A}^N(\mathbf{x_2}) \sum_{s \neq 0} \frac{\psi_s(\mathbf{x_2}) \bar{\psi}_s(\mathbf{x_1})}{E_s - E_0} \gamma \cdot \mathbf{A}^B(\mathbf{x_1}) \psi_0(\mathbf{x_1}) \tag{171}$$

$$= \sum_{s \neq 0} \frac{\gamma \cdot \langle 0 | \mathbf{A}^N | s \rangle \langle s | \mathbf{A}^B | 0 \rangle \cdot \gamma}{E_s - E_0} + \text{c.c.} \tag{172}$$

It should be noted that the last expression is the same as the one obtained from the definition of the polarization propagator. Furthermore, its representation involves a summation on intermediate positive- and negative-energy states. In Figure 9 the time is

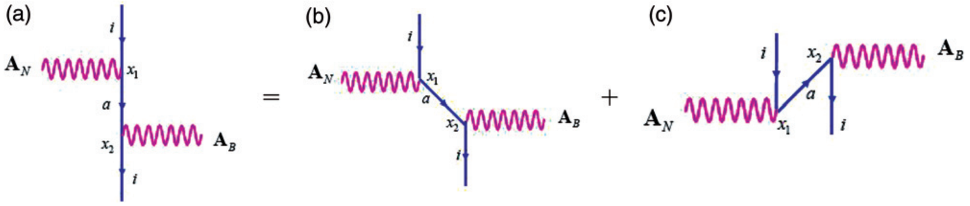

Figure 9. Decomposition of the fermion propagator (a) in terms of Feynman diagrams with forward (b) and backward (c) paths. The solid line represent an electron interacting with external magnetic fields $\boldsymbol{A}_N$ and $\boldsymbol{A}_B$ represented by the wavy lines.

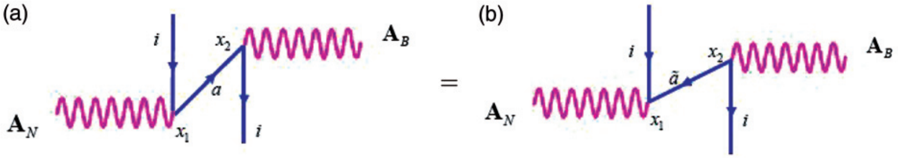

Figure 10. Equivalence between the Feynman diagrams of an electron propagating backward in time and a positron propagating forward in time.

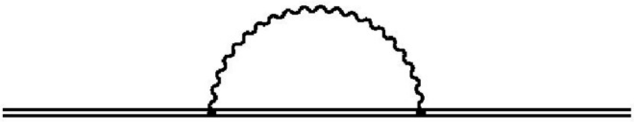

Figure 11. [Colour online] Basic self-energy Feynman diagram.

assumed running from top downward. The straight vertical line between x_1 and x_2 in Figure 9(a) stands for both signs of energy, and it is equivalent to the sum of the (b) and (c) diagrams where the solid broken lines stand for an electron propagating forward in time (i.e. with positive energy) and an electron propagating backward in time (i.e. with negative energy), respectively. Taking into account the way in which the wavefunctions for electrons of negative energy evolve with time, the last graph can also be represented with an opposite direction of the arrow, as in Figure 10. In (a) the electron is scattered backward in time at x_1 due to its interaction with the field $\boldsymbol{A}_N$, and then scattered forward again at x_2 due to $\boldsymbol{A}_B$. This is equivalent to saying that an electron–positron is created at x_2 due to $\boldsymbol{A}_B$ with the positron being annihilated by the electron at x_1 in the field of $\boldsymbol{A}_N$.

Another process of interest occurs when the electron interacts only with a quantized field; i.e. when there is no classical vector potential and neither the initial nor final state have photons, the second-order S-matrix can be represented by a *self-energy* Feynman diagram as sketched in Figure 11. Feynman diagrams represent pictorial representations of processes included in the calculations of the S-matrix. A wavy line represents the photon propagator and a straight line stands for the bound fermion propagator.

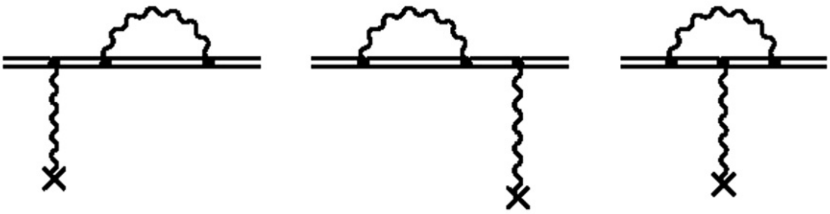

Figure 12. Feynman diagrams *side left* (L), *side right* (R) and *vertex* (V) for self-energy corresponding to the $S^{(3)}_{\epsilon\lambda}$ term.

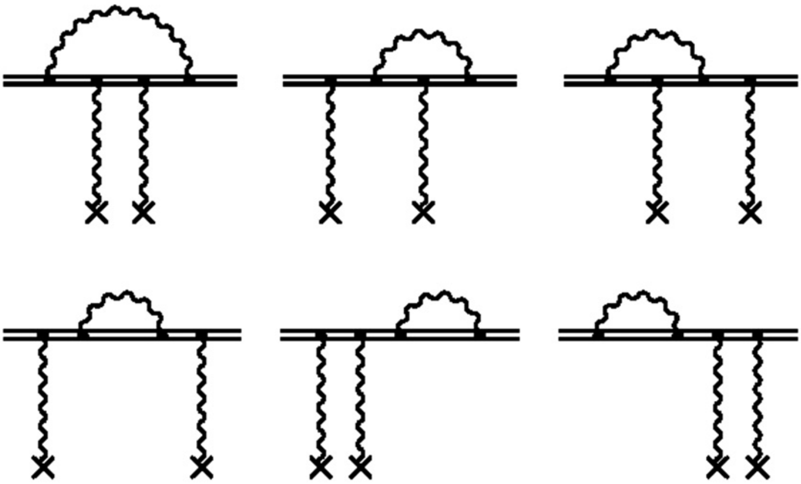

Figure 13. Fourth-order Feynman diagrams *vertex–vertex* (VV), *left–vertex* (LV), *vertex-right* (VR), *left–right* (LR), *left–left* (LL) and *right–right* (RR) contributing to the self-energy correction quadratic in the external field and corresponding to the $S^{(4)}_{\epsilon\lambda}$ term.

In this view, the process of Figure 11 is interpreted as if the electron interacts with a photon by emitting it and reabsorbing it later and contributes with a measurable shift in the energy levels of the bound electron, namely, the self-energy correction.

As an application of the third-order formula (162), Blundell *et al.* [155] calculated self-energy corrections in atomic systems in the presence of an external potential. The fourth-order energy expression (163) was used to obtain self-energy corrections to the NMR parameters. The Feynman diagrams depicted in Figures 12 and 13 appear in the computation of $\Delta E^{(4)}_0$.

For the *n* levels of heavy atoms ($Z > 50$), QED effects are known to cancel $\approx 1\%$ of the relativistic shifts of the one-electron energies. As an estimation of the order of magnitude expected for the QED effects on magnetic properties, Pyykkö and Zhao have used local model potentials to simulate self-energy effects on atomic energy levels and magnetic dipole hyperfine integrals. It was found that the self-energy effect on the ground state hyperfine splitting of Hg^+ is around 1.4%, thus giving $\Delta J/J \approx -3\%$ for the Hg–Hg coupling [156].

5.3. *Antiparticles*

Are antiparticles needed in chemistry? As Dirac stated in the early days of QED, almost the whole of chemistry is included in the physics described by QED or the quantum physics of electrons and electromagnetic fields. If we describe the electron's dynamics within the framework of relativistic quantum mechanics one cannot avoid making a reference to positrons. As mentioned above, the Dirac equation is not a one-body equation but a many-body one. The hole theory predicts the existence of positrons that were observed in 1932, and given that electrons and positrons may annihilate we must abandon the interpretation of the Dirac equation as a wave equation and construct a truly many-body theory which includes particles and antiparticles in a consistent way. This is achieved by the second quantization which polarization propagators use from the very beginning even within the NR domain. Then from the outset or at the end, positrons do and will appear. They could appear as virtual particle–antiparticle pairs created or annihilated, just as virtual orbitals are needed to reproduce bonds properly. Virtual particles (and antiparticles) are such particles that appear in intermediate, unobservable, stages of a process. Only initial and final particles in the diagram represent observable objects and are the well-known real particles.

One can make some transformations to move some of its effects from, say, diamagnetic to paramagnetic contributions in actual calculations, but one should not forget that their influence on property values cannot be eliminated. This fact seems to be similar to what one is used to consider within the NR domain: one always has both terms, diamagnetic and paramagnetic, and one cannot eliminate one of them by modifying the gauge condition. Within the relativistic domain diamagnetism and paramagnetism arise from the same formal source. Indeed they arise from excitation to 'virtual' positive or negative-energy electronic states.

Antiparticles can be used to explain deeper insights into magnetic properties that otherwise would not be observed. How do they appear and what kind of effects may one expect from them? To answer this question we need to go further with the QED formalism applied to calculate magnetic molecular properties.

Equation (171) shows that polarization propagators can be derived from the second-order correction of the S-matrix. The interpretation of the origin of diamagnetic contributions arises from the non-covariant formulation of QED. Diamagnetic terms are obtained as interactions with 'external' fields that may be considered as classical, which produce virtual pair creation and annihilation. It is easy to start with hydrogen-like atoms. In such a case one needs to work only at the PZOA level of approach. The diagrams of Figure 9 show that there are two interactions. Paramagnetic terms arise from excitation to positive-energy unoccupied orbitals or only one-electron excitations. On the other hand, diamagnetic terms arise from excitations which involve two electron–positron pairs; one is created due to the electron interaction with one of the external fields and then annihilated by the interactions with the other external field. The diagram shows the equivalence between the negative-energy electron moving backward in time and the positive-energy positron moving forward in time.

We may ask whether this new formulation brings about new insights, or is it only a kind redefinition of what is well-known?

There is an old approximation that was first formulated by Sternheim in 1962 [157]. One can approximate each excitation to the negative-energy branch by the same number: $2mc^2$. This approximation works quite well for not so heavy atoms. Why is this so? We used this approach 10 years ago [29] and a similar prescription for the development of the LR-ESC formalism [134,135]. We have shown that when working with heavier atoms the development as a series of the inverse of excitation to the negative-energy branch does not fit exactly to the exact inverse. In fact a branch of excitations appears that seems to restrict the whole branch to a well-defined interval of energies. What about the amount of its total contribution? They accounted for more than 95% of the diamagnetic terms [158].

We have shown that diamagnetic terms arise from 'virtual pair-creations' that are then annihilated. In fact there are two pairs involved because in the principal propagators one works at least with two simultaneous excitations (at the SOPPA level there are more than two simultaneous excitations). So, if the energy involved were larger than $4mc^2$ there would be a non-zero probability for a real creation of electron–positron pairs. But, as it should be, this is not the case. As we have shown a few years ago, there are no contributions which have excitation (to the negative-energy branch of the energy spectra) energies equal to or larger than $4mc^2$.

5.4. *Multi-polar QED*

We shall outline now the basics of another formalism developed for the foundation of the QED theory of the nuclear spin–spin coupling tensor. It is closely inspired by the description of one-photon absorption by molecules in multi-polar QED [159]. The total Hamiltonian for bounded electrons in a molecule interacting with quantized electromagnetic fields can be written as

$$H = H_{DF} + H_R + H_I, \tag{173}$$

where H_{DF} is the electronic Hamiltonian at the Dirac–Fock (DF) level of approximation, H_R is the free radiation Hamiltonian, and $H_I = H_I^A + H_I^N + H_I^M$ accounts for the interaction of the radiation with the electrons, and the nuclei N and M, respectively. Using the Coulomb gauge, we can write

$$H_R = \sum_k \hbar\omega a_k^\dagger a_k \tag{174}$$

$$H_{DF} = \sum_i \epsilon_i b_i^\dagger b_i \tag{175}$$

$$H_I^A = ec\int \Psi^\dagger(x)\gamma\cdot \boldsymbol{A}(x)\Psi(x)d^3x, \tag{176}$$

$$H_I^K = -\boldsymbol{\mu}_K \cdot \boldsymbol{B}(\boldsymbol{R}_K), (K = M, N), \tag{177}$$

where $\omega = ck$ is the photon frequency in the mode ($\boldsymbol{k}$, λ), ε_i is the orbital energy of the DF state ϕ_i and $b_i^\dagger$ and b_i are the corresponding creation and annihilation operators. $\Psi = \sum_i b_i\phi_i$ stands for the fermion field operator and $\boldsymbol{A}$ is the second quantized transverse three-dimensional vector potential

$$\boldsymbol{A}(\boldsymbol{r}) = \sum_{\boldsymbol{k}\lambda}\left(\frac{\hbar}{2\varepsilon_0 ckV}\right)^{1/2}\boldsymbol{e}^{(\lambda)}\left(a_{\boldsymbol{k}\lambda}e^{i\boldsymbol{k}\cdot\boldsymbol{r}} + a_{\boldsymbol{k}\lambda}^\dagger e^{-i\boldsymbol{k}\cdot\boldsymbol{r}}\right), \tag{178}$$

where $\boldsymbol{e}^{(\lambda)}(\boldsymbol{k})$ is the unit polarization vector transverse to the wavevector $\boldsymbol{k}$ and V is a normalization volume. Hereafter, the mode dependence of the photon creation and annihilation operators will be implicit. With this choice of gauge, all charge interactions within the molecule defining H_{DF} are instantaneous.

5.4.1. *Operator equation of motion*

It is convenient to transform to the interaction picture, where the Hamiltonian can be written as $H = H_0 + H_I^A$. In this representation, the operators evolve with time according to Heisenberg-like equations of motions depending on the interaction Hamiltonian H_I^A. Photon and fermion Fock operators become $a(t) = \alpha(t)e^{-i\omega t}$, $b_n(t) = \beta_n e^{-i\epsilon_n t}$ and their hermitian conjugate relations for $a^\dagger$ and $b_n^\dagger$.

The electron–radiation interaction Hamiltonian now becomes

$$H_I^A = ec\sum_{ij}\sum_{\boldsymbol{k}\lambda}\left(\frac{\hbar}{2\varepsilon_0 ckV}\right)^{1/2}\boldsymbol{e}\cdot\left(\alpha e^{-i\omega t}\boldsymbol{u}^{(+)ij} + \alpha^\dagger e^{i\omega t}\boldsymbol{u}^{(-)ij}\right)\beta_i^\dagger\beta_j e^{i\omega_{ij}t} \tag{179}$$

where the vectors $\boldsymbol{u}^{(\pm)ij}$ have components $u_r^{(\pm)ij} \equiv \langle i|\alpha_r e^{\pm i\boldsymbol{k}\cdot\boldsymbol{r}}|j\rangle$, and α_r is the r-th Dirac matrix ($r = 1, 2, 3$). The operator equations of motion

$$\begin{aligned} i\hbar\,\dot{\alpha} &= \left[\alpha, H_I^A\right] \\ &= ec\sum_{ij}\left(\frac{\hbar}{2\varepsilon_0\omega V}\right)^{1/2}\boldsymbol{e}\cdot\boldsymbol{u}^{(-)ij}e^{i(\omega+\omega_{ij})t}\beta_i^\dagger(t)\beta_j(t) \end{aligned} \tag{180}$$

$$\begin{aligned} i\hbar\,\dot{\beta}_j &= \left[\beta_j, H_I^A\right] \\ &= ec\sum_{n}\sum_{\boldsymbol{k}\lambda}\left(\frac{\hbar}{2\varepsilon_0\omega V}\right)^{1/2}\beta_n\boldsymbol{e}\cdot\left(\alpha\boldsymbol{u}^{(+)jn}e^{-i(\omega-\omega_{jn})t} + \alpha^\dagger\boldsymbol{u}^{(-)jn}e^{i(\omega+\omega_{jn})t}\right) \end{aligned} \tag{181}$$

can be integrated to give

$$\alpha(t) = \alpha(0) - iec\sum_{ij}\left(\frac{1}{2\varepsilon_0\hbar\omega V}\right)^{1/2}e_r u_r^{(-)ij}\int_0^t e^{i(\omega+\omega_{ij})t'}\beta_i^\dagger(t')\beta_j(t')\mathrm{d}t' \tag{182}$$

$$\begin{aligned} \beta_j(t) = \beta_j(0) - iec\sum_{n}\sum_{\boldsymbol{k}\lambda}\left(\frac{1}{2\varepsilon_0\hbar\omega V}\right)^{1/2}e_r \\ \times\int_0^t dt'\beta_n(t')\left(\alpha(t')u_r^{(+)jn}e^{-i(\omega-\omega_{jn})t'} + \alpha^\dagger(t')u_r^{(-)jn}e^{i(\omega+\omega_{jn})t'}\right). \end{aligned} \tag{183}$$

These coupled equations can be solved by successive iterations to get a solution in terms of powers of the electron charge. Substituting the unperturbed operators $\alpha(0)$ and $\beta_j(0)$ into the right-hand side of Equations (182) and (183) we get the first-order corrections

$$\alpha^{(1)}(t) = -ec\sum_{ij}\left(\frac{1}{2\varepsilon_0\hbar\omega V}\right)^{1/2}e_r u_r^{(-)ij}\frac{e^{i(\omega+\omega_{ij})t} - 1}{\omega + \omega_{ij}}\beta_i^\dagger(0)\beta_j(0) \tag{184}$$

$$\beta_j^{(1)}(t) = ec \sum_l \sum_{\boldsymbol{k}\lambda} \left(\frac{\hbar}{2\varepsilon_0 \hbar \omega V} \right)^{1/2} \beta_l(0) \times \left[\alpha(0) e_r u_r^{(+)jl} \frac{e^{-i(\omega - \omega_{jl})t} - 1}{\omega - \omega_{jl}} - \alpha^\dagger(0) e_r u_r^{(-)jl} \frac{e^{i(\omega + \omega_{jl})t} - 1}{\omega + \omega_{jl}} \right]. \tag{185}$$

On the other hand, the $O(e^2)$ correction $\alpha^{(2)}$ to the photon operator follows from approximating, in the right-hand side of Equation (182), $\beta_i^\dagger(t)\beta_j(t)$ by its first-order approximation $\beta_i^{\dagger(1)}\beta_j(0) + \beta_i^\dagger(0)\beta_j^{(1)}$, with $\beta_i^{\dagger(1)}$ and $\beta_j^{(1)}$ given by Equation (185) and its hermitian conjugate. Then,

$$\begin{aligned} \alpha^{(2)}(t) = \sum_{ijl} \sum_{\boldsymbol{k}'\lambda'} \left(\frac{e^2 c}{2\epsilon_0 \hbar V} \right) \left(\frac{1}{kk'} \right)^{1/2} \beta_i^\dagger(0)\beta_l(0) \\ \Bigg\{ \alpha'(0) \Bigg[\frac{(e_r u_r^{(-)ij})(e'_s u'^{(+)jl}_s)}{\omega' - \omega_{jl}} \left(\frac{e^{-i(\omega' - \omega - \omega_{il})t} - 1}{\omega' - \omega - \omega_{il}} + \frac{e^{i(\omega + \omega_{ij})t} - 1}{\omega + \omega_{ij}} \right) \\ - \frac{(e'_s u'^{(+)ij}_s)(e_r u_r^{(-)jl})}{\omega' - \omega_{ij}} \left(\frac{e^{-i(\omega' - \omega - \omega_{il})t} - 1}{\omega' - \omega - \omega_{il}} + \frac{e^{i(\omega + \omega_{jl})t} - 1}{\omega + \omega_{jl}} \right) \Bigg] \\ + \alpha'^\dagger(0) \Bigg[\frac{(e_r u_r^{(-)ij})(e'_s u'^{(-)jl}_s)}{\omega' + \omega_{jl}} \left(\frac{e^{i(\omega' + \omega + \omega_{il})t} - 1}{\omega' + \omega + \omega_{il}} - \frac{e^{i(\omega + \omega_{ij})t} - 1}{\omega + \omega_{ij}} \right) \\ - \frac{(e'_s u'^{(-)ij}_s)(e_r u_r^{(-)jl})}{\omega' + \omega_{ij}} \left(\frac{e^{i(\omega' + \omega + \omega_{il})t} - 1}{\omega' + \omega + \omega_{il}} - \frac{e^{i(\omega + \omega_{jl})t} - 1}{\omega + \omega_{jl}} \right) \Bigg] \Bigg\}. \end{aligned} \tag{186}$$

It is interesting to analyse the structure of the corrections to the operators α and β in the combined photon–electron Fock space. They affect the form of the magnetic vector potential (178). The zeroth-order operators $\alpha^{(0)}$ correspond to those of a free field. The first-order corrections, $\alpha^{(1)} \sim \beta^{\dagger(0)}\beta^{(0)}$, are electron excitations. Finally, the second-order operators $\alpha^{(1)} \sim \alpha^{(o)}\beta^{\dagger(0)}\beta^{(0)} +$ c.c., both excite electrons and create or annihilate photons. These operators will give us the explicit form of the magnetic field and show that the electron–photon interaction affects the degrees of freedom of the electromagnetic field.

5.4.2. *Magnetic field in the neighbourhood of a nucleus*

From the expressions derived in Section 5.4.1, the contribution of order $O(e^l)$ to the magnetic field at the nuclear position $\boldsymbol{R}_N$ can be calculated as

$$B_p^{(l)}(\boldsymbol{R}_N, t) = i \sum_{\boldsymbol{k}\lambda} \left(\frac{\hbar}{2\varepsilon_0 \omega V} \right)^{1/2} \varepsilon_{mnp} k_m e_n \left(\alpha^{(l)} e^{i(\boldsymbol{k}\cdot\boldsymbol{R}_N - \omega t)} - \alpha^{(l)\dagger} e^{-i(\boldsymbol{k}\cdot\boldsymbol{R}_N - \omega t)} \right), \tag{187}$$

the lowest order approximation being the unperturbed field

$$B_p^{(0)}(\boldsymbol{R}_N, t) = i \sum_{\boldsymbol{k}\lambda} \left(\frac{\hbar}{2\varepsilon_0 \omega V} \right)^{1/2} \varepsilon_{mnp} k_m e_n \left(\alpha(0) e^{i(\boldsymbol{k}\cdot\boldsymbol{R}_N - \omega t)} - \alpha^\dagger(0) e^{-i(\boldsymbol{k}\cdot\boldsymbol{R}_N - \omega t)} \right). \tag{188}$$

Inserting Equation (184) into Equation (187) and summing over the polarization directions, we get

$$B_p^{(1)}(\boldsymbol{R}_N,t) = i\sum_{\boldsymbol{k}}\sum_{ij}\left(\frac{e}{2\epsilon_0 kV}\right)\varepsilon_{mnp}k_m\beta_i^{\dagger}(0)\beta_j(0)$$

$$\left(u_n^{(+)ij}(N)\frac{e^{i\omega_{ij}t}-e^{i\omega t}}{\omega-\omega_{ij}} - u_n^{(-)ij}(N)\frac{e^{i\omega_{ij}t}-e^{-i\omega t}}{\omega+\omega_{ij}}\right) \tag{189}$$

where $u_n^{\pm ij}(N) \equiv \langle i|\alpha_n e^{\pm i\boldsymbol{k}\cdot\boldsymbol{r}_N}|j\rangle$, and $\boldsymbol{r}_N = \boldsymbol{r} - \boldsymbol{R}_N$ is the electron position relative to the nucleus N. As usual, summation over the wavevector $\boldsymbol{k}$ is made by replacing $V^{-1}\sum_{\boldsymbol{k}} \to (2\pi)^{-3}\int d^3k$ with $d^3k = k^2dk\,d\Omega$. Integration over the angular variables gives

$$B_p^{(1)}(\boldsymbol{R}_N,t) = \frac{e}{8\pi^2 i\epsilon_0 c}\sum_{ij}\varepsilon_{mnp}\nabla_m^N\beta_i^{\dagger}(0)\beta_j(0)$$

$$\times\langle i|\frac{\alpha_n}{r_N}\int_0^{\infty}dk(e^{ikr_N}-e^{-ikr_N})\left(\frac{e^{ick_{ij}t}-e^{-ickt}}{k+k_{ij}}+\frac{e^{ick_{ij}t}-e^{ickt}}{k-k_{ij}}\right)|j\rangle \tag{190}$$

where the derivatives ∇_m^N are taken with respect to the nuclear coordinates $\boldsymbol{R}_N$. Finally, evaluating the integrals in the complex k-plane, we get

$$B_p^{(1)}(\boldsymbol{R}_N,t) = \frac{\mu_0}{4\pi}ec\sum_{ij}\varepsilon_{mnp}\langle i|\nabla_m^N\left(\frac{e^{-ik_{ij}(r_N-ct)}}{r_N}\right)\alpha_n|j\rangle\beta_i^{\dagger}(0)\beta_j(0), \tag{191}$$

if $t > r_N/c$, and 0 if $t < r_N/c$, reflecting the causal nature of the fields.

Inserting Equation (186) into Equation (187), and summing again over the polarization directions, transforming the sum over the wavevector into an integral and integrating the angular variables, we get the correction to the field up to order e^2:

$$B_p^{(2)}(\boldsymbol{R}_N,t) = \sum_{ijl}\sum_{\boldsymbol{k}\boldsymbol{k}'\lambda'}\left(\frac{1}{2\epsilon_0\hbar\omega' V}\right)^{1/2}\frac{e^2}{8\pi^2 i\epsilon_0}\varepsilon_{mnp}\nabla_m\beta_i^{\dagger}(0)\beta_j(0) \tag{192}$$

$$\times\left\{\alpha'(0)\left[\frac{e_r' u_r'^{(+)ij}}{\omega'-\omega_{ij}}\langle j|I^{(+)}(k'-k_{il},k_{jl})\frac{\alpha_n}{r_N}|l\rangle - \langle i|I^{(+)}(k'-k_{il},k_{ij})\frac{\alpha_n}{r_N}|j\rangle\frac{e_r' u_r'^{(+)jl}}{\omega'+\omega_{jl}}\right]\right.$$

$$+\alpha'^{\dagger}(0)\left[\langle i|I^{(-)}(-k'-k_{il},\,-k_{ij})\frac{\alpha_n}{r_N}|j\rangle\frac{e_r' u_r'^{(-)jl}}{\omega'+\omega_{jl}}\right.$$

$$\left.\left.-\frac{e_r' u_r'^{(-)ij}}{\omega'+\omega_{ij}}\langle j|I^{(-)}(-k'-k_{il},\,-k_{jl})\frac{\alpha_n}{r_N}|l\rangle\right]\right\} \tag{193}$$

for times $t > r_N/c$, where

$$I^{(\pm)}(q',q'') = \int_{-\infty}^{\infty}dk\big(e^{ikr_N}-e^{-ikr_N}\big)\left(\frac{e^{-icq't}-e^{\pm ickt}}{k\pm q'}-\frac{e^{\pm icq''t}-e^{\pm ickt}}{k-q''}\right), \tag{194}$$

while $B_p^{(2)}(\boldsymbol{R}_N) = 0$ if $t < r_N/c$.

5.4.3. *Response theory*

We shall now evaluate the effect of the presence of nucleus M on the interaction of nucleus N with the perturbed magnetic field obtained in Section 5.4.2.

The perturbative expansion of the magnetic field obtained in Section 5.4.2 gives rise to a corresponding expansion of the **$\boldsymbol{B}$**-dependent Hamiltonians H_I^M and H_I^N in powers of the electron charge

$$H_I^K = H_I^{K(0)} + H_I^{K(1)} + H_I^{K(2)} + \cdots \quad (K = M, N). \tag{195}$$

These expansions include (up to order $\mathcal{O}(e^2)$) the effect of the electron–radiation interaction. Let us write the state of the electron-field system in the presence of the nucleus M as $\Xi(t)$. It satisfies the Schrödinger-like equation of motion

$$i\hbar \frac{d\Xi}{\mathrm{d}t} = (H_0 + H_I^M)\Xi(t). \tag{196}$$

The expectation value of the Hamiltonian H_I^N, at time t, becomes then

$$\langle \Xi(t)|H_I^N(t)|\Xi(t)\rangle = \langle \Xi(t)|H_I^{N(0)}(t) + H_I^{N(1)}(t) + H_I^{N(2)}(t) + \cdots|\Xi(t)\rangle. \tag{197}$$

In order to determine the influence of the perturbation produced by the nucleus M on this expectation value, we solve Equation (196) expanding the state Ξ in terms of the complete set of states of H_{DF} and H_R

$$\{\Phi_0\Psi_0, \Phi_{\boldsymbol{k}\lambda}\Psi_0, \Phi_0\Psi_a^r, \Phi_{\boldsymbol{k}\lambda}\Psi_a^r, \ldots\} \tag{198}$$

where Φ_0 is the photon vacuum state, $\Phi_{\boldsymbol{k}\lambda} = a_{\boldsymbol{k}\lambda}^\dagger \Phi_0$ represents one-photon states in the $(\boldsymbol{k}\lambda)$ mode, etc. On the other hand, Ψ_0 is the Dirac–Fock ground state of energy E_0, and $\Psi_a^r = b_r^\dagger b_a \Psi_0$ are singly-excited (with respect to Ψ_0) Slater determinants, $\Psi_{ab}^{rs} = b_s^\dagger b_b \Psi_a^r$ are doubly excited Slater determinants, etc.

Hence, the state Ξ becomes

$$\begin{aligned}\Xi(t) = {} & \Phi_0\Psi_0 + \sum_{\boldsymbol{k}\lambda} c_{\boldsymbol{k}\lambda}(t)\Phi_{\boldsymbol{k}\lambda}\Psi_0 + \sum_{ar} c_a^r(t)\Phi_0\Psi_a^r \\ & + \sum_{\boldsymbol{k}\lambda}\sum_{ar} c_{a;\boldsymbol{k}\lambda}^r(t)\Phi_{\boldsymbol{k}\lambda}\Psi_a^r + \sum_{\boldsymbol{k}\lambda,\boldsymbol{k}'\lambda'} c_{\boldsymbol{k}\lambda\boldsymbol{k}'\lambda'}(t)\Phi_{\boldsymbol{k}\lambda}\Phi_{\boldsymbol{k}'\lambda'}\Psi_0 \\ & + \sum_{abrs} c_{ab}^{rs}(t)\Phi_0\Psi_{ab}^{rs} + \cdots\end{aligned} \tag{199}$$

where the coefficients of this expansion satisfy the equations of motion

$$\begin{aligned} i\hbar\, \dot{c}_{\boldsymbol{k}\lambda}(t) &= \langle \Phi_{\boldsymbol{k}\lambda}\Psi_0|H_I^M|\Phi_0\Psi_0\rangle + \sum_{\boldsymbol{k}'\lambda'} c_{\boldsymbol{k}'\lambda'}(t)\langle \Phi_{\boldsymbol{k}\lambda}\Psi_0|H_I^M|\Phi_{\boldsymbol{k}'\lambda'}\Psi_0\rangle \\ &\quad + \sum_{ar} c_a^r(t)\langle \Phi_{\boldsymbol{k}\lambda}\Psi_0|H_I^M|\Phi_0\Psi_a^r\rangle + \cdots \\ &= \langle \Phi_{\boldsymbol{k}\lambda}\Psi_0|H_I^{M(0)} + H_I^{M(2)}|\Phi_0\Psi_0\rangle + c_{\boldsymbol{k}\lambda}(t)\langle \Psi_0|H_I^{M(1)}|\Psi_0\rangle \\ &\quad + \sum_{ar} c_a^r(t)\langle \Phi_{\boldsymbol{k}\lambda}\Psi_0|H_I^{M(2)}|\Phi_0\Psi_a^r\rangle + \cdots \end{aligned} \tag{200}$$

$$\begin{aligned} i\hbar\,\dot{c}^{r}_{a}(t) &= \langle\Phi_0\Psi^r_a|H^M_I|\Phi_0\Psi_0\rangle + \sum_{\boldsymbol{k}\lambda} c_{\boldsymbol{k}\lambda}(t)\langle\Phi_0\Psi^r_a|H^M_I|\Phi_{\boldsymbol{k}\lambda}\Psi_0\rangle \\ &\quad + \sum_{ar} c^r_a(t)\langle\Phi_0\Psi^r_a|H^M_I|\Phi_0\Psi^r_a\rangle + \cdots \\ &= \langle\Phi_0\Psi^r_a|H^{M(1)}_I|\Phi_0\Psi_0\rangle + \sum_{\boldsymbol{k}\lambda} c_{\boldsymbol{k}\lambda}(t)\langle\Phi_0\Psi^r_a|H^{M(2)}_I|\Phi_{\boldsymbol{k}\lambda}\Psi_0\rangle \\ &\quad + \sum_{ar} c^r_a(t)\langle\Phi_0\Psi^r_a|H^{M(1)}_I|\Phi_0\Psi^r_a\rangle + \cdots \end{aligned} \tag{201}$$

$$\begin{aligned} i\hbar\,\dot{c}^{r}_{a;\boldsymbol{k}\lambda}(t) &= \langle\Phi_{\boldsymbol{k}\lambda}\Psi^r_a|H^M_I|\Phi_0\Psi_0\rangle + \sum_{\boldsymbol{k}\lambda} c_{\boldsymbol{k}\lambda}(t)\langle\Phi_{\boldsymbol{k}\lambda}\Psi^r_a|H^M_I|\Phi_{\boldsymbol{k}\lambda}\Psi_0\rangle \\ &\quad + \sum_{ar} c^r_a(t)\langle\Phi_{\boldsymbol{k}\lambda}\Psi^r_a|H^M_I|\Phi_0\Psi^r_a\rangle + \cdots \\ &= \langle\Phi_{\boldsymbol{k}\lambda}\Psi^r_a|H^{M(2)}_I|\Phi_0\Psi_0\rangle + \sum_{\boldsymbol{k}\lambda} c_{\boldsymbol{k}\lambda}(t)\langle\Phi_{\boldsymbol{k}\lambda}\Psi^r_a|H^{M(1)}_I|\Phi_{\boldsymbol{k}\lambda}\Psi_0\rangle \\ &\quad + \sum_{ar} c^r_a(t)\langle\Phi_{\boldsymbol{k}\lambda}\Psi^r_a|H^{M(0)}_I + H^{M(2)}_I|\Phi_0\Psi^r_a\rangle + \cdots \end{aligned} \tag{202}$$

It should be noted that these coupled equations have to fulfil the initial conditions $c_{\boldsymbol{k}\lambda}(-\infty)=0$, $c^r_a(-\infty)=0$, $c^r_{a;\boldsymbol{k}\lambda}(-\infty)=0$, so that $\Xi(-\infty)=\Psi_0\Phi_0$, and can be solved iteratively considering an expansion of the coefficients $c_{\boldsymbol{k}\lambda}$, c^r_a and $c^r_{a;\boldsymbol{k}\lambda}$ in powers of e.

From the order of the Hamiltonian H^M_I it can be seen that $c_{\boldsymbol{k}\lambda}$ is, at least, of order $\mathcal{O}(e^0)$, while c^r_a and $c^r_{a;\boldsymbol{k}\lambda}$ are, at least, of order $\mathcal{O}(e^1)$. Furthermore, the iterative solution of Equations (200), (201), and (202) depend linearly, quadratically, cubically, etc. on H^M_I. Restricting ourselves to linear terms, we get the solutions

$$\begin{aligned} c^{(0)}_{\boldsymbol{k}\lambda}(t) &= -\frac{i}{\hbar}\int_{-\infty}^{t}\langle\Phi_{\boldsymbol{k}\lambda}\Psi_0|H^{M(0)}_I(t')|\Phi_0\Psi_0\rangle\mathrm{d}t' \\ c^{r(1)}_{a}(t) &= -\frac{i}{\hbar}\int_{-\infty}^{t}\langle\Phi_0\Psi^r_a|H^{M(1)}_I(t')|\Phi_0\Psi_0\rangle\mathrm{d}t' \\ c^{r(2)}_{a;\boldsymbol{k}\lambda}(t) &= -\frac{i}{\hbar}\int_{-\infty}^{t}\langle\Phi_{\boldsymbol{k}\lambda}\Psi^r_a|H^{M(2)}_I(t')|\Phi_0\Psi_0\rangle\mathrm{d}t' \\ c^{(2)}_{\boldsymbol{k}\lambda}(t) &= -\frac{i}{\hbar}\int_{-\infty}^{t}\langle\Phi_{\boldsymbol{k}\lambda}\Psi_0|H^{M(2)}_I(t')|\Phi_0\Psi_0\rangle\mathrm{d}t'. \end{aligned} \tag{203}$$

Hence,

$$\begin{aligned} \delta\langle H^N_I\rangle &= \langle\langle H^{N(0)}_I(t) + H^{N(2)}_I(t); H^{M(0)}_I(t') + H^{M(2)}_I(t')\rangle\rangle + \langle\langle H^{N(1)}_I(t); H^{M(1)}_I(t')\rangle\rangle \\ &\quad + \langle\langle H^{N(2)}_I(t); H^{M(2)}_I(t')\rangle\rangle + \text{c.c.} + \cdots \end{aligned} \tag{204}$$

where c.c. and $\cdots$ denote, respectively, complex conjugate and non-bilinear terms in H^M_I and H^N_I. Due to the orthogonality of the set of states (198) not every possible combination of the matrix elements of the perturbations occurs. It should also be noted that the expectation value of H^N_I at time t depends on the matrix elements of H^M_I at every time t', with $t' \leq t$, i.e. it is a time correlation function. Equation (204) gives formally the expression of the (linear) response of the nuclear spin N to the perturbation of nuclear spin M. It differs from the usual linear response theory in the fact that the field degrees of freedom are included. As is well known, response theory is equivalent to perturbation theory when the perturbations become static, i.e. time-independent, and represents a straightforward generalization of the definition of molecular properties for time-dependent perturbations [160].

5.4.4. *Effective nuclear spin–spin interaction*

The response theory outlined in the previous section can be used to obtain an effective nuclear spin–spin interaction. Phenomenologically, in NMR spectroscopy, the energy shift bilinear in the nuclear spins $\boldsymbol{I}_N$ and $\boldsymbol{I}_M$ defines the nuclear spin coupling tensor $D_{pq}(N,M)+J_{pq}(N,M)$ according to

$$E^{(2)} = h\big(J_{pq}(N,M) + D_{pq}(N,M)\big)I_{Np}I_{Mq}, \tag{205}$$

where D_{pq} and J_{pq} are named the *direct* and *indirect* (i.e. via the electrons) coupling tensor, respectively; the nuclear magnetic moment is related to the nuclear spin by $\boldsymbol{\mu}_K=\gamma_K\hbar\boldsymbol{I}_K$, $(K=M,N)$, γ_K being the magnetogyric ratio of nucleus K.

Equation (204) allows us to define a quantum field T_{pq} analogous to the coupling tensor by factoring out the nuclear spins

$$\delta\langle H_I^N\rangle = hT_{pq}I_{Np}I_{Mq}, \tag{206}$$

with

$$T_{pq} = \gamma_N\gamma_M\frac{h}{(2\pi)^2}\langle\langle B_p(\boldsymbol{R}_N,t);\, B_q(\boldsymbol{R}_M,t')\rangle\rangle. \tag{207}$$

Using the expressions for $\boldsymbol{B}=\sum_a\boldsymbol{B}^{(a)}$ derived in Section 5.4.2, the various contributions to the tensor $T_{pq}=\sum_{ab}T_{pq}^{(a,b)}$ can be calculated as follows

$$T_{pq}^{(a,b)} = \gamma_N\gamma_M\frac{h}{(2\pi)^2}\langle\langle B_p^{(a)}(\boldsymbol{R}_N,t);\, B_q^{(b)}(\boldsymbol{R}_M,t')\rangle\rangle. \tag{208}$$

5.4.5. *e^0 order term*

The leading term in T_{pq} is the lowest (e^0) order contribution $T_{pq}^{(0,0)}$. This corresponds to the case of interaction of the magnetic moments with the non-perturbed radiation field. As can be seen from Equation (204) and since no interactions with the electrons occur, this corresponds to transitions from the unperturbed ground states $|\Phi_0\Psi_0\rangle$ to the intermediate states $|\Phi_{\boldsymbol{k}\lambda}\Psi_0\rangle$. So, Equation (208) gives

$$T_{pq}^{(0,0)} = \gamma_N\gamma_M\frac{h}{(2\pi)^2}\frac{\mu_0}{4\pi}\left[\frac{\delta_{pq}R_{MN}^2 - 3X_{MN,p}X_{MN,q}}{R_{MN}^5}\right], \tag{209}$$

where $X_{MN,i}$ is the i-th component of the vector $\boldsymbol{R}_{MN}=\boldsymbol{R}_M-\boldsymbol{R}_N$, and $R_{MN}=|\boldsymbol{R}_{MN}|$.

5.4.6. *e^2 order terms*

The possible contributions quadratic in the electron charge are $T_{pq}^{(1,1)}$ and $T_{pq}^{(0,2)}+T_{pq}^{(2,0)}$, which we grouped according to the order of the fields involved. Note that the operator $\boldsymbol{B}^{(1)}$

acts on the fermion states while $\boldsymbol{B}^{(2)}$ changes both the fermion states and the photon number. As noted previously in a non-relativistic context, this is an operator having no classical analogue [161]. The operator $\boldsymbol{B}^{(1)}$ only acts on the fermion Fock space. Hence, the ground and intermediate states are, respectively, $|\Phi_0\Psi_0$ and $|\Phi_0\Psi_a^r\rangle$ (see Equation 204). Inserting the operator $\boldsymbol{B}^{(1)}$ (Equation 191), and summing over the polarization directions by using of the identity

$$\sum_{\lambda} \boldsymbol{k} \times \boldsymbol{e}^{(\lambda)}\left(\alpha \cdot \boldsymbol{e}^{(\lambda)}\right) = \boldsymbol{k} \times \boldsymbol{\alpha}, \tag{210}$$

and transforming the $\boldsymbol{k}$-summation into an integral, we get

$$T_{pq}^{(1,1)} = \left(\frac{\mu_0}{4\pi} ec\right)^2 \sum_{ar} \varepsilon_{mnp}\varepsilon_{rsq}\langle a|\nabla_m\left(\frac{e^{-ik_{ar}r_N}}{R_N}\right)\alpha_n|r\rangle \times \frac{1}{\epsilon_a - \epsilon_r}\langle r|\nabla_r\left(\frac{e^{ik_{ar}r_M}}{R_M}\right)\alpha_s|a\rangle. \tag{211}$$

The term $T_{pq}(B^{(0)}, B^{(2)}) \equiv T_{pq}^{(0,2)} + T_{pq}^{(2,0)}$ depends on the second-order field, which is an operator acting in the combined fermion–photon space. However, it enters into $T_{pq}(B^{(0)}, B^{(2)})$ with $B^{(0)}$ which does not change the fermion state. So, the intermediate states are of the form $|\Phi_{\boldsymbol{k}\lambda}\Psi_0\rangle$, i.e. single occupation of photon modes and electrons in the DF ground state. Then, after some manipulations, Equation (208) gives [17,18]

$$\begin{aligned} &T_{pq}(B^{(0)}, B^{(2)}) \\ &\quad = \sum_{ja}\left(\frac{\mu_0 ec}{4\pi}\right)^2 \frac{1}{\epsilon_a - \epsilon_j}\epsilon_{lmp}\epsilon_{rsq} \\ &\quad\left\{\langle aj\rangle(\alpha_r^{(1)}\nabla_s^M)(\alpha_l^{(2)}\nabla_m^N)\left[\frac{1-e^{-ik_{ja}(r_{2N}-ct)}}{r_{1M}r_{2N}}\theta(r_{1M}-r_{2N}) + \frac{1-e^{ik_{ja}(r_{1M}-ct)}}{r_{1M}r_{2N}}\theta(r_{2N}-r_{1M})\right]|nj\rangle\right. \\ &\quad\left. + \langle aj\rangle(\alpha_l^{(1)}\nabla_m^N)(\alpha_r^{(2)}\nabla_s^M)\left[\frac{1-e^{ik_{ja}(r_{1N}-ct)}}{r_{1N}r_{2M}}\theta(r_{2M}-r_{1N}) + \frac{1-e^{-ik_{ja}(r_{2M}-ct)}}{r_{1N}r_{2M}}\theta(r_{1N}-r_{2M})\right]|ja\rangle\right\} \end{aligned} \tag{212}$$

for times such that ct is greater than any of the distances r_{1N}, r_{2N}, r_{1M} or r_{2M}.

5.4.7. *Comparison to classical-field theory*

It is instructive to consider the relation between the quantum-field (Q) coupling tensor T_{pq} defined in the previous section with the usual classical-field (C) one, namely, the tensor K_{pq} of NMR spectroscopy. Note that Q-expressions consist finally of one-electron operators without reference to the photon frequencies. However, their influence can be traced out through the dependence on the energy differences in the exponents. As is usual, the C-expressions are recovered as these differences approach zero. Let us consider successively the $T_{pq}^{(1,1)}$ and $T_{pq}(B^{(0)}, B^{(2)})$ tensors.

Exponential functions of Equation (211) show that the leading contributions to the tensor $T_{pq}^{(1,1)}$ are those having $k_{ar} \ll 1$, since otherwise the exponentials turn out to be rapidly oscillating and the matrix elements give vanishing contributions. Since a and r

represent occupied and virtual states, respectively, and their energy differences must be $|\epsilon_a - \epsilon_r| \ll 2mc/\hbar$, the virtual states r are essentially positive-energy states. Then

$$T_{pq}^{(1,1)} \simeq \left(\frac{\mu_0}{4\pi}ec\right)^2 \sum_a^{occ} \sum_r^{(+)} \varepsilon_{mnp}\varepsilon_{rsq} \langle a|\nabla_m\left(\frac{1}{R_N}\right)\alpha_n|r\rangle \frac{1}{\epsilon_a - \epsilon_r} \langle r|\nabla_r\left(\frac{1}{R_M}\right)\alpha_s|a\rangle + c.c. \tag{213}$$

On the other hand, Equation (212) shows that the most important contributions to $T_{pq}(B^{(0)}, B^{(2)})$ come from the low-lying negative-energy states for which $k_{ja} \simeq 2mc/\hbar$, so that the exponential functions oscillate rapidly and the numerators can be replaced by unity. Then,

$$\begin{aligned} &T_{pq}(B^{(0)}, B^{(2)}) \\ &\quad \simeq \sum_a^{occ} \sum_j^{(-)} \left(\frac{\mu_0 ec}{4\pi}\right)^2 \frac{1}{\epsilon_a - \epsilon_j} \epsilon_{lmp}\epsilon_{rsq} \\ &\quad \left\{ \langle aj \rangle (\alpha_r^{(1)} \nabla_s^M)(\alpha_l^{(2)} \nabla_m^N) \left(\frac{1}{r_{1M} r_{2N}}\right) |aj\rangle + \langle aj \rangle (\alpha_l^{(1)} \nabla_m^N)(\alpha_r^{(2)} \nabla_s^M) \left(\frac{1}{r_{1N} r_{2M}}\right) |ja\rangle \right\} \\ &\quad = \sum_{ja} \left(\frac{\mu_0 ec}{4\pi}\right)^2 \frac{1}{\epsilon_a - \epsilon_j} \epsilon_{lmp}\epsilon_{rsq} \\ &\quad \left\{ \langle a|(\alpha_r \nabla_s^M) \frac{1}{r_M} |j\rangle \langle j|(\alpha_l \nabla_m^N) \frac{1}{r_N} |a\rangle + \langle a|(\alpha_l \nabla_m^N) \frac{1}{r_N} |j\rangle \langle j|(\alpha_r \nabla_s^M) \frac{1}{r_N} |a\rangle \right\}. \end{aligned} \tag{214}$$

It should be noted that the matrix elements of Equations (213) and (214) can be reduced to their non-relativistic form by using the approximate relation between the large (L) and small (S) two-component spinors of the four-component Dirac wavefunctions

$$|\psi^S\rangle \simeq \frac{\boldsymbol{\sigma} \cdot \boldsymbol{p}}{2mc} |\psi^L\rangle, \tag{215}$$

where $|\psi\rangle = \left|\begin{matrix}\psi^L \\ \psi^S\end{matrix}\right\rangle$ for positive-energy and $|\psi\rangle = \left|\begin{matrix}\psi^S \\ \psi^L\end{matrix}\right\rangle$ for negative-energy wavefunctions, with the standard representation of the Dirac matrices $\boldsymbol{\alpha}$ in terms of Pauli matrices $\boldsymbol{\sigma}$

$$\boldsymbol{\alpha} = \begin{pmatrix} 0 & \boldsymbol{\sigma} \\ \boldsymbol{\sigma} & 0 \end{pmatrix} \tag{216}$$

to give

$$\langle a|\nabla_m\left(\frac{1}{R_N}\right)\alpha_n|r\rangle \simeq \frac{1}{2mc} \langle \alpha^L|\{\nabla_m\left(\frac{1}{R_N}\right)\alpha_n, \sigma_i p_i\}|r^L\rangle \tag{217}$$

when r is a positive-energy state and $\{A, B\} = AB + BA$ represents the anticommutator between A and B; and

$$\langle a|\nabla_m\left(\frac{1}{R_N}\right)\alpha_n|j\rangle \simeq \langle \alpha^L|\nabla_m\left(\frac{1}{R_N}\right)\alpha_n|j^L\rangle \tag{218}$$

when j is a negative-energy state.

It should also be pointed out that in Ramsey's non-relativistic theory, paramagnetic terms (FC, PSO and SD) arise from second-order perturbation theory, while the single diamagnetic spin–orbit term DSO is obtained from first-order perturbation theory. However, in the relativistic domain, as discussed by Sternheim [157] and Aucar *et al.* [29], the operators are linear in the nuclear spins; hence, there is no contribution from first-order perturbation theory to the nuclear spin–spin coupling. In this case, the coupling is an effect completely accounted for by second-order perturbation theory. The non-relativistic DSO term is an approximation to that part of the (second-order) expression including only intermediate negative-energy states. In line with this, Equation (214) is the relativistic C-expression with negative energy (of order $-2mc^2$) states j, which has been shown to give the non-relativistic DSO term [29,157].

6. Concluding remarks

In this review we have tried to show what polarization propagators are, and what one can learn by studying NMR spectroscopic parameters with them; within NR, relativistic and QED theories. The beautiful quantum feature of this tool, which consider all likely pathways through which a perturbation could reach a given place of a system being initiated in a different place, is expressed in the analysis and calculation of molecular properties by including what are called *coupling pathways*. They consist of all excitations that are allowed to contribute to a given property calculation.

Even though polarization propagators have exactly the same formal definition (a nice feature of them), they give different insights depending on the regime to which they are applied. On the other hand, calculations that start within the relativistic regime will end up in the correct NR values when one makes c go to infinity. This is a special characteristic of polarization propagators that is in line with what the founder of propagators, Richard Feynman, wanted when he was looking for a way to introduce the formalism of quantum theory from more classical tools like the principle of least action. We want to highlight this feature because it is quite transparent in this case and involves new considerations that should be fulfilled. As an example, **J**-couplings are produced by mechanisms that are electron-spin restricted in the NR regime though spin is no longer a good quantum number within the relativistic regime. So how can we obtain such contributions starting from the relativistic expressions? One should include time-reversal symmetry which is a kind of generalization of spin symmetry. By doing this one starts from pseudo-singlet expressions and ends up naturally in two kinds of electron-spin-dependent terms, of singlet and triplet type.

One of the main goals of relativistic polarization propagators is the unification of all electronic mechanisms that produce the NMR spectroscopic parameters in only one. Indeed such a mechanism is exactly the same for paramagnetic and diamagnetic terms. So within the relativistic regime it is nonsense to split them up into two. There is only one mechanism that is not of diamagnetic or paramagnetic type. One can get both of them, but after making an approximation. Then diamagnetism and paramagnetism are understood as something completely different from what we know from the NR world. This is also more nicely seen within the QED theory which shows that paramagnetic-like contributions arise from excitations to 'virtual' positive-energy states and diamagnetic-like contributions arise from excitations to 'virtual' negative-energy electronic states. This distinction is complete at the PZOA level of approach but has a mix of contributions of both excitations whenever electron correlation is considered: that 'virtual' excitations are completely equivalent to 'virtual' electron–positron creation and annihilation. This is something completely new but makes a lot of sense. It is like an extension of the concept of 'virtual' bondings or antibondings that are necessary to well-define a bond. When going to a relativistic theory one should consider sooner or later the fact that positrons could exist, and such existence may have an influence on the molecular system even though there is not enough energy to make them real particles. One additional explanation that arises from our QED theory is related to the fact that diamagnetic-like contributions can be completely described by an interval of excitation energies: $2mc^2 \leq |\varepsilon_i - \varepsilon_{\tilde{a}}| < 4mc^2$. This should be the case because otherwise one would get real electron–positron pairs which is not possible because there is not enough energy available.

The NR rule that paramagnetic-like contributions to the magnetic shielding of rare gases are zero is not fulfilled within the relativistic regime. We have shown here, for the first time, that there is a more general rule that includes the paramagnetic-like contribution to the magnetic shielding of the elements belonging to the same row of the periodic table.

Another interesting feature that arises within the QED theory is the fact that the gauge invariance of the shielding is equivalent to covariance. From a non-covariant QED one gets diamagnetic-like and paramagnetic-like terms, but we all know that only the covariant formulation of QED is right; and this implies that both diamagnetic and paramagnetic-like terms should be summed up to obtain a covariant formulation.

Within the NR domain we have shown that using polarization propagators one can get reliable results and also a deep understanding of several conspicuous properties of NMR spectroscopic parameters. The sign of **J** could be understood as arising from the relative sign of phases between occupied and virtual electron states at the site of nuclei for the FC mechanism. This is independent of the distance between the coupled nuclei and generalizes (which means that it includes) the previous model of Dirac and Peeney. Another interesting finding only obtained with polarization propagators is the explanation of the Karplus rule through a new kind of entanglement which will be developed in more detail in future publications. We have given some other studies that include cooperative effects, long-range couplings (of the order of a few nanometres distant) and the proton transfer mechanism in Schiff bases.

Polarization propagators are nice theoretical tools that give a deep insight on the physics behind the electronic structure of molecular processes. The beauty and simplicity of its equations within the relativistic regime, its natural NR limit and its relationship with QED theory, and its predictive power and versatility to explain different mechanisms that intervene in the origin of NMR spectroscopic parameters, makes them one of the most powerful theoretical tools for studying these molecular properties.

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