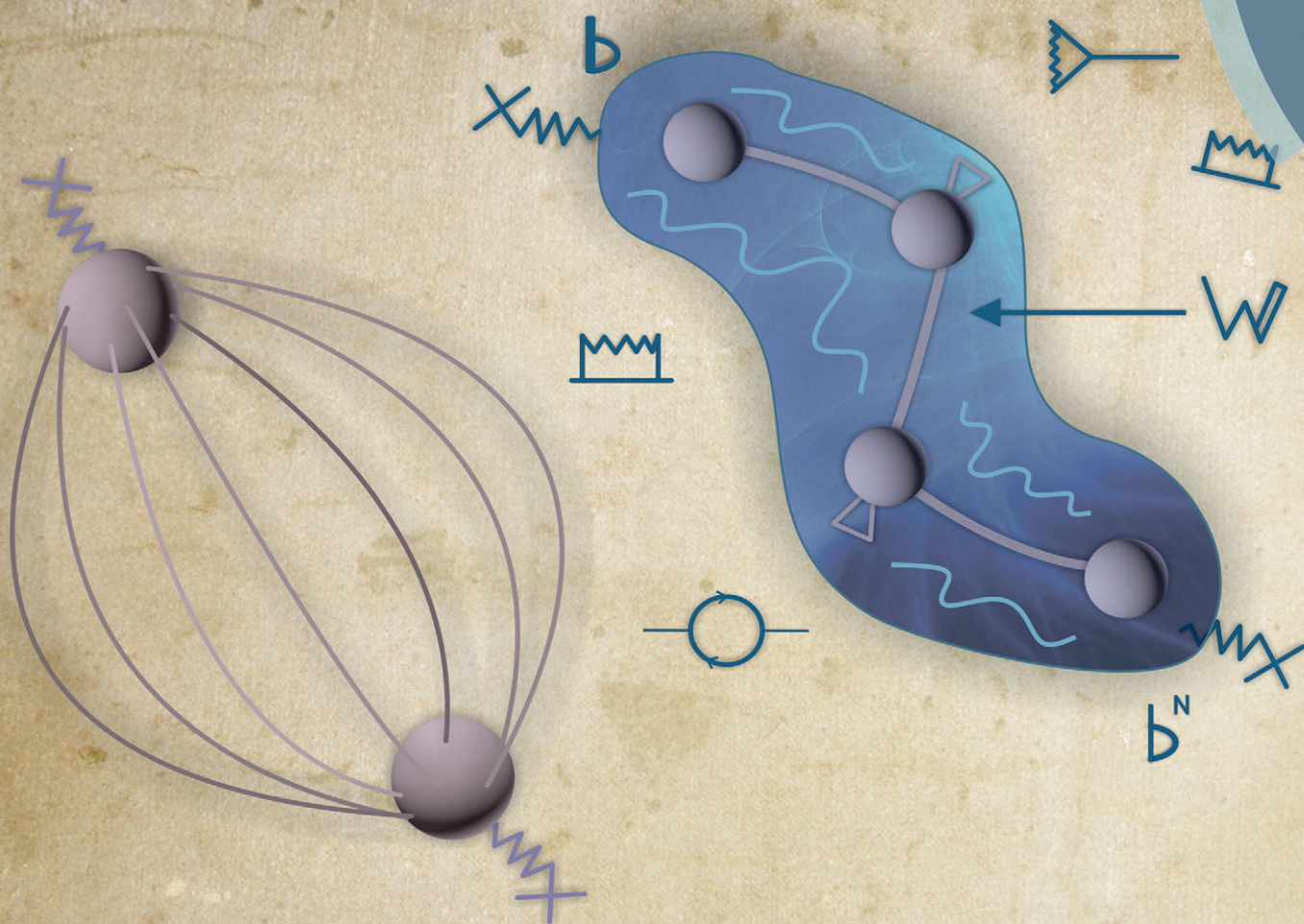


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PERSPECTIVE

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Toward a QFT-based theory of atomic and molecular properties

Toward a QFT-based theory of atomic and molecular properties

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Gustavo A. Aucar^{ab}

The search for a QED-based (and then QFT-based) formalism that brings solid grounds to the whole area of relativistic quantum chemistry was just implicit in the first decades of the quantum theory. During the last few years it was shown that it is still unclear how to derive a well-defined N -electron relativistic Hamiltonian, and also the way negative-energy states may contribute to electron correlation. Furthermore, the relationship among electron correlation and radiative QED corrections is even more difficult to guess. These are few of the fundamental problems that need to be solved before such a program of research is finished within the wavefunction approach to quantum physics. The polarization propagator formalism was developed as an alternative approach to study atomic and molecular properties within both regimes, relativistic and nonrelativistic. In this article we expose how far away one can go today working with polarization propagators, until including QED (and afterwards QFT) effects. We will uncover its deepest formal origin, the path integral formalism, which explains why polarization propagators can be written formally the same in both regimes. This will also explain why the NR limit is obtained scaling the velocity of light to infinity. We shall introduce a few basic aspects of elementary propagators to show what they have in common with polarization propagators. Then we shall remark on the most important news that appears with the latter ones. Within the relativistic regime the contributions of negative energy orbitals to electron correlation are straightforwardly included. New insights on the relationship between spin and time-reversal operators are also given, together with an ansatz on how to consider both, QED and electron correlation effects on the same grounds. We focus here on the treatment of NMR spectroscopic parameters within such a formalism, that is still not broadly used by the quantum chemistry community. Most of the other response properties can be treated in a similar manner.

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1 Introduction

In the search for a QED-based theory to describe atomic and molecular properties one first needs to learn how to properly define or consider some dynamical variables that just appears in relativistic quantum chemistry. Among these one can mention the definition of a relativistic many-electron Hamiltonian, the way the negative-energy states contribute to the electron correlation and how to include QED effects and electron correlation on the same theoretical grounds. These long-standing difficulties and some new developments on polarization propagators theory justify the search for an alternative proposal to that of the usual wavefunction approach.

The occurrence of positive-energy and negative-energy states in the solutions of the Dirac equation are related with particles

and antiparticles (electrons and positrons, respectively), and so with creation and annihilation of both particles. How should negative-energy states be included in the description of atomic and molecular properties? Do they have any meaning for the explanation of a chemical (low-energy) process, if real antiparticles are not available?

From a chemical point of view it is hard to realize the importance of considering the influence of electron-positron pairs on the molecular properties. There is still an interesting and long standing controversy on whether negative-energy states (which do introduce the concept of electron-positron pair creation) should not be considered on calculations due to the high energy necessary to create real positrons or be included from the outset as generating virtual particles.^{1–11} This controversy is still underway though some new proposals have recently been published.¹² We are also introducing here new arguments that may shed some more light on it.

The appearance of negative energy states in the framework of relativistic quantum chemistry and physics was always a source of difficulties. They were treated in different manners

^a Institute for Modeling and Innovative Technology, IMIT (CONICET-UNNE), Argentina. E-mail: gaa@unne.edu.ar

^b Physics Department - Natural and Exact Science Faculty, Northeastern University of Argentina, Avda Libertad 5460, W3404AAS, Corrientes, Argentina

through: (a) well-defined positive-energy projectors, (b) unitary transformations based on the spirit of the Foldy–Wouthuysen transformation though with several improvements, or (c) properly applying polarization propagators.

By using positive-energy projectors Sucher was one of the first to discuss what is known as the no-pair Hamiltonians.¹³ He was engaged in deriving a relativistic many-body Hamiltonian from QED and was also able to show explicit expressions for the energy level shifts that arise from the effects of virtual photons and virtual electron–positron pairs. Appropriate projectors were also found useful when looking for relativistic corrections to magnetic properties at two-component levels, starting from four-component ones.^{5,14–16} There are few methodologies developed to obtain appropriate unitary transformations for block diagonalizing the relativistic Hamiltonian^{17–22} or expressing all working equations in terms only on the “large” components.^{8,23–31} In a recent review Saue has discussed in some detail the whole set of relativistic Hamiltonians available in quantum chemistry.³²

We should also mention several other new 4- and 2-components methodologies that during the last few years were developed and implemented for including relativistic effects in molecular electric and magnetic properties, within both wavefunction and DFT approaches. They were published in regular articles^{9,33–40} and also in review articles.^{8,11,41–43} In a few of them small though significant effects like nuclear-size effects were studied.^{44–48}

All previous considerations show a growing interest to go one step further and introduce QED effects also on properties.^{12,49} Few recent articles that include QED effects on the atomic properties^{50–52} or attempts to explain how one may do it for molecular properties^{53–56} were published. Lindgren also introduced a new approach in a book.⁵⁷ In his recent article¹² Kutzelnigg mentioned that there are indications of a *change of paradigm* in the sense that for getting the correct Hamiltonian one may try in opposition of what was previously looked for, *e.g.* by introducing clear cut approximations of the QED Hamiltonian, each of which can be studied exactly. The way it was done before was to start from a *full* QED and then construct a Hamiltonian. We suggest here to choose a different road, meaning the application of the path integral formalism. We are going to present effective QED-based Hamiltonians (including perturbative Hamiltonians) in a Liouvillian framework in order to introduce QED effects on the response properties in a many-body atomic or molecular system.

This article will focus on some new theoretical insights arising from the polarization propagator formalism, and some of its applications to a few specific magnetic properties that are very much influenced by relativistic effects: the NMR spectroscopic parameters. Its application to most other second order properties could be pursued in a similar manner.

Norman Ramsey was the first to propose a consistent non-relativistic theory for such parameters.^{58–60} He found several theoretical mechanisms for describing the interaction among nuclei and the electronic environment that gave accurate results when calculations were performed with high-level methods on only light-atom containing molecules. After a few decades it was realized that when heavy-atoms are included in the model

molecular systems relativistic effects should (must) be included (depending on the weight of the atoms).^{61,62} In addition to that Pyykkö and Zhao⁶³ suggested that QED effects on NMR parameters may be of the same size as solvent effects on heavy-atom containing molecules.

A higher-level of theory for including QED effects in the spectroscopic parameters was published by Romero and Aucar more than ten years ago.^{53,54} They did it based on two different theoretical schemes arriving to formal expressions which are however still not implemented in computational codes. No clear indications were proposed on how to handle electron correlation and relativistic effects on the same grounds and in actual calculations being the full theory formally sound.⁷ Right now there is no other general QED-based theory for calculation of both NMR spectroscopic parameters though Pachucki and coauthors proposed a theory for including QED effects on magnetic shieldings of hydrogen-like ions.⁶⁴

A theoretical explanation of any quantum phenomenon requires a coherent formalism from which one should be able to describe and predict the evolution of the quantum system under study, and afterwards the prediction of the likely results of the measurements. To learn about the spectroscopic properties of an atomic or molecular quantum system one should make it possible that the system does interact with internal or external fields. From the analysis of some specific responses one then obtains a pattern from which to explain or describe those properties.

The principles of quantum mechanics can be explicitly formulated by two different and equivalent formalisms: (a) the most used in atomic and molecular physics, for which the dynamical (classical) variables are replaced by linear operators acting on wavefunctions or state vectors which belong to a given Hilbert space. Basic commutator relationships between the elementary dynamical variables, the position and its canonical conjugate linear momentum are well defined. This formalism is due to Schrödinger, Heisenberg, Dirac, and others; and (b) the path integral formalism (first developed by Richard Feynman) where the propagator is the basic dynamical variable. This formalism is mainly used in quantum field theory. It offers a straightforward though quite unconventional way to describe how in quantum physics, a perturbation (transmitted through virtual particles or virtual excitations) goes from a given space-time point to another one.

One of the aims of this article is to show how polarization propagators can be derived from the path integral formalism, and so which are the elements they have in common with all other propagators. We shall stress the relationship of the Green functions with the Feynman’s formulation of quantum mechanics. It will not be possible to do it in all details here but we will expose it in such a way that one can grasp the basic knowledge needed to understand what is at the basis of the relativistic polarization propagator theory. This fundamental step will permit us to go one step forward and propose its formulation within the QED framework and, afterwards, it will also indicate how one can go back to their NR limit in a nice and natural way.

We shall start giving a brief introduction of the well-known aspects of the path integral formalism, and how the Green

functions are obtained from it. We introduce the concept of non-interacting and interacting propagators, and their generating functionals. This first section will give a theoretical support to the following sections. Polarization propagators are then introduced with their main features. Its usual definition and the statement of a theorem about how they can be derived from the path integral formalism, meaning the MO representative of the Green's function corresponds to the quantum correlation between two perturbative interactions. This last point is given here for the first time and is one of the main novelties of this article. This finding gives us new insights on what polarization propagators are and how are they connected with previous and sound knowledge.

Then we give a brief introduction of the theory of relativistic polarization propagators^{1,3,7} highlighting the way electron correlation is properly included in them. Furthermore we will show some properties of new pseudo-singlet and pseudo-triplet operators that become traditional singlet and triplet NR operators when the velocity of light is scaled to infinity. In the last section we show a transparent relationship between the *S*-matrix formalism and polarization propagators and finally we propose an ansatz for including both the QED and electron correlation effects on the same grounds.

2 The path integral formalism for quantum physics

We introduce in this section the basic language that gives support to the fact that polarization propagators have the same formal definition within both domains, relativistic and non-relativistic. Furthermore we shall highlight the main features of some powerful theoretical tools that were mainly developed within the quantum field theory, QFT and are now necessary to introduce in quantum chemistry.

2.1 Basic features and definitions

In classical physics the equation of motion for a *N*-particle system can be obtained by applying the least action principle: one should be able to write the actual Lagrangian of the system, include it in the action *S* and then minimize it. The Lagrangian *L* is defined as the difference between the kinetic and potential energies.

Let us consider first the evolution of a given one-particle system in a one-dimensional space between two points, A and B, as shown in Fig. 1. The particle could make its displacement through any available path. The action is written then as

$$S = \int_{t_A}^{t_B} dt L(q, \dot{q}, t) \quad (1)$$

q and \dot{q} being the generalized coordinate and the generalized velocity, respectively. Applying the least action principle, one finds that there is only one path that the particle must follow: $q_c(t)$.

What would happen in quantum physics? The basic assumption is that the particle could follow any available path. In fact one must consider the whole universe of the likely paths, which should also include paths where the particle travels

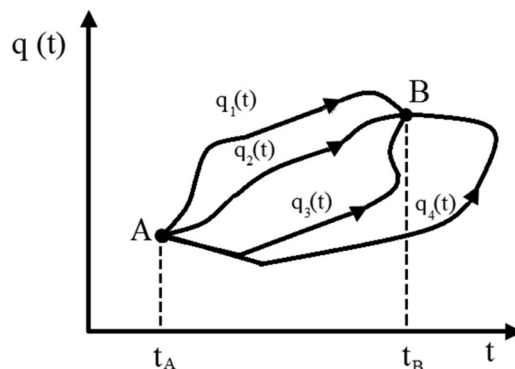


Fig. 1 Different pathways for a particle in a one-dimensional trajectory.

backward in time as happens to the path q_4 in Fig. 1. This is the starting point of the path integral formalism, and was suggested and later developed by Richard Feynman.

Let us see how the equations of motion are obtained for quantum systems. In quantum mechanics the dynamical variables, like position of the particle becomes an operator $\hat{q}(t)$. In what follows it is better to work within the Heisenberg or the interaction pictures where the operators explicitly depend on time. It is easier to consider any available trajectory in those pictures.

For the actual path that a particle shall follow to be known, measurements need to be done. So the eigenvalues of the position eigenstates should be determined,⁶⁵

$$\hat{q}|q'(t=0)\rangle = q'|q'(t=0)\rangle \quad (2)$$

The eigenvalues of the position operator at any given time are obtained from the evolved eigenstate

$$|q'(t')\rangle = e^{-\frac{i}{\hbar}\hat{H}t'}|q'(t=0)\rangle = e^{-\frac{i}{\hbar}\hat{H}t'}|q'\rangle \quad (3)$$

\hat{H} being the Hamiltonian operator of the system.

The probability amplitude that the particle (system) being in a position (initial state, Ψ_A) $q_A(t_A)$ would be found in another position (final state, Ψ_B) $q_B(t_B)$ is computed as

$$P(q_A, q_B) = N^2 |A(q_A, q_B)|^2 \quad (4)$$

where *N* is a normalization constant, and

$$A(q_A, q_B) = \langle q_B(t_B) | q_A(t_A) \rangle = \langle q_B | e^{\frac{i}{\hbar}\hat{H}(t_B-t_A)} | q_A \rangle \quad (5)$$

is the transition or probability amplitude. This amplitude contains a complete description of the quantum system.

If \hat{H} is of the form

$$\hat{H}(p, q) = \frac{1}{2m} p^2 + V(q) \quad (6)$$

it can be shown that

$$\langle q_B(t_B) | q_A(t_A) \rangle = N \int_{t_A}^{t_B} Dq e^{\frac{i}{\hbar}S[q; t_B, t_A]} \quad (7)$$

where $Dq = \prod_{i=1}^{\infty} dq_i$ and *N* is a normalization constant. The action $S[q; t_B, t_A]$ is a functional of a particular path, *q*, but also a function of the end points t_B and t_A . Functional integrals

mean that the integration is taken over all functions $q(t)$ and it gives a number. Eqn (7) is the Feynman path integral and gives the probability amplitude as a sum over histories.

The probability amplitude of eqn (7) is also known as a propagator and is equivalent to

$$\begin{aligned} \langle q_B(t_B) | q_A(t_A) \rangle &\propto \sum_{\text{all possible paths, } q_i} e^{\frac{i}{\hbar} S[q_i; t_B, t_A]} \\ &= \lim_{n \rightarrow \infty} \int_{q_A}^{q_B} dq_1 \dots dq_n e^{\frac{i}{\hbar} \int_{t_A}^{t_B} L(q_1, \dot{q}_1) dt} \dots e^{\frac{i}{\hbar} \int_{t_A}^{t_B} L(q_n, \dot{q}_n) dt} \end{aligned} \quad (8)$$

The propagator depends on the value of the function $q(t)$ at all points. Not all paths, q_i are equally likely. The classical path makes S stationary under a small change of the path. So, in its vicinity there will appear a constructive addition of phases represented by the closely related values of $S[q; t_B, t_A]$. The contribution of all other paths is zero because their contributions are cancelled among themselves.

2.2 Propagators for quantum fields

Right now, we have considered the evolution within a non relativistic framework of a quantum system, by the measurement of the position of point particles at any time which then produce the trajectory $q(t)$. The passage of the NR description of a point particle position $q(t)$ to a relativistic quantum field $\phi(x^\mu)$ may be done by replacing q by ϕ and t by $x^\mu = (\mathbf{r}, t)$. The quantum field $\phi(x^\mu)$ describes a system with an infinite number of degrees of freedom because at each time, ϕ has an independent value at each point in space. In what follows we will rename the space-time position x^μ as x to simplify notation. Its meaning is such that, when working within a NR framework they will represent position and time separately. On the other hand, when working within a relativistic framework $x^0 = ct$ and the other 3-coordinates will represent the space point \mathbf{r} . As is usual in QFT, c is set equal to 1 when there is no explicit reference to it.

We need to work with fields because in the framework of relativistic quantum theory even the one-particle wave function becomes an operator. Both, the Klein–Gordon, KG and the Dirac equations describe quantum fields, for bosons and fermions respectively. The appearance of negative-energy states is related with the existence of antiparticles and force us to reinterpret both equations as describing the evolution of many-particle systems.

In any case one can obtain the KG or the Dirac equation through the application of the Euler–Lagrange equation. One only needs to define adequately the Lagrangian density function, $\mathcal{L}(\phi, \dot{\phi}, \nabla\phi)$.

Eqn (7) can be generalized to the case of quantum fields as

$$\langle \phi_B(t_B) | \phi_A(t_A) \rangle \propto \sum_{\text{all possible fields, } \phi} e^{\frac{i}{\hbar} S[\phi; t_B, t_A]} \quad (9)$$

In the absence of any external perturbation the system will stay in its ground or vacuum state, $|0\rangle$ at both times, initial t_A

and final t_B . The propagator of eqn (9) shall now describe the evolution of a system where one virtual particle (bosonic or leptonic) is created at a space-time position x_A and annihilated at a different space-time position x_B . In the same manner one may also consider an equivalent phenomenon for which virtual excitations are transmitted from one space-time to another.

In QFT the ground-state to ground-state transition amplitude of the free (or independent) particle is usually written as

$$\begin{aligned} Z_0 &= \langle 0, t_B | 0, t_A \rangle \\ &= N \int D\phi e^{\frac{i}{\hbar} S[\phi; t_B, t_A]} = N \int D\phi e^{\frac{i}{\hbar} \int d^4x \mathcal{L}(\phi)} \end{aligned} \quad (10)$$

where the initial and final times are explicitly shown. In this case the evolving field is the vacuum or the ground-state. The (infinitely many) trajectories mean that quantum fluctuations of the ground state are likely produced on top of the “classical” ground-state. The amplitudes for propagating (virtual) particles, which refer to excitations about the ground state, are calculated as the product of fields weighted by the $\exp(iS/\hbar)$. This topic will be expanded in Section 4.

For future developments and understandings of what the polarization propagators refer to we shall consider now the way in which the inclusion of a perturbation do modify the probability amplitude Z_0 .

2.3 The evolution of a perturbed scalar field

Let's consider the specific case of an scalar field whose Lagrangian density \mathcal{L}_0 is

$$\mathcal{L}_0 = \frac{1}{2} (\partial_\mu \phi \partial^\mu \phi) - V(\phi) \quad (11)$$

where the operator $\partial_\mu \partial^\mu$ is the well known D'Alembertian operator. We follow the presentations of Ryder⁶⁶ and Zee.⁶⁷ When the potential is $V(\phi) = 1/2m^2\phi^2$, the Lagrangian density \mathcal{L}_0 will be the adequate function from which the scalar field excitations without interactions among themselves are obtained. If the potential V contain terms with a different potential dependence of ϕ (like third or fourth) it shall imply that the interactions among the scalar field excitations shall be included. This is an important point that will be dealt with in more detail in Section 2.5.

In order to consider the effect of a perturbation J on the ground state of the quantum system, we should modify the Lagrangian density as

$$\mathcal{L} \rightarrow \mathcal{L} + J\phi \quad (12)$$

meaning that the field ϕ has a source J . There will appears an excitation in the perturbed system in a given space-time that will disappears in another space-time. In this case the transition amplitude becomes

$$\begin{aligned} Z_0(J) &= \int D\phi e^{\frac{i}{\hbar} \int d^4x [1/2(\partial_\mu \phi \partial^\mu \phi - m^2 \phi^2)] + J\phi} \\ &= \int D\phi e^{\frac{i}{\hbar} \int d^4x [-1/2\phi(\partial_\mu \partial^\mu + m^2)\phi + J\phi]} \end{aligned} \quad (13)$$

being the last term obtained from integrating by parts. Its formal solution can be grasped from a relationship with the discrete case (see pages 273–275 of ref. 65)

$$\int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \dots \int_{-\infty}^{\infty} dq_1 dq_2 \dots dq_N e^{i\mathbf{q}\mathbf{A}\mathbf{q} + i\mathbf{J}\mathbf{q}} = \left(\frac{(2\pi i)^N}{\det[\mathbf{A}]} \right)^{1/2} e^{-\frac{i}{2}\mathbf{J}\mathbf{A}^{-1}\mathbf{J}} \quad (14)$$

\mathbf{A} being a matrix and \mathbf{q} a vector. Matrix \mathbf{A} is equivalent to the differential operator $-(\partial_\mu \partial^\mu + m^2)$. Then, eqn (13) can be rewritten as

$$\begin{aligned} Z_0(J) &= Z_0(J=0) e^{-i/2 \int \int dx^4 dy^4 J(x) \Delta_F(x-y) J(y)} \\ &= Z_0(J=0) e^{iW(J)} \end{aligned} \quad (15)$$

Given that the transition amplitudes are normalized the factor $Z_0(J=0)$ is not relevant.

The equation that defines \mathbf{A}^{-1}

$$\mathbf{A}\mathbf{A}^{-1} = \mathbf{I} \text{ or } \sum_j \mathbf{A}_{ij} \mathbf{A}_{jk}^{-1} = \delta_{ik} \quad (16)$$

has its equivalence in the field case

$$-(\partial_\mu \partial^\mu + m^2) \Delta_F(x-y) = \delta^{(4)}(x-y) \quad (17)$$

where $\Delta_F(x-y)$ is known as the free-particle Feynman propagator. The propagator $\Delta_F(x-y)$ is related with a Green function as follows, $G(x,y) = i\Delta_F(x-y)$ and the vacuum to vacuum (or ground-state to ground-state) transition amplitude $Z_0(J)$ is the generating functional for the free (or independent) particle Green function. As can be seen from eqn (17) the Feynman propagator is clearly the inverse of an operator

$$\Delta_F(x-y) = -(\partial_\mu \partial^\mu + m^2)^{-1} \quad (18)$$

whose analytic expression can be obtained within the momentum space. The Feynman propagator is also the inverse of the operator that appears in the quadratic term of the Lagrangian function (see eqn (13)). This last statement can be taken as a definition of a propagator (see page 216 of ref. 66).

Considering that

$$\delta^{(4)}(x-y) = \int \frac{d^4 k}{(2\pi)^4} e^{ik(x-y)} \quad (19)$$

its solution is

$$\Delta_F(x-y) = \int \frac{d^4 k}{(2\pi)^4} \frac{e^{ik(x-y)}}{k^2 - m^2 + i\epsilon} \quad (20)$$

The prescription $i\epsilon$ is needed in order to solve the integration over k .

By expanding the exponential factor of eqn (15) one finds a series of terms, which represent the propagation of one particle between the sources, the propagation of two particles between sources and so on. Then we have at hand a many-particle theory. Each term of this series is a Green function; so that $Z_0(J)$ is a generating functional for the Green functions of the theory.

Let's analyze the first term of the series which represent the propagation of one particle between the sources placed on two space-time points, x and y

$$-i/2 \int \int dx^4 dy^4 J(x) \Delta_F(x-y) J(y) \quad (21)$$

Introducing the Fourier transform of $J(x)$

$$J(x) = \frac{1}{(2\pi)^4} \int d^4 k e^{ikx} J(k) \quad (22)$$

one finds that eqn (21) can be written as

$$-i/2 \int \frac{d^4 k}{(2\pi)^4} J^*(k) \frac{1}{k^2 - m^2 + i\epsilon} J(k) \quad (23)$$

Now, if $J(x) = J_1(x) + J_2(x)$ where $J_1(x)$ and $J_2(x)$ are concentrated in two different regions of the space-time framework one shall have four terms in the last equation. If the self-energy terms are not considered one obtains the following analytic expressions for eqn (21)

$$-i/2 \int \frac{d^4 k}{(2\pi)^4} J_2^*(k) \frac{1}{k^2 - m^2 + i\epsilon} J_1(k) \quad (24)$$

The calculation of this integral will give a non-vanishing contribution only when there is a significant overlap between $J_1(x)$ and $J_2(x)$ in its Fourier transformation together with the constraint that within the region of such overlap ($k^2 - m^2$) is close to zero. The physics behind this theory is the following: there is a source in the space-time region 1 whose perturbation to the field is transmitted to the whole space-time framework but absorbed later on in the space-time region 2. The perturbation is transmitted by (virtual) particles like photons or electrons that are created in region 1 and annihilated in region 2 or *vice versa*.

For electromagnetic fields, ϕ is replaced by the vector potential \mathbf{A}_μ . For spinor fields there will be two fields, ψ and $\bar{\psi}$.

Equivalent procedures as that considered above give the photon propagator or the electron propagator when the Lagrangian is the appropriate one. Such propagators represent the transmission of elementary excitations of a field.

2.4 The 2-point correlation function and the generating functional, W

We are interested in the analysis of the propagator of an excitation that is created in a given spacetime (say x_A) and annihilated in another spacetime (say x_B). The Feynman propagator or causal propagator is a correlation function that takes care of the physical sense of time. Its definition is

$$\Delta_F(x_B - x_A) = -i \langle 0 | T \phi(x_B) \phi^\dagger(x_A) | 0 \rangle \quad (25)$$

where T represent the time-ordering operator, $\phi^\dagger(x_A)$ creates a particle from the vacuum or the ground state at the space-time x_A and $\phi(x_B)$ annihilates such particle at the space-time x_B ; the field operator $\phi(x)$ is a complex scalar (like the KG) field.

Then the Feynman propagator can be calculated as

$$\Delta_F(x_B - x_A) = -i \begin{cases} \langle 0 | \phi(x_B) \phi^\dagger(x_A) | 0 \rangle & \text{if } t_B > t_A \\ \langle 0 | \phi^\dagger(x_A) \phi(x_B) | 0 \rangle & \text{if } t_A > t_B \end{cases} \quad (26)$$

The second line describes the propagator of a virtual anti-particle that travels from space-time x_B to space-time x_A .

The Feynman propagator and so the 2-point Green function can be also obtained from the path integral formalism. It can be proven that (see ch. 14 of ref. 65)

$$\langle 0, t_f | T[\phi(t_A) \phi(t_B)] | 0, t_i \rangle = N \int D\phi \phi(t_A) \phi(t_B) e^{\frac{i}{\hbar} \int_{t_i}^{t_f} L dt} \quad (27)$$

It is worth to mention that on the lhs one has operator fields, and on the rhs there are c -number fields. The meaning of that identity is the following: for each path represented by a given field ϕ the correlation between the actual values of the field at different times is weighted by an exponential of the action. When $t_i \rightarrow -\infty$ and $t_f \rightarrow \infty$ the last equation becomes the path integral definition of the Feynman propagator.

From the last fundamental identity one can obtain a relationship between Generating functionals and Feynman propagators. Let us consider again the functional $Z_0[J]$

$$Z_0[J] = \int D\phi e^{\frac{i}{\hbar} \int d^4x (\mathcal{L} + J\phi)} \quad (28)$$

Its first functional derivatives with respect to J are

$$\frac{\delta Z_0[J]}{\delta J(x_A)} = i \int D\phi \phi(x_A) e^{\frac{i}{\hbar} \int d^4x (\mathcal{L} + J\phi)} \quad (29)$$

$$\frac{\delta^2 Z_0[J]}{\delta J(x_A) \delta J(x_B)} = i^2 \int D\phi \phi(x_A) \phi(x_B) e^{\frac{i}{\hbar} \int d^4x (\mathcal{L} + J\phi)}$$

so that

$$\begin{aligned} \left. \frac{\delta^2 Z_0[J]}{\delta J(x_A) \delta J(x_B)} \right|_{J=0} &= i^2 \int D\phi \phi(x_A) \phi(x_B) e^{\frac{i}{\hbar} \int d^4x (\mathcal{L}(\phi))} \\ &= -\langle 0 | T\phi(x_A) \phi(x_B) | 0 \rangle \end{aligned} \quad (30)$$

This second derivative of the functional is then equal to $i\Delta_F(x_A - x_B)$.

We have seen that $Z_0[J]$ is the generating functional of the Greens function (which include all connected and disconnected Feynman diagrams) of the theory. What about the functional $W[J]$? From eqn (15)

$$W[J] = -i \ln Z_0[J] \quad (31)$$

Applying to this equation a second-order functional derivative:

$$\frac{\delta^2 W[J]}{\delta J(x_A) \delta J(x_B)} = \frac{i}{Z_0^2} \frac{\delta Z_0}{\delta J(x_A)} \frac{\delta Z_0}{\delta J(x_B)} - \frac{i}{Z_0} \frac{\delta^2 Z_0}{\delta J(x_A) \delta J(x_B)} \quad (32)$$

For $J = 0$ we obtain

$$\left. \frac{\delta Z_0}{\delta J(x)} \right|_{J=0} = 0, \quad Z_0[0] = 1 \quad (33)$$

and so

$$\left. \frac{\delta^2 W[J]}{\delta J(x_A) \delta J(x_B)} \right|_{J=0} = -i \left. \frac{\delta^2 Z_0}{\delta J(x_A) \delta J(x_B)} \right|_{J=0} = -\Delta_F(x_A - x_B) \quad (34)$$

This shows that the functional W generates the propagator that has no disconnected part. Then it is W that one want to calculate. Such functional is related with the polarization propagator as will be seen in Section 3.5.

2.5 From non interacting (free) to the interacting propagators

In previous sections we worked out the free particle propagators and its generating functionals. Meaning propagators that arise from generating functionals where the potential energy is quadratic. In such cases the equations of motion for the field operators are linear. The effect of the external perturbation is propagated by ϕ , which couple the external sources. The particles associated with the field operator ϕ do not interact each other. When the unperturbed Lagrangian contain anharmonic terms the equation of motion for the field operators will become nonlinear, meaning that the particles arising from the field operator ϕ and propagates the perturbation, do interact each other. In quantum chemistry it would imply that electron correlation must be included.

Let us write again the generating functional of eqn (13) though now with a potential $u(\phi)$ that may contain an anharmonic term

$$Z[J] = \int D\phi e^{\frac{i}{\hbar} \int d^4x [1/2(\partial_\mu \phi \partial^\mu \phi) + u(\phi) + J\phi]} \quad (35)$$

If $u(\phi) = -m^2 \phi^2 + \lambda/4! \phi^4$ the generating functional becomes $Z[J] \rightarrow Z[J, \lambda]$ (see p. 48 of ref. 67), where

$$\begin{aligned} Z[J, \lambda] &= \sum_{s=0}^{\infty} \frac{1}{s!} J(x_1) \dots J(x_s) \\ &\times \int D\phi \phi(x_1) \dots \phi(x_s) e^{\frac{i}{\hbar} \int d^4x [1/2(\partial_\mu \phi \partial^\mu \phi - m^2 \phi^2) - \frac{\lambda}{4!} \phi^4]} \\ &= Z[0, 0] \sum_{s=0}^{\infty} \frac{1}{s!} J(x_1) \dots J(x_s) G^{(s)}(x_1 \dots x_s) \end{aligned} \quad (36)$$

In this way the 2-point Green function can be written as

$$\begin{aligned} G(x_A, x_B) &= \frac{1}{Z[0, 0]} \int D\phi \phi(x_A) \phi(x_B) \\ &\times e^{\left\{ \frac{i}{\hbar} \int d^4x [1/2(\partial_\mu \phi \partial^\mu \phi - m^2 \phi^2)] - \frac{\lambda}{4!} \phi^4 \right\}} \end{aligned} \quad (37)$$

Now we give a final remark on the path integral formalism and its relationship with Green functions. For $\lambda = 0$, the 2-point Green function reduces to $i\Delta_F(x_A - x_B)$, the free (or independent) particle propagator. The propagator $\Delta_F(x_A - x_B)$ describes the propagation of elementary particles between x_A and x_B in the absence of any interaction between them. On the other hand, the 2-point Green function $G(x_A, x_B)$ describes the propagation of elementary particles between x_A and x_B in the presence of interactions between them.

3 Polarization propagators

What can we do if we want to deal with the propagation of the effect of an electric or magnetic perturbation within the whole electronic framework of an atomic or molecular system? Is it possible to do it applying the path integral formalism? How?

To answer such questions we should go one step ahead of what we have learned right now working with fundamental propagators, and introduce the same principles and rules but in bounded and correlated systems. We shall deal with the transmission of basic virtual excitations through the whole atom or molecule. They would have a similar flavor as the fundamental virtual particles whose transmission was treated in previous sections.

Previous works published by Jens Oddershede and coauthors,^{68,69} and ourselves^{1,3,7} are merged here in a concise way. We will give a brief introduction to the basic aspects of the formalism of polarization propagators. One can always start up with the usual definition of the polarization propagators, as the ground-state average value of the time-ordered product of two operators written in its second-quantized form; this is quite well adapted to what we pursue. Given that we want to consider the propagation of perturbative bosonic excitations within a molecular system based on basic excitation operators, we should define then a basis of operators on which all operators should be applied.

Once the equation of motion for the polarization propagators is written one can use the superoperator formalism to obtain its solutions in a compact way. Some strategies developed long time ago are still useful to write down the actual matrix expressions used in computational codes. As was previously shown^{1,7} the definition of polarization propagators is not restricted to a given regime, be it relativistic or non relativistic. We will show in this section that polarization propagators can be safely derived from the path integral formalism and this is the deepest underlying theoretical reason for the application of the same definition in both regimes.

Then we go one step further to relate what we have obtained analytically in previous sections with what can be obtained in a basis of excitation operators. These results are among the most important of this article and shall be given in Section 3.5. They show how the Feynman formalism can be applied to any response theory on many-body systems.

3.1 Second-quantization and superoperator formalisms

The second-quantization formalism is especially useful when one wants to handle atomic and molecular problems mostly in an algebraic way. Operators and wavefunctions can both be treated as operators, and so the equations of motion are expressed in an entirely algebraic way. There are algebraic rules which all basic creation and annihilation operators should fulfil. These operators are defined in such a way that

$$a_a^\dagger a_i |0\rangle = |\Psi_i^a\rangle \quad (38)$$

being Ψ_i^a a monoexcited N-electron state. The indices a, b, \dots , refer to unoccupied Hartree-Fock, HF or Dirac-Hartree-Fock, DHF orbitals and i, j, \dots , stand for occupied HF or DHF orbitals.

We define a complete operator manifold \mathbf{h} from which one can generate all excited states of a given N-electron molecular system: $\mathbf{h}|0\rangle = |\mathbf{n}\rangle$. If $|0\rangle$ is the reference state which usually is a self consistent field, SCF, the number conserving operator manifold may be written as,

$$\mathbf{h} = \{\mathbf{h}_2, \mathbf{h}_4, \dots\} \quad (39)$$

where

$$\begin{aligned} \mathbf{h}_2 &= \{a_a^\dagger a_i, a_i^\dagger a_a\}; \\ \mathbf{h}_4 &= \{a_a^\dagger a_b^\dagger a_i a_j, a_j^\dagger a_i^\dagger a_b a_a\}, \text{ etc.} \end{aligned} \quad (40)$$

Any one-electron operator P can be written as

$$P = \sum_{p,q} P_{pq} a_p^\dagger a_q, \quad (41)$$

or, by using spin-adapted excitation operators,⁶⁸

$$P = \sum_{p,q} P_{pq} E_{pq} \quad (42)$$

Assuming a Hilbert space of dimension n spanned by n independent vectors, there are n^2 independent operators. The basis operators span an operator's space of dimension n^2 called Liouville space. There is a close analogy between the Hilbert space spanned by the state functions and the Liouville space spanned by the corresponding linear operators. The Liouville space also forms an operator's algebra where the product of two operators is well defined.

One can then introduce superoperators which define operator relations in the above mentioned Liouville space. An special relation among superoperator operators valid for any operator A is the commutator:

$$\hat{H}A \equiv [H, A] \quad (43)$$

The basic linear operators which span the Liouville space form an operator algebra. In line with this the superoperators in turn form an algebra, since they span a vector space of dimension $n^2 \times n^2$ where products like the previous commutators are defined.

Any pair of operators P, Q , etc. are elements in a superoperator space with a well-defined binary product

$$(P|Q) = \langle 0|[P^\dagger, Q]|0\rangle \quad (44)$$

Within the superoperator formalism the inverse of an operator can be written in terms of matrices. So, the inner projection of the superoperator resolvent $(E\hat{I} - \hat{H}_0)^{-1}$ is

$$(E\hat{I} - \hat{H}_0)^{-1} = |\tilde{\mathbf{h}}\rangle(\mathbf{h}|E\hat{I} - \hat{H}_0|\tilde{\mathbf{h}})^{-1}\langle\mathbf{h}| \quad (45)$$

assuming that \mathbf{h} span a complete operator space.

This way of writing the operators is especially suited to work out the actual equations and oriented to obtain explicit formulas to be implemented in computational codes.

3.2 Definition of polarization propagators

Given two operators $P(x_A)$ and $Q(x_B)$ that may be field operators and describe excitations on the electronic ground-state of a molecular system, the polarization propagator is defined as

$$\begin{aligned} i\langle\langle P(x_A); Q(x_B) \rangle\rangle &= \hbar\langle 0|T(P(x_A)Q(x_B))|0\rangle \\ &= \hbar\theta(t_A - t_B)\langle 0|P(\mathbf{r}_A)Q(\mathbf{r}_B)|0\rangle \\ &\quad + \hbar\theta(t_B - t_A)\langle 0|Q(\mathbf{r}_B)P(\mathbf{r}_A)|0\rangle \end{aligned} \quad (46)$$

where x_A and x_B stand for the space-time points $x_A = (\mathbf{r}_A, t_A)$ and $x_B = (\mathbf{r}_B, t_B)$, respectively. This definition of polarization propagators is independent on whether the underlying theoretical framework is relativistic or NR,¹ even though its formulation was given for the first time within a NR regime.^{70–72} This is a remarkable fact that gives support to what was observed in previous articles treating propagators within the relativistic regime.^{3,7,73} The reference state $|0\rangle$ will properly be chosen according to the regime considered.

Since the polarization propagator has the same basic quantum nature as a wave function 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.⁶⁸ Afterwards one transform time-dependent expressions to their corresponding energy-dependent framework in order to make use of this tool in spectroscopic problems.

Operators P and Q are expressed in the interaction picture and obeys a Heisenberg-like equation of motion. So the equation of motion for polarization propagators in the energy framework is

$$\langle\langle P; Q \rangle\rangle_E = (P|\tilde{\mathbf{h}})(\mathbf{h}|E\hat{I} - \hat{H}_0|\tilde{\mathbf{h}})^{-1}(\mathbf{h}|Q) \quad (47)$$

This is the final expression of the equation of motion that needs to be solved, though it cannot be done within an full excitation operator manifold. It is equivalent to the Dyson equation though written in a matricial representative form.

Then, using the manifold decomposition of eqn (39), this last eqn (47) can be written in a matrix form as

$$\langle\langle P; Q \rangle\rangle_E = \begin{pmatrix} \mathbf{P}_a^\dagger & \mathbf{P}_b^\dagger & \dots \end{pmatrix} \begin{pmatrix} \mathbf{M}_{aa} & \mathbf{M}_{ab} & \dots \\ \mathbf{M}_{ba} & \mathbf{M}_{bb} & \dots \\ \dots & \dots & \dots \end{pmatrix}^{-1} \begin{pmatrix} \mathbf{Q}_a \\ \mathbf{Q}_b \\ \dots \end{pmatrix}, \quad (48)$$

where

$$\mathbf{P}_a = (P|\mathbf{h}_a), \quad (49)$$

and

$$\mathbf{M}_{ab} = (\mathbf{h}_a|E\hat{I} - \hat{H}_0|\tilde{\mathbf{h}}_b). \quad (50)$$

We can write eqn (48) in a more compact way

$$\langle\langle P; Q \rangle\rangle_E = \mathbf{b}^P \mathbf{M}^{-1} \mathbf{b}^Q \quad (51)$$

The factor \mathbf{M}^{-1} of the rhs of eqn (48) is known as the *principal* propagator, while \mathbf{b}^P and \mathbf{b}^Q are the property matrix elements or, as they were named within the semi-empirical models, the *perturbators*.⁷⁴ The principal propagator depends

only on both the electronic molecular system as a whole and the spin (time-reversal within the relativistic regime) dependence of the perturbators, but it is independent of the particular response property under study. It gives the whole excitation pathway for the transmission of the interaction between the external perturbations related with the property matrix elements, through the unperturbed electronic system. They are like the streamlines through which the perturbation is transmitted. Furthermore the external perturbations intervene explicitly only on the perturbators though indirectly on principal propagator through its spin (or time reversal)-dependence.

3.3 Perturbative expansion

One cannot solve the equation of motion for polarization propagators in an exact manner. It was shown by Oddershede and coauthors⁶⁸ that eqn (51) can perturbatively be expanded as a function of the fluctuation potential V . The order in perturbation theory is shown explicitly through the superoperator $E\hat{I} - \hat{H}_0$ where $\hat{H}_0 = \hat{F} + \hat{V}$, and implicitly through the reference states used to evaluate the superoperator binary product.

The superoperator \hat{F} stands for the Fock or Dirac-Fock super operator, and \hat{V} is the fluctuation 2-particle super operator that do contain Coulomb and may also contain Breit or other interactions including QED corrections. As usual the Hamiltonian H_0 describe only the internal interactions of the electronic system.

The order of the reference state in perturbation theory comes from the expansion of such state using the Rayleigh-Schrödinger perturbation theory. The zeroth-order state is the SCF solution

$$|0\rangle = \Omega(|\text{SCF}\rangle + |0^1\rangle + |0^2\rangle + \dots) \quad (52)$$

Ω being a normalization constant and $|0^i\rangle$ the i th order correction to the SCF state. The first order correction to the $|\text{SCF}\rangle$ state may be written as

$$|0^1\rangle = \frac{1}{4} \sum_{ab,ij} \kappa_{ij}^{ab}(1) a_a^\dagger a_b^\dagger a_i a_j |\text{SCF}\rangle \quad (53)$$

where

$$\kappa_{ij}^{ab}(1) = (bi\|aj)(\varepsilon_i + \varepsilon_j - \varepsilon_b - \varepsilon_a)^{-1} \quad (54)$$

are the first order Rayleigh-Schrödinger correlation coefficients and $(bi\|aj) = (bi|aj) - (bj\|ai)$

Perturbators are then written as

$$(P|\hat{\mathbf{h}}_1) = \Omega^2 \langle \text{SCF} + 0^1 + \dots | [P^\dagger, \hat{\mathbf{h}}_1] | \dots + 0^1 + \text{SCF} \rangle \quad (55)$$

The lowest order for this perturbator is zero

$$(P|\hat{\mathbf{h}}_2) = \Omega^2 \langle \text{SCF} | [P^\dagger, \hat{\mathbf{h}}_2] | \text{SCF} \rangle \quad (56)$$

and so, the polarization propagator at zeroth-order will be composed of both, perturbators and principal propagators at zeroth-order. To first order one shall have perturbators at zeroth-order and the principal propagator at first order; and so on.

The lowest non-vanishing contribution for \mathbf{h}_4 to first-order terms are

$$\langle P|\hat{\mathbf{h}}_4\rangle = \Omega^2(\langle \text{SCF} | [P^\dagger, \hat{\mathbf{h}}_4] | 0^1 \rangle + \langle 0^1 | [P^\dagger, \hat{\mathbf{h}}_4] | \text{SCF} \rangle) \quad (57)$$

The consistent polarization propagator till first order is known as the random phase approximation, RPA, and is composed of perturbators at zeroth-order and the matrices of the principal propagator till order one. Such RPA approximation is obtained when $|\text{SCF}\rangle = |\text{HF}\rangle$ or $|\text{DHF}\rangle$ (the Hartree–Fock or Dirac–Hartree–Fock state) and $\mathbf{h} = \mathbf{h}_2$. This is such that only the following two supermatrices, \mathbf{A} and \mathbf{B} should be considered,

$$\begin{aligned} \mathbf{A}_{ai,bj}(0,1) &= \mathbf{A}_{ai,bj}(0) + \mathbf{A}_{ai,bj}(1) \\ &= -\langle 0 | [a_i^\dagger a_a, [a_b^\dagger a_j, H_0]] | 0 \rangle \\ &= \delta_{ab} \delta_{ij} (\varepsilon_a - \varepsilon_i) + (ai||jb) \end{aligned} \quad (58)$$

and

$$\mathbf{B}_{ai,bj}(1) = -\langle 0 | [a_i^\dagger a_a, [a_j^\dagger a_b, H_0]] | 0 \rangle = (ib||ja) \quad (59)$$

3.4 The polarization propagators and the NMR spectroscopic parameters

Any static (dynamical) second-order molecular property, *i.e.*, those arising from a second-order correction to the energy and depending on two external static (time dependent) fields, can be calculated by using polarization propagators.

This is apparent from the following equation

$$E_{PQ}^2 = 1/2 \text{Re} \langle \langle H^P; H^Q \rangle \rangle_{E=0} \quad (60)$$

where H^P and H^Q are the interaction Hamiltonians related with 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.⁷⁵ The complete Hamiltonian is then

$$H = H_0 + H_{1,\text{NMR}} \quad (61)$$

being

$$\begin{aligned} H_{1,\text{NMR}} &= \sum_{\text{KL}} \{ \boldsymbol{\mu}_{\text{K}} \cdot (\mathbf{D}_{\text{KL}} + \mathbf{J}_{\text{KL}}) \cdot \boldsymbol{\mu}_{\text{L}} \} \\ &+ \sum_{\text{K}} \{ \boldsymbol{\mu}_{\text{K}} \cdot (1 - \boldsymbol{\sigma}_{\text{K}}) \cdot \mathbf{B} \} \end{aligned} \quad (62)$$

where $\boldsymbol{\mu}_{\text{K}}$ is the nuclear dipole moment of nucleus K, \mathbf{D}_{KL} and \mathbf{J}_{KL} are the direct and indirect nuclear spin coupling tensors, $\boldsymbol{\sigma}_{\text{K}}$ the nuclear magnetic shielding of nucleus K and \mathbf{B} 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 \mathbf{J}), and on a nuclear dipole moment and the external magnetic field (for $\boldsymbol{\sigma}$). Since the nuclear magnetic moments $\boldsymbol{\mu}_{\text{K}}$ are proportional to the nuclear spins \mathbf{I}_{K} , the magnetic interaction energy between the coupled nuclei depend on \mathbf{I}_{K} and \mathbf{I}_{L} , and is expressed as

$$E_{\text{KL}}^{(2)} = h \mathbf{I}_{\text{K}} \cdot \mathbf{J}_{\text{KL}} \cdot \mathbf{I}_{\text{L}} \quad (63)$$

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

$$E_{\text{K}}^{(2)} = -h \mathbf{I}_{\text{K}} \cdot \boldsymbol{\sigma}_{\text{K}} \cdot \mathbf{B} \quad (64)$$

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

$$E_{PQ}^{(2)} = \sum_{n \neq 0} \left\{ \frac{\langle 0 | H^P | n \rangle \langle n | H^Q | 0 \rangle}{E_0 - E_n} \right\} \quad (65)$$

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 \mathbf{B} ; their explicit forms were given elsewhere⁷ for \mathbf{J} -couplings and $\boldsymbol{\sigma}$. It is worth to mention that in order to have a non-vanishing result, both Hamiltonians must have the same time-reversal symmetry.⁷⁶

As shown in eqn (60) and (65) paramagnetic contributions to both NMR spectroscopic parameters can be obtained within non relativistic polarization propagator theory. The diamagnetic contribution is calculated as a ground-state expectation value. It should be noted that mixing perturbations with different electron spin dependence gives vanishing results.⁷⁶ When considering electron spin dependent Hamiltonians, the excitation energies of eqn (65) shall be restricted to that of singlet or triplet type. In the same manner will the principal propagator of eqn (50) be restricted. Then, in the case of J -couplings there will be two kind of terms: (i) electron spin-dependent terms which are related with triplet principal propagators: ${}^3\text{M}^{-1}$ and (ii) electron spin-independent terms which are calculated with singlet principal propagators: ${}^1\text{M}^{-1}$.

Then, there are five contributions to the indirect nuclear spin coupling tensor which depend on the electron–nucleus interaction mechanism involved.

$$\mathbf{J} = \mathbf{J}^{\text{FC}} + \mathbf{J}^{\text{SD}} + \mathbf{J}^{\text{PSO}} + \mathbf{J}^{\text{FC/SD}} + \mathbf{J}^{\text{DSO}} \quad (66)$$

being FC the Fermi contact, SD the spin dipolar, PSO the paramagnetic spin–orbital and DSO the diamagnetic spin–orbital. When calculated by the non relativistic polarization propagator theory each one of the first three terms are written as

$$\mathbf{J}_{\text{KL}}^{\text{X}} = \gamma_{\text{K}} \gamma_{\text{L}} \langle \langle \mathbf{V}_{\text{K}}^{\text{X}}; \mathbf{V}_{\text{L}}^{\text{X}} \rangle \rangle_{E=0} \quad (67)$$

where X = FC, SD or PSO. In eqn (66) $\mathbf{J}^{\text{FC/SD}}$ only contributes for systems in solid state phase, so it will not be considered here, while \mathbf{J}^{DSO} is isotropic. All terms of eqn (67) 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), and so on.⁶⁸

As just mentioned above there is a relationship among the perturbative Hamiltonians of eqn (65) with electronic mechanisms that underlies both spectroscopic parameters, J -couplings and shieldings. We first consider the non-relativistic Fermi contact mechanism for J -couplings since it is the simplest. Then we shall consider its

relativistic counterpart which is due to a unique mechanism.

$$H^{\text{FC}} = \sum_{\text{K}} \gamma_{\text{K}} \mathbf{I}_{\text{K}} \cdot \mathbf{V}_{\text{K}}^{\text{FC}} \quad (68)$$

being

$$\mathbf{V}_{\text{K}}^{\text{FC}} = \frac{8}{3} \pi \mu_{\text{B}} \hbar g_{\text{e}} \sum_i \delta(r_{i\text{K}}) s_i \quad (69)$$

the corresponding Fermi contact perturbator, and μ_{B} the nuclear magneton, γ_{K} the magnetogyric ratio of nucleus K and g_{e} the electronic g -factor.

On the other hand there is only one relativistic perturbative Hamiltonian used for the calculation of J -couplings (see Section 4.3)

$$H_1 = \sum_{\text{K}} \gamma_{\text{K}} \mathbf{I}_{\text{K}} \cdot \mathbf{V}_{\text{K}}^{\text{Rel}} \quad (70)$$

being

$$\mathbf{V}_{\text{K}}^{\text{Rel}} = -\frac{e}{c} \hbar \left(\frac{\boldsymbol{\alpha} \times \mathbf{r}_{\text{K}}}{r_{\text{K}}^3} \right) \quad (71)$$

The vector $\boldsymbol{\alpha}$ represents the Dirac operator.

3.5 Polarization propagators from the path integral formalism

Is it possible to apply the whole machinery developed in Section 2 to get the generating functional of the two-time Green's function or polarization propagator?

Let's go back now to discrete variables. We can do it considering $\phi(x)$ as the coordinate representative of a vector in a Hilbert space, and $A(x, y)$ the coordinate representative of an operator on the same space. If the basis vectors $|x\rangle$ satisfy the closure relation

$$\int d^4|x\rangle \langle x| = 1 \quad (72)$$

we shall get the following inner products as

$$(J, \phi) \equiv \langle J | \phi \rangle = \int d^4x J(x) \phi(x) \quad (73)$$

$$(\phi, A\psi) \equiv \langle \phi | A | \psi \rangle = \int d^4x d^4y \phi(x) A(x, y) \psi(y)$$

being $\phi(x) = \langle x | \phi \rangle$ and $A(x, y) = \langle x | A | y \rangle$.

Applying them we are able to obtain the solution of the following Gaussian functional integral,

$$\begin{aligned} Z_{[J]} &= \int D\phi e^{-\frac{1}{2}(\phi, A\phi) + (J, \phi)} \\ &= \frac{1}{\sqrt{\det A}} e^{\frac{1}{2}(J, A^{-1}J)} \end{aligned} \quad (74)$$

Then it is sound to define the following generating functional for the polarization propagator used to calculate the J -coupling corresponding to the FC NR mechanism,

$$\begin{aligned} Z_{[V_{\text{K}}^{\text{FC}}, V_{\text{L}}^{\text{FC}}]} &= \int (D|\tilde{\mathbf{h}}|) e^{|\tilde{\mathbf{h}}|(\mathbf{h}|E\hat{I} - \hat{H}_0^{\text{Sch}}|\tilde{\mathbf{h}})(\mathbf{h}| + (V_{\text{K}}^{\text{FC}}|\tilde{\mathbf{h}})(\mathbf{h}| + (V_{\text{L}}^{\text{FC}}|\tilde{\mathbf{h}})(\mathbf{h}|} \\ &= Z_{[V_{\text{K}}^{\text{FC}}=0, V_{\text{L}}^{\text{FC}}=0]} e^{iW[V_{\text{K}}^{\text{FC}}, V_{\text{L}}^{\text{FC}}]} \end{aligned} \quad (75)$$

where

$$W_{[V_{\text{K}}^{\text{FC}}, V_{\text{L}}^{\text{FC}}]} = (V_{\text{K}}^{\text{FC}}|\tilde{\mathbf{h}})(\mathbf{h}|E\hat{I} - \hat{H}_0^{\text{Sch}}|\tilde{\mathbf{h}}^{-1})^{-1}(\mathbf{h}|V_{\text{L}}^{\text{FC}}) \quad (76)$$

The Hamiltonian \hat{H}_0^{Sch} is the NR Schrödinger Hamiltonian for the unperturbed atomic or molecular system.

The last equation resemble eqn (24) with $(V_{\text{K}}^{\text{FC}}|\tilde{\mathbf{h}})$ replacing the source \mathbf{J}_2 and $(\mathbf{h}|V_{\text{L}}^{\text{FC}})$ the source \mathbf{J}_1 . It is then uncovered that eqn (76) is the MO representative of the Green's function that corresponds to the quantum correlation between two perturbative interactions acting on a molecular system. They can be related with J -couplings. Its physical meaning is the following: there are a finite number of (virtual) excitations that are created in a spatial region close to nucleus K; they are transmitted to the whole electronic molecular framework and then absorbed in a spatial region close to the nucleus L. The polarization propagator describes how such a density disturbance propagates in an interacting system. The principal propagator is the Green representative of the propagation of such basic virtual excitations.

The formal definition of the generating functional of eqn (75) does not depend on the space-time framework within which the evolution of the system is described. It is formally the same within both, the relativistic and NR domain. It gives then new avenues for introducing QED effects. Indeed the generating functional W_J is valid in any regime where an unperturbed Hamiltonian is well defined.

Within the relativistic regime one can define an appropriate generating functional for J -couplings

$$\begin{aligned} Z_{[V_{\text{K}}^{\text{Rel}}, V_{\text{L}}^{\text{Rel}}]} &= \int D|\tilde{\mathbf{h}}| \\ &\times e^{|\tilde{\mathbf{h}}|(\mathbf{h}|E\hat{I} - \hat{H}_0^{\text{D}}|\tilde{\mathbf{h}})(\mathbf{h}| + (V_{\text{K}}^{\text{Rel}}|\tilde{\mathbf{h}})(\mathbf{h}| + (V_{\text{L}}^{\text{Rel}}|\tilde{\mathbf{h}})(\mathbf{h}|} \\ &= Z_{[V_{\text{K}}^{\text{Rel}}=0, V_{\text{L}}^{\text{Rel}}=0]} e^{iW[V_{\text{K}}^{\text{Rel}}, V_{\text{L}}^{\text{Rel}}]} \end{aligned} \quad (77)$$

where

$$W_{[V_{\text{K}}^{\text{Rel}}, V_{\text{L}}^{\text{Rel}}]} = (V_{\text{K}}^{\text{Rel}}|\tilde{\mathbf{h}})(\mathbf{h}|E\hat{I} - \hat{H}_0^{\text{D}}|\tilde{\mathbf{h}})^{-1}(\mathbf{h}|V_{\text{L}}^{\text{Rel}}) \quad (78)$$

The operator manifold \mathbf{h} is well defined within the relativistic framework as will be shown in the next section. \hat{H}_0^{D} stands for the unperturbed atomic or molecular relativistic Hamiltonian.

From the last development a natural understanding of what were called, within the non-relativistic framework, the *perturbative propagation pathways* do appears. In the case of indirect J -couplings they were named *coupling pathways*.⁷⁴ When this concept is extended to the relativistic regime it is also found that its physical meaning continues being the same. In fact it gives strong support on what was shown previously: relativistic propagators go smoothly to its NR counterpart when $c \rightarrow \infty$. The *perturbative propagation pathways* can be written within the NR or the relativistic framework, in such a way that they can be transformed one into the other applying the usual "classical" transformation.

It is worth to emphasize that eqn (51) represents the solution of the equation of motion in the energy domain.

Then if one starts from the relativistic representative of the double-time Green's function of eqn (78) one can obtain its NR counterpart only making $c \rightarrow \infty$. This means that what one is doing is to apply the transformation to each of the three different factors of eqn (51) and so each factor goes to its NR counterpart.¹

In addition we want to highlight here the fact that the integral in eqn (7) can be solved by the method of the stationary phase, identifying the classical path q_{cl} from the stationary condition of the principle of least action

$$\left. \frac{\delta}{\delta q(t)} (S[q(t)]) \right|_{q_{\text{cl}}} = 0 \quad (79)$$

where S is the action.

From eqn (7) and what was shown in this subsection one can say that starting with different functionals W that are related with every excitation one can obtain the equations of motion. In other words, applying the principle of least action one do get the equation of motion for each excitation.

In our case this would be the same as the functional derivative of the generating functional $W[V]$, which give the quantum equations of motion for the Green's functions known as the Schwinger–Dyson equations.

4 Polarization propagators within an appropriate relativistic framework

The analysis of molecular properties of heavy-atom containing molecules requires new mathematical tools. Space and time are unified as space-time and the Schrödinger equation is not valid any longer and should be replaced by the Dirac equation which in turn should be written in a covariant form. There is one special feature that one needs to treat carefully: there are solutions of this last equation with negative-energy states. So, if possible there would be excitations to both branches of the energy spectra. The possibility to consider excitations to the negative energy states have been a source of confusion and difficulties. Perhaps the main inconvenience comes from conceptual difficulties. Today they can be properly handled.^{7,12,56}

Looking for the solutions of the Dirac equation for one-particle systems one finds that they refer to a many-body equation. The free-particle Dirac equation is written in a non-covariant form as⁷

$$H^{\text{free}}\psi(\mathbf{x}) = (c\boldsymbol{\alpha}\cdot\mathbf{p} + \beta mc^2)\psi(\mathbf{x}) = E\psi(\mathbf{x}) \quad (80)$$

where β and $\boldsymbol{\alpha} = (\alpha_x, \alpha_y, \alpha_z)$ 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

$$\boldsymbol{\alpha} = \begin{pmatrix} \mathbf{0} & \boldsymbol{\sigma} \\ \boldsymbol{\sigma} & \mathbf{0} \end{pmatrix}, \quad \beta = \begin{pmatrix} \mathbf{1} & \mathbf{0} \\ \mathbf{0} & -\mathbf{1} \end{pmatrix} \quad (81)$$

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

$$(\gamma^\mu p_\mu - mc)\psi(x) = 0 \quad (82)$$

where $\gamma^0 \equiv \beta$, $\gamma^i \equiv \beta\alpha^i$, $\gamma^\mu = (\gamma^0, \boldsymbol{\gamma})$ and $p_\mu \left(\frac{E}{c}, -\mathbf{p} \right)$, so that $\gamma^\mu p_\mu = \gamma^0 p_0 - \boldsymbol{\gamma}\cdot\mathbf{p}$.

Covariance means that such equation will have the same form when written in any inertial frame of reference. Being an scalar, the left hand side of eqn (82) is invariant under a Lorentz transformation. Then it is easier to get its energy spectra. So for one Dirac particle at rest ($\mathbf{p} = 0$) eqn (82) is written as

$$\gamma^0 p_0 \psi = mc\psi \quad \text{or} \quad p_0 \psi = mc\gamma^0 \psi \quad (83)$$

Given that the operator γ^0 has doubly degenerate eigenvalues ± 1 , one obtains two positive-energy solutions and two negative-energy solutions. When $p \neq 0$ there are doubly degenerate eigenvalues of $E = \pm(m^2c^4 + p^2c^2)^{1/2}$.

Dirac was the first to propose that one should consider the negative-energy branch as being full of electrons. This awkward proposal was the breakthrough to start thinking more deeply on what the vacuum is and mainly on how to handle such a many-body system. In the early days of quantum mechanics non-stable solutions could be found without considering the negative-energy branch as fully occupied. In fact this feature pointed out to the existence of another particle that obeys the same equation but with opposite electric charge, the positron.

4.1 Empty-Dirac and QED pictures

As shown in Section 3.2 the actual implementation of the formalism of propagators hangs on the completeness of the operator manifold \mathbf{h} . Then within the relativistic domain one should properly consider the whole one-particle energy-spectra. Two formally equivalent pictures are used at the moment: the empty-Dirac and the QED. In the first case one considers that the branch of negative-energies is empty so that electronic excitations to it are allowed. The negative-energy states are not reinterpreted as positronic states. On the other hand, in the QED picture one only works with positive-energy unoccupied states, electronic and positronic, and occupied electronic states.

The second quantized form of any relativistic operator \hat{O} within the “empty Dirac” approach is written as,⁷⁷

$$\hat{O} = \sum_{pq} O_{pq} \hat{a}_p^\dagger \hat{a}_q + O_{p\bar{q}} \hat{a}_p^\dagger \hat{a}_{\bar{q}} + O_{\bar{p}q} \hat{a}_{\bar{p}}^\dagger \hat{a}_q + O_{\bar{p}\bar{q}} \hat{a}_{\bar{p}}^\dagger \hat{a}_{\bar{q}} \quad (84)$$

where the tilde on Roman indices means orbitals which belongs to the negative-energy branch. There are two branches of unoccupied electronic spinors, the usual and positive, and the negative.

In the particle-hole picture

$$\begin{aligned} \hat{b}_p^\dagger &= \hat{a}_p^\dagger; \quad \hat{b}_p = \hat{a}_p & \text{when } \varepsilon_p > 0 \\ \hat{b}_{\bar{p}}^\dagger &= \hat{a}_{\bar{p}}; \quad \hat{b}_{\bar{p}} = \hat{a}_{\bar{p}}^\dagger & \text{when } \varepsilon_p < 0 \end{aligned} \quad (85)$$

the operator \hat{O} (also named as Fock space operator^{12,56}) is written in our own nomenclature as

$$\hat{O} = \sum_{pq} O_{pq}^{ee} \hat{b}_p^\dagger \hat{b}_q + O_{p\bar{q}}^{ep} \hat{b}_p^\dagger \hat{b}_{\bar{q}}^\dagger + O_{\bar{p}q}^{pe} \hat{b}_{\bar{p}} \hat{b}_q + O_{\bar{p}\bar{q}}^{pp} \hat{b}_{\bar{p}} \hat{b}_{\bar{q}}^\dagger \quad (86)$$

On the other hand, in the QED picture the negative energy states are reinterpreted according to the QED approach as

positive energy positrons. The operators are written in normal-ordered form as

$$: \hat{O} := \sum_{pq} O_{pq}^{ee} \hat{b}_p^\dagger \hat{b}_q + O_{pq}^{ep} \hat{b}_p^\dagger \hat{b}_q^\dagger + O_{pq}^{pe} \hat{b}_p \hat{b}_q - O_{pq}^{pp} \hat{b}_p \hat{b}_q^\dagger = \hat{O}^{\text{QED}} \quad (87)$$

The unoccupied spinors may be electronic or positronic. For the last spinors we use creation (annihilation) operators \hat{b}^\dagger (\hat{b}).

When calculating the property matrix elements of eqn (49) with operators expanded in any of both pictures one gets the same c -numbers. This will be shown in the Section 4.3, as we shall also give the actual supermatrix expressions of matrices A and B defined previously in Section 3.3. In this way the principal propagator can be divided in four blocks depending on which are the excitation operators considered.

4.2 Kramer's excitation operators

Within the relativistic domain spin is not any longer a good quantum number. The spin symmetry can be recovered by what was baptized as Kramer's operators.^{76,77} These operators fulfil different commutation relationship as compared with previous excitation operators like the spin-adapted excitation operators of eqn (42), though they form the most useful basis for expanding operators in the relativistic domain.

The Kramer's time-reversal adapted operators form a basis for superoperators algebra. They are of two types: \hat{X}^\pm . The one body operators that are time-reversal symmetric and Hermitian (like the Hamiltonian) are represented by \hat{X}^+ . Time-reversal anti-symmetric and Hermitian operators as the perturbative operators entering in the calculation of magnetic properties with propagators are represented by \hat{X}^- .

Any one-electron operator can be written in terms of time-reversal restricted basic excitation operators, the \hat{X} operators, known as Kramer's single replacement operators.⁷⁶⁻⁷⁸ There are two types of X operators, depending on both the symmetry under time-reversal and the hermitian conjugation of the operators, say \hat{X} , being represented as an expansion on the \hat{X} operator basis.

$$\begin{aligned} \hat{X}_{pq}^s &= \hat{a}_p^\dagger \hat{a}_q + s \hat{a}_q^\dagger \hat{a}_p, \\ \hat{X}_{\bar{p}q}^s &= \hat{a}_{\bar{p}}^\dagger \hat{a}_q - s \hat{a}_q^\dagger \hat{a}_{\bar{p}}, \\ \hat{X}_{p\bar{q}}^s &= \hat{a}_p^\dagger \hat{a}_{\bar{q}} - s \hat{a}_{\bar{q}}^\dagger \hat{a}_p, \end{aligned} \quad (88)$$

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

$$\hat{O} = \sum_{pq} \left[O_{pq} \hat{X}_{pq}^+ + \frac{1}{2} \left(O_{p\bar{q}} \hat{X}_{p\bar{q}}^+ + O_{\bar{p}q} \hat{X}_{\bar{p}q}^+ \right) \right] \quad (89)$$

If the operator \hat{O} is time-reversal anti-symmetric or anti-Hermitian, it should be expanded in terms of X^- . This is the case for the binary products involving *perturbators* (see eqn (49)) because they are time-reversal anti-symmetric.

Principal propagators can be written with explicit spin-symmetry in them. They are usually of singlet- or triplet-type. Do exist in the relativistic framework similar tensor operators? The answer is affirmative.⁷⁶ They are the pseudo-singlet excitation operator,

$$\hat{R}_{ai}^\pm(0, 0) = \frac{1}{\sqrt{2}} \left[\hat{X}_{ai}^\mp \mp \hat{X}_{ia}^\mp \right] \quad (90)$$

and the pseudo-triplet tensor operator

$$\begin{aligned} \hat{R}_{ai}^\pm(1, 0) &= \frac{1}{\sqrt{2}} \left[\hat{X}_{ai}^\pm \mp \hat{X}_{ia}^\pm \right] \\ \hat{R}_{ai}^\pm(1, 1) &= -\hat{X}_{ai}^\pm \\ \hat{R}_{ai}^\pm(1, -1) &= \hat{X}_{ai}^\pm \end{aligned} \quad (91)$$

In the next section we will emphasize one interesting behavior of the principal propagator that appears when written in this last basis of pseudo-singlet and pseudo-triplet tensors.

4.3 Relativistic formalism

The interaction of an N-electron system with an external magnetic field is accounted for by the minimal coupling prescription. Its explicit expression is $\mathbf{p} \rightarrow \mathbf{p} + e\mathbf{A}$, leading to the introduction of the perturbative Hamiltonian

$$H_1 = ec\boldsymbol{\alpha} \cdot \mathbf{A} \quad (92)$$

where $\mathbf{A} = \mathbf{A}^N + \mathbf{A}^B$ is the sum of the nuclear and the external vector potentials

$$\mathbf{A}^N = \frac{1}{c^2} \sum_{\mathbf{K}} \frac{\mu_{\mathbf{K}} \times \mathbf{r}_{\mathbf{K}}}{r_{\mathbf{K}}^3} \quad (93)$$

and

$$\mathbf{A}^B = \frac{1}{2} \mathbf{B} \times \mathbf{r}_G = \frac{1}{2} (\mathbf{B} \times \mathbf{r} - \mathbf{R}_G) \quad (94)$$

\mathbf{R}_G is the gauge origin, $\mathbf{r}_{\mathbf{K}} = \mathbf{r} - \mathbf{R}_{\mathbf{K}}$, and \mathbf{r} and $\mathbf{R}_{\mathbf{K}}$ are the coordinates of the positions of the electron and the nucleus K, respectively. Then eqn (92) can be written as

$$\begin{aligned} H_1 &= ec\boldsymbol{\alpha} \cdot \left\{ \frac{1}{c^2} \sum_{\mathbf{K}} \frac{\mu_{\mathbf{K}} \times \mathbf{r}_{\mathbf{K}}}{r_{\mathbf{K}}^3} + \frac{1}{2} \mathbf{B} \times \mathbf{r}_G \right\} \\ &= -\frac{e}{c} \hbar \sum_{\mathbf{K}} \gamma_{\mathbf{K}} \mathbf{I}_{\mathbf{K}} \cdot \left(\frac{\boldsymbol{\alpha} \times \mathbf{r}_{\mathbf{K}}}{r_{\mathbf{K}}^3} \right) - \frac{ec}{2} \mathbf{B} \cdot (\boldsymbol{\alpha} \times \mathbf{r}_G) \end{aligned} \quad (95)$$

From eqn (60), (92) and (95), the second-order perturbative correcting terms to the energy are written as

$$\begin{aligned} E^{(2)} &= \frac{1}{2} \text{Re} \langle \langle H_1; H_1 \rangle \rangle \\ &= \frac{1}{2} \frac{e\hbar^2}{c} \sum_{\mathbf{KL}} \gamma_{\mathbf{K}} \gamma_{\mathbf{L}} \mathbf{I}_{\mathbf{K}} \cdot \text{Re} \left\langle \left\langle \frac{\boldsymbol{\alpha} \times \mathbf{r}_{\mathbf{K}}}{r_{\mathbf{K}}^3}; \frac{\boldsymbol{\alpha} \times \mathbf{r}_{\mathbf{L}}}{r_{\mathbf{L}}^3} \right\rangle \right\rangle \cdot \mathbf{I}_{\mathbf{L}} \\ &\quad + \frac{e^2 \hbar}{2} \sum_{\mathbf{K}} \gamma_{\mathbf{K}} \mathbf{I}_{\mathbf{K}} \cdot \text{Re} \left\langle \left\langle \frac{\boldsymbol{\alpha} \times \mathbf{r}_{\mathbf{K}}}{r_{\mathbf{K}}^3}; \boldsymbol{\alpha} \times \mathbf{r}_G \right\rangle \right\rangle \cdot \mathbf{B} + \dots \end{aligned} \quad (96)$$

From the last equation, the full relativistic expressions of the NMR spectroscopic parameters are obtained as

$$\mathbf{J}_{\text{KL}} = \frac{e^2 \hbar^2}{h} \gamma_{\text{K}} \gamma_{\text{L}} \left\langle \left\langle \frac{\boldsymbol{\alpha} \times \mathbf{r}_{\text{K}}}{r_{\text{K}}^3}; \frac{\boldsymbol{\alpha} \times \mathbf{r}_{\text{L}}}{r_{\text{L}}^3} \right\rangle \right\rangle \quad (97)$$

and

$$\sigma_{\text{K}} = e^2 \left\langle \left\langle \frac{\boldsymbol{\alpha} \times \mathbf{r}_{\text{K}}}{r_{\text{K}}^3}; \boldsymbol{\alpha} \times \mathbf{r}_{\text{G}} \right\rangle \right\rangle \quad (98)$$

From these equations one observes that there is only one electronic mechanism involved in describing each of both NMR spectroscopic parameters. There is no formal distinction between dia and paramagnetic terms,³ even though one can recover what is well-known within the NR regime by making $c \rightarrow \infty$.

In what follows it is better to change the nomenclature of creation and annihilation operators

$$\hat{a}_i^\dagger \hat{a}_i \rightarrow \hat{a}^\dagger \hat{i}, \quad \hat{a}_i^\dagger \hat{a}_a \rightarrow \hat{i}^\dagger \hat{a}, \dots \quad (99)$$

So, the restricted excitation operator manifold \mathbf{h}_2 of eqn (40) shall be written as

$$\mathbf{h}_2 = \left\{ \hat{a}^\dagger \hat{i}, \hat{i}^\dagger \hat{a}, \hat{a}^\dagger \hat{i}, \hat{i}^\dagger \hat{a} \right\} \quad (100)$$

where now two more basic excitation operators do appears as compared with eqn (40): $\hat{a}^\dagger \hat{i}$ which represent a pair annihilation and $\hat{i}^\dagger \hat{a}$ which stand for pair creation.

The actual expressions of the perturbators are obtained as follows

$$\begin{aligned} \langle 0 | [\hat{P}, \hat{a}^\dagger \hat{i}] | 0 \rangle &= \sum_{pq} P_{pq}^{ee} \{ \delta_{qa} \langle 0 | \hat{p}^\dagger \hat{i} | 0 \rangle - \delta_{pi} \langle 0 | \hat{a}^\dagger \hat{q} | 0 \rangle \} \\ &\quad - \sum_{\bar{p}\bar{q}, \bar{p}\bar{q}} \left\{ P_{\bar{p}\bar{q}}^{ep} \delta_{pi} \langle 0 | \hat{a}^\dagger \hat{q} | 0 \rangle + P_{\bar{p}\bar{q}}^{pe} \delta_{qa} \langle 0 | \hat{p}^\dagger \hat{i} | 0 \rangle \right\} \\ &= P_{ia}^{ee} \end{aligned} \quad (101)$$

The contributions of the last three terms are zero, so only the first term survives. Similar expressions are found for the excitations $\hat{i}^\dagger \hat{a}$, $\hat{a}\hat{i}$ and $\hat{i}\hat{a}$ and the property matrix elements will be $-P_{ai}^{ee}$, P_{ia}^{ep} and $-P_{ai}^{pe}$, respectively.

Within the QED picture one obtain the same results. It means that one can work safely with any of both equivalent pictures for getting actual expressions of the polarization propagators. Then the perturbators at RPA level of approach can be blocked as,

$$\begin{aligned} \tilde{\mathbf{P}} &= \left(\hat{P}^\dagger | \hat{\mathbf{h}}_2 \right) = \langle 0 | \left[\hat{P}^\dagger, \hat{\mathbf{h}}_2 \right] | 0 \rangle \\ &= \left(-\tilde{P}_{ai}^{ee} \tilde{P}_{ai}^{ep*} - \tilde{P}_{ai}^{pe} \tilde{P}_{ai}^{pe*} \right) = \left(\tilde{\mathbf{P}}^{ee} \tilde{\mathbf{P}}^{pe} \right) \end{aligned} \quad (102)$$

In line with what was worked out above some new matrix elements of supermatrices \mathbf{A} and \mathbf{B} must be considered due

to the new branch of negative-energy states. At RPA level of approach they are

$$\begin{aligned} \mathbf{A}_{\hat{a}\hat{i}, \hat{i}\hat{a}}^{pe, pe}(0, 1) &= -\langle 0 | \left[\hat{i}^\dagger \hat{a}, \left[\hat{b}^\dagger \hat{j}, H_0 \right] \right] | 0 \rangle \\ &= -\delta_{\hat{a}\hat{b}} \delta_{ij} (\varepsilon_{\hat{a}} - \varepsilon_i) + \left(\hat{a}\hat{i} | \hat{j}\hat{b} \right) \end{aligned} \quad (103)$$

$$\begin{aligned} \mathbf{A}_{\hat{a}\hat{i}, \hat{i}\hat{a}}^{ee, ee}(0) &= 0 \\ \mathbf{A}_{\hat{a}\hat{i}, \hat{i}\hat{a}}^{ee, pe}(1) &= \left(\hat{a}\hat{i} | \hat{j}\hat{b} \right) - \left(\hat{a}\hat{b} | \hat{j}\hat{i} \right) \\ \mathbf{B}_{\hat{a}\hat{i}, \hat{i}\hat{a}}^{ee, pe}(1) &= \left(\hat{i}\hat{b} | \hat{j}\hat{a} \right) - \left(\hat{i}\hat{a} | \hat{j}\hat{b} \right) \end{aligned} \quad (104)$$

One can get new insights on what they mean from the easiest diagrams of the (ee, ee) part. Such diagrams are obtained for $a = b$ and $i = j$. They are related with the usual NR excitations to positive-energy electronic states. In a similar manner their equivalent diagrams for the (pe, pe) part are obtained when $\hat{a} = \hat{b}$ and $i = j$. They refer to the creation (by $\hat{i}^\dagger \hat{a}$) and annihilation (by $\hat{a}^\dagger \hat{i}$) of virtual electron–positron pairs in two different space-time points. This “exchange” process has been treated by Mohr and coauthors for the inclusion of nuclear polarization effects on the energy spectrum of electronic systems in an equivalent way (see Section 6.1 of ref. 79)

The contribution of the matrix elements of the supermatrices \mathbf{A} and \mathbf{B} belonging to the off-diagonal parts are quite small. There are no diagonal elements for them due to $\delta_{\hat{a}\hat{b}} = 0$. Still they are nonzero.

The equation of motion of relativistic polarization propagators are more conveniently written in the Kramer's basis as

$$\langle \langle \hat{P}; \hat{Q} \rangle \rangle_E = \left(\hat{P}^\dagger | \hat{\mathbf{X}}^+ \right) \left(\hat{\mathbf{X}}^+ | E\hat{I} - \hat{H}_0 | \hat{\mathbf{X}}^+ \right)^{-1} \left(\hat{\mathbf{X}}^+ | \hat{Q} \right) \quad (105)$$

Perturbators do contain two types of elements that can so be arranged in two different sub-blocks. We mean vector elements which contain unoccupied positive-energy states and vector elements which contain unoccupied negative-energy states. The vector elements with excitations to positive-energy MOs are

$$\begin{aligned} \tilde{\mathbf{P}}^{ee} &= \left(\hat{P}^\dagger | \hat{\mathbf{X}}_{ia}^+ \right) = \sum_{pq} P_{pq} \langle 0 | \left[\hat{X}_{pq}^-, \hat{X}_{ia}^+ \right] | 0 \rangle + \dots \\ &= \sum_{pq} P_{pq} \left\{ \delta_{qi} \langle 0 | \hat{X}_{pa}^+ | 0 \rangle - \delta_{ap} \langle 0 | \hat{X}_{iq}^+ | 0 \rangle \right\} = -2P_{ai}^{ee} \end{aligned} \quad (106)$$

Each vector element P_{ai}^{pe} is formally the same though the orbital a is replaced by \hat{a} .

At RPA level of approach the new elements of the supermatrix \mathbf{A} are written in the X-basis as

$$\begin{aligned} \mathbf{A}_{\hat{a}\hat{i}, \hat{i}\hat{a}}^{ee, ee} &= -\langle 0 | \left[\hat{X}_{ai} \left[\hat{X}_{jb}, \hat{H}_0 \right] \right] | 0 \rangle \\ \mathbf{A}_{\hat{a}\hat{i}, \hat{i}\hat{a}}^{pe, pe} &= -\langle 0 | \left[\hat{X}_{\hat{a}\hat{i}} \left[\hat{X}_{\hat{b}\hat{j}}, \hat{H}_0 \right] \right] | 0 \rangle \end{aligned} \quad (107)$$

The matrix elements of \mathbf{B} are constructed in a similar manner.

When considering excitations from an occupied MO to both the positive- and negative-energy MOs one shall get an equivalent expression to that of eqn (48),

$$\langle\langle \hat{P}; \hat{Q} \rangle\rangle_E^R = (\mathbf{P}^{ee}, \mathbf{P}^{pe}) \begin{pmatrix} \mathbf{M}^{ee,ee} & \mathbf{M}^{ee,pe} \\ \mathbf{M}^{pe,ee} & \mathbf{M}^{pe,pe} \end{pmatrix}^{-1} \begin{pmatrix} \mathbf{Q}^{ee} \\ \mathbf{Q}^{pe} \end{pmatrix} \quad (108)$$

The matrix elements belonging to the supermatrices of subblocks $\mathbf{M}^{ee,pe}$ and $\mathbf{M}^{pe,ee}$ are much smaller than the other elements belonging to the subblocks (ee, ee) and (ep, ep) .

4.4 A proper non relativistic limit

As was shown in the first paper on relativistic polarization propagators¹ both, the relativistic perturbators and the principal propagators go to their NR limit when $c \rightarrow \infty$. In such a case one starts with only one electronic mechanism and ends up with four, of both singlet and triplet-type. How is this possible?

When the principal propagator is written in the tensorial basis defined in eqn (90) and (91) one has to deal with two types of binary products, pseudo-singlet and pseudo-triplet. Each of them will go to their NR limit when $c \rightarrow \infty$, meaning that, for the singlet case and time-reversal variant perturbators the principal propagator will have the following behavior

$$\begin{aligned} \left(\hat{R}_{ai}^-(0, 0 | E\hat{I} - \hat{H}_0 | \hat{R}_{bj}^-(0, 0) \right) \Big|_{E=0} &= -2({}^1\mathbf{A}_{ai,bj} + {}^1\mathbf{B}_{ai,bj}) \\ &+ (\bar{i}b|\bar{j}a) + \dots - (\bar{a}b|\bar{j}i) \dots \\ &\rightarrow_{c \rightarrow \infty} -2({}^1\mathbf{A}_{ai,bj} + {}^1\mathbf{B}_{ai,bj}) \end{aligned} \quad (109)$$

For the triplet case it follows that each component has the appropriate NR behavior. In the case of the (1, 0) component

$$\begin{aligned} \left(\hat{R}_{ai}^-(1, 0 | E\hat{I} - \hat{H}_0 | \hat{R}_{bj}^-(1, 0) \right) \Big|_{E=0} &= -2({}^3\mathbf{A}_{ai,bj} - {}^3\mathbf{B}_{ai,bj}) \\ &+ (\bar{i}b|\bar{j}a) + \dots \rightarrow_{c \rightarrow \infty} -2({}^3\mathbf{A}_{ai,bj} - {}^3\mathbf{B}_{ai,bj}) \end{aligned} \quad (110)$$

In order to show the behavior just mentioned above we have performed the calculation of $J(\text{Sn-I})$ for SnH_3I within the relativistic and NR domain, with exactly the same basis set and geometry. In the first case it was done applying the DIRAC⁸⁰ code with the velocity of light scaled by a factor λ . The results of calculations with $\lambda = 10$ nicely match with the NR values obtained with the DALTON code.⁸¹ As shown in Table 1 the total NR value obtained from the sum of the triplet (FC + SD) and singlet (PSO + DSO) mechanisms is close to the

Table 1 Contributions to $J(\text{SnI}; \text{SnH}_3\text{I})$ and $J(\text{CBr}; \text{CH}_3\text{Br})$ at relativistic RPA and NR RPA level of approach. All values are in Hz

	Relativistic ^a		Non-relativistic			
	$\lambda = 1$	$\lambda = 10$	FC + SD	PSO	DSO	Total
$J(^{119}\text{Sn } ^{127}\text{I})$	2144.87	948.42	796.44	160.19	-0.01	956.62
$J(^{13}\text{C } ^{79}\text{Br})$	-62.42	-48.17	-82.72	33.35	0.05	-49.32

^a λ is the scaling factor of the velocity of light.

relativistic value with c scaled 10 times. When J is scaled 10 times, $J(\text{SnI}; \text{SnH}_3\text{I}) = 948.42$ Hz, and its NR calculated value is 956.62 Hz. In the case of $J(\text{CBr})$ we got -48.17 and -49.32 Hz, respectively.

Within the relativistic domain some well-established “non-relativistic-based” concepts shall be redefined or even avoided. In the same manner as the concepts of space and time are unified in the new space-time concept making a deep change of what they mean within the NR domain, or the spin dependence that is avoided and its operators are replaced by operators with a given time reversal symmetry, diamagnetic and paramagnetic contributions are transformed in a unique and different kind of contribution. What is its new physical meaning is still not very well understood. Based on our theory one can realize that the NR-type of paramagnetic contribution are related with virtual electronic excitations like the $(i \rightarrow a, j \rightarrow b)$ perturbative pathways. On the other hand the NR-type of diamagnetism do arise from virtual electron-positron pair creations and annihilations, e.g. $(i \rightarrow \bar{a}, j \rightarrow \bar{b})$ perturbative pathways. These diamagnetic and paramagnetic NR-type of contributions may be transformed one into the other type as a function of the velocity of light as shown below.

To obtain the usual NR diamagnetic and paramagnetic type of contributions to the nuclear magnetic shieldings one should neglect the contributions that come from the (ee, pe) and (pe, ee) subblocks of the principal propagator. In such a case the total contribution obtained from the subblock ee, ee will go to the paramagnetic term in the NR limit when $c \rightarrow \infty$. In the same manner, the total contribution of the (pe, pe) subblock goes to the NR diamagnetic value.

As observed in Fig. 2 the NR-type of the paramagnetic contributions strongly depend (in a way more pronounced than the diamagnetic contribution) on the scaled speed of light. The paramagnetic $\sigma^p(\text{I})$ is positive when calculated within the relativistic regime (meaning that its contribution becomes NR diamagnetic-like). In the case of $\sigma^p(\text{Rn})$ there is a difference of around 11 000 ppm (!) among its values when the velocity of light is scaled from $\lambda = 1$ to $\lambda = 10$. In the NR regime $\sigma^p(\text{Rn}) \cong 0$

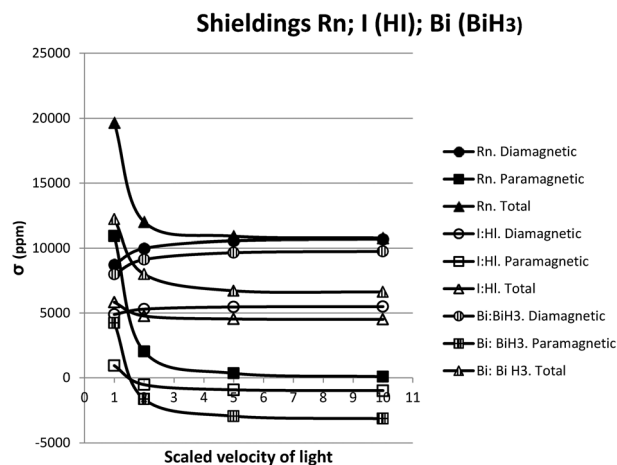


Fig. 2 Relativistic and NR shieldings of Rn, I and Bi. Its dependence with the scaled velocity of light.

ppm as is well-known it should be. Similar behavior was shown previously in ref. 7. The nuclear magnetic shielding dependence of Bi in BiH₃ with the velocity of light is similar to that of Rn and also to iodine, though in this last case the variation is less pronounced.

5 Bound-QED theory for atomic and molecular properties

The natural next step for improving the level of our theory is concerned with the introduction of QED effects. The best way to do it is still under development. We shall give here some insights on what to do as a first step. They are related with previous works developed by Lindgren,⁵⁷ Shabaev⁸² and Mohr and coauthors.⁷⁹

More than ten year ago we published two formalisms which would permit the inclusion of QED corrections on magnetic molecular properties.^{53,54} They are formally sound, but have some difficulties striving on practical or formal problems: some integrals were not solved, and there were no clear indication on how to introduce electron correlation effects.

5.1 Fundamentals

The equation which describes the electronic behavior of atomic and molecular systems takes into account the electron–nucleus and electron–electron interaction by means of electrostatic fields. This is enough to provide, to a large extent, agreement with experimental data. However, some quite small discrepancies are measurable. They indicate that the quantum effects of the electromagnetic fields can be treated as perturbations to the solutions of the equation which consider classical fields as zeroth-order. This is the basis of the *bound state QED*. Within this formalism the total electromagnetic field is splitted-up 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-annihilation of virtual particles).

Quantum electrodynamics of bound state systems is usually formulated in the so-called *Furry bound interaction picture*.⁸³ In this picture, one starts from the solutions $\psi_n(x)$ to the Dirac equation in the potential $a^\mu(x)$ (such as the nuclear potential, for instance) described by the Hamiltonian H_0 . We consider as the best option the *Fuzzy picture*^{3,32} in which the no pair or zeroth-order Hamiltonian is dynamically redefined during the wave function optimization process, such that it adapts to the average repulsion between the electrons, as defined in the used wave function approximation. Then one enforces that the energy should be stationary with respect to the mixing of positive-energy and negative-energy electronic orbitals. E is minimized for rotations between occupied electronic orbitals and unoccupied positive-energy orbitals, and E is maximized for orbital rotations between occupied orbitals with unoccupied negative-energy orbitals. In this case the external Coulombic nuclear-electron interaction is introduced in the SCF procedure.

$$H_0\psi(x) = \left(i\hbar\gamma^\mu\partial_\mu + \frac{e}{c}\gamma^\mu a_\mu - mc \right)\psi(x) = 0 \quad (111)$$

The interactions between an external classical or quantized electromagnetic field and Dirac fields are given by

$$H'(t) = -\frac{e}{c} \int d\mathbf{r} j^\mu(x) A_\mu(x). \quad (112)$$

where the electron current $j^\mu(x) = \bar{\psi}(x)\gamma^\mu\psi(x)$. In the bound-state QED the Dirac current is not normal ordered because one should consider the equal time contraction between fermionic operators. Otherwise one should not include the vacuum-polarization corrections.⁷⁹

Expansion of the Dirac field in terms of a complete set of zeroth-order solutions $\psi_n(x) = \psi_n(\mathbf{r})e^{-iE_n t/\hbar}$ of the Dirac equation in the potential $a^\mu(x)$, and the promotion of the coefficients of the expansion to creation and annihilation operators, allows us to hold the particle interpretation. Hence, the operator \hat{a}_n (\hat{b}_m^\dagger) annihilates (creates) electrons (positrons) in the unperturbed bound states ψ_n (ψ_m) with $E_n > 0$ ($E_m < 0$).⁷

Then the electron–positron field can be written as

$$\psi(x) = \sum_{E_n > 0} a_n \psi_n(x) + \sum_{E_m > 0} b_m^\dagger \psi_m(x), \quad (113)$$

or

$$\begin{aligned} \hat{\psi}(x) &= \sum \hat{a}_r^\dagger(t) \bar{u}_r(\mathbf{r}) + \sum \hat{b}_r^\dagger \bar{v}_r(\mathbf{r}) \\ \hat{\psi}(x) &= \sum \hat{a}_s(t) u_s(\mathbf{r}) + \sum \hat{b}_s^\dagger v_s(\mathbf{r}) \end{aligned} \quad (114)$$

where $\bar{\psi}(x) = \psi^\dagger \gamma^0$, and the functions u and v refer to positive and negative energy solutions of eqn (113), respectively.

For actual calculations of magnetic molecular properties, both the empty-Dirac and the QED pictures are formally equivalent; so in what follows we will continuously work within the empty-Dirac picture to introduce QED corrections.

5.2 S-matrix formalism and polarization propagators

The main interest in the bound state problem is the calculation of level shifts. In the approach by Gell-Mann and Low⁸⁴ and Sucher⁸⁵ the interaction Hamiltonian $H_I(t)$ is replaced by an adiabatically damped one

$$H_I^\varepsilon(x) = \int d^3x e^{-\varepsilon|x^0|} j^\mu(x) A_\mu(x). \quad (115)$$

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

$$\Delta E_0 = \lim_{\varepsilon \rightarrow 0, \lambda \rightarrow 1} \frac{\partial}{\partial \lambda} \frac{\langle 0 | S_{e,\lambda} | 0 \rangle_c}{2 \langle 0 | S_{e,\lambda} | 0 \rangle_c} + \text{const.} \quad (116)$$

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

$$S_{e,\lambda} = 1 + \sum_{k=1}^{\infty} \frac{(-i\lambda)^k}{k!} \int d^4x_1 \dots \int d^4x_k T \{ H_I^\varepsilon(x_1) \dots H_I^\varepsilon(x_k) \}. \quad (117)$$

$T\{H_I^\varepsilon(x_1) \dots H_I^\varepsilon(x_k)\}$ is the *time-ordered product* (i.e., $x_1^0 < x_2^0 < \dots < x_k^0$) of the operators $H_I^\varepsilon(x_1) \dots H_I^\varepsilon(x_k)$.

It could be instructive to analyze the second-order level shift yet from another point of view. Since for NMR applications we are interested in the effect of two external magnetic fields the relevant term is

$$S_{\epsilon\lambda}^{(2)} = \frac{(-i\lambda)^2}{2!} \int d^4x_1 d^4x_2 T\{\mathcal{H}_I(x_A)\mathcal{H}_I(x_B)\} \quad (118)$$

and so,

$$\begin{aligned} \langle 0|S_{\epsilon}^{(2)}|0\rangle &= -\frac{1}{2!} \int_{-\infty}^{\infty} dt_A \int_{-\infty}^{\infty} dt_B \langle 0|T(\mathcal{H}_I(t_A)\mathcal{H}_I(t_B))|0\rangle \\ &= \frac{i}{2!} \int_{-\infty}^{\infty} dt_A \int_{-\infty}^{\infty} dt_B \langle\langle \mathcal{H}_I(t_A); \mathcal{H}_I(t_B) \rangle\rangle \end{aligned} \quad (119)$$

This is a very important relationship between the second-order S -matrix and the polarization propagator.

Let's consider in more detail the polarization propagator that appears in the last line of the last equation. We assume that both perturbative external fields, represented by H_1 of eqn (95) are treated as classical. We will give explicit expressions for only one of both external fields.

$$H_1^N(t_A) = -\frac{e}{c} \hbar \sum_{\mathbf{K}} \gamma_{\mathbf{K}} \mathbf{I}_{\mathbf{K}} \cdot \int d\mathbf{r}_A \bar{\psi}(x_1) V_{\mathbf{K}}^N \psi(x_A) \quad (120)$$

The last integral is written in second-quantized language as

$$\begin{aligned} &= \sum_{r,s} \left(\hat{a}_r^\dagger(t_A) \hat{a}_s(t_A) \langle u_r | V_{\mathbf{K}}^N | u_s \rangle + \hat{a}_r^\dagger(t_A) \hat{b}_s^\dagger(t_A) \langle u_r | V_{\mathbf{K}}^N | v_s \rangle \right. \\ &\quad \left. + \hat{b}_r(t_A) \hat{a}_s(t_A) \langle v_r | V_{\mathbf{K}}^N | u_s \rangle + \hat{b}_r(t_A) \hat{b}_s^\dagger(t_A) \langle v_r | V_{\mathbf{K}}^N | v_s \rangle \right) \\ &= \sum_{r,s} \left(V_{\mathbf{K},rs}^{N,ee} \hat{a}_r^\dagger(t_A) \hat{a}_s(t_A) + V_{\mathbf{K},rs}^{N,ep} \hat{a}_r^\dagger(t_A) \hat{b}_s^\dagger(t_A) \right. \\ &\quad \left. + V_{\mathbf{K},rs}^{N,pe} \hat{b}_r(t_A) \hat{a}_s(t_A) + V_{\mathbf{K},rs}^{N,pp} \hat{b}_r(t_A) \hat{b}_s^\dagger(t_A) \right) \end{aligned} \quad (121)$$

Then, from what was shown in Section 4.3 the principal propagator will be constructed with the ee , ep and pe excitation terms.

The (ee, ee) block of the principal propagator is then related with time ordered product of basic excitation operators,

$$\begin{aligned} &\langle\langle \hat{a}_r^\dagger(t_A) \hat{a}_s(t_A); \hat{a}_p^\dagger(t_B) \hat{a}_q(t_B) \rangle\rangle \\ &= i \langle 0|T(\hat{a}_r^\dagger(t_A) \hat{a}_s(t_A) \hat{a}_p^\dagger(t_B) \hat{a}_q(t_B)) \end{aligned} \quad (122)$$

Considering a one-electron system and applying the 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 in 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 there are no photon propagator since the electromagnetic field is treated as a classical one.

There are two terms with two-fermion contractions. They will give the basic electron propagators. When including higher order radiative corrections to them, like the whole set of proper self-energy corrections, one would obtain the full electron propagator which introduce the mass renormalization. The full electron propagator is finally related with the free electron propagator and the proper self-energy term (see page 193 of ref. 65).

From the previous analysis one realize that QED effects can be introduced in the calculation of atomic or molecular properties when they are performed applying the polarization propagator formalism. Its relationship with the S -matrix formalism is a clear indication of this statement.

5.3 QED corrections within the polarization propagator formalism

As was shown above there are a simple relationship between polarization propagators at both regimes, relativistic and non-relativistic. In line with that finding we shall advice that QED effects shall be included separately in its two main factors: the perturbators and the principal propagator. How to do it?

First we consider the electron correlation arising from negative energy orbitals. At zeroth order of approach only the matrix elements of the $\mathbf{A}(0)$ supermatrix do contribute to the principal propagator. They are composed of diagonal elements which only contain the inverse of the excitation energies between one occupied atomic or molecular orbital (say i) to any of two unoccupied orbitals (say a or \bar{a}). At RPA level there are two more terms in the matrices of the principal propagators, $\mathbf{A}(1)$ and $\mathbf{B}(1)$. Electron-correlation corrections are so included in these last matrices up to first order. Further corrections appear when working up to second-order level of approach as shown in Sections 3.2 and 3.3. In this way the contribution of negative-energy states to the electron correlation effects at consistent first order of polarization propagators will be included through each matrix element of e.g. $\mathbf{A}_{\bar{a}i, \bar{b}j}(1)$ and $\mathbf{B}_{\bar{a}i, \bar{b}j}(1)$.

QED corrections can be introduced to the principal propagator matrix elements considering that the leading QED effects are important only for the deep-core electrons, in an atom-based description of electronic molecular systems. On the other hand, the QED corrections to perturbators should arise from the matrix elements of eqn (102). They may be calculated at different levels within perturbation theory.

From the considerations above we are able to introduce the following ansatz for the calculation of QED effects on atomic or molecular response properties:

- (1) Work out all one-electron relativistic eigenstates and eigenvalues of the electronic system within the Fuzzy picture.
- (2) The leading QED effects (VP, SE, . . .) should be considered separately within both the principal propagator and the perturbators matrices. For the principal propagators we assume that only the deep-core atomic or molecular orbital energies should be modified.

So, the occupied orbital energies of eqn (58) and (104) shall be replaced by $\varepsilon_i^{\text{QED}}$.

(3) Even at RPA level of approach QED effects will also modify the perturbators. There will appear contributions like the single-vertex contributions of ref. 52. In such a case two terms would appear: the hyperfine-vertex, hfs-vertex, contribution and the Zeeman-vertex contribution. The first vertex contribution is obtained from the term representing the renormalized part of the 3-point vertex which consider the electron interaction with the hfs field. The second vertex contribution is defined analogously to the hfs one.

(4) Going up to second-order in perturbation theory of polarization propagators some electron correlation and QED corrections will also appear in the perturbators through the correlation coefficients κ of eqn (54) where ε_i and ε_j shall be replaced by $\varepsilon_i^{\text{QED}}$ and $\varepsilon_j^{\text{QED}}$. Perturbed-orbital contributions must also be included.

5.4 The NMR nuclear magnetic shielding within the QED framework

As mentioned above the NMR spectroscopic parameters are among the most influenced by relativistic effects due to they strongly depends on the electronic density “at the site” of the nucleus. On the other hand they become observables when an external magnetic field is applied.

The covariant theory of polarization propagators shows that there is only one electronic mechanism involved. Within this formalism it is not possible any longer to obtain the NR-like paramagnetic and diamagnetic contributions by themselves. On the other hand such a separation is recovered when the off-diagonal matrix elements are neglected. This is straight forwardly observed when the polarization propagators are expressed in a non-covariant form.^{3,7}

The principal propagator matrix does contain the information of the electronic system as a whole. So, one can guess that the magnetic behavior of the atomic or molecular system shall be in it. The principal propagator can be divided into four-blocks (see eqn (108)). The diagonal subblocks are related with the usual paramagnetic (up and left, diagonal) contribution and the usual diamagnetic (down and right, diagonal) contribution. The last contribution does arise from two-perturbed terms where virtual creation and annihilation of electron-positron pairs are involved.

We should stress here that such virtual “exchange” process of electron-positron creation and annihilation should be related with the physical origin of the diamagnetic contributions. This is not a typical QED effect. There is a similar mechanism known as nuclear polarization that contributes to the electronic Lamb shift.⁷⁹ This last mechanism gives additional contributions to the energy shift of electron bound states. It is expressed as a new term which describes the interaction of the Dirac vacuum with virtual nuclear excitations: an electron which is in the occupied negative energy continuum can be virtually excited into the occupied, say $1S_{1/2}$ -state at different spacetime points *via* the interaction with virtual nuclear excitations, while the present electron and the positron will annihilate each other. This is a kind of “exchange” process.

In our case the source of the “exchange” is the interaction of the vacuum with any of both magnetic fields, arising from the vector potentials \mathbf{A}^N and \mathbf{A}^B .

There is another interesting feature that is related with what was written above: the appearance of a branch of energies within which all virtual excitation, from occupied electronic states to negative-energy states are contained. As shown in ref. 86 the interval $2mc^2 \leq \varepsilon_i - \varepsilon_{\bar{a}} < 4mc^2$ gives the total contribution to σ^d , and this does not depend of the model compound studied. The energy at disposal involved in such excitations to the negative-energy electronic branch cannot be higher than the value from which real electron-positron pairs shall be produced.

On the other hand the NR paramagnetic-type of contributing terms arise from the excitations to positive-energy electronic states. The dependence of these terms with the scaled value of the velocity of light is more pronounced than in the case of the diamagnetic terms as shown in Fig. 2. The paramagnetic-like behavior of the three nuclei studied is similar though $\sigma^p(\text{Rn})$ and $\sigma^p(\text{Bi})$ are more influenced by relativistic effects. In the case of Bi and I, its NR paramagnetic-like behavior becomes diamagnetic-like within the relativistic regime.

The off-diagonal terms of the relativistic polarization propagator are quite small. They are zero within the NR domain. They do not contain matrix elements of $\mathbf{A}(0)$. Then there is no leading QED correcting terms on them.

6 Conclusions and outlook

During the last few years several attempts to introduce relativistic quantum methods in a QED framework were published. One of the main difficulties is related to merging electron correlation and QED effects on the same theoretical framework.

The path integral formalism was developed long time ago as an alternative to the wave function based formalism. Both are completely equivalent though the first one is mostly applied by the quantum field community of physicist, and the second one is more traditionally applied by quantum chemist and molecular physicist. Polarization propagators are in between of both communities. Calculations of atomic and molecular response properties with polarization propagators at second-order level of approach, SOPPA, are among the most reliable. They are still not widely applied by the quantum chemist by perhaps historical reasons.

We have shown in this article the sound formal origin of polarization propagators. This formalism was developed in the early '70s within the NR domain, and then extended to the relativistic regime 20 years ago. From now on QED effects can naturally be introduced in polarization propagators and also, the quantum field framework arise as its natural framework. Its derivation from an effective generating functional would have broad applications in the field of many-body systems.

The generalization of polarization propagators to the relativistic framework (right now implemented at first-order or RPA) gave new insights on the understanding of the physical origin

of magnetic molecular properties. Diamagnetic and paramagnetic contributions, which arise from completely different electronic mechanisms within the NR regime are now unified. They are produced by the same mechanism which is still not completely understood. One of the reasons for this is our “NR way of thinking”. It is hardly seen how to grasp physical insights on magnetic properties without going down from 4-component to 2-component formalism. As an example, in a proper relativistic framework the spin is not any longer a good quantum number, so spin-orbit effects cannot be used to explain any physical situation within the full relativistic formalism.

The path integral formalism is the natural quantum language that gives solid grounds to derive polarization propagators. We have shown here how to do it and what we have learned doing it: there is a rule to write propagators within the path integral formalism as a representation. One can work out generating functionals from which to obtain double-time Green functions or polarization propagators. The physical insight that is intrinsic to the path integral formulation of quantum mechanics is nicely applied in our propagators.

When a given atomic or molecular system is perturbed by an external perturbation, its transmission to the whole quantum system will consider the whole branch of excitations allowed to do so. There will be several *perturbative propagation pathways*. At consistent first-order they are defined by excitations which contain two occupied atomic or molecular orbitals and two unoccupied ones. When both occupied orbitals are equal, and both unoccupied orbitals are also equal, they define the diagonal matrix elements of the principal propagator. Such elements are the largest, so they will give the main propagation pathways. In this context QED effects can be naturally introduced. We suggested here an ansatz as a first step in this direction. Next steps should include QED on the perturbators. What appears as the most important finding is the treatment of QED and electron correlation on the same and powerful formalism.

Within the relativistic regime new operators shall replace the spin-adapted tensor operators. They are the well-known Kramer's operators that span a new basis. When the matrices of the principal propagator are expressed in this last tensor basis, they become the NR spin-adapted matrices, when $c \rightarrow \infty$. This finding gives strong support on what the Kramers operators mean, and also on the physical information that the principal propagator contain at any regime.

We have uncovered why polarization propagators are defined with exactly the same formal expressions within both regimes, relativistic and non-relativistic: it is due to its foundations on the path integral formalism. From this new theoretical framework it would be possible to find out new roads for including QED and electron correlation on atomic and molecular properties.

After several decades of continuous developments, the beauty and fruitfulness of polarization propagators are the source for always going one step further in our yet unfinished program. It may be that this last step becomes in one of the most influential for the near future.

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