Relativistic and QED effects on NMR magnetic shielding constant of neutral and ionized atoms and diatomic molecules\textsuperscript{a)}

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We show here results of four-component calculations of NMR $\sigma$ for atoms with $10 \leq Z \leq 86$ and their ions, within the polarization propagator formalism at its random phase level of approach, and the first estimation of QED effects and Breit interactions of those atomic systems by using two theoretical effective models. We also show QED corrections to $\sigma(X)$ in simple diatomic HX and $X_2$ ($X = \text{Br, I, At}$) molecules. We found that the $Z$ dependence of QED corrections in bound-state many-electron systems is proportional to $Z^5$, which is higher than its dependence in H-like systems. The analysis of relativistic ee (or paramagnetic-like) and pp (or diamagnetic-like) terms of $\sigma$, expose two different patterns: the pp contribution arise from virtual electron-positron pair creation/annihilation, and the ee contribution is mainly given by $1s \rightarrow ns$ and $2s \rightarrow ns$ excitations. The QED effects on shieldings have a negative sign and their magnitude is larger than 1% of the relativistic effects for high-$Z$ atoms like Hg and Rn, and up to 0.6% of its total four-component value for neutral Rn. Furthermore, percentual contributions of QED effects to the total shielding are larger for ionized than for neutral atoms. In molecule, the contribution of QED effects to $\sigma(X)$ is determined by its highest-$Z$ atoms, being up to $-0.6\%$ of its total $\sigma$ value for astatine compounds. It is found that QED effects grow faster than relativistic effects with $Z$.

Keywords: Relativistic effects, ee and pp contributions, diatomic molecules

I. INTRODUCTION

Nuclear magnetic resonance (NMR) spectroscopy is a powerful experimental technique used, among many other applications, to identify chemical compounds and predict their molecular structures. Precise calculations of both of its relevant spectroscopic parameters, the NMR shielding constant, $\sigma$, and the J-coupling (indirect spin-spin coupling) constant, are highly challenging. They require to consider several intra- and intermolecular effects with the proper theories and state-of-the-art models.\textsuperscript{1-4}

There are few leading electronic effects, such as the electron correlation and relativistic effects, that should be included in order to get an accurate theoretical reproduction of the nuclear magnetic shieldings. In the case of heavy-atom containing molecules it is known that relativistic effects may be as large as the non-relativistic (NR) contributions.\textsuperscript{5,6} Furthermore, it was recently shown that electron correlation effects within a four-component DFT scheme and relativistic effects may not be independent each other, for NMR spectroscopic parameters.\textsuperscript{6,7} When one looks for the most accurate results, the effects of the nuclear size and quantum electrodynamic (QED) corrections must be included.\textsuperscript{8,9} The nuclear charge distribution effects on shieldings may be of the order 3% to 6% in heavy-atom containing molecules as HAt and PbIH\textsubscript{3}.\textsuperscript{7,10}

The first theoretical models developed to introduce QED effects (the self-energy part) on $\sigma$, were presented by Romero and Aucar.\textsuperscript{11,12} In those models the main difficulties were related with solutions of formal expressions and implementations, like the integrals for the fourth level of the scattering matrix. During the last couple of years few attempts were made to estimate quantitatively the influence of QED effects on shielding of H-like and He-like systems.\textsuperscript{13-15} Rudziński et al.\textsuperscript{13} have published relativistic and QED corrections to the shielding of $\text{He}^+\text{He}$, derived from the Breit-Pauli Hamiltonian. They concluded that QED corrections are non-negligible, being 1% of the relativistic contribution. These findings are in line with previous suggestions of Pyynkö and Zhao\textsuperscript{16}. Afterward, Yerokhin et al.\textsuperscript{14,15} have presented the results of \textit{ab initio} calculations for several H-like ions in the range of $8 \leq Z \leq 92$, considering various QED contributions to $\sigma$, as well as Bohr-Weisskopf and quadrupole corrections. They found that QED corrections, related to total $\sigma$, are in the range from $-0.002\%$ for $8\text{O}^{7+}$ to $-0.7\%$ for $83\text{Br}^{82+}$ (being also about 1% of the relativistic part). The Bohr-Weisskopf corrections, meaning the effect induced by the spatial distribution of the nuclear magnetic moments, and the quadrupole corrections are of the same...
order of magnitude as the QED effects for H-like ions.\textsuperscript{14,15} In Refs. 13, 14 and 15 the first reliable results were given, but only for 1- and 2-electron atomic systems. Theoretical treatments used in both references are fully relativistic, being that of Ref. 13 based on the non-relativistic QED expansion (only the zeroth-order approximation is obtained non-relativistically). The difficulties are such that there are no actual calculations published in the literature with estimations of such effects on $\sigma$ for many-electron systems.

Among different formalisms that were developed to introduce QED effects on atomic systems,\textsuperscript{17–21} there is the polarization propagator one which was recently derived from the path integral version of quantum theory.\textsuperscript{22} This fact gives new insights on how to include QED and correlation effects altogether, through the consideration of the effects of external perturbations on a many-body quantum system that is described within a QED-based theoretical framework. Within the polarization propagator formalism perturbative (external) effects can be described by using the knowledge of the unperturbed though correlated many-body quantum system.

Recently we published preliminary results concerning the estimation of QED effects on NMR shielding constant for He-like and Be-like atomic systems with $10 \leq Z \leq 86$.\textsuperscript{23} In that work we presented a model by which QED corrections, obtained by Yerokhin et al. for H-like atoms, are scaled to those ionic systems.\textsuperscript{14,15} Such procedure is similar to the way QED effects are usually introduced in multi-electron atoms.\textsuperscript{24} We also estimated the Gaunt corrections to the molecular orbital energies of few diatomic molecules, i.e. HX ($X = Br, I, At$).\textsuperscript{25}

As a next step in our research program to include QED effects on atomic and molecular properties, in this manuscript we give an estimation of QED effects on shielding of neutral and ionic atoms with $10 \leq Z \leq 86$, and diatomic halogen molecules by using an extension of our previous approach. To our knowledge there is no other estimation of QED effects on nuclear shielding of molecular systems. Our results show that QED effects may be measurable. At the moment highly accurate absolute values of NMR shieldings in some gas-phase molecules can be obtained by experiments. Their error bars may be less than the values of QED corrections for heavy-atom containing molecules.\textsuperscript{26–29}

We also include the analysis of the physical mechanisms that are involved in both relativistic terms, ee (or paramagnetic-like) and pp (or diamagnetic-like). We shall show that the origin of the pp-like term may be understood, within the polarization propagator formalism, as due to the propagation of virtual electron-positron pairs.\textsuperscript{6,22,30} This is shown through the analysis of the nuclear shielding of ions of the same nucleus.

In the following sections we will present two different models for including QED effects on shielding of ionic and neutral atoms, together with diatomic molecules. We shall consider relativistic contributions to the shieldings of those systems and propose a $Z$-dependence for QED effects on the shieldings of neutral atoms. We shall also show the pattern that QED corrections follows in all those systems.

II. THEORETICAL MODELS AND COMPUTATIONAL DETAILS

In this section we sketch few basic expressions of the underlying theoretical method used for relativistic calculations. Then we present two models for including QED effects on magnetic shieldings. The first one is the same as given previously,\textsuperscript{23} and the second one is less accurate though useful for our purpose. Computational details are also given.

A. The NMR shieldings

Within the polarization propagator formalism, the shielding constant of nucleus $K$, $\sigma(K)$, is written at first consistent order of approach or random phase approximation (RPA) as\textsuperscript{6}

$$\sigma(K) = (b^K b^*K) \left( A \begin{bmatrix} B & A^* \end{bmatrix}^{-1} \begin{bmatrix} b^*B \\ bB \end{bmatrix} \right) \tag{1}$$

where $K$ corresponds to the nuclear magnetic moment index, $B$ is the external magnetic field, and Gaussian cgs system of units are used. There are two different terms on the rhs of Eq. (1). The first one and the last one are so-called perturbators, $b$, and the matrix in the middle correspond to the principal propagator, $P = M^{-1}$, being matrices $A$ and $B$ written within the second quantization language as,

$$A_{ia,jb} = -\langle 0| [a_i^\dagger a_i, [a_j^\dagger a_j, H_0]]|0 \rangle = \delta_{ia} \delta_{ij} (\varepsilon_a - \varepsilon_i) + \langle a_j|ib \rangle = A_{ia,jb}(0) + A_{ia,jb}(1) \tag{2}$$

and

$$B_{ia,jb} = \langle 0| [a_i^\dagger a_i, [a_j^\dagger a_j, H_0]]|0 \rangle = -\langle ij|ab \rangle. \tag{3}$$

Subscripts $a, b, \ldots$ refer to canonical unoccupied Dirac-Hartree-Fock (DHF) orbitals and $i, j, \ldots$ stands for canonical occupied DHF orbitals and $H_0$ refers to the unperturbed electronic Hamiltonian.

Eq. (1) is valid within both regimes, relativistic and NR, though the actual expressions of its three factors depends on the framework one works in. In what follows all expressions will be given within the relativistic framework.

Both perturbators are written as

$$b^K_{ia} = \left( i \frac{\alpha \times r_K}{r_K^2} \right)_a, \quad b^B_{jb} = \langle j |\frac{\alpha \times r_G}{2} |b \rangle \tag{4}$$

where $r_G = r - R_G$ being $R_G$ the gauge origin, and $r_K = r - R_K$, being $R_K$ the position of nucleus K. They
are related with excitations from occupied to unoccupied orbitals. In the relativistic regime the set of unoccupied orbitals is splitted into two subsets, the positive and negative branch of energies. Excitations from occupied electronic states to negative (pp) and positive (ee) energy solutions are related with the pp or diamagnetic-like, \( \sigma^{pp} \), and ee or paramagnetic-like, \( \sigma^{ee} \), contributions to \( \sigma \).\(^{22,30}\)

As mentioned in Ref. 23 actual calculations are not performed using Eq. (1) but an algorithm that solves the product among the inverted matrix of the principal propagator (which is the inverse of the electronic Hessian) and one of the perturbators

\[
\sigma(K) = \sum_{ia,jb} (b^K_{ia} b^{*K}_{ia}) (M^{-1})_{ia,jb} (b^B_{jb} b^{*B}_{jb})
\]

\[
= \sum_{ia} (b^K_{ia} b^{*K}_{ia}) (X^B_{ia} X^{*B}_{ia}) = \sum_{ia} \sigma_{ia}(K)
\]

All the information related to the principal propagator and one of the two perturbators is contained in the matrix \( X \). The way it is formally derived and implemented in the four-component \( \text{DIRAC} \) code is explicitly given in Ref. 31.

### B. Estimating QED effects – model A

This model was first proposed in Ref. 23. We have made a consideration that leading QED corrections to both, perturbators and principal propagators are enough to estimate an order of magnitude for QED corrections to shieldings.

In the papers of Yerokhin et al.\(^{14,15} \) the NMR shielding constants for H-like ions are calculated within Rayleigh-Schrödinger sum-over-states perturbation theory by considering virtual excitations from ground \( 1s_{1/2} \) state to excited \( n_s1/2 \) electronic Dirac states. This model is based on earlier works of Moore\(^{32} \) and Pyper\(^{33} \). In Yerokhin et al. work the QED correction to the shielding constant is calculated as a sum of various vacuum polarization (VP) and self energy (SE) contributions and expressed in terms of the function \( D(Z\alpha) \) as

\[
\Delta \sigma^{QED} = \Delta \sigma^{SE} + \Delta \sigma^{VP}
\]

\[
\Delta \sigma^{SE} = \alpha^2(Z\alpha)^3 D_{SE}(Z\alpha)
\]

\[
\Delta \sigma^{VP} = \alpha^2(Z\alpha)^3 D_{VP}(Z\alpha)
\]

where \( \Delta \sigma^{VP} \) collects VP influence on both electronic orbital properties (perturbed-orbital contribution, \( \Delta \sigma^{VP,po} \)) and hyperfine interaction (\( \Delta \sigma^{VP,\text{mag}} \)), i.e.

\[
\Delta \sigma^{VP} = \Delta \sigma^{VP,po} + \Delta \sigma^{VP,\text{mag}}
\]

\[
= \alpha^2(Z\alpha)^3 D_{VP,po}(Z\alpha) + \alpha^2(Z\alpha)^3 D_{VP,\text{mag}}(Z\alpha)
\]

Then the ratio

\[
R_D = \frac{D_{VP,po}(Z\alpha)}{D_{VP}(Z\alpha) + D_{SE}(Z\alpha)} = \frac{\Delta \sigma^{VP,po}}{\Delta \sigma^{QED}}
\]

is a relative contribution of perturbed-orbital VP contribution to total QED effect.

In our study we assume that the pattern of SE to VP effects ratio, expressed by \( D_{SE}(Z\alpha) \), \( D_{VP}(Z\alpha) \), and \( D_{VP,po}(Z\alpha) \) coefficients, is similar for H-like and many-electron atomic systems. That happens in the case of orbital energies – compare, e.g., Ref. 34 and supplement of Ref. 35. The VP influence on principal propagator is equivalent to adding VP energy correction to appropriate orbitals energies. The perturbed-orbital VP influence on perturbators can be reproduced in many-electron atoms by comparing calculations with and without Uehling potential included in self-consistent field (SCF) process. Let us make the following ratios

\[
C_B(\frac{DCB}{DCBV}) = \frac{(n_1k_1m_1 \alpha \times r_{n_2k_2m_2})_{DCBV}}{(n_1k_1m_1 \alpha \times r_{n_2k_2m_2})_{DCB}}
\]

\[
= \frac{(R^{(1)}(n_1k_1n_2k_2))_{DCBV}}{(R^{(1)}(n_1k_1n_2k_2))_{DCB}}
\]

and

\[
C_K(\frac{DCB}{DCBV}) = \frac{(n_1k_1m_1 \alpha \times r_{n_2k_2m_2})_{DCBV}}{(n_1k_1m_1 \alpha \times r_{n_2k_2m_2})_{DCB}}
\]

\[
= \frac{(R^{(-2)}(n_1k_1n_2k_2))_{DCBV}}{(R^{(-2)}(n_1k_1n_2k_2))_{DCB}}
\]

being both indices \( DCB \) and \( DCBV \) mean wavefunctions calculated in a self-consistent manner by using Dirac–Coulomb–Breit Hamiltonian without and with adding the Uehling potential, respectively. Besides \( R^{(n)} \) are the radial integrals defined as

\[
R^{(n)}(n_1k_1n_2k_2) = \int_0^\infty r^n (P_{n_1k_1}Q_{n_2k_2} + Q_{n_1k_1}P_{n_2k_2}) dr
\]

being \( P_{nk} \) and \( Q_{nk} \) the radial parts of the one-electron wavefunction (Dirac bispinor). The \( C_K(\frac{DCB}{DCBV}) \) and \( C_B(\frac{DCBV}{DCB}) \) factors count the VP effects on both perturbators of Eq. (4). It is worth to mention that \( C_K(\frac{DCB}{DCBV}) \) factors are larger than \( C_B(\frac{DCBV}{DCB}) \) factors or, in other words, the expectation value of \( \alpha \times r \) operator is more influenced by VP than the one for \( \alpha \) or \( r \) operator. Then the coefficient \( C^{VP/DC} \) expressed as

\[
C^{VP/DC} = C_K(\frac{DCBV}{DCB})C_B(\frac{DCBV}{DCB}) - 1
\]

accounts for perturbed-orbital VP influence on both perturbators. Index DC means the Dirac–Coulomb–Breit level of theory, without QED corrections. We should also mention that factors \( C^{VP/DC} \) in each of the following group of excitations: \( ns - n's, np_{1/2} - np_{1/2}, \)
After short derivations:
\[
\Delta \varepsilon_{ia} = \xi_{ia}^{DC} - \varepsilon_a^{DC}, \quad \Delta \varepsilon_{ia}^{VP} = \Delta \varepsilon_{ia}^{V} - \varepsilon_a^{VP} \quad \text{for simplification. Then using Eq. (1)}
\]
\[
\sigma_{ia}^{DC+VP,po} = \frac{m_{ia}^{DCV}}{\Delta \varepsilon_{ia} + \Delta \varepsilon_{ia}^{VP}} = \frac{m_{ia}^{DC}}{\Delta \varepsilon_{ia} + \Delta \varepsilon_{ia}^{VP}} + \sigma_{ia}^{V,po}
\]
\[
= \sigma_{ia}^{DC} + \sigma_{ia}^{V,po} = \frac{m_{ia}^{DC}}{\Delta \varepsilon_{ia} + \Delta \varepsilon_{ia}^{VP}} + \sigma_{ia}^{V,po} \quad \text{(16)}
\]

After short derivations:
\[
\Delta \sigma_{ia}^{V,po} = \frac{m_{ia}^{DC} (C_{ia}^{VP/DC} - \Delta \varepsilon_{ia}^{VP})}{\Delta \varepsilon_{ia} + \Delta \varepsilon_{ia}^{VP}} \quad \text{(17)}
\]

Next, we can write:
\[
\sigma_{ia}^{DC+QED} = \sigma_{ia}^{DC} + \Delta \sigma_{ia}^{QED} = \sigma_{ia}^{DC} + \sigma_{ia}^{QED} C_{ia}^{QED/DC}
\]
\[
= \sigma_{ia}^{DC} + \sigma_{ia}^{V,po} \frac{\Delta \sigma_{ia}^{QED}}{\Delta \sigma_{ia}^{V,po}} \quad \text{(18)}
\]

where the scaling coefficients \(C_{ia}^{QED/DC}\) is introduced. Finally, linking Eq. (17) and Eq. (18) we obtain the \(C_{ia}^{QED/DC}\) coefficient in the form
\[
C_{ia}^{QED/DC} = \left( \frac{C_{ia}^{VP/DC} - \Delta \varepsilon_{ia}^{VP}}{1 + \Delta \varepsilon_{ia}^{VP}} \right) R_D^{-1} \quad \text{(19)}
\]
when \(a\) is a positive-energy unoccupied state. If \(a\) is one of the negative-energy unoccupied states, \(C_{ia}^{QED/DC} = 0\). For simplicity we used the factor \(\Delta \varepsilon_{ia}^{VP} = \Delta \varepsilon_{ia}^{VP}/\Delta \varepsilon_{ia}\).

Then we are able to rewrite Eq. (6) to include leading-order QED effects within polarization propagator formalism at zeroth- and first-order level of approach:
\[
\sigma_{ia}^{DC+QED}(K) = \sum_{i=\text{inner }s\text{-type}, \quad a=\text{unoccupied }s\text{-type}} \sigma_{ia}^{DC}(K) \left( 1 + C_{ia}^{QED/DC} \right)
\]
\[
+ \sum_{i=\text{inner }s\text{-type}, \quad a\neq \text{unoccupied }s\text{-type}} \sigma_{ia}^{DC}(K)
\]
\[
+ \sum_{i \neq \text{inner }s\text{-type}, \quad a} \sigma_{ia}^{DC}(K) \quad \text{(20)}
\]

In this equation the amplitudes for excitations between atomic or molecular orbitals are scaled by coefficients \(C_{ia}^{QED/DC}\).

The more general approach\(^{30}\) considers excitations from occupied electronic states to both positive- (electronic) and negative-energy (positronic) unoccupied Dirac states, resulting in the ee and pp contributions, respectively. In order to ensure the compatibility between the approaches of Yerokhin \textit{et al}. and ours, we implemented QED corrections only to the ee term of shielding. Coefficients \(D_{SE}, D_{VP}, D_{VP,po}\) have been calculated for H-like systems, in such a way that the use of \(C_{ia}^{QED/DC}\) factor is justified only for \(ns - n's\) excitations. Assuming that the pattern of SE to VP effects ratio is similar for each \(ns\) subshell, as happens in the case of orbital energies (see supplement of Ref. 35), we extended our model for excitations from \(ns\) subshells with \(n > 1\).

\section{C. Estimating QED effects – model B}

There are few approaches to estimate the influence of QED effects on orbital energies, in many-electron atoms.\(^{24,35}\) The original idea of Bethe\(^{36}\) linked the QED contribution to \(ns\) orbital energies with the electron density at the site of the nucleus. We test this simple model in the case of QED contributions to shielding constants:
\[
\Delta \sigma_{H_{Hyd}}^{QED} = \Delta \sigma_{H_{Hyd}}^{QED} \sum_n \rho(0)_{ns} \sum_a \sigma_{ns,a}^{H_{Hyd}} \quad \text{(21)}
\]

where \(\Delta \sigma_{H_{Hyd}}^{QED}\) is calculated by Eq. (7), according to Ref. 15, and \(\sigma_{ia}\) was defined in Eq. (5) (\(a\) is an unoccupied electronic state).

\section{D. QED effects on the shielding constants of nuclei in molecules}

For the calculation of nuclear shieldings in molecules within polarization propagators, the occupied and vacant atomic orbitals, AOs, \(i, j\) and \(a, b\), respectively, are replaced by their molecular orbitals, MOs, counterparts. In order to estimate their QED effects we assume that:

- They will modify the contributions due to perturbators but not much the matrix elements of the principal propagator. Then we can use the same criterium for including QED effects in molecules as used for atoms; meaning, by applying coefficients \(C_{ia}^{QED/DC}\)

- They are mostly due to excitations arising from the occupied MOs that are built from \(s\)-type GTO. These MOs are \(\sigma\) bonding and antibonding orbitals. Furthermore, the inner occupied MOs are close in energy to the inner AOs of the atom to whom that nucleus belongs. Then we can use \(C_{ia}^{QED/DC}\) for
including QED effects due to the innermost s-type MOs.

In order to be more clear about the way we included the ee contributions to the shielding on molecules, it is better to rearrange the summation of the rhs of Eq. (20) into two parts. The one that include QED effects on top of contributions of the ns−n’s MOs excitations and another one that only consider relativistic contributions. This scheme of calculation will be given more explicitly in the next section.

E. Computational details

1. MCDF method

The calculation of \( C(DCBV_{DCB}) \) coefficients, the radial integrals defined in Eq. (14), and QED contributions to the orbital energies were performed by means of MCDFGME code release 2005. This four-component code is based on the well-established Multiconfigurational Dirac–Fock (MCDF) approach.

The methodology of MCDF calculations performed in the present studies is similar to the one published earlier, in several papers (see, e.g., 37, 38). The effective Dirac–Coulomb–Breit Hamiltonian for an N-electron system is expressed by

\[
\hat{H} = \sum_{i=1}^{N} \hat{h}_D(i) + \sum_{j>i=1}^{N} V_{ij}
\]

where \( \hat{h}_D(i) \) is the Dirac one-particle operator for \( i \)-th electron and the terms \( V_{ij} \) account for the effective electron-electron interactions.

An atomic state function (ASF) with the total angular momentum \( J \), its z-projection \( M \), and parity \( p \) is assumed in the form

\[
\Psi_s(JMP) = \sum_m c_m(s) \Phi(\gamma_m JMP)
\]

where \( \Phi(\gamma_m JMP) \) are configuration state functions (CSF), \( c_m(s) \) are the configuration mixing coefficients for state \( s \), \( \gamma_m \) represents all information required to uniquely define a certain CSF. The CSF is a Slater determinant of Dirac 4-component bispinors:

\[
\Phi(\gamma_m JMP) = \sum_i d_i \begin{vmatrix} \psi_1(1) & \cdots & \psi_1(N) \\ \vdots & \ddots & \vdots \\ \psi_N(1) & \cdots & \psi_N(N) \end{vmatrix}
\]

where the \( \psi_i \) is the one-electron wavefunctions and \( d_i \) coefficients are determined by requiring that the CSF is an eigenstate of \( \hat{J}^2 \) and \( \hat{J}_z \). The one-electron wavefunction is defined as

\[
\psi_{n,\kappa,j} = \frac{1}{r} \left( P_{n,\kappa}(r) \cdot \Omega^{m_{\kappa,j}}_{n,\kappa,j}(\theta, \phi) \right)
\]

where \( \Omega^{m_{\kappa,j}}_{n,\kappa,j}(\theta, \phi) \) is a angular 2-component spinor and \( P_{n,\kappa}(r) \) and \( Q_{n,\kappa}(r) \) are large and small radial part of the wavefunction, respectively.

The electron-electron interaction term is a sum of the Coulomb interaction \( \hat{V}^C_{ij} \) operator and the transverse Breit \( \hat{V}^B_{ij} \) operator:

\[
\hat{V}_{ij} = \hat{V}^C_{ij} + \hat{V}^B_{ij}
\]

where the Coulomb interaction operator is \( \hat{V}^C_{ij} = 1/r_{ij} \), and the Breit operator

\[
\hat{V}^B_{ij} = -\alpha_j \cdot \alpha_j e^{i\omega_{ij}r_{ij}}/r_{ij} - (\alpha_j \cdot \nabla_j)(\alpha_j \cdot \nabla_j) e^{i\omega_{ij}r_{ij}} - 1/\omega_{ij}r_{ij}
\]

where \( \omega_{ij} = (\varepsilon_i - \varepsilon_j)/c \) is the frequency of one virtual photon exchanged (\( \varepsilon_i \) and \( \varepsilon_j \) are orbital energies of interacting electrons).

The Uehling potential, being the first term of vacuum polarization contribution of order \( \alpha(Z_0) \), in the case of finite nuclear size and spherical symmetric nuclear charge distribution \( \rho(\vec{r}) \) can be expressed as:

\[
U(\vec{r}) = -\frac{2}{3} \frac{Z_0^2 e^2}{m r} \int_0^\infty d^3r' r' \rho(\vec{r}') \int_0^\infty d^3r'' |r - r''| K_0\left( \frac{2mc}{h} |r + r''| \right)
\]

where the function \( K_0(x) \) is defined as:

\[
K_0(x) = \int_1^\infty dt e^{-xt} \left( \frac{1}{t^3} + \frac{1}{2t^5} \right) \sqrt{t^2 - 1}
\]

The Uehling potential in atomic self-consistent field calculations that can be treated perturbatively or in self-consistent way. In the last case, the regular Hartree–Fock equations (where \( \hat{F} \) is a Fock operator according to Dirac–Coulomb–Breit Hamiltonian, \( \psi_k \) is an one-electron wavefunction (orbital), and \( \varepsilon_k \) is an orbital energy.)

\[
\hat{F} \psi_k = \varepsilon_k \psi_k
\]

are transformed into new Hartree–Fock equations

\[
(\hat{F} + U) \psi'_k = \varepsilon'_k \psi'_k
\]

where Uehling potential, \( U \), is added to eigenvalue equation, and \( \psi'_k \) and \( \varepsilon'_k \) are modified orbital and orbital energy, respectively.

The radial integrals specified in Eq. 14 have been calculated by using intrinsic function of MCDFGME code.
2. NMR shielding constant calculations

The calculations of NMR shielding constants were performed by means of the DIRAC code release 2017.\textsuperscript{44} The Gaussian nuclear charge distribution was used.\textsuperscript{45} We used for Ne, Ar,\textsuperscript{46} Br, Kr, I, Xe, At, and Rn\textsuperscript{47} the dyall.acv4z basis set and for Zn,\textsuperscript{48} Cd,\textsuperscript{49} and Hg,\textsuperscript{50} the dyall.cv4z basis set. NR values of $\sigma$ were obtained performing pseudo-nrelativistic calculations by assuming the speed of light as $c = 100c_0$ (being $c_0 = 137.0359998$ a.u.).

Because the DIRAC code has issues related to open-shell systems, the $\sum_a \sigma_{s,a}^{H\text{yd}}$ values in Eq. (21) are actually extracted from calculations performed for point-like H-like systems\textsuperscript{43} and corrected by finite nuclear size (FNS) effect by using proportionally values of FNS (calculated by DIRAC code) for He-like ions.

Four-component calculations of shieldings are based on the Dirac–Coulomb and Dirac–Coulomb–Gaunt Hamiltonians. Due to actual implementations in the DIRAC code, Gaunt contributions to the shieldings are partially included in both kind of terms of Eq. (5). They are included in the matrix elements of the principal propagator through the orbital energies (occupied and virtual). For perturbers they are included through the matrix elements of the Fock matrix that is one-index transformed. There are no Gaunt contributions included in the two-electron elements of the principal propagator.\textsuperscript{31} Furthermore, we should highlight that the Breit electron-electron interactions are replaced by Gaunt integrals, i.e. the retardation terms are neglected. We assume that Gaunt interactions provide a useful approximation to the Breit interactions; they were found to be an order of magnitude larger than the retardation contributions.\textsuperscript{25}

Linear response calculations were performed within the relativistic polarization propagator approach at the random phase level of approach (RPA). Two-electron integrals containing only small component basis functions, the (SS)(SS) integrals, were included in all calculations.

In all cases, the uncontracted Gaussian basis sets were used with the common gauge-origin (CGO) approach. The small component basis sets for relativistic calculations were generated by applying the unrestricted kinetic balance prescription (UKB).

In the DIRAC code MOs are expanded in a gaussian basis set in such a way that $s$-type, $p$-type, etc gaussian functions are used. Then Large and Small $s$-type components are expanded in a set of $s$-type gaussian functions so that we can use the scaled $C_{1s,ns}^{QED/DC}$, $C_{2s,ns}^{QED/DC}$, . . . coefficients for including QED corrections arising from the innermost $s$-type MOs. For the molecules analyzed here, we found that the first term on the rhs of Eq. (20) dominates over the second term, i.e. the contribution of excitations starting from inner $s$-type MO that end up on s-type unoccupied MOs is very high (larger than 90%):

$$\sum_{i=\text{inner } s\text{-type, } a=\text{unoccupied } s\text{-type}} \sigma_{i,a}^{DC}(K) > 0.9$$

Then, in practice, we calculate $\sigma^{DC+QED}$ by using simplified form of Eq. (20):

$$\sigma^{DC+QED}(K) = \sum_{i=\text{inner } s\text{-type}, a}\sigma_{i,a}^{DC+QED}(K) + \sum_{i\neq\text{inner } s\text{-type}, a}\sigma_{i,a}^{DC}(K)$$

with the error of calculations about 5%. We used the special output of DIRAC code to make such kind of analysis. We show how to actually do it in Supplementary Information for I$_2$ molecule.

The gauge origin of the external magnetic potential was placed at the molecular center of mass in all the NMR shielding calculations. Furthermore, when necessary the shieldings were calculated for the anions rather the neutral atoms in order to have closed-shell systems.

Experimental bond distances were extracted from Ref.\textsuperscript{51} for HBr, HI, Br$_2$ and I$_2$. For HAt and At$_2$, optimized distances were employed, and calculated at DHF level of approach. The internuclear distances are: 1.4145 Å (HBr), 1.6090 Å (HI), 2.2811 Å (Br$_2$), 2.6663 Å (I$_2$), 1.7117 Å (HAt) and 2.9627 Å (At$_2$).

III. RESULTS AND DISCUSSIONS

We shall show first results at RPA level of approach of four-component calculations of shielding for neutral atoms and ions separated in paramagnetic-like and diamagnetic-like as is usual within the NR regime. This analysis will show the origin of novel behaviors that appear for the first time in the present work. Relativistic effects are then analyzed and compared with NR contributions. Gaunt contributions (which are partially included as mentioned in the previous Section) to the relativistic effects are also given. The pattern of QED contributions to the atomic and diatomic molecular systems are then given, together with the analysis of which excitations are more involved. In our previous article\textsuperscript{23} we have included only few of total excitations. We shall end up with the analysis of the dependence of QED effects on the shielding of atoms and molecules, and compare them with relativistic and NR effects.
TABLE I. NMR shielding constants (without QED contributions), but employing the Dirac–Coulomb–Gaunt Hamiltonian for Ne, Ar, Zn, Kr, and Cd neutral atoms, and their ions. $\sigma^i$ means total shielding and $\sigma^{pp}$ and $\sigma^{ee}$ mean diamagnetic-like and paramagnetic-like terms, respectively. $\sigma_{\text{Lamb}}$ stand for numbers calculated by the Lamb expression. $n_{el}$ is the number of electrons in the ion.

| $Z$ | $n_{el}$ | $\sigma^i$ (ppm) | $\sigma^{pp}$ (ppm) | $\sigma^{ee}$ (ppm) | $\sigma_{\text{Lamb}}$ (ppm) |
|-----|---------|-----------------|-------------------|-------------------|------------------|
| 10  | 2       | 348.8549        | 338.1047          | 10.7510           | 342.3263         |
|     | 4       | 421.3373        | 409.6371          | 11.7004           | 400.4438         |
| 10  | 557.1123| 545.1253        | 11.9870           | 553.3895          |                  |
| 18  | 2       | 656.4766        | 598.0950          | 58.3816           | 628.4583         |
|     | 4       | 803.1269        | 738.6204          | 64.5065           | 755.8693         |
| 10  | 1156.6681| 1090.1447      | 66.5234           | 1124.4790         |                  |
|     | 1195.9558| 1128.6501      | 67.3058           | 1158.8409         |                  |
| 12  | 1273.1343| 1205.4665      | 67.6679           | 1245.6581         |                  |
| 30  | 2       | 1196.1820       | 924.0793          | 272.1072          | 1073.2685        |
|     | 4       | 1465.2827       | 1162.2390         | 303.0437          | 1309.4299        |
| 10  | 2149.9452| 1833.8730      | 316.0722          | 1988.8222         |                  |
| 12  | 2240.5185| 1918.4602      | 322.0582          | 2072.9267         |                  |
| 18  | 2466.5450| 2141.9852      | 324.5598          | 2277.2334         |                  |
| 30  | 2708.5417| 2380.5594      | 327.9823          | 2564.3647         |                  |
| 36  | 2       | 1522.3339       | 1055.0074         | 467.3265          | 1305.3292        |
|     | 4       | 1861.1178       | 1339.3208         | 521.7970          | 1598.4356        |
| 10  | 2176.8037| 2171.1266      | 545.6771          | 2450.7825         |                  |
| 12  | 2835.1619| 2728.0196      | 557.1423          | 2547.4234         |                  |
| 18  | 3315.6392| 2573.5528      | 562.0864          | 2819.8878         |                  |
| 30  | 3520.6708| 2952.8542      | 567.8166          | 3252.5333         |                  |
| 36  | 3584.5022| 3014.7361      | 569.7661          | 3324.2802         |                  |
| 48  | 2       | 2358.6725       | 1247.4817         | 1111.1908         | 1797.8509        |
|     | 4       | 2865.7675       | 1619.5662         | 1246.2014         | 2213.7973        |
| 10  | 4082.0625| 2770.4307      | 1311.6345         | 3403.7627         |                  |
| 12  | 4263.8099| 2920.9406      | 1342.8093         | 3550.2714         |                  |
| 18  | 4718.6823| 3360.6799      | 1358.0024         | 3966.4257         |                  |
| 30  | 5382.5622| 4006.6724      | 1375.8898         | 4669.1920         |                  |
| 36  | 5537.2706| 4157.2339      | 1380.0368         | 4817.9820         |                  |
| 48  | 5712.6538| 4328.3407      | 1384.3131         | 5020.0663         |                  |

A. Relativistic and non-relativistic contributions

We should first mention that all relativistic calculations were performed using the Dirac–Coulomb–Gaunt Hamiltonian. Tables I and II collect calculated NMR shielding constants (without QED contributions) for closed-shell 10Ne, 18Ar, 30Zn, 36Kr, 48Cd, 54Xe, 80Hg, and 86Rn neutral atoms, and their selected closed-shell ions. We included in them both contributions, $\sigma^{pp}$ and $\sigma^{ee}$, which are equivalent to diamagnetic-like and paramagnetic-like terms well defined within the NR framework.30 For low- and medium-Z atoms, the diamagnetic-like term contributes more than the paramagnetic-like one, but for high-Z atoms this behavior is reversed.

One can see that the diamagnetic-like contributions strongly depend on the actual number of electrons that are bonded to the ionized atoms ($n_{el}$), but the paramagnetic dependence on them is much smaller. These differences show that they arise from two different physical origins.

The major contributions to $\sigma^{ee}$ arise from electron-electron excitations that start from the 1s shell, even for neutral atoms. The next important part of those excitations start from the 2s shell (and then appears those starting from higher ns shell for high-Z atoms). For example, for Be-like ($n_{el}=4$) Ne the e-e excitations from the 1s shell contribute 82.42% and excitations from the 2s shell contribute 17.58%. For Be-like Rn these numbers are 65.29% and 34.71% respectively. For neutral Ne ($n_{el}=10$) the e-e excitations from the 1s shell contribute 82.57% and excitations from the 2s shell contribute 13.69%. For neutral Rn ($n_{el}=86$) these numbers are 52.35% and 21.16% respectively. One can see that with increasing $Z$ the percentual contributions from 2s shell excitations increase and those from the 1s shell decrease.

The percentage of contributions to the relativistic value of $\sigma^{ee}$ of He-, Be-, Ne- like and Rn neutral atoms are shown in Fig. 1. For He-like Rn the excitation 1s $\rightarrow$ 2s (1s $\rightarrow$ 3s) contributes $\approx 25.4\% \quad (\approx 5.6\%)$. The other important contributions arises from excitations to the
They do not depend on the occupation number of the spectra, and all inner and middle shells do it with a significant value (as opposite to $\sigma^{ee}$ part, where $1s$ and $2s$ contribute together 75–90\% to $\sigma^{ee}$). In order to be more explicit let us analyze the way $\sigma^{pp}$ is built for the neutral Rn. Excitations that start in $1s$ and $2s$ AOs contribute with $\approx 12.68\%$ and $7.27\%$, respectively, of the total value of the shielding (i.e. $6.34\%$ and $3.63\%$ per each electronic occupation of both $ns$ AOs, respectively). The $2p$ AOs contribute with $\approx 26.85\%$ (4.47\% per electron), and the absolute value of those contributions are almost independent of whether one consider the neutral or the ionized Rn, meaning that it depends only on $Z$. Then, all other subshells will contribute with values that are almost the same for a given nucleus. This behavior explains why $\sigma^{pp}$ grows continuously when the highly ionized atom is becoming less ionized.

From this previous analysis, and given that within our formalism $\sigma^{pp}$ can be understood as due to the propagation of virtual electron-positron pairs, that involve negative-energy electronic orbitals together with positive-energy electronic orbitals, we are able to state that $\sigma^{pp}$ "strongly depends" on the occupation number of electrons in each subshell, and the value of $Z$.

In the work of Lamb\textsuperscript{52} there was pointed out that the diamagnetic contribution to the non-relativistic shielding is connected to the ground-state expectation value of the electrostatic potential. This was further reported in Helgaker \textit{et al.}\textsuperscript{53} paper, in which the simple formula for the shielding of spherically symmetrical closed-shell atoms with the gauge origin in nuclear position of the atom, was written and called Lamb expression:

$$
\sigma = \frac{\alpha^2}{3} \langle 0 | \frac{1}{r} | 0 \rangle
$$

Even though in those previously mentioned papers it was not explicitly written, on the ground of our new under-
standings one may realize that the shielding for the whole atom is a sum of shielding contributions from particular shells. This approach may allow us to simply analyze the variation of $\sigma$ with occupation of particular shells, on NR level of theory. The shielding numbers calculated by using Eq. (34) and expectation values of $1/r$ from MCDF-calculated orbitals are presented also in Tables I and II, marked as $\sigma_{\text{Lamb}}$. The numbers calculated by Lamb expression agree well, within ten percent, with pp results for shielding constants of atoms calculated by DIRAC code with $Z \leq 30$. For higher-Z atoms, the relativistic effects become important and so the difference between both kind of calculations become higher. For neutral atoms that difference is much smaller than for ionic atoms. In the case of neutral Hg the difference is close to 25% but for He-like Hg such a difference is as high as three times.

Tables III and IV collect NR results for NMR shielding constants of selected atoms and their ions. It can be seen that the paramagnetic-like term goes to zero within the NR framework as it should be. For neutral atoms, the relativistic part of shielding constant, meaning $\sigma_{\text{R-NR}} = \sigma - \sigma_{\text{Lamb}}$, contributes from 1% for Ne to 45% for Rn to the total $\sigma$. For ions these numbers are even higher because inner shells are more influenced by relativistic effects than outer shells.

Gaunt contributions to $\sigma^t$ (meaning the difference in $\sigma^t$ value calculated with and without Gaunt term included in SCF process) are also given in Tables III and IV. We observe that they grow in absolute values from higher to lower ionized atoms. Its values are the largest for neutral atoms.

We observe that Gaunt contributions to $\sigma$ are not dependent on relativistic effects. They are $\approx -2\%$ of the relativistic effect for Ar and $\approx -0.3\%$ for Rn. The fact that the percentage of Gaunt contributions goes down when compared with relativistic effects on $\sigma$ is related with the increase of relativistic effects. When $\sigma$ is compared with $\sigma^{NR}$ it is observed that $\sigma^{Gaunt} \approx -0.05\%$ of $\sigma^{NR}$ for Ar and $\approx -0.2\%$ of $\sigma^{NR}$ for Rn. Another interesting finding is that $\sigma^{Gaunt}$ change its sign between

| $Z$ | $n_{\text{el}}$ | $\sigma_{\text{NR}}$ (ppm) | $\sigma_{\text{R-NR}}$ (ppm) | $\sigma_{\text{Lamb}}$ (ppm) | $\sigma_{\text{Gaunt}}$ (ppm) |
|-----|-----------------|-----------------|-----------------|-----------------|-----------------|
| 54  | 2               | 1905.9422       | 1001.0494       | 34.4359         | -1.9922         |
| 4   | 2368.4125       | 1151.3490       | 32.7110         | -2.7048         |
| 10  | 3678.3718       | 1250.3932       | 25.3693         | -5.6492         |
| 12  | 3859.4636       | 1288.6275       | 25.0312         | -6.0481         |
| 18  | 4366.7104       | 1317.3961       | 23.1768         | -6.8464         |
| 30  | 5146.0275       | 1343.9251       | 20.7078         | -8.1215         |
| 36  | 5355.9689       | 1353.2726       | 20.2306         | -8.2457         |
| 48  | 5591.8795       | 1359.8798       | 19.5617         | -8.7942         |
| 54  | 5642.0615       | 1370.5069       | 19.8543         | -9.0639         |
| 80  | 2               | 2828.7900       | 4505.8992       | 61.4322         | 1.6319          |
| 4   | 3522.0704       | 5265.5525       | 59.9201         | -0.4348         |
| 10  | 5524.3437       | 5711.4566       | 50.8327         | -9.7077         |
| 12  | 5808.0173       | 5914.5940       | 50.4546         | -10.8804        |
| 18  | 6623.0491       | 6052.2564       | 47.7484         | -14.1050        |
| 30  | 7974.2459       | 6179.4126       | 43.6595         | -17.7444        |
| 36  | 8383.5148       | 6231.2183       | 42.7682         | -18.6334        |
| 46  | 8866.2448       | 6255.8162       | 41.3686         | -20.1192        |
| 60  | 9414.2095       | 6281.4881       | 40.0204         | -21.0645        |
| 80  | 9729.8925       | 6313.9461       | 39.5435         | -22.3831        |
| 86  | 2               | 3041.7961       | 6205.8031       | 67.1072         | 5.0326          |
| 4   | 3788.2603       | 7289.0735       | 65.8017         | 2.8784          |
| 10  | 5950.2979       | 7904.1760       | 57.0514         | -9.5504         |
| 12  | 6257.2620       | 8195.2311       | 56.7032         | -11.1096        |
| 18  | 7143.6821       | 8386.9389       | 54.0026         | -15.4192        |
| 30  | 8626.6467       | 8561.4539       | 49.8104         | -19.9342        |
| 36  | 9030.9652       | 8635.7416       | 48.8814         | -21.2242        |
| 46  | 9625.7345       | 8686.2746       | 47.3831         | -23.1337        |
| 60  | 10270.2984      | 8701.8602       | 45.8665         | -24.2527        |
| 80  | 10682.6048      | 8758.8185       | 45.0524         | -25.8796        |
| 86  | 10727.9376      | 8932.1352       | 45.4329         | -27.5181        |

TABLE III. Non-relativistic results for NMR shielding constants for Ne, Ar, Zn, Kr, and Cd neutral atoms, and their ions. $\sigma_{\text{R-NR}}$ means the relativistic shift, i.e., $\sigma_{\text{R-NR}} = \sigma - \sigma_{\text{Lamb}}$. Gaunt contribution to the $\sigma^t$ is also elucidated (Gaunt contribution is included in $\sigma_{\text{R-NR}}$ but given in separate column for its further analysis).

TABLE IV. Like Table III, but for Xe, Hg, and Rn neutral atoms, and their ions.
Be-like and Ne-like Rn and between He-like and Be-like Hg.

B. QED contributions for neutral atoms and ions

Tables V and VI collect QED contributions, calculated with model A, to $\sigma^{ee}$ for selected atoms and their ions. The QED contributions, $\sigma^{QED}$, were split into parts according to particular types of e-e excitations: $1s \rightarrow 2s$ (only for He-like atomic systems), $1s \rightarrow ns$ ($n > 2$), $2s \rightarrow ns$, $3s \rightarrow ns$, and $4s \rightarrow ns$. We used three $C^{QED/DC}$ coefficients in present work: $C_{1s,2s}^{QED/DC}$, $C_{1s,n,s}^{QED/DC}$ (assuming $\alpha \simeq 0.35\Delta E_{1s}/E_{1s}^{DC}$ and $\beta \simeq 0.35\Delta E_{1s}/E_{1s}^{DC}$), and $C_{2s,n,s}^{QED/DC}$ (assuming $\alpha \simeq 0.35\Delta E_{2s}/E_{2s}^{DC}$ and $\beta \simeq 0.35\Delta E_{2s}/E_{2s}^{DC}$; used for $2s \rightarrow ns$, $3s \rightarrow ns$, and $4s \rightarrow ns$ excitations). With Dirac code one can calculate both bounded and unbounded though discretized electronic orbitals, but we assume that QED effects on excitations from the inner orbitals to highly excited, bounded or unbounded though discretized orbitals are the same (QED effects arises from strong electric field near nucleus).

As stated before in Refs. 14 and 15, QED contributions to NMR shielding constants have negative sign. The $\sigma^{QED}$ is almost independent of the number of electrons in ion. It is because a major part of e-e excitations occur from inner $1s$ and $2s$ shells, that are more influenced by QED effects. Even if contributions from $1s$ and $2s$ shells decrease a little with $n_{el}$, the contributions from $3s$ and $4s$ shells arise instead. As one can see from Tables V and VI, the $\sigma^{QED}$ contributes to $\sigma$ from $-0.0011\%$ for Ne to $-0.51\%$ for Rn. For neutral atoms $\sigma^{QED}$ scales like $Z^{2}$, a dependence that is weaker than that of H-like atoms for which $\sigma^{QED}$ scales like $Z^{4.15}$.

QED effects contribute to $\sigma^{R-NR}$ from $-0.10\%$ for Ne to $-1.13\%$ for Rn. Note that $\sigma^{QED}/\sigma^{R-NR}$ ratio grows almost linearly with Z for neutral atoms. The $\sigma^{QED}/\sigma^{R-NR}$ ratio depends also on the number of electrons: the higher the number of electrons in ion, the lower the ratio $\sigma^{QED}/\sigma^{R-NR}$. The contribution to $\sigma$ of QED effects is larger than that of Gaunt for higher Z atoms. The $\sigma^{QED}/\sigma^{Gaunt}$ ratio depends on the number of electrons; the higher number of electrons in ion, the lower $\sigma^{QED}/\sigma^{Gaunt}$ ratio. For neutral atoms, the $\sigma^{QED}/\sigma^{Gaunt}$ ratio grows like $Z^{2.4}$.

In Table VII we present the contributions of QED effects to $\sigma^{ee}$ for neutral atoms, calculated with model B. One can see that QED contributions from model B are about 79–97\% of QED contributions from model A, except for Ne and Ar atoms. Results from the less accurate model B show that, by applying model A, we are getting reliable orders of magnitude for QED contributions to NMR shielding constants.

The percentage with which QED effects contribute to the total NMR shielding constants, $\sigma^{QED}/\sigma^{t}$, for neutral atoms (present work) and for H-like atomic systems (Yerokhin et al. work) are presented on Fig. 2. The analysis of uncertainty was performed in our previous paper\textsuperscript{23}.

In Figs. 3 and 4 we observe the pattern of dependence with $Z$ for four terms that contribute to both, $\sigma$ and the total energy. Such terms are: NR, relativistic, QED and Breit/Gaunt.

It is seen that, for $\sigma$, relativistic effects are as large as the NR shieldings when $Z \simeq 86$, though they are smaller when $Z \simeq 10$. On the other hand QED effects grow faster than all the other ones as $Z$ grows. For $Z \simeq 86$ QED effects are less than two orders of magnitude smaller than both, relativistic and NR contributions. Hence, if one wants to reproduce NMR shieldings within less than 1\% of error one must include QED effects.

In Fig. 4 we observe that, the contributions of QED effects and Breit interactions to the total atomic energy of atoms, grow together almost at the same rate. This behavior is different as that observed in Fig. 3, meaning that QED effects are larger for shieldings than for electronic energies of atoms. A similar behavior is also observed for relativistic effects, which are larger for shieldings than for...
TABLE V. QED contributions to $\sigma^{ee}$ (model A) for Ne, Ar, Zn, Kr, and Cd, and their ions.

| Z  | $n_{el}$ | 1s − 2s | 1s − ns | 2s − ns | 3s − ns | 4s − ns | total | $\sigma^{QED}/\sigma^{t}$ | $\sigma^{QED}/\sigma^{R-NR}$ |
|----|---------|---------|---------|---------|---------|---------|-------|----------------|----------------|
| 10 | 2       | −0.0006 | −0.0051 | −0.0011 | −0.0062 | −0.0006 | −0.0057 | −0.0016 | −0.1148 |
| 10 | 4       | −0.0006 | −0.0051 | −0.0011 | −0.0062 | −0.0006 | −0.0057 | −0.0016 | −0.1148 |
| 30 | 2       | −0.1210 | −0.7189 | −0.2110 | −0.7208 | −0.7303 | −0.7109 | −0.7194 | −0.5011 |
| 36 | 2       | −0.2630 | −1.4243 | −0.4451 | −1.4277 | −1.4445 | −1.3997 | −1.4115 | −0.5549 |
| 48 | 2       | −0.9093 | −4.4783 | −1.5564 | −4.4879 | −4.5346 | −4.3585 | −4.3794 | −0.7205 |

FIG. 4. Individual contributions (absolute values) to the total energy for selected atoms.

energies when compared with NR contributions in both cases.

C. QED contribution for diatomic halogen molecules

NMR shielding constants (without QED contributions, but employing a Dirac–Coulomb–Gaunt Hamiltonian) for Br, I, and At halogens nuclei in Br$_2$, I$_2$, and At$_2$ homonuclear molecules, and HBr, HI, and HAt heteronuclear molecules, and Br$^-$, I$^-$, and At$^-$ ions are presented in Table VIII. Because of lack of spherical symmetry, the shielding tensor contributions parallel ($\|\|$) and perpendicular ($\perp$) to the molecular axis are presented. As one can see, $\sigma_{ee}^{\|}$ and $\sigma_{ee}^{\perp}$ differ from each other more than $\sigma_{pp}^{\|}$ and $\sigma_{pp}^{\perp}$. This can be understood by using a relativistic model that relates $\sigma$ with the spin-rotation constants.54–56 There are different contributions to the parallel and perpendicular components of the spin-rotation tensor caused by the change of electron density according to bond formation.

QED contributions to $\sigma^{ee}$ are collected in Table IX. We performed calculations of Br$^-$, I$^-$, and At$^-$ ions instead of the calculations of regular Br, I, and At atoms, because the DIRAC code has issues related with open-shell systems.

One can see in Table IX, that QED contributions to $\sigma(X)$ in X$_2$ molecules (X = Br, I, At) are little smaller.
TABLE VI. Like Table V, but for Xe, Hg, and Rn, and their ions.

| Z | n<sub>el</sub> | 1s − 2s | 1s − ns | 2s − ns | 3s − ns | 4s − ns | total | σ<sup>QED</sup>/σ<sup>t</sup> | σ<sup>QED</sup>/σ<sup>R−NR</sup> |
|---|---|---|---|---|---|---|---|---|---|
| 54 | 2 | −1.5292 | −6.7793 | | | | | | |
| | | | | | | | | | |
| | 4 | | | | | | | | |
| | 10 | | | | | | | | |
| | 12 | | | | | | | | |
| | 18 | | | | | | | | |
| | 30 | | | | | | | | |
| | 36 | | | | | | | | |
| | 48 | | | | | | | | |
| | 54 | | | | | | | | |
| 80 | 2 | −12.1398 | −42.1905 | | | | | | |
| | | | | | | | | | |
| | 4 | | | | | | | | |
| | 10 | | | | | | | | |
| | 12 | | | | | | | | |
| | 18 | | | | | | | | |
| | 30 | | | | | | | | |
| | 36 | | | | | | | | |
| | 46 | | | | | | | | |
| | 80 | | | | | | | | |

TABLE VII. QED contributions to σ<sup>ee</sup> (model B) for Ne, Ar, Zn, Kr, Cd, Xe, Hg, and Rn. "B/A" means σ<sup>QED</sup> (model B)/σ<sup>QED</sup> (model A) ratio.

| Z | 1s − ns | 2s − ns | 3s − ns | 4s − ns | total | σ<sup>QED</sup>/σ<sup>t</sup> | σ<sup>QED</sup>/σ<sup>R−NR</sup> | B/A |
|---|---|---|---|---|---|---|---|---|
| 2-6 | exc. | exc. | exc. | exc. | | | | |
| 10 | −0.0096 | −0.0007 | | | | | | |
| 18 | −0.1130 | −0.0151 | −0.0010 | | | | | |
| 30 | −0.7534 | −0.1380 | −0.0199 | | | | | |
| 36 | −1.4480 | −0.2905 | −0.0506 | | | | | |
| 48 | −4.0903 | −0.9478 | −0.2198 | −0.0302 | −5.2881 | −0.0926 | −0.5268 | 95.3 |
| 54 | −6.2914 | −1.5565 | −0.3960 | −0.0712 | −8.3151 | −0.1186 | −0.6067 | 87.7 |
| 80 | −33.5908 | −11.2176 | −3.7581 | −0.9958 | −49.5623 | −0.3089 | −0.7850 | 76.6 |
| 86 | −52.3454 | −18.8301 | −6.5755 | −1.8721 | −79.6231 | −0.4050 | −0.8914 | 79.2 |

than in the case of X<sup>−</sup> ion. The σ<sup>QED</sup> values for atoms in X<sub>2</sub> molecules are closer to σ<sup>QED</sup> for ions than the σ<sup>QED</sup> values. Furthermore, σ<sup>QED</sup>(X) for X in HX molecules (X = Br, I, At) are closer to its atomic σ<sup>QED</sup> values. It is worth to highlight the fact that σ<sup>ee</sup> becomes more positive (diamagnetic) as relativistic effects increase. This is more pronounced for perpendicular contributions. We also found that the virtual ns → n’s type excitations give a total contribution to σ<sup>ee</sup> that is close to 95% (see Supplementary Information)
Among them one must include QED effects and Breit contributions to the magnetic shieldings, within. Shielings are given in ppm and distance in pm.

HBr

HBr141.45

2945.5229

2913.9614

31.5615

3390.5349

2912.0992

478.4357

2723.0169

2914.8924

−191.8756

I₂

266.63

5512.6072

4975.4177

537.1895

6309.3206

4893.7703

1415.5503

5114.2505

5016.2414

98.0091

I⁻

6795.1202

4887.0379

1908.0823

6795.1202

4887.0379

1908.0823

6795.1202

4887.0379

1908.0823

HI

160.90

5857.8445

4887.6303

970.2142

6553.6279

4886.0641

1667.5637

5509.9528

4888.4133

621.5394

At₂

296.27

16915.9043

8756.1722

8159.7321

15623.7007

8639.6204

6984.0803

17562.0062

8814.4481

8747.5581

At⁻

19162.2480

8627.9157

10534.3322

19162.2480

8627.9157

10534.3322

19162.2480

8627.9157

10534.3322

HAt

171.17

8627.5773

9519.3543

16258.8652

8629.0506

7629.8146

19090.9648

8626.8407

10464.1241

9316 8627

H⁻

−2669 2220

−4016 4720

|σₑₑₑₑ| (pm)

|σⁿ⁻σⁿ⁻| (pm)

TABLE IX. QED contributions to $\sigma^{ee}$ for Br₂, I₂, At₂, HBr, HI, and HAt molecules (per atom) and Br⁻, I⁻, and At⁻ ions.



IV. CONCLUSIONS

When searching for highly accurate atomic and molecular response properties one should consider physical effects that were taken to be vanishingly small few years ago. Among them one must include QED effects and Breit interactions.

As a next step in our research program that aims to include QED effects together with electron correlation on response properties in atoms and molecules, we present here two effective models that were developed to calculate QED effects on top of the paramagnetic-like contributions to the NMR magnetic shieldings of nuclei in many-electron atoms and diatomic molecules. Our results are based on state-of-the-art calculations of QED effects on H-like systems, taken from the works of Yerokhin and collaborators. One of our important findings is related with new insights about the likely physical origin of the paramagnetic-like or ee contribution, and the diamagnetic-like or pp contribution to the magnetic shieldings, within a relativistic framework. The analysis of the physical mechanisms that are involved in them shows that pp contributions can be rationalized as due to virtual electron-positron pair creation/annihilation in such a way that: i) for a given atomic number $Z$, each subshell contributes almost the same value, being the condition for doing it that ii) the subshell be occupied. On the other side, the ee contributions can be understood as mostly due to virtual excitations that start from linear combinations of $s$-type gaussian-type orbitals and do not depend on $n\ell$.

Another important finding is the fact that QED corrections to the NMR shielding constant of many-electron systems can be close or even larger than 1% of the relativistic correction for high-$Z$ atoms. On the other hand its $Z$ dependence is proportional to $Z^5$, being proportional to $Z^4$ for H-like systems. Furthermore, $\sigma^{QED}/\sigma^{NR} \propto Z$. It is worth to mention that QED effects are larger on ions than on neutral atoms for a fixed $Z$.

We also found that, for molecules, most of the main ee excitations involved in the relativistic shielding calculations occur between the lowest molecular orbitals (which are similar to 1$s$ and 2$s$ atomic orbitals) and higher unoccupied orbitals. $σ^{QED}$ is the QED correction to the NMR shielding constant of many-electron systems.
cupied orbitals. This behavior is also found in the main mechanisms contributing to $q^{QED}$. So, its origin is highly atomic for magnetic shieldings in molecules and this is the reason why we were able to apply our models to them.

We have calculated relativistic, non-relativistic, Breit (or a fraction of the total Gaunt) and QED contributions to the shieldings of the following atomic and molecular systems: atoms with 10 ≤ Z ≤ 86 and their ionic closed-shell electronic structures, and X$_2$ and HX (X = Br, I, At) molecules. The Z dependence of those contributions to both, the magnetic shielding constant and the total atomic energy are such that the magnetic shielding constants are more influenced by relativistic and QED effects than the total atomic energies.

At the moment we are trying to extend the application of our models to NMR J-couplings. We now know that the $C_K(DCBV)$ factor is larger than the $C_B(DCBV)$ factor. Thus we expect that QED corrections to J-coupling constants should be larger, or at least of the same size, as QED corrections to NMR shielding constants.

SUPPLEMENTARY MATERIAL

We introduce some supplemental material in few tables. In tables 1, 2, 3, and 4 we show the pattern of contributing excitations (ia) that start in each of the four lowest occupied MO, to the parallel component of the e-e terms of the shielding of iodine nucleus in I$_2$, e.g., $\sigma_{\parallel}(e-e)$(I; I$_2$). The pattern for perpendicular components are similar. We include only contributions that are larger than a very small threshold.

In tables 5 and 6 we show results of the influence, on shielding calculations, due to different Gauge-origins and basis sets.

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