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Review Article

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Relativistic quantum theory for atomic and molecular response properties

First hundred years of quantum mechanics and more than fifty years of response properties

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Abstract: This perspective revisits key developments and challenges in the theoretical description of atomic and molecular electronic properties within the framework of relativistic quantum chemistry. Fundamental conceptual issues arising from the extension of non-relativistic theories to the relativistic domain are discussed, with particular emphasis on four-component formalisms, the treatment and interpretation of negative-energy states, including virtual excitations involving these states, the reinterpretation of operators and observables, and the introduction of weak interactions into this field of research. Special attention is given to the construction of model Hamiltonians as accurately as possible and the analysis of the electronic contributions due to spin-dependent and spin-independent effective Hamiltonians to molecular properties. In this context, the generalization of the spin-symmetry to time-reversal-restricted symmetry is emphasized. Recent methodological advances, including the application of the relativistic polarization propagator theory, are also highlighted.

Keywords: Heavy-atoms; quantum science and technology; relativistic quantum chemistry; representation of operators; response properties; time-reversal symmetry; weak interactions.

Introduction

The development, during the years previous to 1925, and then, the publication of a new form of quantum theory by Erwin Schrödinger within a non-relativistic (NR) framework,[1] together with his early formulation of time-independent perturbation theory published the same year (1926),[2] started the development of a fascinating and ever growing area of research known as atomic and molecular response theory. This is related to the nature and magnitude of the response of a given quantum system to an external (and weak compared with the unperturbed energy of the system) perturbation.

When considering heavy-atom containing quantum systems, like heavy-element containing molecules, the proper wave equation needed to describe them is the one proposed few years later than the Schrödinger's wave equation, in 1928, by Paul A. M. Dirac[3] for one-electron systems, which is known ever since as the Dirac equation.

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This expression was then generalized to *N*-electron quantum systems by Bertha Swirles.[4] The Dirac equation contained such new physical concepts and mathematical complexities in the wave equations that it took some decades to find reliable numerical results for atomic and molecular systems. Indeed, there is a quotation from a Dirac's paper of 1929 that expresses its first prophecy about what would come after: "*The underlying physical laws necessary for the mathematical theory of a large part of physics and the whole of chemistry are thus completely known, and the difficulty is only that the exact application of these laws leads to equations much too complicated to be soluble*".[5]

The problem first posed to atomic physicists and then to quantum chemists, and worked out during the last century, is related to finding mathematical solutions to the new set of equations. They contain a negative energy branch that requires being treated with caution, since solutions must explain the atomic stability. It was urgent to know how to deal with them and how to solve them more efficiently. Within the quantum chemistry community, such an impetus is still under development with similar characteristics as appeared early on. What mattered most was to find theoretical results as close as possible to experimental findings, one of the earliest struggles that enforced the birth of quantum physics.

As is well known, this was not the only challenge that the fathers of the new physics clearly recognized from the outset and that scientists who wanted to computationally model atomic and molecular properties based on a relativistic framework had to face later. In what follows we will mention and treat in some detail only few of them, especially the ones that are more related with physical insights of interest to the quantum chemistry community: i) Relativistic operators that are related to observables are expressed as four-dimensional vector operators, not as three-dimensional ones, which makes their interpretation more abstract. This statement is still under debate within the RQC community (see chapter 8.2 of Ref. 6); ii) As a consequence of the four-dimensional nature of the physical observable operators, like the Hamiltonian, the wavefunction became a function of dimension four, known as a four-component (4C) wavefunction. This fact uncovers new physics behind; iii) There is a negative-energy branch in the energy spectra, and so a natural question arises as to how to treat particles that might occupy such negative-energy states in low-energy physics; iv) Within the relativistic regime, the spin of fundamental particles is no longer a good quantum number, so a question arises: how is this operator related to its well-defined analogous NR operator? v) How to build up workable Hamiltonians that resemble all kinds of electromagnetic (or, more generally, electromagnetic and weak) interactions? And, how are they related to the previously used Hamiltonians that are valid within the NR domain? and vi) How can atomic and molecular response properties be calculated and analyzed within the 4C framework, and compared against calculations and analyses performed within an NR-based scheme?

Although only briefly, we will attempt to provide some answers to these questions as they arose over the years. We will focus on a few key points or cornerstones that address special difficulties concerning mathematical solutions or understandings of the physics behind these phenomena. We will also introduce some of our developments within relativistic quantum chemistry (RQC).

Relativistic quantum chemistry

When the building of the quantum physics formalism was in its early stages, there was a strong impetus to ensure its consistency with the principles of special relativity. These principles indicate that: i) the laws of physics have the same form when written in any inertial reference frame, and ii) the speed of light in vacuum is constant, regardless of the speed of its source. From the first principle, it can be stated that the equations governing all fundamental processes in nature must be invariant with respect to Lorentz transformations and, subsequently, that space-like and time-like coordinates must be treated on equal footing.

By merging quantum theory with special relativity, relativistic quantum physics suddenly emerged and, with it, some completely new physical insights that are not yet completely understood within the broad area of quantum chemistry.

The development of the quantum theory required a high degree of acceptance of completely new ideas and, at the time, unexplored mathematical tools to express them. This happened first when the quantum ideas were written within an NR framework, but it was still more shocking when written within a proper relativistic framework. The fact that the one-particle Dirac Hamiltonian (appropriate for particles of "spin-1/2") must be written as an operator of (at least) dimension 4 means that each of its dynamical variables must also be written as 4×4 matrices. Then, a one-to-one relationship among dynamical variables in both regimes, relativistic and NR, is hardly found within the abstract Hilbert space of operators and states. There is no fully appropriate way to do so, and then, one must find the best ways of matching both representations of observables.

In the following sections, we provide the basic elements and mention some weaknesses and subtleties that we have to deal with in the now mature RQC area of research.

Basic elements: equations of motion, operators and wavefunctions

Within the wave formulation of quantum mechanics, the basic equation of motion that expresses the evolution of the quantum state of a given system (whether composed of one or many particles) is expressed as

$$i\hbar \frac{\partial \psi}{\partial t} = \widehat{H}\, \psi, \tag{1}$$

where $i = \sqrt{-1}$ is the imaginary unit and $\hbar = h/(2\pi)$ is the reduced Planck constant. The Hamiltonian operator $\widehat{H}$ is related to the energy of the quantum system under study.

When the relativistic constraints are not imposed (*i.e.*, when the system is studied using a NR formalism), the kinetic energy term in the Hamiltonian has an inverse dependence on the square of the spatial coordinates of the particle(s) in the system, while the left-hand side of eq. 1 shows an inverse dependence on time. In such a theoretical framework, when the system consists of a single particle that is exposed to conservative forces, the Hamiltonian can be written as $\widehat{H} = \widehat{p}^2/(2M) + \widehat{V}$, where the first term on the right-hand side (rhs) of this expression is the NR kinetic energy operator (with $\widehat{\mathbf{p}}$ being the linear momentum operator of the particle, and M its rest mass) and the second is the potential energy operator, associated to the interaction of the particle with the forces to which it is subject.

On the other hand, when relativistic constraints are introduced, the Hamiltonian operator $\widehat{H}$ in eq. 1 must satisfy the requirement that both space-like and time-like variables are treated on equal footing. Therefore, the kinetic energy operator must now be inversely proportional to the spatial coordinates of the particle(s). The fulfillment of this strict constraint results (in the standard 4-component representation) in the appearance of four new variables in the kinetic energy operator, known as the Dirac matrices α_x, α_y, α_z, and β, which all anti-commute with each other.

Another important issue to consider when properly treating many-electron quantum systems within a relativistic framework is that the time variables associated with each electron are different, since there is no absolute time common to all of them. For practical reasons, in the computational modeling of atomic and molecular properties in relativistic contexts, a common time framework is typically assumed for all electrons (*i.e.*, retardation effects are neglected). This assumption is sufficient to obtain good agreements between theoretical and experimental results, after applying additional theoretical constraints.

For simplicity, it is better to start dealing with the non-covariant expression of the free electron Dirac equation, which is given by

$$\widehat{h}^{\mathrm{D-free}}\, \Psi(\boldsymbol{r}, t) = \left(c\, \boldsymbol{\alpha} \cdot \widehat{\boldsymbol{p}} + \beta mc^2\right) \Psi(\boldsymbol{r}, t) = i\hbar \frac{\partial}{\partial t} \Psi(\boldsymbol{r}, t), \tag{2}$$

being $\boldsymbol{r}$ the electron position, m the electron rest mass and c the speed of light in vacuum. Since $\widehat{h}^{\mathrm{D-free}}$ is independent of time, its eigenstates are stationary and can be written as a product of a spatial-dependent and a time-dependent function, *i.e.*, $\Psi(\boldsymbol{r}, t) = \psi(\boldsymbol{r}) \exp(-iE\, t/\hbar)$.[7] This implies that the time-independent free-electron Dirac equation can be written as

$$\left(c\, \boldsymbol{\alpha} \cdot \widehat{\boldsymbol{p}} + \beta mc^2\right) \psi(\boldsymbol{r}) = E\, \psi(\boldsymbol{r}), \tag{3}$$

where the eigenvalues of $\widehat{h}^{\mathrm{D-free}}$ correspond to the energies $E = E(\boldsymbol{p})$ of the electron. Within the standard representation, the Dirac matrices $\boldsymbol{\alpha} = (\alpha_x, \alpha_y, \alpha_z)$ and β are expressed as 4×4 matrices, whose explicit forms are given in terms of the 2×2 Pauli matrices $\boldsymbol{\sigma} = (\sigma_x, \sigma_y, \sigma_z)$ as

$$\boldsymbol{\alpha} = \begin{pmatrix} \emptyset_2 & \boldsymbol{\sigma} \\ \boldsymbol{\sigma} & \emptyset_2 \end{pmatrix} \quad \text{and} \quad \beta = \begin{pmatrix} \mathbb{1}_2 & \emptyset_2 \\ \emptyset_2 & -\mathbb{1}_2 \end{pmatrix}, \tag{4}$$

with $\emptyset_2$ and $\mathbb{1}_2$ being the 2×2 zero and identity matrices, respectively, and

$$\sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad \sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \quad \sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}. \tag{5}$$

It is possible to split the set of solutions to eq. 3 (all of which are 4C wavefunctions, also known as bispinors since the spinors refer to 2C wavefunctions) into two subsets. One of them contains all the eigenstates whose solutions have positive energy, while the other is comprised of the negative energy solutions. The positive-energy wavefunctions can be written as

$$\psi_+(\boldsymbol{r}) = \begin{pmatrix} \psi_1^{\mathrm{L}}(\boldsymbol{r}) \\ \psi_2^{\mathrm{L}}(\boldsymbol{r}) \\ \psi_1^{\mathrm{S}}(\boldsymbol{r}) \\ \psi_2^{\mathrm{S}}(\boldsymbol{r}) \end{pmatrix} = \begin{pmatrix} \psi^{\mathrm{L}}(\boldsymbol{r}) \\ \psi^{\mathrm{S}}(\boldsymbol{r}) \end{pmatrix}. \tag{6}$$

The nomenclature used in eq. 6, where L and S stand for large and small, respectively, arises from the fact that, in the NR limit, the upper components of these wavefunctions are larger than the lower ones, since[8]

$$\left(\psi^{\mathrm{S}}\right)^{\dagger}\psi^{\mathrm{S}} \to \frac{1}{4}\left(\frac{v}{c}\right)^{2}\left(\psi^{\mathrm{L}}\right)^{\dagger}\psi^{\mathrm{L}}. \tag{7}$$

On the other hand, in the case of negative energy states, the two spinors (upper and lower) satisfy a similar relationship with each other, but since in this case the upper spinors will be the small components of the 4C wavefunctions while the lower ones will be their large components, the superscripts S and L of eq. 6 will be interchanged.

In the case of a single electron subject to electromagnetic interactions with external fields, one should start from the time-dependent Dirac equation. Replacing $\widehat{H}$ in eq. 1 by the Hamiltonian

$$\widehat{h}^{\mathrm{D-EM}} = c\ \boldsymbol{\alpha} \cdot \left[\widehat{\boldsymbol{p}} + e\boldsymbol{A}(\boldsymbol{r})\right] + \beta mc^2 - e\,\Phi(\boldsymbol{r}), \tag{8}$$

where e is the elementary charge, and $\Phi(\boldsymbol{r})$ and $\boldsymbol{A}(\boldsymbol{r})$ are the scalar electric and vector magnetic potentials at the position of the electron, respectively (note that the interaction with the electromagnetic fields is introduced by applying minimal coupling).[9,10] The Dirac equation is, in this case,

$$i\hbar\,\frac{\partial\psi(\boldsymbol{r},t)}{\partial t} = \widehat{h}^{\mathrm{D-EM}}\ \psi(\boldsymbol{r},t) \tag{9}$$

By multiplying now both sides of this equation by β/c one obtains the covariant (*i.e.*, Lorentz invariant) expression for the above Dirac equation, which reads

$$\left[\gamma^{\mu}\pi_{\mu} - mc\,\mathbb{1}_4\right]\psi(x^{\mu}) = 0, \tag{10}$$

were a more convenient notation of contravariant, a^{μ}, and covariant, a_{μ}, 4-vectors was used.[8] In this way $\mathbb{1}_4$ is the 4×4 identity matrix, and $x^{\mu} = (ct, \boldsymbol{r})$ is the 4-vector position. It is wealthy to remark that all covariant and contravariant 4-vectors are connected through the Minkowski tensor metric, whose elements $\eta_{\mu\nu} = \eta^{\mu\nu}$ (in orthonormal basis) are such that $a_{\mu} = \eta_{\mu\nu}\, a^{\nu}$, with $\eta_{00} = -\eta_{11} = -\eta_{22} = -\eta_{33} = 1$ and $\eta_{\mu\nu} = 0$ for $\mu \neq \nu$.

As easily seen, in eq. 10 there is a new 4-vector: $\gamma^{\mu} = (\gamma^0, \boldsymbol{\gamma})$, whose components in the standard representation are $\gamma^0 = \beta$ and $\boldsymbol{\gamma} = \beta\boldsymbol{\alpha}$. Furthermore, $\pi_{\mu} = p_{\mu} + eA_{\mu}$ is the 4-vector mechanical momentum, where

$$p_{\mu} = i\hbar\partial_{\mu} = i\hbar\frac{\partial}{x^{\mu}} = i\hbar\left(\frac{\partial}{\partial(ct)}, \nabla\right) = (p_0, -\boldsymbol{p}) = \left(\frac{E}{c}, -\boldsymbol{p}\right) \tag{11}$$

is the covariant form of the 4-vector canonical momentum, and $A_\mu = (\Phi/c, -\boldsymbol{A})$ is the covariant form of the 4-vector potential. They fulfill the relations $\gamma^\mu p_\mu = \gamma^0 p_0 - \boldsymbol{\gamma}\cdot\boldsymbol{p}$ and $\gamma^\mu A_\mu = \gamma^0(\Phi/c) - \boldsymbol{\gamma}\cdot\boldsymbol{A}$, respectively.

Now, any equation of motion is said to be covariant when it has the same form in any inertial frame of reference. The left-hand side of eq. 10 is invariant under a Lorentz transformation because it is a 4-scalar quantity, and therefore it is simple to obtain its energy spectrum. For a single Dirac particle at rest (*i.e.*, when $\boldsymbol{p} = \boldsymbol{0}$) and in the absence of electromagnetic fields (*i.e.*, for $A^\mu = 0$), eq. 10 can be rewritten as

$$\gamma^0 p_0\,\psi = mc\,\psi \quad \text{or} \quad p_0\,\psi = mc\gamma^0\,\psi. \tag{12}$$

Since the operator γ^0 has two doubly degenerate eigenvalues (each with values ±1), one obtains two positive-energy and two negative-energy solutions from eq. 12. Then, according to eq. 2, if the free electron is not at rest ($\boldsymbol{p} \neq \boldsymbol{0}$), there will be two doubly degenerate eigenstates, with eigenenergies $E = \pm\sqrt{m^2c^4 + p^2c^2}$.

The free-electron Dirac equation is a key expression in RQC, being it the only one based on sufficiently good theoretical grounds. To study one-electron atoms or molecules, one must consider the potential energies arising from the electromagnetic interactions that occurs between the electron and a single nucleus (for atoms) or between the electron and each of the nuclei in the system (in the case of molecules).

Although the electron-nucleus interaction associated with the Coulomb electrostatic potential produced by fixed nuclei is only an approximate description of the real interaction between these particles, valid only within the clamped-nuclei approximation, common practice in RQC is to consider these potential energies as arising from the classical Coulomb electrostatic interactions. Then, for an electron in the electrostatic field produced by M clamped nuclei, the one-electron time-independent Dirac Hamiltonian is expressed as

$$\widehat{h}^{\mathrm{D}}(\boldsymbol{r})\,\psi(\boldsymbol{r}) = \left(c\,\boldsymbol{\alpha}\cdot\boldsymbol{p} + \beta mc^2 - \mathbf{1}_4\sum_{K=1}^{M} e\,\Phi_K(\boldsymbol{r})\right)\psi(\boldsymbol{r}), \tag{13}$$

where

$$\Phi_K(\boldsymbol{r}) = \frac{1}{4\pi\varepsilon_0}\int \frac{\rho_K(\boldsymbol{r}')}{|\boldsymbol{r}-\boldsymbol{r}'|}\,\mathrm{d}\boldsymbol{r}'. \tag{14}$$

In eq. 14, $\Phi_K(\boldsymbol{r})$ is the instantaneous Coulomb potential operator produced by nucleus K at the position of the electron, ε_0 is the vacuum permittivity, and $\rho_K(\boldsymbol{r}')$ is the charge density distribution of nucleus K at an arbitrary position $\boldsymbol{r}'$.

The energy spectra and bispinors that arise from solving eq. 13 are usually the starting point for getting the solutions of N-electron atomic or molecular systems. In line with this, the N-electron wavefunctions are commonly written in terms of one-electron wavefunctions using, *e.g.*, Slater-type determinants. The use of eq. 13 to write an N-electron wavefunction of an N-electron atomic or molecular systems in the clamped-nuclei approximation as an Slater-type determinant solution was first guessed by Swirles.[4] Considering that all internal magnetic interactions (*i.e.*, the electron-electron Breit interactions and also higher-order interactions) can be neglected, she proposed to use the 4C wavefunction for a single electron in a central field as a starting point.

It is possible to extend Swirles' proposal to include electron-electron Breit interactions,[11] such that the N-electron time-independent wavefunction $\Psi(\boldsymbol{r}_1, \boldsymbol{r}_2, \ldots, \boldsymbol{r}_N)$ be the solution of the following equation for M clamped nuclei,

$$\widehat{H}_0^{\mathrm{DCB}}\,\Psi(\boldsymbol{r}_1,\boldsymbol{r}_2,\ldots,\boldsymbol{r}_N) = E_0\,\Psi(\boldsymbol{r}_1,\boldsymbol{r}_2,\ldots,\boldsymbol{r}_N), \tag{15}$$

where

$$\widehat{H}_0^{\mathrm{DCB}} = \sum_{i=1}^{N}\widehat{h}_i^{\mathrm{D}} + \mathbb{1}_4\sum_{i<j}^{N} V_{ij}^{\mathrm{CB}} + \mathbb{1}_4\sum_{K<L}^{M} V_{KL}^{\mathrm{C}}. \tag{16}$$

The first term on the rhs of eq. 16 is a sum of the one-electron Hamiltonians of eq. 13, whose summation runs over all the N electrons in the system. Besides, V_{ij}^{CB} and V_{KL}^{C} stand for the Coulomb-Breit electron-electron and Coulomb nucleus-nucleus interaction energies, respectively, for electrons i and j, and nuclei K and L. As noted above, these potential energies are considered within classical fields. In the Coulomb gauge, they can be written, respectively, as

$$V_{ij}^{\mathrm{CB}} = \frac{1}{4\pi\varepsilon_0}\frac{e^2}{r_{ij}}\left[1 - \frac{1}{2}\left(\boldsymbol{\alpha}_i \cdot \boldsymbol{\alpha}_j + \frac{(\boldsymbol{\alpha}_i \cdot \boldsymbol{r}_{ij})\,(\boldsymbol{\alpha}_j \cdot \boldsymbol{r}_{ij})}{r_{ij}^2}\right)\right] \tag{17}$$

and

$$V_{KL}^{\mathrm{C}} = \frac{1}{4\pi\varepsilon_0}\frac{Z_K Z_L e^2}{R_{KL}}, \tag{18}$$

where $\boldsymbol{r}_{ij} = \boldsymbol{r}_i - \boldsymbol{r}_j$ is the position of electron i relative to electron j (with absolute value $r_{ij} = |\boldsymbol{r}_{ij}|$), $\boldsymbol{R}_{KL} = \boldsymbol{R}_K - \boldsymbol{R}_L$ is the position of nucleus K with respect to nucleus L (with $R_{KL} = |\boldsymbol{R}_{KL}|$), and Z_K and Z_L the atomic numbers of nuclei K and L, respectively. The potential energy of the repulsive interaction between each pair of nuclei has been taken as interactions between point nuclei. This approximation is perfectly justified by applying Gauss's law, considering that the distance between the centers of any two nuclei in a molecule is approximately five orders of magnitude greater than the mean square radius of any nucleus, and that the charge distributions for this approximation can be assumed to be spherically symmetric.

The electron-electron Coulomb-Breit interaction energy presented in eq. 17 does not satisfy Lorentz invariance. However, since the Lorentz-invariant interaction arising from quantum electrodynamics (QED), *i.e.*, from considering the emission and absorption of virtual photons, when retaining only the two lowest orders in perturbation theory, becomes computationally infeasible, it is necessary to resort to approximations. Given its small magnitude in situations of chemical interest, it is reasonable to neglect the effects arising from the retardation of the electron-electron interaction due to the finite speed of its transmission. This approximation, which implies considering zero frequency of the exchanged photon (*i.e.*, $\omega = 0$), leads to eq. 17. This equation can also be seen as the sum of three contributions within the Coulomb gauge: the charge-charge instantaneous Coulomb interaction (first term of eq. 17), the current-current instantaneous Gaunt interaction

$$V_{ij}^{\mathrm{Gaunt}} = -\frac{1}{4\pi\varepsilon_0}\frac{e^2}{r_{ij}}\,\boldsymbol{\alpha}_i \cdot \boldsymbol{\alpha}_j, \tag{19}$$

and a remaining term, which comes from an additional gauge contribution,[7,12]

$$V_{ij}^{\mathrm{gauge}} = \frac{1}{4\pi\varepsilon_0}\frac{e^2}{2\,r_{ij}}\left(\boldsymbol{\alpha}_i \cdot \boldsymbol{\alpha}_j - \frac{(\boldsymbol{\alpha}_i \cdot \boldsymbol{r}_{ij})\,(\boldsymbol{\alpha}_j \cdot \boldsymbol{r}_{ij})}{r_{ij}^2}\right). \tag{20}$$

We stress here our broad accord with the following statement by Werner Kutzelnigg: "*[In] relativistic quantum chemistry […] one starts from an ad hoc relativistic many-electron Hamiltonian (for which there is no unique prescription), the relation of which to QED is often unclear, and which is largely justified by a compromise of good performance and feasibility*."[13]

Key steps for solving the Dirac equation in atoms and molecules

Since eqs. 13 and 15 were first proposed, several key steps were necessary to do to obtain reliable and useful solutions. From the very beginning, difficulties arose with the formalism and also with its implementation. The emergence of these solutions took a long time to occur, meaning that several years, even decades, passed before they were proposed and then accepted. Readers interested in more detail are invited to have a look at Refs. 14, 15 to follow in more detail the development of relativistic quantum chemistry over the last century. Some of the most recent developments, along with setting forth some of the unsolved problems in RQC, are mentioned in Refs. 13, 16–19.

In addition to the considerations given above, we should mention a methodology that probably is one of the most widely used for including, in some way, relativistic effects into practical calculation.[20] It assumes that the chemistry of an element is only determined by its valence electrons. In this scheme the core electrons remain essentially inert and at most playing an indirect role in the description of the chemistry of a given molecule. It is known as the effective core potential (ECP) being its main virtue the considerable reduction of the computational effort in calculations by avoiding the costly explicit treatment of the atomic cores in the calculations and, at the same time, an implicit treatment of the major relativistic effects for the valence. The method of relativistic ECP is treated in some extend in Refs. 19–21.

As we mentioned in the previous section, the first step of the formalisms developed to solve eq. 15 was given by Bertha Swirles in 1935. She proposed a relativistic model Hamiltonian for *N*-electron systems resembling what was, at that time, routinely used within the NR domain. In 1967, Yong-Ki Kim published the first relativistic self-consistent-field theory for closed-shell atoms,[22] applying the usual NR basis-set expansion technique for large (L-) and small (S-) spinors in terms of Slater-type basis functions, though getting problems with the variational stability of the solutions. Those problems were solved more than a decade later, in 1984, by Stanton and Havrillak,[23] and a few years later, Ian Grant and Harry Quiney proposed a well-defined method to solve the one-electron Dirac equation for atoms, modeling the Coulomb electron-nucleus interaction by using point-like nuclear charge density distributions.[24] The kinetic balance prescription, which relates large and small components of 4C wavefunctions, was found to be related to the minimax principle discovered by James Talman,[25] which has been used routinely since then in 4C molecular codes.

By the late 1970s, few semi-empirical molecular codes that depended on heavy atom parameters were available, such as the relativistically parametrized extended Hückel method (REX).[26] By using them, it was possible to introduce relativistic effects into molecular calculations, although the first proper 4C molecular code appeared in the early 1980s. Results with the first version of the Molecular Fock-Dirac (MOLFDIR) program package were published in 1986.[27] After that milestone, all-electron relativistic calculations on polyatomic molecules became feasible. We must emphasize the influence of the development of the (nowadays) open-source DIRAC code (which stands for "Direct Iterative Relativistic All-electron Calculations") on the entire relativistic quantum chemistry community. It was written mainly by Trond Saue, Lucas Visscher, Hans J. Aa. Jensen, Radovan Bast, and Andre S. P. Gomes.[28,29] It enabled all-electron calculations of molecular properties using relativistic quantum chemical methods since its first version in 1996.[30,31]

Novelties, weaknesses and subtleties

Following the discovery of the Dirac equation, several new and unexpected physical insights emerged for one-electron atomic systems, as well as for *N*-electron atoms or molecules. In this section, we will mention a few of the numerous novelties, weaknesses, and subtleties that we assume are of general interest to the broader quantum chemistry community.

Novelties

The relativistic version of the quantum theory has some very interesting new features, among which we mention the following:

(a) The appearance of a negative energy branch in the energy spectra, which arises after solving the time-dependent Dirac equation. This fact enables the prediction of the antielectron (known as positron) particles by Paul Dirac, which were first observed experimentally by Carl D. Anderson in August 1932,[32] a few years after its prediction.

(b) As can be observed in eqs. 2, 13, and 15, the physical variables are expressed by matrix operators, whose minimum dimension is four. Therefore, in this representation, the wavefunction has four components.

(c) The spin-orbit (SO) correcting terms to the NR energies or physical properties arise naturally after applying a transformation of the basic elements of the Dirac formalism from 4C to 2C theory. This fact makes the SO mechanism a mechanism that contains more than one term, meaning spin-orbits with contributions of one-body, two-body, *etc.* Those SO mechanisms are intrinsically included in the 4C expressions.[7,19]

(d) A formal treatment of particle/antiparticle creation/annihilation must be included in one form or another because they can be observed in high-energy physics, when enough energy is available. While these creation/annihilation phenomena will not be explicitly observed in the low-energy domain, their effects must be taken into account.

All these novelties must be considered in low-energy physics phenomena, meaning in the problems studied with RQC methods. We believe it is important to highlight here that, within the quantum chemistry community, it is common to attempt to understand most low-energy physics phenomena in terms of known NR mechanisms. This approach (which we call "NR way of thinking") has been applied for the past 70 years in spectroscopic studies with satisfactory results, and this is one of the reasons why the understanding and use of novel relativistic concepts does not easily permeate the community, especially given that 2C semi-relativistic formalisms are often sufficient to explain many of the observed relativistic effects. In any case, sooner or later, we must accept that the full relativistic mechanisms (4C mechanisms) are the ones that better express and give the deepest physical insights into the most fundamental quantum chemical processes.

Strong restrictions

Several important constraints arise when quantum mechanics is expressed within the relativistic regime. These are related to the fact that some preliminary knowledge is lost in this domain, or at least cannot be understood as well as in the more widely studied (within the framework of quantum chemistry) NR context. Below, we list those that we consider to be the most significant:

(a) The exact expression for the relativistic many-body Hamiltonian is so far unknown (and will probably remain unknown for the foreseeable future).[13] This fact makes the Hamiltonian used within the relativistic regime emerge from the outset as a model Hamiltonian.

(b) Given the weakness mentioned in the previous point, the usual top-down approach should probably be replaced by a bottom-up approach. This means that one can choose to move *from less accurate expressions for the Hamiltonians to more precise models.*

(c) Equation 15 cannot be expressed in a Lorentz covariant form because:
  i) Each particle must have its own time coordinates.
  ii) The Hamiltonian cannot be expressed in a closed form (electrons interact mediated by virtual photons, which implies that there are no instantaneous interactions).

(d) Relativistic effects can be greater than 100 % of the NR energy or property values. This means that perturbation theory must be used with great caution.

(e) In the case of magnetic properties, there is no exact relationship within the relativistic domain between the paramagnetic-like contribution (also called *ee* contribution, as will be discussed later) to the NMR shielding tensor of a given nucleus *K*, $\boldsymbol{\sigma}_K^{ee}$, and the electronic (*ee*) part of the nuclear spin-rotation (NSR) tensor of the same nucleus in the same molecule, $\boldsymbol{M}_K^{\mathrm{elec},\,ee}$.[33,34] An exact relationship is apparent within the NR domain.[35,36] This fact makes it necessary to rely on a bottom-up procedure to obtain a suitable relationship between some pairs of response properties, a procedure that will be mentioned in Section "Two complementary procedures: top-down and bottom-up".

Operators vs. representation of operators

Among the subtleties underlying common quantum expressions, when working within the relativistic framework, it is the preponderance of the meaning of the operator representation over the meaning of their abstract expressions. Some examples are shown below:

(a) The physical meaning of the one-electron Dirac Hamiltonian operator compared to its representation in a given space.

In the NR domain, energy is usually written as the sum of two terms representing kinetic energy and potential energy. We may then ask ourselves about what would happen within the relativistic domain. In other words, can these two NR terms be generalized to the relativistic regime with the same meaning?

$$E^{\mathrm{NR}} = T^{\mathrm{NR}} + V^{\mathrm{NR}} \quad \rightarrow \quad E^{\mathrm{R}} \overset{?}{=} T^{\mathrm{R}} + V^{\mathrm{R}}.$$

In order to answer such a query, we can tell that it is more meaningful to work within an operator representation than to work with operators themselves. So, in our case, the representation of the energy operator associated with a relativistic bound state $|\psi\rangle$ of a single electron in a central potential within a 4C regime is such that it goes to its NR values when $c \rightarrow \infty$:

$$\langle\psi|h^{\mathrm{D}}|\psi\rangle = \langle\psi|\left(c\boldsymbol{\alpha}\cdot\mathbf{p} + (\beta - \mathbb{1}_4)mc^2 + \mathbb{1}_4\ V\right)|\psi\rangle \overset{c\rightarrow\infty}{\rightarrow} E^{\mathrm{NR}},$$

where we have aligned the rest energy term to the NR energy scale.

(b) Is it possible to obtain a well-defined NR one-electron angular momentum operator from a relativistic operator? The relativistic operator $\beta(\boldsymbol{r}\times c\boldsymbol{\alpha})$ is a good candidate, but it is not a constant of motion because it does not commute with the unperturbed relativistic Hamiltonian. Then, one cannot use it to search for a meaningful relationship among the 4C and NR angular momentum operators. One of the most feasible and reliable ways of obtaining a 4C operator representation of angular momenta is to apply the following identity:[8]

$$m\langle\psi|\left(\boldsymbol{r}\times c\boldsymbol{\alpha}\right)|\psi\rangle = \langle\psi|\beta\left(\boldsymbol{r}\times\mathbf{p}\right)|\psi\rangle + \hbar\langle\psi|\beta\boldsymbol{\Sigma}|\psi\rangle, \tag{21}$$

which is not valid at the (Heisenberg-type) operator level.

Grandy was smart enough to work with one of the earliest attempts to define a 4C magnetic dipole moment operator, $\boldsymbol{\mu}$, in terms of the 4C position and 4C velocity operators to obtain the following equality:

$$\langle\psi|\boldsymbol{\mu}|\psi\rangle = \frac{e}{2mc}\langle\psi|\beta\boldsymbol{L}^{\mathrm{R}}|\psi\rangle + \frac{e}{mc}\langle\psi|\beta\boldsymbol{S}^{\mathrm{R}}|\psi\rangle. \tag{22}$$

This equation shows that one could consider the 4C representation of the magnetic dipole moment operator $\boldsymbol{\mu} = (e/2)\boldsymbol{r}\times c\boldsymbol{\alpha}$, as the sum of two terms: one containing the 4C representation of the orbital angular momentum $(\boldsymbol{L}^{\mathrm{R}} = \mathbb{1}_4\ (\boldsymbol{r}\times\boldsymbol{p}) = -i\hbar\ \mathbb{1}_4\ (\boldsymbol{r}\times\nabla))$, and another containing the 4C representation of the electron spin ($\boldsymbol{S}^{\mathrm{R}} = (\hbar/2)\ \boldsymbol{\Sigma} = (-i\hbar/4)\ \boldsymbol{\alpha}\times\boldsymbol{\alpha}$).

This is a very interesting finding, because we can now realize that the 4C magnetic dipole moment operator $\boldsymbol{\mu}$ (used often within the relativistic domain) could likely contain two terms: one that is “spin-like-independent” and another one that is “spin-like-dependent”.

Virtual processes including negative-energy states

In high-energy physics, one must consider that, when enough energy is available in an appropriate experiment, particle-antiparticle pairs can be created or annihilated. What would happen if there were not enough energy available? Can processes in which these pairs are neither created nor annihilated due to a lack of enough energy, as happens with the likely population of unoccupied states of an atom or molecule, be considered virtual?

When considering magnetic properties such as NMR spectroscopic parameters within a relativistic framework, negative-energy contributions to NMR shielding calculations (in a sum-over-state formulation) were shown to be related to their diamagnetic contributions.[15,37–39] On the other hand, when using relativistic polarization propagator theory (RelPPT),[40] 4C diamagnetic-like contributions are found to arise from matrix elements of tensor operators that are calculated between positive-energy occupied molecular orbitals (MO) and negative-energy unoccupied MOs.[39,41] There are some other interesting explanations about the origin of the contributions of the negative-energy branch of the energy spectra to magnetic properties.[15,42,43]

At the random phase approximation (RPA), one of the subsets of the excitation manifold of operators can be related to virtual excitations/de-excitations between positive-energy one-electron states and negative-energy one-electron states. This fact was interpreted in our research group as processes related to the creation/

annihilation of virtual pairs. One of the earliest findings supporting this assumption was published in 2005.[44] It was found that the "*branch of negative-energy virtual excitations […] contribute with almost all the total value of* σ^d. *This branch of energies is* $-4mc^2 \leq \epsilon_{\bar{s}} \leq -2mc^2$", where σ^{d} is the diamagnetic contributions to the NMR isotropic shielding constant and $\epsilon_{\bar{s}}$ is the $\bar{s}$-MO energy. This finding shows that the physical processes that could explain the diamagnetic contribution to σ within a relativistic framework do not have enough energy available for the creation of electron-positron pairs because, at the RPA level of theory, there are two virtual excitations involved.

It may be useful to recall that, within the relativistic domain, only one electronic mechanism is involved in each of the two main NMR spectroscopic parameters. Therefore, for relativistic calculations of NMR shieldings there is no A^2 term in the magnetic perturbative Hamiltonian, so that the paramagnetic and diamagnetic terms arise from the same linear perturbative Hamiltonian, whose matrix elements are calculated between excitations considering unoccupied electronic states of positive energy (for paramagnetic-like terms) and unoccupied states of negative energy (for diamagnetic-like terms).

Time-reversal symmetric operators generalizing NR spin-symmetric operators

Since the earliest times of the quantum physics the spin is considered a fundamental property of the electron, ubiquitous in NR quantum chemistry. Besides, it is well known that when NR operators have a well-defined spin symmetry, this feature is exploited to reduce computational costs. The spin symmetry of NR operators is also used to appropriately express their matrix elements. But when relativity is properly introduced, one lose the possibility to work with a universally accepted spin operator.[45] While different theoretical considerations lead to different expressions of spin operators, the definite relativistic spin operator must be justified by experimental evidence. The correspondence between experimental measurement procedures and mathematical spin operators remains a completely open question.[46]

Spin is no longer a good quantum number in RQC, and therefore, well-behaved relativistic operators cannot be written with such a symmetry. This could lead to a significant loss of efficiency in relativistic calculations, which would be desirable to avoid. As mentioned in the book of Dyall and Faegri,[7] "time-reversal symmetry takes the place of spin symmetry …Time-reversal symmetry includes the spin symmetry of NR systems, but there are significant differences from spin symmetry for systems with a Hamiltonian that is spin-dependent". In fact, one can recover the spin-like symmetry through the use of the time-reversal restricted operators, known as Kramer operators which give the most compact representation of an operator.[7] More than 30 years ago, it was shown that such a discrete symmetry, time reversal, generalizes the spin-restricted symmetry in the sense that, among other advantages, the matrix representation of the relativistic operators can be performed within the R-restricted representation. From it the spin-restricted representation of that operators can be naturally obtained within the NR limit.[47,48] From that first proposal, several powerful Kramer's restricted formalisms were developed to make calculations more efficient.[49,50] This has also been the case in the implementation of the relativistic coupled-cluster methodology.[51]

Spin-orbit interactions as one of several spin-dependent relativistic corrections

Starting from the Dirac one-electron Hamiltonian, one can obtain the first-order relativistic corrections to it by applying perturbation theory. There are several procedures for doing it, but the point here is that one always obtains three perturbative Hamiltonians: two that are spin-independent (mass-velocity and Darwin Hamiltonians) and one that is spin-dependent (SO Hamiltonian). Typically, perturbation theory is not extended further, and as such, one may consider that there is only one type of spin-orbit (SO) term, referring to expressions involving all variations of the interactions between spin angular momentum operators and orbital angular momentum operators.[52]

Then, the SO corrections arise when the perturbation theory is written using the $(1/c)$ parameter within an NR framework. Such a correction does not appear explicitly in a 4C framework, as happens with the spin angular momentum operators known as spin operators for short. What one can safely say is that, in a relativistic framework, the SO corrections are one of the likely correcting terms that are implicitly included in what we may call "pseudo-spin-dependent" (or just "spin-dependent") corrections.

The influence of electron spin-dependent contributions on atomic and molecular energies, as well as on many other properties, has been studied using various formalisms. In a 4C framework, a modified Dirac operator[53] allows for a separation of the Dirac Hamiltonian in spin-free (SF) and spin-dependent terms,[54] so that the transformed SF Hamiltonian, with several terms in common with the Breit-Pauli Hamiltonian, can be used in a 4C variational procedure. The spin-dependent terms in the Hamiltonian can then be included or suppressed. This can be partially addressed by describing the electronic wavefunction in such a way as to include the one-body Pauli SO interaction within it by perturbation theory. This provides results that are in close agreement with experimental data for light-element-containing systems,[52,55–57] but for systems containing one or more heavy nuclei, this description leads to inaccurate and therefore unreliable results.

Theories and models for 4C and 2C studies

As mentioned in the Introduction, merging the requirements of the two most influential physical theories formalized at the beginning of the last century, the quantum theory and the special theory of relativity, uncovered a completely new conception of the material world. Such a conception was inserted on top of both theories, but perhaps taken separately. This may be why it took so long for scientists to begin questioning themselves deeply about the completely new physical insights generated by relativistic quantum physics. In fact, the first ideas concerning this separation were given in the first sentence of Dirac's seminal paper of 1929 (Italian emphasis is ours): "The general theory of quantum mechanics is now almost complete, *the imperfections that still remain being in connection with the exact fitting in of the theory with relativity ideas*. These give rise to difficulties *only when high-speed particles are involved, and are therefore of no importance in the consideration of atomic and molecular structure and ordinary chemical reactions*, in which it is, indeed, usually sufficiently accurate if one neglects relativity variation of mass with velocity and assumes only Coulomb forces between the various electrons and atomic nuclei".[5] This means that he seems to assumes that the bold ideas behind both theories should be taken separately, and also that the chemistry is based only on what happens to valence electrons, which do not have high-speed.

Relativistic effects have consequences that are observables, and are, as Pekka Pyykkö express it: "more common than we think".[58] They could be "visible", like the color of gold, or intrinsic, like the values of the NMR spectroscopic parameters of heavy-atom containing molecules.[14,17]

Searching for the best path to include relativistic effects on the treatment of quantum systems, one can adopt two different, though complementary, ways of doing it. In what follows in this section, we give some of the most commonly used procedures, though stressing the fact that quantifying relativistic effects is not the whole story. As mentioned in Section "Novelties", some novelties and subtleties which are still not fully understood. Therefore, we will try to provide some insights on how one can overcome these challenges. Furthermore, at the end of this section, we introduce some of the basic theoretical aspects related to the treatment of weak interactions in phenomena associated with low-energy physics, an area of research whose theoretical and experimental development has seen significant growth in recent decades.

Two complementary procedures: top-down and bottom-up

Nature satisfies relativistic postulates. This means that they must be included in one form or another. One can start from exact (perturbed or unperturbed) relativistic Hamiltonians and then propose approximations through different approaches. This procedure is known as "top-down." One can also start from the NR limits of these operators and add relativistic corrections by introducing perturbative Hamiltonians. This procedure is known as "bottom-up." Both have strengths and weaknesses.

The reliability of top-down procedures depends on knowledge of the exact relativistic expressions from which one starts, and this condition is fulfilled only in very few cases and with a small number of degrees of freedom. In the case of the relativistic N-electron Dirac-Coulomb Hamiltonian, all electromagnetic interactions are treated classically. If these interactions were considered according to the postulates of QED, it would not be possible to use an exact Hamiltonian, and then a bottom-up procedure must be used to include QED effects.[13,59]

The opposite and most usual procedures for obtaining the relativistic effects of any physical property consist of using perturbation theory on top of the unperturbed Schrödinger-type solutions. There are a large number of models and theories that use this type of procedure; some of them will be mentioned in Section "Two-component formalisms for describing energy spectra and molecular response properties". Here we will only mention one of the newest developments that permit us to find a few relationships among atomic or molecular properties that include relativistic effects at different levels of approximation. They were found using the bottom-up procedure, taking the Linear Response within the Elimination of the Small Components (LRESC) model as the basic model.[60] They are: i) the NMR magnetic shielding ($\boldsymbol{\sigma}_K$) and NSR ($\boldsymbol{M}_K$) tensors of a given nucleus K,[61,62] and ii) the rotational $\boldsymbol{g}$ and magnetic susceptibility or magnetizability ($\boldsymbol{\chi}$) tensors.[63]

Computational codes based on four-component theory

The calculation of response properties at the 4C level usually starts from generalizing the 2C theories and models. Most of the wave functions-based methods available for 2C molecular property calculations were reviewed in Ref. 64. A more extensive treatment of the theories and models used to calculate molecular properties can be found in Ref. 6. At the moment, there are only a few implementations of 4C formalisms, of which we can mention the following ones:

(a) DIRAC,[29]
(b) RESPECT,[65]
(c) BERTHA,[66]
(d) BDF,[67]
(e) UTCHEM,[68]
(f) PYSCF,[69]
(g) CHRONUSQ.[70]

The pioneering DIRAC code is one of the first relativistic quantum chemistry computational programs ever available, and it is also one of the most widely used nowadays for calculating molecular properties in a 4C relativistic context. This code contains some functionalities implemented based on the relativistic polarization propagator theory, to which we will dedicate Section "Polarization propagators". Through this discussion, we seek to highlight some discoveries of electronic mechanisms underlying molecular properties in relativistic contexts, which have been identified thanks to the use of this methodology.

Two-component formalisms for describing energy spectra and molecular response properties

The development of any formalism whose goal is to apply quantum theory to atomic and molecular systems usually starts by focusing on getting the electronic structure as accurately as possible, and then, in a second stage, it is applied to the calculation and analysis of response properties. This is not always the case, as happened with some semi-relativistic models which were oriented from the outset to response properties using only perturbation theory and some other mathematical tools.

We start this section by mentioning some of the 2C formalisms that were developed for describing the energy spectra, and afterwards, we will mention a few semi-relativistic models that were oriented towards the search for response properties.

Historically, the development of these two- or one-component methods sought to take advantage of all the machinery used in the NR regime, specifically for describing dynamic and non-dynamic electron correlation, calculating response properties, and describing excited states.

The first method that accomplished to reproduce exactly the one-electron energies of the 4C Dirac method was derived by Kenneth Dyall, who presented the Normalized Elimination of the Small Component (NESC) methodology as the first 2C semi-relativistic approach in 1997,[71] based on his previous proposal to separately analyze contributions from the spin-free part of the modified Dirac Hamiltonian and its spin-dependent part.[54] A crucial aspect for this development was the expression of the Dirac equation in matrix form.

Quasi-relativistic methods can be classified as either operator-based or matrix-based,[72,73] and both formulations that use exact-two-component (X2C) Hamiltonians are equivalent.[74] Relativistic methods can also be divided into perturbative and nonperturbative,[64] but the distinction between the two groups is blurred in many cases.

Given their importance in the development of RQC area of research, we mention them, though only briefly:

- The infinite order Douglas-Kroll-Hess theory (DKH),[75] that allows for a generalized transformation up to an arbitrary order and whose original idea dates back to 1974 and is due to Douglas and Kroll,[76] and extended by Hess[77,78] to low orders.
- The Infinite-Order Two-Component (IOTC) method,[79] which introduces nonsingular 2C Hamiltonians via a free-particle Foldy–Wouthuysen transformation[80] followed by a block-diagonalizing transformation, which was also converted into matrix algebra.[81]
- The Zeroth Order Regular Approximation (ZORA) method,[82,83] based on a regular approximation to the relativistic Hamiltonian. If a normalization of the wave function is carried out, at infinite order, it leads to the Infinite Order Regular Approximation (IORA) method.[84] Both are based on the same Hamiltonian but use different wave function metrics.
- Zou, Filatov, and Cremer (ZFC) recently addressed and solved some computational problems needed to obtain solutions to the NESC equations,[85] which allowed the method to be applied to the routine calculation of first-order and second-order response properties, and extended it to a 2C version that includes SO coupling effects.[86,87]
- Within the framework of the spin-free (SF)-X2C theory, Gauss and Cheng developed the SFX2C-1e scheme to calculate molecular geometries, vibrational frequencies, and magnetic properties at the level of Dirac-exact methods.[88–90]
- Recently, an efficient and numerically accurate matrix approach was presented to correct both scalar-relativistic and spin–orbit two-electron picture-change effects (arising within an X2C Hamiltonian framework).[91] It constitutes a 2C approach that holds the accuracy of the 4C results at a fraction of its computational cost. The picture-change effects are related to the required transformation of all the operators, related to the transformation of the Hamiltonian, used to achieve decoupling of the positive and negative energy solutions with independent 2C wavefunctions.[92]

Relativistic effects on several second-order response properties have also been studied in detail, analyzing the physical mechanisms involved, using the LRESC model, which was originally introduced to investigate NMR shielding tensors.[93] Among these properties, we can mention the NSR tensors,[33] the molecular rotational g-tensors and magnetic susceptibility (or magnetizability),[63] and the parity-violating (PV) contributions to NMR shieldings and NSR tensors.[94] Besides, it was also applied to study first-order properties, like the electric field gradients (EFG).[95]

Within the LRESC model, the individual electronic mechanisms giving rise to relativistic contributions (at different orders in perturbation theory in c^{-2}) can be easily classified into those that depend explicitly on the electronic spin and those that do not. This makes it possible to unambiguously identify the nature of the main relativistic contributions to each molecular property. The application of this method shows, for instance, that a SO-dependent contribution is dominant in describing the relativistic effects of the anisotropic parameters for the NMR shielding tensor.[96,97] In a framework that includes all the NR and leading-order relativistic terms within a series expansion in c^{-2}, this contribution is a quadratic response function within the NR polarization propagator theory, involving three triplet operators (SO, total NR electronic spin angular momentum, and the sum of Fermi-contact and spin-dipole operators), and it was named SO-S contribution.[98]

Recently, two different ways of including such an SO-related mechanism for the NMR shielding anisotropic parameters for molecules of any symmetry were explored.[97] The results rely on the so-called M–V model, which reveals a relationship between the NSR and NMR shielding tensors in a 4C relativistic context.[61,62] The so-called SO-S mechanism was generalized to a 4C expression in the quest to find the relation between the NSR and the NMR shielding tensors in the relativistic domain.[62] This analysis led to a mechanism within the relativistic 4C framework, whose NR limit is zero and whose lowest-order relativistic contribution is the aforementioned SO-S mechanism. Last but not least, it is worth mentioning that it has recently been shown that a similar mechanism (*i.e.*, within a series expansion in terms of c^{-2}, a quadratic response between three triplet operators involving both the electron spin operator and the SO interaction) explains most of the relativistic effects in the parity-violating contributions to both, the NMR shielding and NSR tensors.[94]

Among other methodologies to describe relativistic effects on NMR shielding tensors, a perturbation theory approach developed within the Breit-Pauli perturbation theory (BPPT) within the no-pair approximation, *i.e.*, based on the no-pair Hamiltonian presented by Fukui *et al.*,[99] was proposed by Manninen *et al.*[100] In the case of anisotropic shielding, the BPPT methodology allows identifying the relativistic corrections responsible for most of these effects.[101] However, the SO-S mechanism, which is formally obtained within the LRESC model,[98,102] is included *ad hoc* in BPPT (taking it from the LRESC formalism) since it plays a decisive role in heavy-element containing systems.[103]

For electric properties, electron-spin-dependent corrections are also crucial in describing relativistic effects in heavy-atom containing systems. Applying similar ideas that led to the LRESC model, it was observed that all first-order relativistic corrections to the EFG tensor, in an expansion in terms of the fine-structure constant, are spin-independent.[95] Further developments of this formalism made it possible to identify all second-order spin-dependent mechanisms that contribute to the EFG, showing its importance for accurately describing relativistic effects on that property.[104,105] The importance of SO effects in the EFG was emphasized previously by Pyykkö through the so-called spin-orbit tilting effect, which also occurs in light atoms bound to heavy atoms.[106] Within direct perturbation theory, the importance of SO effects in the same electric property was also studied, showing that they can lead to a significant improvement in the description of the property.[107]

Polarization propagators

Quantum theory does have several formal languages to be expressed.[108] One refers to Paul A. M. Dirac and Richard Feynman, who introduced the path-integral formalism, from which all measurable quantum objects can be obtained.[109,110]

Feynman propagators, which are among the main theoretical tools used within quantum field theory, were first introduced for describing the scattering of high-energy particles, which are considered uncoupled between them. On the other hand, in quantum chemistry, one usually deals with describing the evolution of electronic molecular structures after being perturbed by small external perturbations. In these cases, there is not enough energy available to create/destroy electrons/positrons. The theoretical description of the propagation of such perturbations in statistical physics was initially proposed by Dmitry N. Zubarev in 1960.[111] Jens Oddershede and coauthors applied this theory to boson-like external perturbations on molecules by defining a two-time Green function which are related to mathematical objects known as polarization propagators.[112] Such a theory was first developed within the NR domain and, after some time, extended to the relativistic domain.[40]

Relativistic and NR polarization propagators

In this section, we want to emphasize that explicit expressions for NR polarization propagators can be obtained from their relativistic generalization. Therefore, the relativistic and NR values of the properties calculated with polarization propagators theory can be naturally obtained using the same formalism and computational code. This means that no transformation is required, other than making c go to ∞; this is very similar to what is done to obtain NR values from relativistic expressions in classical physics.

As mentioned above, we must be aware that the polarization propagator's equation of motion is based exclusively on quantum physics. This implies that such an equation does not depend on the regime in which it is written, and so it must be valid in any of them.[40]

It is known that the mathematical object known as (NR or relativistic) polarization propagator is written as[113]

$$\langle\langle\, V^P; V^Q \,\rangle\rangle_E^{\mathrm{R}} = \left(V^{P\dagger}|\widetilde{\mathbf{h}}\right)\mathbf{M}^{-1}\left(\mathbf{h}|V^Q\right) = \widetilde{\mathbf{P}}\ \mathbf{M}^{-1}\ \mathbf{Q}, \tag{23}$$

where the first and last elements of the rhs of eq. 23 are the *perturbators* and the object in the middle is the *principal propagator*. For static properties, $E = 0$, whereas in the case of dynamical properties, $E = \hbar\omega$. What makes those propagators valid within the relativistic or the NR domain is the framework in which each element is written.

When considering the RelPPT, each element (perturbators and principal propagator) is written through the application of a manifold of excitation operators **h** containing two different types of virtual excitations: excitations between occupied and unoccupied positive-energy one-electron states, denoted as *ee*, and excitations and de-excitations between occupied and unoccupied negative-energy one-electron states, denoted as *ep* or *pe*. The virtual excitations *ep* and *pe* stand for the virtual annihilation and creation of electron-positron pairs.

Therefore, eq. 23 can be more explicitly rewritten as[41]

$$\langle\langle\, V^P; V^Q \,\rangle\rangle_E^{\mathrm{R}} = \left(\widetilde{\mathbf{P}}^{ee}\ \ \widetilde{\mathbf{P}}^{ep}\ \ \widetilde{\mathbf{P}}^{pe}\right)\begin{pmatrix} \mathbf{M}^{ee,ee} & \mathbf{M}^{ee,ep} & \mathbf{M}^{ee,pe} \\ \mathbf{M}^{ep,ee} & \mathbf{M}^{ep,ep} & \mathbf{M}^{ep,pe} \\ \mathbf{M}^{pe,ee} & \mathbf{M}^{pe,ep} & \mathbf{M}^{pe,pe} \end{pmatrix}^{-1}\begin{pmatrix} \mathbf{Q}^{ee} \\ \mathbf{Q}^{ep} \\ \mathbf{Q}^{pe} \end{pmatrix}. \tag{24}$$

Actual calculations are performed by applying perturbation theory on the way the elements of **P**, **Q**, and **M** are calculated. This requires that the unperturbed Hamiltonian matrix be written as: $\mathbf{H}_0 = \mathbf{F} + \mathbf{V}$, being **F** the Fock or Dirac-Fock matrix and **V** the fluctuation potential matrix.[112] The first-order approach is known as the random phase approximation (RPA). This is defined in such a way that, in eq. 23, the fluctuation potential appears at first order, and the manifold of excitation operators contains only particle-hole and hole-particle excitations. Therefore, the approximation $\mathbf{h} = \mathbf{h}_2$ holds, with

$$\mathbf{h}_2^{ee} = \left\{a_a^\dagger a_i, a_i^\dagger a_a\right\}, \quad \mathbf{h}_2^{ep} = \left\{a_i^\dagger a_{\tilde{a}}\right\} \quad \text{and} \quad \mathbf{h}_2^{pe} = \left\{a_{\tilde{a}}^\dagger a_i\right\}, \tag{25}$$

where the subindex i stands for the occupied MOs, while the subindex a $(\tilde{a})$ represents the unoccupied MOs belonging to the positive (negative) branch of the energy spectrum.

To discuss the formalism of principal propagators and perturbators, we first show the formal explicit expressions for the perturbators and how they are calculated, and then, we focus on some of the matrix elements of the principal propagator. Some of the three blocks of the perturbators (*ee*, *ep*, and *pe*) are

$$\begin{aligned} \widetilde{\mathbf{P}}^{ee} &= \left(\mathbf{P}^\dagger \,|\, \widetilde{\mathbf{h}}^{ee}\right) = \langle 0|\,[\mathbf{P}, \mathbf{h}^{ee}]\,|0\rangle \\ \widetilde{\mathbf{P}}^{ep} &= \left(\mathbf{P}^\dagger \,|\, \widetilde{\mathbf{h}}^{ep}\right) = \langle 0|\,[\mathbf{P}, \mathbf{h}^{ep}]\,|0\rangle \\ &\dots \\ \mathbf{Q}^{pe} &= (\mathbf{h}^{pe} \,|\, \mathbf{Q}) = \langle 0|\,[\mathbf{h}^{pe}, \mathbf{Q}]\,|0\rangle. \end{aligned} \tag{26}$$

It is seen that the actual expressions of the MO-based perturbator matrices are obtained by solving integrals like the ones given in eq. 26. The explicit matrix elements of a given perturbator, like $\widetilde{\mathbf{P}}^{ee}$, for instance, are

$$(\widetilde{\mathbf{P}}^{ee})_{ia} = \langle 0|\left[P, a_a^\dagger a_i\right]|0\rangle = P_{ia}^{ee}. \tag{27}$$

Similar expressions can be found for the matrix elements arising from all other excitation operators, *i.e.*, $a_i^\dagger a_a$, $a_i^\dagger a_{\tilde{a}}$, and $a_{\tilde{a}}^\dagger a_i$. Then, at the RPA level of approach, both perturbators are written as

$$\widetilde{\mathbf{P}} = \left(\mathbf{P}^\dagger \,|\, \widetilde{\mathbf{h}}_2\right) = \langle 0|[\mathbf{P}, \mathbf{h}_2]|0\rangle = \left(\widetilde{\mathbf{P}}^{ee}\ \ \widetilde{\mathbf{P}}^{ep}\ \ \widetilde{\mathbf{P}}^{pe}\right), \tag{28}$$

$$\mathbf{Q} = (\mathbf{h}_2 \,|\, \mathbf{Q}) = \langle 0|\,[\mathbf{h}_2, \mathbf{Q}]\,|0\rangle = \begin{pmatrix} \mathbf{Q}^{ee} \\ \mathbf{Q}^{ep} \\ \mathbf{Q}^{pe} \end{pmatrix}. \tag{29}$$

Now we show some of the matrix elements of the sub-matrices belonging to the inverse of the principal propagator:

$$\begin{aligned}\mathbf{M}^{ee,ee}_{ia,jb} &= \mathbf{A}_{ai,bj}(0,1) + \mathbf{B}_{ai,bj}(1)\\ \mathbf{M}^{ep,ep}_{i\tilde{a},j\tilde{b}} &= \mathbf{A}_{\tilde{a}i,\tilde{b}j}(0,1) + \mathbf{B}_{\tilde{a}i,\tilde{b}j}(1)\\ &\dots\\ \mathbf{M}^{pe,pe}_{\tilde{i}a,\tilde{j}b} &= \mathbf{A}_{a\tilde{i},b\tilde{j}}(0,1) + \mathbf{B}_{a\tilde{i},b\tilde{j}}(1),\end{aligned} \tag{30}$$

where 0 and 1 in the matrices **A** and **B** means the times the fluctuation potential appears in them. The explicit expressions of some of the matrix elements are

$$\begin{aligned}\mathbf{A}^{pe,pe}_{\tilde{a}i,\tilde{b}j}(0,1) &= -\langle 0|\left[a_i^\dagger a_{\tilde{a}}, \left[a_{\tilde{b}}^\dagger a_j, H_0\right]\right]|0\rangle\\ &= \delta_{\tilde{\mathrm{ab}}}\delta_{ij}\left(\varepsilon_{\tilde{a}} - \varepsilon_i\right) + \langle\widetilde{a}j \parallel i\widetilde{b}\rangle\\ &= \mathbf{A}^{pe,pe}_{\tilde{a}i,\tilde{b}j}(0) + \mathbf{A}^{pe,pe}_{\tilde{a}i,\tilde{b}j}(1)\\ \mathbf{B}^{pe,pe}_{\tilde{i}a,\tilde{b}j}(1) &= \langle ij||\widetilde{b}\widetilde{a}\,\rangle\,.\end{aligned} \tag{31}$$

Once the explicit matrix expressions of both the relativistic perturbators and the principal propagator are known, one can ask oneself about their NR limit. A long time ago, it was shown that the off-diagonal elements of the super-matrices **A** and **B** (*i.e.*, those elements for which $i \neq j$ or $a \neq b$) are quite small; they are of order $\mathscr{O}(c^{-1})$, while the diagonal matrix elements are of order $\mathscr{O}(c^0)$.[39] Thus, the principal propagator shown in eq. 24 can be divided into both diagonal and non-diagonal contributions to the super matrices.

Neglecting the off-diagonal elements of **M**, the linear response in eq. 24 becomes

$$\langle\langle V^P; V^Q\rangle\rangle^{\mathrm{R}}_E \approx \widetilde{\mathbf{P}}^{ee}(\mathbf{M}^{ee,ee})^{-1}\mathbf{Q}^{ee} + \widetilde{\mathbf{P}}^{ep}(\mathbf{M}^{ep,ep})^{-1}\mathbf{Q}^{ep} + \widetilde{\mathbf{P}}^{pe}(\mathbf{M}^{pe,pe})^{-1}\mathbf{Q}^{pe}. \tag{32}$$

The first term of the rhs of eq. 32 is related to the "*ee*" or "paramagnetic-like" contribution to the response function (since in the case of magnetic properties, its NR limit gives their paramagnetic contributions), while the sum of the second and third terms is related to its "*pp*" or "diamagnetic-like" contribution.[39] As shown by the prescriptions underlying the validity of eq. 32, the best manner to obtain the "*ee*" and "*pp*" contributions that are closest to its equivalent NR paramagnetic and diamagnetic contributions requires approximating the full matrix **M**. In other words, within the relativistic domain, there is no way to disentangle the paramagnetic and diamagnetic contributions from magnetic properties, which are, on the contrary, well defined within the NR domain. Furthermore, they arise as an "artifact" that appears only when working within the NR regime. It is worth emphasizing here that these two different type of contributions are not (*i.e.*, they cannot be) well defined in relativistic theory. In such a theory such a distinction is unavoidable due to the principal propagator is obtained as an inverse of the matrix **M** that contains all kind of excitations.

Regarding magnetic properties that can be expressed in terms of relativistic linear responses, whose NR contributions are well known, it is worth noting what happens with the NMR *J*-coupling tensors. *J* couplings are expressed in the NR regime as the sum of four well-defined mechanisms (which are four NR linear responses), usually called FC, SD, PSO, and DSO. The sum of these four mechanisms constitutes an approximation of this property, valid only in an NR context. They merge into a single response within the relativistic domain. A more detailed discussion of how the *ee* and *pp* terms are taken into account in 4C calculations is given in Ref. 48.

In classical physics, the natural procedure for obtaining the NR limit of all physical magnitudes is to scale the speed of light to infinity. Applying this procedure to relativistic propagators, we observe that

$$\mathbf{P}^{\mathrm{R}} \overset{c\to\infty}{\longrightarrow} \mathbf{P}^{\mathrm{NR}}$$

$$\mathbf{Q}^{\mathrm{R}} \overset{c\to\infty}{\longrightarrow} \mathbf{Q}^{\mathrm{NR}} \tag{33}$$

$$\mathbf{M}^{\mathrm{R}} \overset{c\to\infty}{\longrightarrow} \mathbf{M}^{\mathrm{NR}}. \tag{34}$$

This fact has important and deep consequences, not only because propagators are one of the most coherent ways of calculating relativistic properties, but also because they can provide new grounds for a better understanding of the physics behind the calculations of atomic or molecular linear response properties within a relativistic framework. Moreover, from a fully theoretical point of view, we have at hand a powerful quantum theory that permits us to naturally relate the physical magnitudes described within the relativistic framework with their NR equivalent magnitudes.[41,113]

Let us now see how the matrix elements of a paramagnetic-like, or *ee*, contribution to the NMR *J*-coupling constant go to its NR counterpart (the paramagnetic contribution) when the speed of light c is scaled to infinity. As mentioned above, the perturbator *ee* terms account for virtual excitations between MOs that belong, both occupied and unoccupied, to the positive-energy branch of the energy spectra.

As an example, we show the case of the external perturbative Hamiltonian arising from the electromagnetic interaction (in the Coulomb gauge) between the electrons and the nuclear magnetic moment due to the nuclear spin of a given nucleus, say K,

$$H_K = \sum_i c\boldsymbol{\alpha}_i \cdot e\left(\frac{\mu_0}{4\pi}\frac{\boldsymbol{\mu}_K \times \boldsymbol{r}_{iK}}{r_{iK}^3}\right), \tag{35}$$

where the sum runs over all the electrons i in the system. When a point-like magnetic dipole moment density (or magnetization) distribution is used, the magnetic dipole moment of nucleus K is given by $\boldsymbol{\mu}_K = \gamma_K \boldsymbol{I}_K$. Here, $\boldsymbol{r}_{iK} = \boldsymbol{r}_i - \boldsymbol{R}_K$ is the position vector operator of electron i relative to nucleus K (with absolute value $r_{iK} = |\boldsymbol{r}_{iK}|$), and $\gamma_K = \frac{e}{2m_p} g_K$ and g_K are the gyromagnetic ratio and nuclear g-factor of nucleus K, respectively. In addition, μ_0 is the vacuum magnetic permeability, and m_p is the proton rest mass.

The matrix elements of the perturbative Hamiltonian H_K with respect to the unperturbed positive-energy one-electron states $|j\rangle$ and $|b\rangle$ can be directly related to the matrix elements of well-known NR operators, according to the following expressions:

$$\begin{aligned}
\langle j|H_K|b\rangle &= \gamma_K \boldsymbol{I}_K \cdot \langle j|\boldsymbol{V}_K^{\mathrm{R}}|b\rangle \\
&= \gamma_K \boldsymbol{I}_K \cdot \langle j|\sum_i \left[\frac{\mu_0}{4\pi}\, e\left(\frac{\boldsymbol{r}_{iK}}{r_{iK}^3} \times c\boldsymbol{\alpha}_i\right)\right]|b\rangle \\
&\overset{c\to\infty}{=} \gamma_K \boldsymbol{I}_K \cdot \langle j^{\mathrm{NR}}|\sum_i \left[\frac{\mu_0}{4\pi}\frac{e}{2m}\left\{\frac{\boldsymbol{r}_{iK}}{r_{iK}^3} \times \boldsymbol{\sigma}_i, \boldsymbol{\sigma}_i \cdot \boldsymbol{p}_i\right\}\right]|b^{\mathrm{NR}}\rangle \\
&= \gamma_K \boldsymbol{I}_K \cdot \left[\langle j^{\mathrm{NR}}|\boldsymbol{V}_K^{\mathrm{FC}} + \boldsymbol{V}_K^{\mathrm{SD}} + \boldsymbol{V}_K^{\mathrm{PSO}}|b^{\mathrm{NR}}\rangle\right],
\end{aligned} \tag{36}$$

with $|j^{\mathrm{NR}}\rangle$ and $|b^{\mathrm{NR}}\rangle$ being two NR spinors. Besides, {, } stands for the anti-commutator of two operators.

The NR matrix elements of eq. 36 were obtained by applying the elimination of small components procedure, in which the small components of the one-electron wavefunctions are expressed in terms of the large components.[41] One must realize that the NR limit of the 4C Hamiltonian H_K matrix elements is well defined. In fact, in such a limit, this particular perturbative operator becomes the sum of the following three NR perturbative Hamiltonians: $H_K^{\mathrm{FC}} + H_K^{\mathrm{SD}} + H_K^{\mathrm{PSO}}$ (where the superscripts stand for Fermi contact, spin dipolar, and paramagnetic spin-orbit contributions, respectively). These three terms have different electronic spin-dependence: the first two are spin-dependent, whereas the last one is spin-independent.

To finish this section on relativistic polarization propagators, we want to highlight some of the most important novelties uncovered by the RelPPT:

(a) The theory of polarization propagators can be expressed in the same formal way in both domains: relativistic and NR.
(b) Both the NR expressions and values of the response molecular properties are obtained within RelPPT only by applying the condition $c \to \infty$ in the relativistic expressions and calculations.
(c) Polarization propagators can be derived from the path integral formalism.[114]

(d) When the off-diagonal matrix elements of the super matrix **M** are discarded, the *ee* terms correspond to the well-defined new paramagnetic-like contributions, while the *pp* terms give the new diamagnetic-like contributions. Both are closely related to their well-known NR counterparts.

(e) Diamagnetic-like and paramagnetic-like terms are unified in only one contribution. There are only virtual excitations to be considered. From this concept, it appears that “paramagnetic-like” or “diamagnetic-like” contributions depend on whether the excitations go to the positive-energy MOs (“*ee*” contributions) or to/from negative-energy MOs (“*pp*” contributions).

(f) There is a fundamental relationship between spin-symmetry and time-reversal symmetry that allows the relativistic polarization propagators to be expressed in terms of quasi-singlet type and quasi-triplet type operators, which have the time-reversal symmetry included in them.[48]

Weak interactions in low-energy physics

The Standard Model (SM) of particle physics describes successfully most of the known fundamental interactions occurring in nature in terms of elementary particles (although, despite its theoretical robustness, it cannot describe some important observations, such as the matter-antimatter asymmetry in the universe, neutrino oscillations, and the existence and nature of dark matter and energy, between others).[115] When studying atoms and molecules, *i.e.*, low-energy physics phenomena, effective Hamiltonians must be used to deal with many of these interactions. Those effective Hamiltonians are constructed from theoretical foundations arising from particle physics, which are in turn supported by experimental results.

Although electromagnetic and weak interactions are merged in high-energy physics phenomena (above 200 GeV), representing two different aspects of a single electroweak interaction, it is justifiable to treat them separately within low-energy physics. Electromagnetic interactions, described by QED, preserve the discrete symmetries of charge conjugation, parity, and time reversal. However, some weak interactions violate space parity symmetry, as first postulated by Lee and Yang,[116] and subsequently demonstrated experimentally by Wu *et al.*[117]

The study of the atomic and molecular consequences of spatial inversion symmetry violations serves not only to test the SM but is also useful in the ongoing searches for new physics.[118,119] Furthermore, since the early 1960s, there have been many attempts to identify a relationship between PV effects and molecular chirality.[120–122] Although it is well-known that PV effects are significantly enhanced in heavy-element-containing molecules,[123,124] despite numerous attempts in this direction, these effects have not yet been experimentally observed in molecular systems.[125–131] Chiral molecules have the particular advantage compared with atomic systems, that parity violating effects can be measured as energy differences between the nonidentical mirror-image molecules in various energy regimes.[132] Experiments searching for molecular PV effects opened a new window into fundamental aspects of the SM, and might contribute to a better understanding of the fundamental laws of physics.[132–136]

To understand whether there is a clear correlation between molecular chirality and PV effects, various methodologies have been developed. Some rely on quantifying the degree of chirality using geometric descriptors,[137–139] while other are based on the electronic wavefunction.[140,141] Recently, the correlation between PV effects and the electronic degree of chirality was suggested, based on molecular results within the 4C relativistic framework.[142] An absolute configuration-sensitive chirality measure must be a time-even pseudoscalar.[135] The electron chirality density would provide a natural convention for specifying absolute chirality,[143] but while the PV contributions to the molecular energy (E^{PV}) depend strongly on the chirality of the electron density at distances very close to the nuclei,[124] the chirality of the total electron density requires integration of the density over the entire molecule.[144]

In the relativistic framework, the effective PV electron-nucleus interaction operator, corresponding to the lowest-order Z^0 boson exchange between electrons and nucleons, is given by[145–147]

$$\widehat{H}^{\mathrm{PV}}_{\mathrm{eff}} = \sum_{i,K} \frac{G_{\mathrm{F}}}{2\sqrt{2}c_0}\, Q_{\mathrm{w},K}\, c\gamma_i^5\, \varrho_K(\boldsymbol{r}_i) + \sum_{i,K} \frac{G_{\mathrm{F}}}{2\sqrt{2}\hbar c_0}\, \kappa_K\, c\boldsymbol{\alpha}_i \cdot \boldsymbol{I}_K\, \varrho_K(\boldsymbol{r}_i). \tag{37}$$

In eq. 37, the nucleons were considered as NR objects,[146,148] and two values of c appear, which are equal to each other in the 4C relativistic domain ($c = c_0$), but only c_0 is fixed to the actual speed of light in vacuum when the NR limit prescription $c \to \infty$ is applied.[40,94] This expression, where the sums run over all electrons i and nuclei K in the system, shows that PV interactions arise from both nuclear spin-dependent (NSD) and nuclear spin-independent (NSI) mechanisms, shown in the first and second terms on the rhs of eq. 37, respectively. In particular, there are three contributions to the NSD PV term:[119,149] one arises from the exchange of Z^0-bosons in neutral-current interactions involving nucleonic axial-vector (*i.e.*, pseudovector) currents and electronic polar-vector currents.[150] Another contribution originates in the perturbation of the nuclear-spin independent PV weak interaction (corresponding to the weak nuclear charge Q_W), by the hyperfine coupling.[151] The third contributing mechanism comes from the electromagnetic interaction between the nuclear anapole moment (which is a magnetic moment generated by PV nucleonic currents) and the electrons.[146,152–154] While all three mechanisms contribute to the second term in eq. 37, and do so through three different contributions to the factor κ_K, the most important in heavy-element containing systems are the first and third of those mentioned above.

In eq. 37, G_F is the Fermi coupling constant, whose value is $G_F/(\hbar c_0)^3 = 1.1663787 \times 10^{-5}$ GeV^{-2}, or equivalently $G_F \simeq 2.222516 \times 10^{-14} E_h a_0^3$.[155] $Q_{W,K} = Z_K\left(1 - 4\sin^2\theta_W\right) - N_K$ is the weak nuclear charge, with Z_K and N_K being the number of protons and neutrons of nucleus K, respectively. The sine-squared weak mixing angle, $\sin^2\theta_W$ is 0.23122.[155] Furthermore, the pseudo-scalar $\gamma^5 = i\gamma^0\gamma^1\gamma^2\gamma^3$ chirality operator and the Dirac matrices $\boldsymbol{\alpha}$ operate on bispinors of electron i; $\mathbf{r}_i$ is the position of electron i with respect to the coordinate origin, $\varrho_K(\boldsymbol{r}_i)$ is the number density distribution of nucleus K at the position of electron i, which can be related to the nuclear charge density by $\varrho_K(\boldsymbol{r}_i) = \rho_K(\boldsymbol{r}_i)/(Z_K e)$. Following a common choice in the molecular physics community, it is possible to define $\kappa_K = -2\lambda_K\left(1 - 4\sin^2\theta_W\right)$, where λ_K is a nuclear state-dependent parameter (which is estimated to be of order 1–10 for heavy nuclei[153]). The nuclear anapole moment contribution and the contribution arising from electron-axial-vector nucleon-polar-vector neutral-current interactions, among others, can be incorporated through an appropriate choice of the coupling constant λ_K.[156]

Using perturbation theory, and considering the PV Hamiltonian of eq. 37 as a perturbation to the Dirac-Coulomb (or Dirac-Coulomb-Breit) Hamiltonian, the first-order perturbative contribution to the electronic energy (*i.e.*, E^{PV}) can be calculated as the expectation value of eq. 37 over the exact (or, according to Hellmann–Feynman theorem, variational) solutions of the Dirac–Coulomb–Breit equation. This contribution is zero for non-chiral molecules. However, the two enantiomeric forms of a chiral system have a nonzero energy contribution arising from PV interactions, of equal magnitude but opposite sign.[157] In the absence of external magnetic fields, since $\boldsymbol{\alpha}_i$ is a time-reversal odd operator, the NSD term in eq. 37 reduces to a sum of terms over the nucleonic spins that cancel in pairs, leaving a contribution arising only from the unpaired spin.[148] In general, this contribution represents less than 1 % of the one coming from the NSI term. Contributions arising from electron-electron (vector-pseudovector) neutral-current interactions will be smaller than the homologous ones arising from electron-nucleon interactions, and can therefore be safely ignored.[147,158]

Within the semi-relativistic Breit-Pauli approximation, in which the unperturbed and perturbed Hamiltonians are expanded in a power series in terms of c^{-2} by applying the elimination of small components approach, the lowest-order contribution to the 4C expression of E^{PV} is a linear response based on NR orbitals which involves, on the one hand, the SO interaction and, on the other, the zeroth-order (electron spin-dependent) contribution to the NSI PV Hamiltonian (*i.e.*, the first term on the rhs of eq. 37).[123]

On the other hand, expectation value calculations of the NSI-PV 4C Hamiltonian show that in the relativistic domain E^{PV} is dominated by intra-atomic contributions,[159] due both to the presence of $\varrho(\boldsymbol{r})$ in such a Hamiltonian, and to the coupling of the large and small components of the Dirac bi spinors produced by the chirality operator γ^5. The PV energy then arises from the mixing of valence $s_{1/2}$ and $p_{1/2}$ MOs with a common nuclear center.

Spectroscopic parameters

When working within a relativistic regime, some spectroscopic parameters are formally expressed in terms of 4C operators that do not yet have a completely clear meaning, unlike in an NR context. This is because the 4C operators representing observables are expressed (in the standard representation) as 4-dimensional square matrices involving Dirac matrices, which can be non-diagonal. As a consequence, we can mention the breaking of well-established NR formal relationships between some pairs of molecular properties. This is the case of the NMR shielding and NSR constants,[160] and also of the rotational g-tensors and magnetizabilities, which in an NR context have common contributions, related to each other by equality relations. These relationships do not hold in the relativistic regime.[33,63]

In particular, the theoretical NR relationship between the NSR and NMR shielding tensors is based on Larmor's theorem (the same occurs with the relationship between rotational g-tensors and magnetizabilities), which states a formal equivalence, within NR dynamics, between the Hamiltonians of a single particle in either a uniformly rotating frame or a uniform magnetic field, up to first order in the field strength.[10] However, when the relativistic formalism is applied to study electronic density distributions, this equivalence does not hold anymore, as it was observed experimentally.[160] This has raised a long-standing interest in finding out whether it is possible to generalize the well-known Flygare's NR relationship to a relativistic domain. A preliminary result was published more than a decade ago.[161] More recently, by studying the relativistic electronic mechanisms affecting each of these properties within the LRESC model,[102] it has been possible to propose a successful 4C relativistic generalization of the NR relationship.[62,63]

Parity-conserving spectroscopic response parameters

Among the most studied molecular spectroscopic parameters in closed-shell systems are the two main NMR properties, which are strongly affected by relativistic effects: the shielding tensor $\boldsymbol{\sigma}_K$ of a given nucleus K and the indirect nuclear spin-spin coupling tensor between nuclei K and L, $\boldsymbol{J}_{KL}$. Both show a special dependence on the (off-diagonal) Dirac matrices $\boldsymbol{\alpha}$.

More generally, it is possible to focus not only on these two but also on other molecular properties of electronic closed-shell systems that can be expressed as linear responses within the RelPPT. Some of them are bilinear in one or two of the following external perturbations: the nuclear spins, an external uniform magnetic field $\boldsymbol{B}_0$, and the molecular rotational angular momentum $\boldsymbol{L}$. In molecular spectroscopy, these molecular parameters are defined in terms of the following effective Hamiltonians:[162,163]

$$H^{\text{eff-NMR}} = -\sum_K \gamma_K \boldsymbol{I}_K \cdot (\boldsymbol{1} - \boldsymbol{\sigma}_K) \cdot \boldsymbol{B}_0 + \sum_{K<L} \frac{1}{\hbar^2} \boldsymbol{I}_K \cdot \boldsymbol{J}_{KL} \cdot \boldsymbol{I}_L \tag{38}$$

$$H^{\text{eff-NSR}} = -\sum_K \frac{1}{\hbar^2} \boldsymbol{I}_K \cdot \boldsymbol{M}_K \cdot \boldsymbol{L} \tag{39}$$

$$H^{\text{eff-B}} = -\frac{\mu_N}{\hbar} \boldsymbol{L} \cdot \boldsymbol{g} \cdot \boldsymbol{B}_0 - \frac{1}{2} \boldsymbol{B}_0 \cdot \chi \cdot \boldsymbol{B}_0, \tag{40}$$

where $\mu_N = \frac{e\hbar}{2m_{\mathrm{p}}}$ is the nuclear magneton.

In eqs. 39 and 40, the NSR tensor $\boldsymbol{M}_K$, the rotational g tensor $\boldsymbol{g}$, and the magnetizability χ can be written as sums of nuclear and electronic contributions (*i.e.*, $\boldsymbol{M}_K = \boldsymbol{M}_K^{\text{nuc}} + \boldsymbol{M}_K^{\text{elec}}$, $\boldsymbol{g} = \boldsymbol{g}^{\text{nuc}} + \boldsymbol{g}^{\text{elec}}$, and $\chi = \chi^{\text{nuc}} + \chi^{\text{elec}}$, respectively). Using a rigid rotor model to describe the motion of nuclei in an NR context,[33] and employing the Dirac formalism within the Born-Oppenheimer approximation to describe the electronic structure, expressions for all these molecular properties (or their electronic contributions, when it is the case) have been proposed in recent years, in the context of static RelPPT (*i.e.*, for $E = 0$, see eq. 23).[33,39,40,63,102,164] They are:

$$\boldsymbol{J}_{KL} = \left(\frac{\mu_0}{4\pi}\right)^2 e^2\hbar^2\, \gamma_K \gamma_L \,\mathrm{Re}\,\langle\langle\, \frac{\boldsymbol{r}_K \times c\boldsymbol{\alpha}}{|\boldsymbol{r}_K|^3} ;\, \frac{\boldsymbol{r}_L \times c\boldsymbol{\alpha}}{|\boldsymbol{r}_L|^3} \,\rangle\rangle_0 \tag{41}$$

$$\boldsymbol{\sigma}_K = \frac{\mu_0}{4\pi} \frac{e^2}{2} \,\mathrm{Re}\,\langle\langle\, \frac{\boldsymbol{r}_K \times c\boldsymbol{\alpha}}{|\boldsymbol{r}_K|^3} ;\, \boldsymbol{r}_{\mathrm{GO}} \times c\boldsymbol{\alpha} \,\rangle\rangle_0 \tag{42}$$

$$\boldsymbol{M}_K^{\text{elec}} = \frac{\mu_0}{4\pi} \frac{e^2\hbar^2}{2m_{\mathrm{p}}} g_K \,\mathrm{Re}\,\langle\langle\, \frac{\boldsymbol{r}_K \times c\boldsymbol{\alpha}}{|\boldsymbol{r}_K|^3} ;\, \boldsymbol{J}^{\mathrm{R}} \,\rangle\rangle_0 \cdot \boldsymbol{I}^{-1} \tag{43}$$

$$\boldsymbol{g}^{\mathrm{elec}} = m_{\mathrm{p}}\,\mathrm{Re}\,\langle\langle\, \boldsymbol{r}_{\mathrm{GO}} \times c\boldsymbol{\alpha}\,;\, \boldsymbol{J}^{\mathrm{R}}\,\rangle\rangle_0 \cdot \boldsymbol{I}^{-1} \tag{44}$$

$$\chi^{\mathrm{elec}} = -\frac{e^2}{4}\,\mathrm{Re}\,\langle\langle\, \boldsymbol{r}_{\mathrm{GO}} \times c\boldsymbol{\alpha}\,;\, \boldsymbol{r}_{\mathrm{GO}} \times c\boldsymbol{\alpha}\,\rangle\rangle_0, \tag{45}$$

where $\boldsymbol{r}_{\mathrm{GO}} = \boldsymbol{r} - \boldsymbol{R}_{\mathrm{GO}}$ is the electron position vector relative to the (arbitrary) gauge origin of the magnetic potential, $\boldsymbol{J}^{\mathrm{R}} = \boldsymbol{L}^{\mathrm{R}} + \boldsymbol{S}^{\mathrm{R}} = \mathbb{1}_4\, \boldsymbol{r}_{\mathrm{CM}} \times \boldsymbol{p} + (\hbar/2)\boldsymbol{\Sigma}$ is the total relativistic electronic angular momentum operator around the molecular center of mass (CM), and $\boldsymbol{I}^{-1}$ is the inverse molecular moment of inertia from the CM. One detail to note is that the electronic contribution to the NSR tensor as given by eq. 43 (to which a term independent of the electronic variables, $\boldsymbol{M}_K^{\mathrm{nuc}}$, is added to get the total $\boldsymbol{M}_K$) is only valid at the molecular equilibrium geometry.[33] Outside of equilibrium, other contributions, both nuclear and electronic, must be taken into account, including SO terms based on Thomas precession associated with the nuclear spin.[33,35,102,165]

To derive eqs. 41–45, use has been made of the relation[34,166]

$$E_0^{(2)}\left(\hat{H}'\right) = \frac{1}{2}\mathrm{Re}\,\langle\langle\,\hat{H}'\,;\hat{H}'\,\rangle\rangle_0, \tag{46}$$

where $E_0^{(2)}(\hat{H}')$ is the second-order correction to the ground-state molecular energy in perturbation theory, due to a (static) perturbative Hamiltonian $\hat{H}'$ (which can in turn be a sum of different perturbation terms).[40,93,112]

The first 4C relativistic calculations of NMR shieldings and spin-spin coupling constants were carried out in the late 1990s,[39,164] and therefore these parameters have been extensively studied in the next decades. Although the RelPPT has also been applied to calculate linear responses associated with electric properties, such as dipole polarizabilities,[167] here we focus on magnetic and rotational properties. In this regard, it is worth mentioning that in 2013, the magnetizability tensor of some molecular systems, and in particular its dependence on the gauge origin, was studied.[168] A gauge-including atomic orbitals prescription (in a manner analogous to what has been done in the NR case) was proposed to eliminate this dependence. Both the NMR shielding and magnetizability tensors are independent of the gauge origin when the basis set is complete; however, this limit can never be exactly reached in practice.[15,169]

In recent years, both the relativistic theory and its first computational applications have been proposed with studies of NSR tensors,[33,170] rotational *g*-tensors, and magnetizabilities.[63] In the case of rotational properties (*i.e.*, $\boldsymbol{M}_K$ and $\boldsymbol{g}$), it is worth noting that contributions from electron-nucleus Breit interactions were shown to be negligible.[171]

The relativistic formal expression of the NSR tensors is a generalization of Flygare's NR theory,[35] and simultaneously addresses some questions related to the validity of the NR expression of this property in a relativistic framework.[161] Shortly after this theory was proposed, other independent formalisms were published,[172] with identical results within the same approach. Furthermore, it was shown that combining the relativistic expression for the NSR tensor with Flygare's NR relationship between this property and the NMR shielding tensor yields shielding predictions that are far from the values obtained by calculating this property using 4C methods.[173] This problem can be fully solved by applying the M–V model.[34,62]

Relativistic electronic mechanisms in PV contributions to spectroscopic parameters

In recent decades, many research projects have focused on searching for molecules suitable for detecting frequency shifts caused by PV weak interactions. These studies include, among others, parameters such as NMR nuclear magnetic shielding and indirect nuclear spin-spin coupling, as well as NSR tensors. During these years, it has not only been shown that the contributions to NSR and NMR shielding constants arising from PV effects strongly depend on relativistic effects,[174–176] but also that the main electronic mechanisms that play crucial roles in some of those effects have been unambiguously identified.[94] Furthermore, current and past experimental searches for PV effects in chiral molecules, as well as theoretical predictions that strength and support those searches, have been conducted looking for resonance frequency splittings in NMR, rotational, vibrational, and electronic spectroscopy.[174–194] Despite the ever-increasing precision of those experiments, so far it has not been possible to detect PV effects in chiral molecules.

Among the relativistic second-order molecular properties mentioned in Section “Parity-conserving spectroscopic response parameters”, those most likely to be affected by PV effects are the *J* coupling, the NSR, and the shielding constants. Since the PV-NSI contributions are expected to be at least two orders of magnitude smaller than the PV-NSD counterparts in heavy-element containing systems,[178] it is usually assumed that the latter will be the only ones that need to be considered. They give the following contributions:[175,193,194]

$$J_{KL}^{\mathrm{PV-NSD}} = \frac{\mu_0}{4\pi}\,\frac{e^2\,\hbar\,G_{\mathrm{F}}}{4\sqrt{2}\,m_{\mathrm{p}}\,c_0}\left[\kappa_K g_L \mathrm{Re}\,\langle\langle\, \varrho_K(\boldsymbol{r})\,c\boldsymbol{\alpha};\ \frac{\boldsymbol{r}_L\times c\boldsymbol{\alpha}}{|\boldsymbol{r}_L|^3}\,\rangle\rangle_0 + \kappa_L g_K \mathrm{Re}\,\langle\langle\, \varrho_L(\boldsymbol{r})\,c\boldsymbol{\alpha};\ \frac{\boldsymbol{r}_K\times c\boldsymbol{\alpha}}{|\boldsymbol{r}_K|^3}\,\rangle\rangle_0\right] \tag{47}$$

$$\boldsymbol{\sigma}_K^{\mathrm{PV-NSD}} = \frac{m_{\mathrm{p}}\,G_{\mathrm{F}}}{2\sqrt{2}\,\hbar\,c_0}\,\frac{\kappa_K}{g_K}\,\mathrm{Re}\,\langle\langle\, \varrho_K(\boldsymbol{r})\,c\boldsymbol{\alpha};\ \boldsymbol{r}_{\mathrm{GO}}\times c\boldsymbol{\alpha}\,\rangle\rangle_0 \tag{48}$$

$$\boldsymbol{M}_K^{\mathrm{PV-NSD}} = \frac{\hbar\,G_{\mathrm{F}}}{2\sqrt{2}\,c_0}\,\kappa_K\,\mathrm{Re}\,\langle\langle\, \varrho_K(\boldsymbol{r})\,c\boldsymbol{\alpha};\ \boldsymbol{J}^{\mathrm{R}}\,\rangle\rangle_0\cdot\boldsymbol{I}^{-1}. \tag{49}$$

It is worth noting that, in a power series expansion in c^{-2}, the zeroth-order contributions to eqs. 47–49 are recovered by applying the limit $c\rightarrow\infty$, keeping c_0 fixed. The zeroth-order expressions recovered by applying this limit exactly match those proposed in the 1980s, first by Gorshkov *et al.* (although these authors have not written explicitly the complete formal expressions, they have nicely described the origin of each of them, giving associated estimations of their orders of magnitude),[178] and later by Barra and coworkers.[179]

While experimental searches for signatures of molecular PV effects continue, there has been significant theoretical progress in the understanding of the electronic mechanisms underlying PV effects in those response properties. In this regard, for instance, it has recently been possible to identify the main relativistic mechanisms that enhance PV effects in NSR and NMR shielding tensors. They arise from SO effects which, in terms of NR orbitals, can be written as quadratic responses involving three triplet operators: the NR electron spin operator, the SO interaction, and the electron SD term arising from the lowest-order contribution to the PV NSD Hamiltonian.[94] As a result of this finding, it has been possible to probe that there is a very close formal relationship between the PV contributions to these two properties. Consequently, if these effects are known for any of these two properties, it is possible to determine the equivalent effects in the other, by simply adding (or subtracting) a 4C linear response calculation, which involves the usual relativistic generalization of the electron spin operator, $\boldsymbol{S}^{\mathrm{R}}$.

Concluding remarks

One hundred years have elapsed since the publication of the formalism of NR quantum theory, and a little less since its relativistic generalization (albeit highly restricted to one-electron systems) was proposed. Theories of atomic and molecular response properties appeared long after those seminal papers, although more than 50 years have passed since then.

In this work, we aimed to celebrate these anniversaries and review and analyze some of the key aspects and subtleties underlying the development of atomic and molecular theory within the well-established framework of RQC. We highlighted some of the main conceptual and methodological challenges that have historically arisen when NR studies were extended to relativistic frameworks. In addition, we present a few selected developments and physical insights that our research group has contributed over the years to the RQC area of research, particularly regarding the calculation and interpretation of the origin of relativistic effects in molecular response properties. In line with all this, we have focused on some of the main difficulties that have arisen in the application of the postulates of special relativity to quantum chemistry. We wanted to shed some light on these issues, and we discussed and clarified them as much as possible, providing an overview of how they have been (and still are in the case of some of them) exposed and strengthened over the years. We briefly mention some of them:

(1) Spin is not a good quantum number within RQC, so there are no formal expressions capable of reproducing all the properties that it must have in the relativistic regime. In this domain, time-reversal symmetry replaces spin symmetry, opening new roads for producing formalisms that exploit this characteristic to reduce computational costs and to explore what the meaning and usefulness of the well-known singlet and triplet NR operators might be in a relativistic context.

(2) In the foreseeable future, there is no possibility of getting Lorentz invariant *N*-electron Hamiltonians. In other words, the best description of a molecular system within a relativistic framework, including QED effects, is not known *a priori.* As a result, the current strategy relies on a bottom-up approach, constructing effective Hamiltonians through *ad hoc* proposals tailored to specific physical contexts.

(3) Within the relativistic framework, the representation of operators is more meaningful than the operators themselves. This makes their interpretation more difficult, but also helps define the best way to obtain NR analogs of relativistic operators. Thus, it is highlighted that the interpretation of observables derived from relativistic operators, as well as their apparent structure, can depend significantly on the representation used.

(4) The advantages that top-down approaches offer over bottom-up approaches, including in some cases the computational efficiency of calculations, are often exploited through the development of two-component methods based on well-defined and reliable formal backgrounds. One of the most widely used semi-relativistic approaches for obtaining energy spectra and properties of molecular systems is the X2C model in any of its versions. Another is the LRESC model, which allows the individual electronic mechanisms of various molecular properties to be calculated and interpreted using NR orbitals. However, the LRESC method can also be considered a valuable starting point for developing bottom-up approaches. In this work, we have demonstrated how this model has allowed us to establish relativistic generalizations of the relationships between response properties that had previously been studied exclusively within an NR framework.

(5) The emergence of negative-energy states and their usefulness are generally difficult to accept within the quantum chemistry community, since it is naturally more accustomed to dealing almost exclusively with positive-energy states. Consequently, excitations to or from negative-energy states are often interpreted simply in terms of orbital "rotations" that facilitate SCF procedures. However, the deeper physical meaning of the negative-energy spectrum after optimization is usually not considered. This issue became particularly evident with the development of relativistic polarization propagators, where virtual excitations involving one-electron negative-energy states show that diamagnetic contributions to magnetic properties are due to virtual pair creation/annihilation within the relativistic domain. Further exploration of these aspects could provide more valuable insights into the role of negative-energy states in relativistic quantum chemistry.

(6) The interactions that have been accurately described and formulated within the Standard Model are only those that occur between elementary particles. These interactions have been included in low-energy physics through brilliant proposals for effective Hamiltonians, the application of which has led to promising results. However, as calculations have become more precise, the need for certain modifications to these Hamiltonians has become apparent to better describe interactions involving systems of composite particles, such as atomic nuclei.

(7) Electroweak interactions, traditionally considered negligible in theoretical chemistry, have gained increasing importance in recent decades as theoretical models and experimental techniques reach ever-higher levels of precision. The fundamental role that weak interactions play in subtle spatial symmetry-breaking phenomena within molecular systems, and their relationship to new effects such as chirality in these systems, is becoming increasingly relevant.

Looking ahead, we foresee a continuing and growing need to develop more consistent, accurate, and computationally efficient methods for calculating and describing relativistic (together with other still less studied though being required to be done so in the next future) effects in atomic and molecular systems. In particular, the refinement of 4C and 2C formalisms, the systematic treatment of electron correlation in the relativistic regime, and the inclusion of QED and weak interactions at the molecular level, remain encouraging challenges. In the near future, advances in these directions are expected to deepen our understanding of fundamental processes and enhance the predictive power of relativistic quantum chemistry.

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