Weak Correlation and Strong Relativistic Effects on the Hyperfine Interaction in Fluorine

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In previous work devoted to *ab initio* calculations of hyperfine structure constants in nitrogen and fluorine atoms, we observed sizeable relativistic effects, a priori unexpected for such light systems, that can even largely dominate over electron correlation. We observed that the atomic wave functions calculated in the Breit-Pauli approximation describe adequately the relevant atomic levels and hyperfine structures, even in cases for which a small relativistic LS-term mixing becomes crucial. In the present work we identify new levels belonging to the spectroscopic terms 2p(3P)3d 2,4(P, D, F) of the fluorine atom, for which correlation effects on the hyperfine structures are small, but relativistic LS-term admixtures are decisive to correctly reproduce the experimental values. The Breit-Pauli analysis of the hyperfine matrix elements nails cases with large cancellation, either between LS pairs for individual hyperfine operators, or between the orbital and the spin-dipole contributions. Multi-configuration Dirac-Hartree-Fock calculations are performed to support the Breit-Pauli analysis.

### I. INTRODUCTION

The development of relativistic theories applied to atoms has greatly contributed to improving the agreement between theory and observation. Among the methods accounting for relativity we can cite the multiconfigurational Hartree-Fock (MCHF) approach with Breit-Pauli (BP) corrections [1,2] and the multiconfigurational Dirac-Hartree-Fock (MCDHF) approach with Breit and QED corrections [3,4]. The methodological developments, combined with the increasing computer resources, allow for accurate calculations of atomic wave functions, which make it possible to study rigorously the balance between electronic correlation and relativistic effects on atomic properties. ATSP2k [5] and GRASP2018 [6] are codes built on, respectively, the MCHF+BP and MCDHF+Breit+QED approaches.

Correlation effects are traditionally presented as being dominant in light atoms, on the basis of the Z-dependent perturbation approach of the non-relativistic Hamiltonian [7], while relativistic effects are expected to be more prominent in heavy atoms, due to the large mean velocity of the inner electrons relatively to the speed of light, when increasing the nuclear charge [4,8]. This picture is definitely too simple, as explicitly expressed two decades ago by Desclaux’s statement [4]: “It is obvious that correlation and relativistic corrections should be included simultaneously in a coherent scheme.” It is nowadays acknowledged that relativity has to be taken into account, even for light atoms [10,11], to obtain accurate predictions of electronic structures.

The effects of relativity on the hyperfine interaction in light atoms have been studied in several works [11,14]. In fully relativistic calculations, as in the MCDHF method, the influence of relativity leads to two effects [15,10]. The first one is a direct effect that results in the contraction of radial orbitals compared to the nonrelativistic ones. The second one, an indirect effect, is a consequence of the first, that manifests itself by an expansion of radial orbitals. Orbitals characterized by low angular momentum l-values, i.e. s and p electrons, undergo the first contraction effect, while orbitals with larger l-values, more efficiently screened due to the relativistic contraction of the s and p shells, are radially outward expanded. These effects, resulting from the application of purely relativistic methods, have a weak influence on the atomic properties of light elements. In the case of the 1s22s2p3d configuration of fluorine (Z = 9), the mean radii of Dirac-Hartree-Fock (DHF) and Hartree-Fock (HF) orbitals, \( \langle r \rangle_{1s}^{\text{DHF}} = 0.17543 \) and \( \langle r \rangle_{1s}^{\text{HF}} = 0.17567 \), differ relatively by 0.14%. This contraction effect in fluorine is rather small in comparison with, e.g. the gold atom, for which the 1s orbital undergoes a relative displacement of the order of 13%, while the 6s-contraction is of the order of 17%, due to the combined direct and indirect effects of relativity [17,18]. In the BP approximation, the radial orbitals are frozen from nonrelativistic calculations, while relativity is captured only through the LS-term mixing for a given J-value. For light atoms, the inclusion of relativistic effects in the BP approximation is generally sufficient to estimate atomic properties accurately.

Large-scale MCHF calculations combined with non-relativistic configuration interaction calculations of hyperfine parameters have been performed successfully in light atoms [13,23]. In some studies, relativity was included to improve the agreement with observation, either through the Breit-Pauli approximation or using the relativistic interaction configurations (RCI) approach [24,27]. In all these works, the relativistic corrections were not negligible, but remained relatively small, changing the hyperfine parameters by less than a few percent. However, unexpected large deviations have been highlighted in the study of hyperfine structures of some levels of the fluorine atom, for

\[
\langle r \rangle_{1s} \quad \langle r \rangle_{2s} \quad \langle r \rangle_{3s} 
\]
which the relativistic effects on the hyperfine constants $A_{3/2}$ and $A_{5/2}$ of the $2p^43p \, ^4P_{0\pi}^{3/2,5/2}$ levels were estimated to be around 30% [28]. Even larger relativistic effects have been found for other levels [14], of the order of 35% for $A(2p^43s \, ^4P_{1/2})$ and, even more spectacular, reaching 182% for $A(2p^43p \, ^4S_{3/2}^{0})$. Aouiri et al. [14] showed that in some cases, although the relativistic effects can be important for the different contributions to the hyperfine interaction, the global effect of relativity may become relatively small due to large cancellation.

The theoretical values of Carette et al. [23] for $A_{3/2}$ and $A_{5/2}$ of the $2p^43p \, ^4P_{3/2}^{3/2,5/2}$ levels, both strongly affected by relativity, were confirmed experimentally [29], while there is no experimental values available to compare with for the other two constants $A(2p^43s \, ^4P_{1/2})$ and $A(2p^43p \, ^4S_{3/2}^{0})$.

Hyperfine constant values for the $2p^4(3P)3d \, ^2S\!+\!1L_J$ levels have been determined recently from concentration modulation spectroscopy experiments [29], and it is worthwhile to investigate how much relativity affects the theoretical estimation. The results obtained in the present work far exceeded our expectations, since the relative differences between the nonrelativistic values and those taking relativity into account reach in some cases several hundreds percent. As an example, the nonrelativistic correlated values, $A(4F_{3/2}) = 1333$ MHz, $A(4F_{5/2}) = 956$ MHz and $A(4F_{7/2}) = 995$ MHz, are dramatically affected by the relativistic BP corrections, which decrease them to $A(4F_{3/2}) = 122$ MHz, $A(4F_{5/2}) = 252$ MHz and $A(4F_{7/2}) = 263$ MHz, in good agreement with the experimental values, respectively, 110 ± 10, 304 ± 50 and 276 ± 10 MHz.

In this work, we investigate and explain the origin of the relativistic effects on the calculated hyperfine constants. We used the multiconfigurational Hartree-Fock (MCHF) method to estimate the hyperfine constants of the $2p^4(3P)3d \, ^2S\!+\!1L_J$ levels, within the framework of a nonrelativistic approach for the optimization of the zero-order wave functions. A simultaneous optimization scheme was applied in the variational nonrelativistic procedure to get a common orbital basis for describing a set of terms that mix in the Breit–Pauli approximation. The relativistic effects are assessed through Breit-Pauli calculations (MCHF+BP). The latter are cross-checked by relativistic configuration interaction (RCI) calculations performed in the Pauli approximation. We also performed fully relativistic MCDHF/RCI calculations based on similar correlation models. These four methods, used for obtaining the relevant electronic wave functions, and the basic theory of hyperfine interaction, are briefly described in Section II.

A. Variational methods

In order to investigate the effects of electronic correlation and relativity on the magnetic dipole hyperfine constant, we used the multiconfiguration Hartree-Fock (MCHF) approach with Breit-Pauli (BP) corrections and the relativistic configuration interaction method (RCI) in the framework of the Pauli approximation (RCI-P). We also used the multiconfiguration Dirac-Hartree-Fock (MCDHF) method combined with the RCI approach.

In the nonrelativistic MCHF method the wave function $\Psi(\gamma\pi LS)$ is a linear combination of configuration state functions (CSFs) $\Phi(\gamma\pi LS)$ having the same parity $\pi$, $L$ and $S$ quantum numbers

$$\Psi(\gamma\pi LS) = \sum_i c_i \, \Phi(\gamma_i\pi LS),$$

where the CSFs are spin-angular-coupled antisymmetric products of one-electron spin-orbitals $\phi$:

$$\phi_{nlm_{l}m_{s}}(r) = \frac{1}{r} P_{nl}(r) Y_{m_{l}}(\theta, \phi) \chi_{m_{s}}.$$

The radial functions $\{P_{nl}(r)\}$ and the mixing coefficients $\{c_i\}$ in (1) are determined by solving iteratively the numerical MCHF radial equations coupled to the eigenvalue problem in the CSFs space, until self-consistency. Since the interactions between several of the terms of the $2p^43d$ configuration are strong, it is important to determine a common set of orbitals for these terms and those that lie below in the spectrum and have the same parity. In this
procedure, referred as simultaneous optimization strategy, the energy functional is a linear combination of energy functionals for the different LS terms \[5\]. Once the one-electron radial functions optimized for the selected states, the BP Hamiltonian matrix is built and diagonalised in the basis of LSJ configuration states belonging to a given parity \(\pi\). The resulting eigenvectors define the intermediate coupling wave functions

\[
\Psi(\gamma\pi J) = \sum_k c_k \Phi(\gamma_k \pi L_k S_k J),
\]

that explicitly illustrates the possible LS mixing for the selected \(J\)-value.

We also performed relativistic configuration interaction (RCI) calculations to determine the mixing coefficients \(\{c_i\}\) of the atomic wave function which, for a state labeled \(\gamma\pi J\), is written as a linear combination of relativistic CSFs

\[
\Phi(\gamma \pi J) = \sum_i c_i \Phi_{\gamma i \pi J},
\]

where the relativistic CSFs are spin-angular coupled antisymmetric products of one-electron Dirac spinors

\[
\phi_{n\kappa m}(r) = \frac{1}{r} \left(\begin{array}{cccc}
P_{n\kappa}(r)\chi_{\kappa m}(\theta, \phi) \\
nQ_{n\kappa}(r)\chi_{-\kappa m}(\theta, \phi)
\end{array}\right).
\]

In the RCI-P method, based on the Pauli limit of the Dirac equation \[30\], the radial function of the small component, \(Q_{n\kappa}(r)\), is estimated from the radial function of the large one, \(P_{n\kappa}(r)\), as:

\[
Q_{n\kappa}(r) \simeq \frac{\alpha^2}{2} \left(\frac{d}{dr} + \frac{\kappa}{r}\right) P_{n\kappa}(r),
\]

where, in our case, the large component radial function \(P_{n\kappa}(r)\) is the nonrelativistic MCHF radial function \(P_{nl}(r)\).

In the MCDHF-RCI method, the small and large radial functions of the one-electron Dirac spinors \[5\] are obtained using the fully relativistic MCDHF version of the multiconfiguration method \[2\] to optimise the relativistic one-electron orbital basis, together with the mixing coefficients.

B. Magnetic dipole hyperfine interaction

The magnetic dipole hyperfine interaction Hamiltonian is given by

\[
H_{\text{hfs}} = T^{(1)} \cdot M^{(1)},
\]

where \(T^{(1)}\) is the dipolar magnetic operator tensor which, in the nonrelativistic framework, is the sum of three terms \[31,32\]

\[
T^{(1)} = \frac{\alpha^2}{2} \sum_{i=1}^N \left\{2I^{(1)}(i) \tilde{r}_i^{-3} - g_s \sqrt{10} C^{(2)}(i) \times s^{(1)}(i) \tilde{r}_i^{-3} + g_s \frac{8}{3} \pi \delta(r_i) s^{(1)}(i)\right\}
\]

corresponding, respectively, to the orbital, spin-dipole and contact contributions, that we will denote \(T_{\text{orb}}^{(1)}, T_{\text{sd}}^{(1)}\) and \(T_{\text{con}}^{(1)}\), i.e.

\[
T^{(1)} = T_{\text{orb}}^{(1)} + T_{\text{sd}}^{(1)} + T_{\text{con}}^{(1)}.
\]

The energy corrections of the fine structure levels are generally expressed in term of the magnetic dipole hyperfine constant \(A_J\) that is proportional to the reduced matrix element of \(T^{(1)}\)

\[
A_J = \frac{\mu_I T}{\sqrt{J(J+1)(2J+1)}} \langle \gamma J | T^{(1)} | \gamma J \rangle.
\]

As suggested by Eq. \[13\], \(A_J\) can be written as

\[
A_J = A_J^{\text{orb}} + A_J^{\text{sd}} + A_J^{\text{con}}.
\]
where the orbital \( A_j^{\alpha b} \), spin-dipolar \( A_j^{\alpha d} \) and contact \( A_j^{\alpha c} \) hyperfine constants can be evaluated using \( \Pi \) when omitting relativistic corrections, and with \( \Phi \) if taking into account relativistic effects through the Breit-Pauli approximation.

In the fully relativistic framework of the MCDHF or RCI approaches, the magnetic electronic tensor operator is (in atomic units) given by \( \Phi \)

\[
T^{(1)} = -i \alpha \sum_{i=1}^{N} \left( \alpha_i \cdot \mathbf{l}_i C^{(1)}(i) \right) e_i^{-2},
\]

(12)

and the \( A_J \) hyperfine constant \( \Pi \) is evaluated using \( \Phi \).

### III. SIMULTANEOUS OPTIMIZATION STRATEGY

According to the NIST Atomic Spectra Database \( \Phi \), the 17 levels of even parity of interest

\[
2p^4(3P)3d \quad 4D_{7/2,5/2,3/2,1/2}, \quad 2D_{5/2,3/2}, \quad 4F_{9/2,7/2,5/2,3/2,1/2}, \quad 2F_{7/2,5/2,3/2,1/2}, \quad 4P_{5/2,3/2,1/2,2}, \quad 2P_{3/2,1/2},
\]

arising from the 6 terms \( 2p^4(3P)3d \) LS, all lie in the narrow spectral window of \([128 064.10 - 128 712.30] \text{ cm}^{-1} \), above the levels arising from the 5 terms

\[
2p^4(3P)3s \quad 4P, \quad 2p^4(3P)3s \quad 2P, \quad 2p^4(1D)3s \quad 2D, \quad 2p^4(3P)4s \quad 4P, \quad 2p^4(3P)4s \quad 2P,
\]

of the same parity. To satisfy the Hylleraas-Undheim-Mac Donald (HUM) theorem \( \Phi \), in the variational procedure, the interaction Hamiltonian matrix should include all low-lying levels of the same \( LS \)-symmetry in the MCHF procedure. Moreover, because of the orbital orthogonality constraints of the ATSP2K package \( \Phi \), a single radial orbital basis has to be obtained for the subsequent BP calculations that mix the levels of the same parity and \( J \)-value. We therefore adopted a simultaneous optimization scheme \( \Phi \) for the MCHF calculations, optimizing simultaneously the \( 6+5=11 \) terms of even parity. The resulting orbital basis is then used to determine the \( J \)-dependent energy levels in the framework of the Breit-Pauli approximation. In the above scheme, the uncorrelated Hartree-Fock (HF) calculation is done based on the \( 11 \) \( LS \) terms arising from the \( \{2p^43d, 2p^43s, 2p^44s\} \) configuration, and results in a common orthonormal set of “spectroscopic” orbitals, \( \{1s, 2s, 2p, 3s, 3d, 4s\} \).

Electron correlation is included by taking the \( \{2p^43d, 2p^43s, 2p^44s\} \) configurations as the multireference (MR), from which single (S) and double (D) excitations are done to increasing orbital active sets to build the SD-MR-MCHF expansions. For each orbital active set (AS), all orbitals, spectroscopic and correlation, are optimized in the MCHF procedure. These calculations are denoted as SD-MR-MCHF[AS], although the latter acronym will be shortened at some places as MR-MCHF[AS], or as (SD)-MR-MCHF[AS] as a discrete reminder, since SD excitations from the MR are considered in all the present calculations. The terminology adapted for the active sets is detailed in reference \( \Phi \). We only recall that the orbital active set (AS) is noted \( [n] \) when no angular limitation applies and \( [nl] \) when angular orbital limitation \( l_{\text{max}} = l \) is introduced.

The relativistic BP wave function expansions are built using the same SD-MR process, but considering CSFs of all \( LS \) symmetries that can be built from the AS and that can mix to each other for a given \( J \)-value. The corresponding notation, SD-MR-BP[AS], will be used in the following.

Table \( \Pi \) reports the excitation energies of the \( 2p^4(3P)3d \text{ } 2S+1L_J \) levels classified according to the NIST database. As already observed above, the levels lie close to each other. The largest difference between levels having the same \( J \)-value does not exceed 385 cm\(^{-1}\) and is found for the energy separation of \( 2D_{5/2} \) and \( 4F_{5/2} \). The smallest energy gap, of the order of 90 cm\(^{-1}\), is observed between \( 2F_{5/2} \) and \( 4P_{5/2} \).

In the same table, the theoretical fine structure values, \( \Delta E_{\text{SD-MR-BP}} \), obtained with the largest \( [9f] \) AS, are compared with the NIST values. For each level, the major contributions to the corresponding Breit-Pauli wave function are also given. All these contributions correspond to CSFs belonging to the \( 2p^4(3P)3d \) configuration, which form the space that we will indicate in the following as the \( \{2p^4(3P)3d \text{ } L'_s S'_l\} \) space. We notice that for all 17 levels, \( \sum c_i^2 \approx 0.97 \), illustrating the fact that the CSFs produced by the S and D excitations from the MR only count for around 3\% of the wave functions. The large values of the mixing coefficients clearly demonstrate strong interactions within the \( \{2p^4(3P)3d \text{ } L'_s S'_l\} \) space. For example, the contribution of the \( 2p^4(3P)3d \text{ } 4F_{3/2}, \text{ } 2D_{3/2}, \text{ } 2D_{3/2}, \text{ } 4P_{3/2} \) states in the composition of \( 2P_{3/2} \) level reaches \( \sum c_i^2 - c_2^2 = 50.4\% \). It is interesting to cite the case of the \( 2F_{5/2} \) level, which loses
A similar simultaneous optimization scheme was used for the MCDHF calculations, called Extended Optimal Level. The nine hyperfine constants and is between the electronic structure calculations. To highlight this fact, we report in Table IV the relative difference in the hyperfine constant values.

| Term | J | Level (cm⁻¹) | ∆E_{NIST} | ∆E_{SD-MR-BP} | Mixing coefficients |
|------|---|--------------|-----------|----------------|---------------------|
| 4D   | 7/2 | 128 064.10 | 0 | 0 | 0.965 3D_{5/2} + 0.340 4P_{5/2} + 0.193 2F_{5/2} |
|      | 5/2 | 128 087.83 | 23.7 | 22.6 | 0.847 3D_{5/2} + 0.326 4P_{5/2} + 0.248 4P_{3/2} - 0.283 2D_{5/2} - 0.083 2F_{5/2} |
|      | 3/2 | 128 122.72 | 58.6 | 56.4 | 0.784 3D_{5/2} - 0.399 2D_{5/2} + 0.282 4P_{3/2} - 0.259 2P_{3/2} + 0.226 4F_{5/2} |
|      | 1/2 | 128 184.99 | 120.9 | 118.6 | -0.831 2D_{5/2} + 0.407 2P_{3/2} - 0.338 2P_{1/2} |
| 2D   | 5/2 | 128 140.48 | 0 | 0 | 0.827 2D_{5/2} + 0.342 2F_{5/2} + 0.283 2P_{3/2} + 0.273 4D_{5/2} - 0.121 4F_{5/2} |
|      | 3/2 | 128 219.83 | 79.4 | 78.1 | -0.717 2D_{5/2} - 0.345 2P_{3/2} - 0.464 2P_{1/2} - 0.338 4D_{5/2} + 0.090 4F_{5/2} |
| 4F   | 9/2 | 128 219.13 | 0 | 0 | 0.958 4F_{5/2} |
|      | 7/2 | 128 514.75 | 295.6 | 299.2 | 0.782 5P_{3/2} + 0.455 5F_{1/2} - 0.391 2D_{3/2} |
|      | 5/2 | 128 525.35 | 306.2 | 309.3 | -0.679 5F_{3/2} + 0.567 5P_{3/2} - 0.387 2D_{5/2} + 0.198 4D_{5/2} - 0.034 4P_{5/2} |
|      | 3/2 | 128 611.92 | 392.8 | 393.6 | 0.821 5P_{3/2} + 0.514 5P_{1/2} - 0.138 4P_{3/2} - 0.020 2D_{5/2} - 0.012 4P_{1/2} |
| 2F   | 7/2 | 128 220.36 | 0 | 0 | 0.853 2P_{3/2} - 0.495 5P_{1/2} + 0.004 4F_{5/2} |
|      | 5/2 | 128 697.89 | 477.5 | 478.9 | -0.442 5P_{3/2} - 0.671 4P_{3/2} - 0.362 5P_{1/2} + 0.372 4D_{5/2} + 0.237 2D_{5/2} |
| 4P   | 1/2 | 128 338.72 | 0 | 0 | 0.815 4P_{3/2} + 0.551 4P_{1/2} - 0.061 5P_{3/2} |
|      | 3/2 | 128 523.28 | 184.6 | 189.7 | 0.762 5P_{3/2} - 0.410 4P_{3/2} - 0.412 2D_{3/2} + 0.232 4P_{3/2} + 0.008 2P_{3/2} |
|      | 5/2 | 128 606.09 | 267.4 | 271.4 | -0.614 5P_{3/2} + 0.575 5P_{1/2} + 0.509 4P_{3/2} + 0.051 2D_{5/2} + 0.030 2P_{3/2} |
| 2P   | 1/2 | 128 712.30 | 0 | 0 | -0.708 5P_{3/2} - 0.525 4P_{3/2} + 0.440 2P_{1/2} |
|      | 3/2 | 128 520.22 | 192.1 | 192.0 | -0.684 5P_{3/2} + 0.489 5P_{1/2} + 0.358 2D_{5/2} - 0.274 4P_{3/2} + 0.249 4F_{5/2} |

Table I: Excitation energies according to the NIST Atomic Spectra Database [32], fine structures ∆E_{NIST} and ∆E_{SD-MR-BP} in cm⁻¹ for 2p⁵(3P)3d²⁸⁺¹L_J levels, and mixing coefficients of the corresponding SD-MR-BP[9f] eigenvectors.

IV. HYPERFINE CONSTANTS CALCULATIONS

¹⁹F has a nuclear spin I=1/2 and a nuclear magnetic moment μ_I = 2.628868 μ_N [43]. The magnetic dipole hyperfine constants A_{J} for all the 17 2p⁵(3P)3d²⁸⁺¹L_J levels, calculated using the single- and double-multireference (SD-MR) expansions with the MCHF, BP, RCI-P and MCDHF-RCI methods, are reported in Tables II and III. For the SD-MR-MCHF and SD-MR-BP approaches, the A_{J} constant value is monitored along the sequence of increasing ASs, from [4] up to [9f], to probe the correlation effects on the hyperfine structures. One observes that the hyperfine constant values quickly converge with the size of the active space. Moreover, the l_{max} = 3 limitation that has been adopted for building the AS, brings an estimated uncertainty contribution of less than 1% for the hyperfine constants, deduced by comparing similar calculations performed with [nq] active set. In other words, the hyperfine constant values quickly converge not only with the size of the active space, but also with the angular momentum value considered for building the correlation orbital active space, a fact that has been observed in many studies, including investigations of the electric field gradient at the nucleus [14, 45]. From Tables II and III we see that electron correlation effects are small. To highlight this fact, we report in Table IV the relative difference between the HF and (SD)-MR-MCHF[9f] hyperfine constants values. This quantity remains smaller than 5% for nine hyperfine constants and is between 6 – 14.5% for the others. Although the description of electron correlation does not seem to be crucial, Tables II and III illustrate the large disagreement between the (SD)-MR-MCHF[9f] theoretical hyperfine constants and the available experimental values [39], except for the constant A(2D_{3/2}). It becomes clear that the origin of this large theory-observation gap should be found somewhere else than in electron correlation. The comparison of the hyperfine constants between BP[HF] and HF (see Table II), or between (SD)-MR-BP[9f] and (SD)-MR-MCHF[9f] (not displayed in the Table), indeed indicates huge relativistic effects. The relative differences reach values of 1872%, 898%, 641%, 300%, and 316% for, respectively, A(2P_{3/2}), A(2F_{3/2}), A(2F_{5/2}), A(4F_{3/2}), A(4F_{5/2}), A(4P_{1/2}). In the same Table, we also report the relative differences between (SD)-MR-MCHF[9f] and BP[HF] hyperfine constants values, which illustrate how much electron excitations beyond the \{2p⁵(3P)3d𝐿_s,𝑆_i\} space model affects the hyperfine constants. Except for the four constants A(4P_{1/2}), A(4F_{5/2}), A(4P_{3/2}) and A(4F_{3/2}) for which the corresponding ratio values are large (58%, 20%, 19% and 74% , respectively), we observe that the
relativistic effects are efficiently captured through the BP calculations limited to the [HF] active space. For almost all levels considered, the BP[HF] and (SD)-MR-BP[9f] hyperfine constants are in good agreement with observation [29]. The MR-RCI-P[9f] results are given in Tables II and III. Since the RCI-P method radially differs from the BP approach, it is interesting to compare the MR-RCI-P[9f] and MR-BP[9f] hyperfine constant values. We can observe that the two sets of results, obtained using the ATSP2K and GRAPPS2018 independent packages, are in excellent agreement with each other. In the same tables, we also report the MR-MCDHF-RCI[9f] results. The global agreement of the latter with the MR-BP[9f] results for the 17 hyperfine constants is 4.7%. The largest differences occur for $A(4P_{3/2})$ and $A(4P_{5/2})$ with relative deviations of 6.8%, 9.4%, 19.7% and 33.3%, respectively.

Large differences between the nonrelativistic and Breit-Pauli results are most likely due to the strong relativistic approach, it is interesting to compare the MR-RCI-P[9f] and MR-BP[9f] hyperfine constant values. We can observe that the two sets of results, obtained using the ATSP2K and GRAPPS2018 independent packages, are in excellent agreement with each other. In the same tables, we also report the MR-MCDHF-RCI[9f] results. The global agreement of the latter with the MR-BP[9f] results for the 17 hyperfine constants is 4.7%. The largest differences occur for $A(4P_{3/2})$ and $A(4P_{5/2})$ with relative deviations of 6.8%, 9.4%, 19.7% and 33.3%, respectively. The largest discrepancies are found for $A(4P_{3/2})$ and $A(4P_{5/2})$. Excluding the last two from this sample, the global theory-observation agreement drops to 3.5%.

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Table II: Hyperfine structure constants (in MHz) of $2p^4(3P)3d$ $^2D$, $^4D$ and $^2P$ calculated with HF and (SD)-MR-MCHF by using the simultaneous optimization strategy, BP[HF], (SD)-MR-BP and (SD)-MR-RCI-P methods. These values are compared with fully relativistic results calculated with the (SD)-MCDHF-RCI method, and with observation.

|          | $A_{3/2}$ | $A_{5/2}$ | $A_{1/2}$ | $A_{3/2}$ | $A_{5/2}$ | $A_{7/2}$ | $A_{1/2}$ | $A_{3/2}$ | $A_{5/2}$ | $A_{7/2}$ | $A_{1/2}$ | $A_{3/2}$ | $A_{5/2}$ | $A_{7/2}$ |
|----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|
| **2D**   |           |           |           |           |           |           |           |           |           |           |           |           |           |           |
| HF       | 1734      | 373       | 3554      | 1422      | 778       | 169       | −3346     | −1435     |           |           |           |           |           |           |
| [4]      | 1618      | 406       | 3330      | 1443      | 832       | 228       | −3345     | −1249     |           |           |           |           |           |           |
| [5f]     | 1437      | 605       | 2876      | 1563      | 1027      | 441       | −3708     | −927      |           |           |           |           |           |           |
| [6f]     | 1744      | 310       | 3643      | 1434      | 762       | 125       | −3232     | −1411     |           |           |           |           |           |           |
| [7f]     | 1678      | 368       | 3479      | 1454      | 812       | 188       | −3319     | −1314     |           |           |           |           |           |           |
| [8f]     | 1674      | 369       | 3471      | 1451      | 811       | 189       | −3317     | −1314     |           |           |           |           |           |           |
| [9f]     | 1675      | 370       | 3472      | 1453      | 813       | 190       | −3320     | −1312     |           |           |           |           |           |           |
| **4D**   |           |           |           |           |           |           |           |           |           |           |           |           |           |           |
| HF       | 1574      | 1066      | 4860      | 2304      | 1474      | 865       | −2354     | −565      |           |           |           |           |           |           |
| [4]      | 1579      | 1076      | 4614      | 2291      | 1494      | 886       | −2271     | −491      |           |           |           |           |           |           |
| [5f]     | 1484      | 1209      | 4465      | 2523      | 1738      | 1081      | −2134     | −292      |           |           |           |           |           |           |
| [6f]     | 1680      | 1033      | 4733      | 2210      | 1402      | 805       | −2348     | −558      |           |           |           |           |           |           |
| [7f]     | 1649      | 1067      | 4658      | 2263      | 1462      | 854       | −2317     | −506      |           |           |           |           |           |           |
| [8f]     | 1652      | 1066      | 4647      | 2260      | 1460      | 852       | −2325     | −503      |           |           |           |           |           |           |
| [9f]     | 1654      | 1067      | 4646      | 2262      | 1461      | 852       | −2327     | −496      |           |           |           |           |           |           |
| **2P**   |           |           |           |           |           |           |           |           |           |           |           |           |           |           |
| HF       |           |           |           |           |           |           |           |           |           |           |           |           |           |           |
| [4]      | 1582 ± 50 | 1046 ± 50 | 4541 ± 50 | 2290 ± 50 | 1481 ± 20 | 793 ± 20 | −2378 ± 80 | −498 ± 80 |           |           |           |           |           |           |
| [5f]     | 1499      | 1066      | 4608      | 2257      | 1463      | 855       | −2312     | −463      |           |           |           |           |           |           |
| [6f]     | 1499      | 1066      | 4608      | 2257      | 1463      | 855       | −2312     | −463      |           |           |           |           |           |           |
| [7f]     | 1499      | 1066      | 4608      | 2257      | 1463      | 855       | −2312     | −463      |           |           |           |           |           |           |
| [8f]     | 1499      | 1066      | 4608      | 2257      | 1463      | 855       | −2312     | −463      |           |           |           |           |           |           |
| [9f]     | 1499      | 1066      | 4608      | 2257      | 1463      | 855       | −2312     | −463      |           |           |           |           |           |           |
Table III: Hyperfine structure constants in (MHz) of $2p^4(^1P)3d$ $^4P$, $^2F$ and $^4F$ calculated with HF and (SD)-MR-MCHF by using the simultaneous optimization strategy, BP[H]F, (SD)-MR-BP and (SD)-MR-RCI-P methods. These values are compared with fully relativistic results calculated with the (SD)-MCDHF-RCI method, and with observation.

|          | $^2P$ | $^4P$ | $^2F$ | $^4F$ |
|----------|-------|-------|-------|-------|
| $A_{1/2}$ | 1574  | −724  | −848  | 1285  |
| $A_{3/2}$ | 1460  | −714  | −841  | 1156  |
| $A_{5/2}$ | 1694  | −634  | −755  | 1178  |
| $A_{7/2}$ | 1693  | −634  | −755  | 1180  |
| $A_{9/2}$ | 1699  | −632  | −753  | 1178  |
| **MR-MCHF** | 1285  | 1437  | 1515  | 1021  |
| **BP[H]F** | 1156  | 1439  | 1295  | 962   |
| **MR-BP** | 1121  | 1390  | 1416  | 950   |
| **MR-RCI-P** | 1334  | 956   | 994   | 1190  |
| **MR-MC-DHF-RCI** | 1337  | 957   | 994   | 1189  |

Table IV: Relative differences in percent between (MR-MCHF[9f], HF), (BP[H]F, HF), and (MR-BP[9f], BP[H]F) hyperfine constants.

|          | $^2D$ | $^4D$ | $^2P$ | $^4P$ | $^2F$ | $^4F$ |
|----------|-------|-------|-------|-------|-------|-------|
| $A_{3/2}$ | 0.8   | 2.1   | 11    | 0.8   | 7.3   | 7.3   |
| $A_{5/2}$ | 3.5   | 4.3   | 14.5  | 12.6  | 9.0   | 6.7   |
| **MR-MCHF[9f]−HF** | 0.8   | 2.1   | 11    | 0.8   | 7.3   | 7.3   |
| **BP[H]F−HF** | 3.5   | 4.3   | 14.5  | 12.6  | 9.0   | 6.7   |
| **MR-BP[9f]−BP[H]F** | 0.8   | 2.1   | 11    | 0.8   | 7.3   | 7.3   |
| **MR-MC-DHF-RCI** | 0.8   | 2.1   | 11    | 0.8   | 7.3   | 7.3   |
| **BP[H]F−BP[H]F** | 0.8   | 2.1   | 11    | 0.8   | 7.3   | 7.3   |

V. M1 HYPERFINE INTERACTION IN THE \{(2p^4(3P)3d \ L_5S_1)\} SPACE

A. Matrix elements

In the present section, we limit the CSFs to the \{(2p^4(3P)3d \ L_5S_1)\} space. The atomic wave function describing the $\gamma LSJ$ states, where $\gamma = 2p^4(^1P)3d$, are therefore written according to Eq. (13) as follows:

$$
\Psi (\gamma 2S^1L_J) = \sum_i c_i \phi (\gamma L_iS_iJ),
$$

where $L_iS_i$ represents any of the six terms listed in Table II corresponding to the same $J$-value. In this approximation, that keeps the 1s and 2s shells closed, there is no contact contribution and the hyperfine constant $A(2S^1L_J)$ of each level $2p^4(^3P)3d$ LSJ is only made of the orbital and spin-dipole contributions, i.e.

$$
A(2S^1L_J) = A^{orb}(2S^1L_J) + A^{sd}(2S^1L_J),
$$
where

\[ A^{orb}(2S+1L_j) = \sum_{ij} A^{orb}_{ij}(\gamma L_i S_i, \gamma L_j S_j) \quad \text{and} \quad A^{sd}(2S+1L_j) = \sum_{ij} A^{sd}_{ij}(\gamma L_i S_i, \gamma L_j S_j) \]

are made of the diagonal \((i = j)\) and off-diagonal \((i \neq j)\) hyperfine interaction matrix elements coupling the CSFs in the basis. \(A^{orb}_{ij}(\gamma L_i S_i, \gamma L_j S_j)\) and \(A^{sd}_{ij}(\gamma L_i S_i, \gamma L_j S_j)\) are proportional, respectively, to the reduced matrix elements \(\langle \gamma L_i S_i | T^{(1)}_{orb} | \gamma L_j S_j \rangle\) and \(\langle \gamma L_i S_i | T^{(1)}_{sd} | \gamma L_j S_j \rangle\) and to the relevant eigenvector coefficient products \(c_i c_j\). They can be written as

\[ A^{orb}_{ij}(\gamma L_i S_i, \gamma L_j S_j) = \frac{1}{2} c_i c_j G_{\mu} \frac{\mu_i}{I} \text{ME}^{orb} \quad \text{and} \quad A^{sd}_{ij}(\gamma L_i S_i, \gamma L_j S_j) = \frac{1}{2} c_i c_j G_{\mu} \frac{\mu_i}{I} \text{ME}^{sd}, \]

with 33, 16

\[ \text{ME}^{orb} = \delta_{S_i S_j} (-1)^{L_i + S_i + J + L_j + 1} 2 \sqrt{(2L_i + 1)(2L_j + 1)(2J + 1)} \frac{L_i S_i J}{J(J+1)} \left\{ \begin{array}{c} L_i \ S_i \ J \\ J \ 1 \ L_j \end{array} \right\} \]

\[ \times \left\{ \begin{array}{c} 1 \\ 2 \\ L_i \\ 1 \ 1 \end{array} \right\} \sqrt{6(2p^4 3P)\|U^{(1)}\| \{ \begin{array}{c} 2p^4 3P \langle 2p | r^{-3} \rangle 2p \\ 2 \ L_j \ 1 \ 2 \end{array} \right\} \sqrt{30}(3d^2 D)\|U^{(1)}\| 3d^2 D \rangle \langle 3d | r^{-3} | 3d \rangle \right\}, \]

and

\[ \text{ME}^{sd} = (-1)^{S_j + L_j + 1/2} \sqrt{(2S_i + 1)(2S_j + 1)(2L_i + 1)(2L_j + 1)(2J + 1)} \frac{L_i S_i J}{J(J+1)} \left\{ \begin{array}{c} L_i \ S_i \ J \\ L_j \ S_j \ J \end{array} \right\} \]

\[ \times \left[ -\sqrt{\frac{6}{5}} \left\{ \begin{array}{c} 1/2 \\ S_i \\ 1 \ 1 \end{array} \right\} \left\{ \begin{array}{c} 1 \\ L_j \ 2 \ 1 \end{array} \right\} \langle 2p^4 3P \|V^{(2)}\| \{ \begin{array}{c} 2p^4 3P \langle 2p | r^{-3} \rangle 2p \\ 2 \ L_i \ 1 \ 2 \end{array} \right\} \langle 3d^2 D \|V^{(2)}\| 3d^2 D \rangle \langle 3d | r^{-3} | 3d \rangle \right\} \right. \]

\[ + \sqrt{\frac{10}{7}} \left\{ \begin{array}{c} 1/2 \\ S_j \ 1 \ 1/2 \end{array} \right\} \left\{ \begin{array}{c} 2 \ 1 \ L_j \ 2 \ 1 \end{array} \right\} \langle 3d^2 D \|V^{(2)}\| 3d^2 D \rangle \langle 3d | r^{-3} | 3d \rangle \right\}. \]

\(G_{\mu} = 95.41068\) is the numerical factor to be used when expressing \(\text{ME}^{orb}\) and \(\text{ME}^{sd}\) in atomic units \((a_0^{-3})\), \(\mu_i\) in nuclear magnetons \((\mu_N)\) and \(A_J\) in units of frequency (MHz) while \(g_e = 2.0023193\) is the electronic g factor corrected for the quantum electrodynamic (QED) effects. \(U^{(1)}\) is the unit tensor operator acting only in the \(L\)-space, and \(V^{(2)}\) is the unit double tensor operator 17. \(nl|r^{-3}|nl\) are the one-electron radial integrals for the active subshells, \(nl = 2p\) and \(3d\). The numerical factors \(\sqrt{6}\) and \(\sqrt{30}\), appearing in 17, correspond to the reduced matrix elements of the angular momentum operator \(\langle l||l^{(1)}||l \rangle\) for \(l = 1\) and \(l = 2\), respectively. In the same way, the numerical factors \(-\sqrt{6/5}\) and \(-\sqrt{10/7}\), appearing in 18, correspond to the reduced matrix elements of the renormalized spherical harmonic \(\langle l||l^{(2)}||l \rangle\) for \(l = 1\) and \(l = 2\) (compare the structure of eqs. (27) and (31) in 33).

### B. Detailed analysis

The numerical values of the products of the mixing coefficients \(c_i c_j\), the electronic matrix elements, \(\text{ME}^{orb}\) 17 and \(\text{ME}^{sd}\) 18, as well as the results of the formulas 14, 15 and 16 are reported in Tables 11 and 12 for \(2p^4(3P)3d^2 D_{5/2}\) and \(2p^4(3P)3d^2 D_{3/2}\), respectively. The mixing coefficients of the corresponding eigenvectors are taken from the MR-BP[9f] calculations (see Table 1). The resulting \(A^{orb}_{ij}(\gamma L_i S_i, \gamma L_j S_j)\) and \(A^{sd}_{ij}(\gamma L_i S_i, \gamma L_j S_j)\) values are given in the fourth and sixth columns, respectively. For each \((L_i S_i, L_j S_j)\) relevant pair, the sum of the orbital and spin-dipolar contributions is reported in the very last column. At the bottom of the table, we give the total values of the orbital and spin-dipolar hyperfine constants, together with their resulting sum respectively, from the contribution of the matrix elements in the \(2p^4(3P)3d\ L_i S_i\) space and from HF and MR-BP[9f] calculations. As already indicated previously, the hyperfine contact interaction is strictly zero in the \(2p^4(3P)3d\ L_i S_i\) space, but not anymore in the spaces associated with the HF calculations in the simultaneous optimisation scheme for \(2p^4(3P)3d^2 P, 3P, \) and \(2D\) states, that involve the contamination by CSFs with one electron \(3s\) or \(4s\). The same observation can be done for the (SD)-MR-BP[9f] calculations for all states \(2p^4 3d\ LS\), for which the opening of the \(1s^2\) and \(2s^2\) subshells switches on the contact contribution through the spin-polarization excitation mechanism 48. The latter, however,
remains rather small. Indeed, as one can see in the two Tables I and II, the contribution of the contact interaction does not exceed 1% in the HF calculations and is of the order of 2% in the MR-BP[9f] calculations. The experimental values are given in the last line.

The two tables illustrate the large effects of terms mixing on the orbital and spin-dipole constants through the factors $c_i c_j$. For example for the state $^2D_{3/2}$, the contributions to the orbital hyperfine constant of two non-diagonal matrix elements, ($^2D, ^2P$) and ($^4P, ^4D$), which are respectively equal to 428 MHz and 487 MHz are of the same order of magnitude as that of the main matrix element ($^2D, ^2D$) which is 447 MHz. The total contribution of the mixing states to the constant $A^{orb}(^2D_{3/2})$ is 646 MHz, or 59% of a total of 1093 MHz, despite a compensation effect estimated to 354 MHz, due to the mixing with other LS-component. Mixing effects on the spin-dipolar $A^{sd}(^2D_{3/2})$ constant are reduced by cancellation effects. Their contribution to the total hyperfine constant is of the order of 47%. The term-mixing effect on the total hyperfine constants depend on the relative sign of the orbital and spin-dipole contributions resulting from each matrix element. They are often reduced due to opposite signs, inducing strong cancellation. In the case of $A(^2D_{3/2}) = 1618$ MHz, these effects are of the order of 47%. Finally, the value of $A(^2D_{3/2})$ obtained using the $\{2p^4(^3P)3d \, L_i S_i\}$ space represents 98% of the value resulting from the MR-BP[9f] calculation, which is based on a space formed by 1 114 108 CSFs. We then deduce that most of the relativistic effects due to mixing effects are captured by the single $\{2p^4(^3P)3d \, L_i S_i\}$ space. The results corresponding to the two calculations BP[HF] and MR-BP[9f] are in good agreement with the experiment.

For the level $^2D_{5/2}$ (Table III), the HF hyperfine constants values, $A_{5/2}^{orb}$ and $A_{5/2}^{sd}$, change, respectively, from 607 to 827 MHz and from $-236$ to 186 MHz, when using the BP[HF] model, equivalent to a variation of the total $A(^2D_{5/2})$ constant from 371 MHz to 1013 MHz. We notice a particularly important effect on the spin-dipole interaction. This effect is mainly due to the two matrix elements ($^2D, ^2F$), ($^2D, ^4D$) of the spin-dipole operator, which increase the spin-dipole contribution, respectively, by 280 MHz and 119 MHz. Note that among the $^2D_{5/2}$ eigenvector LS-composition, the contribution of $^{2}F_{5/2}$ to the constant $A_{5/2}$ is 641 MHz, which corresponds to 63% of the total value.

In Tables IV, V and VI we report in details, for all the other considered levels, the contributions of the hyperfine orbital (orb), spin-dipolar (sd) constants, their sum (orb + sd) for each matrix element, as well as the totals $A^{orb}, A^{sd}$, and $A_{J}$. In the penultimate row we report the MR-BP[9f] values, that we compare with observation [29] in the last row, when available.

The value of the $c_1$ coefficient in the development of the wave functions from Table I is a good indicator of the importance of the relativistic effects. If the coefficients $c_i$ are deduced from a Breit-Pauli calculation limited to the $\{2p^4(^3P)3d \, L_i S_i\}$ space such that $\sum c_i^2 = 1$, the weight $c_1^2$ can be written as follows:

$$c_1^2 = \frac{A^{orb}(LS, LS)}{A^{orb}(2S+1L_J)[HF]} = \frac{A^{sd}(LS, LS)}{A^{sd}(2S+1L_J)[HF]} = \frac{A_{J}(LS, LS)}{A^{2S+1L_J}[HF]},$$

where $c_1^2 = 1$ would correspond to a Hartree-Fock calculation. When $|c_1| = 0.442$ (see Table I), with the following values: $A^{orb}(^2F, ^2F) = 323$ MHz, $A_{5/2}^{sd}(^2F, ^2F) = -77$ MHz, $A_{5/2}^{sd}(^4F, ^4F) = 246$ MHz and $A^{orb}(^2F_{5/2})[HF] = 1691$ MHz, $A^{sd}(^2F_{5/2})[HF] = -406$ MHz, $A(^2F_{5/2})[HF] = 1285$ MHz (see Table VI). We can observe however that the relations (19) are not perfectly verified because the $c_i$ coefficients reported in Table I are taken from the SD-MR-BP[9f] eigenvectors and therefore do not fully satisfy $\sum c_i^2 = 1$. The large difference between the two values of $A_{5/2}^{orb}(^2F, ^2F)$ and $A^{sd}(^2F_{5/2})[HF]$ indicates a significant contribution from the other matrix elements, as it can be seen in Table IX (column 10 entitled “orb + sd”).

For all states, the hyperfine constants calculated using MR-BP[9f] or MR-RCI-P[9f] agree very well with observation, except for $A(^21/2)$, and $A(^23/2)$, as already commented at the end of Section IV. For the first case ($A(^21/2)$), Table IV illustrates a huge cancellation between the two diagonal contributions, $A_{1/2}(^2P, ^2P) = -993$ MHz and $A_{1/2}(^4P, ^4P) = 1022$ MHz, leaving much room to the off-diagonal coupling matrix element $A_{1/2}(^2P, ^4D) = -516$ MHz. For the second case ($A(^23/2)$), the fact that this hyperfine constant is the smallest one (in absolute value) amongst the 15 experimental values can be easily understood from the very large cancellation between the orbital and spin-dipole contributions, as demonstrated by Table IX. The use of the $\{2p^4(^3P)3d \, L_i S_i\}$ space combined with the $c_i$ coefficients of the MR-BP[9f] eigenvector made it possible to demonstrate very clearly the effects of the term-mixing on the hyperfine constants. In some cases, like $^4F_{3/2}$ and $^4P_{3/2}$ for example, the $\{2p^4(^3P)3d \, L_i S_i\}$ limited space is not large
enough to obtain a good agreement with the [9f]-space result, but is sufficient to demonstrate the importance of the mixtures.

Table V: Values of $A_{1/2}^{orb}(\gamma L_i S_i, \gamma L_j S_j)$, $A_{1/2}^{orb}(2D_{3/2})$, $A_{3/2}^{sd}(\gamma L_i S_i, \gamma L_j S_j)$ $A_{1/2}^{sd}(2D_{3/2})$, $A_{3/2}^{sd}(\gamma L_i S_i, \gamma L_j S_j)$ and $A(2D_{3/2})$ in MHz according to the formulas [13, [15, [16].

| $(L_i S_i, L_j S_j)$ | $c_{ij}$ | $ME^{orb}$ | $A_{1/2}^{orb}(\gamma L_i S_i, \gamma L_j S_j)$ | $ME^{sd}$ | $A_{3/2}^{sd}(\gamma L_i S_i, \gamma L_j S_j)$ | $A_{3/2}^{sd}(\gamma L_i S_i, \gamma L_j S_j)$ |
|----------------------|---------|------------|---------------------------------|------|-------------------------------|-------------------------------|
| $(^2P, ^2D)$         | 0.5145  | 3.4612     | 447                             | 3.2288 | 417                          | 804                           |
| $(^4P, ^4D)$         | 0.1187  | -5.7542    | -171                            | 0.1539 | 5                            | -166                          |
| $(^4P, ^4D)$         | 0.2156  | -2.3016    | -124                            | -0.5220 | -28                          | -152                          |
| $(^4P, ^4F)$         | 0.0981  | 9.2212     | 19                              | -3.3199 | 7                            | 12                            |
| $(^4D, ^4D)$         | 0.1143  | 2.3074     | 66                              | 3.2298 | 93                           | 159                           |
| $2 \times (^4P, ^4D)$ | 2x0.2472 | 3.4540 | 428                             | -1.3844 | -172                          | 256                           |
| $2 \times (^2P, ^2D)$ | 2x0.2630 | 00        | 00                              | 0.1549 | 26                           | 26                            |
| $2 \times (^2P, ^2D)$ | 2x0.1165 | 00        | 00                              | -2.3147 | 75                           | 75                            |
| $2 \times (^2P, ^2D)$ | 2x0.2425 | 00        | 00                              | 0.8069 | 98                           | 98                            |
| $2 \times (^4P, ^4D)$ | 2x0.1600 | 00        | 00                              | -0.2242 | -18                          | -18                           |
| $2 \times (^4P, ^4D)$ | 2x0.0310 | 00        | 00                              | -1.1580 | 18                           | 18                            |
| $2 \times (^4P, ^4D)$ | 2x0.1165 | 00        | 00                              | 1.0390 | 61                           | 61                            |
| $2 \times (^4P, ^4D)$ | 2x0.1570 | 6.1800    | 487                             | 00      | 487                          | 487                           |
| $2 \times (^4P, ^4D)$ | 2x0.0304 | 3.8538    | -59                             | 00      | -59                          | -59                           |
| $2 \times (^4P, ^4D)$ | 2x0.0417 | 00        | 00                              | 2.0711 | -43                          | -43                           |

$A^{orb}(2D_{3/2})$ $A^{sd}(2D_{3/2})$ $A^{sd}(2D_{3/2})$

| HF | 910 | 825 | 1734 |
| MR-BP[9f] | 1118 | 563 | 1654 |
| Exp [29] | 1582 ± 50 | | |

† These totals differ from $A^{orb}(2D_{3/2}) + A^{sd}(2D_{3/2})$ because they include the contact contribution, which is not strictly zero in the HF and MR-BP[9f] calculations (see text for more details).

Table VI: Values of $A_{1/2}^{orb}(\gamma L_i S_i, \gamma L_j S_j)$, $A_{1/2}^{orb}(2D_{5/2})$, $A_{3/2}^{sd}(\gamma L_i S_i, \gamma L_j S_j)$ $A_{1/2}^{sd}(2D_{5/2})$, $A_{3/2}^{sd}(\gamma L_i S_i, \gamma L_j S_j)$ and $A(2D_{5/2})$ in MHz according to the formulas [13, [15, [16].

| $(L_i S_i, L_j S_j)$ | $c_{ij}$ | $ME^{orb}$ | $A_{1/2}^{orb}(\gamma L_i S_i, \gamma L_j S_j)$ | $ME^{sd}$ | $A_{3/2}^{sd}(\gamma L_i S_i, \gamma L_j S_j)$ | $A_{3/2}^{sd}(\gamma L_i S_i, \gamma L_j S_j)$ |
|----------------------|---------|------------|---------------------------------|------|-------------------------------|-------------------------------|
| $(^2D, ^2D)$         | 0.6846  | 2.3074     | 396                             | -0.9225 | -158                          | 238                           |
| $(^4P, ^4F)$         | 0.1170  | 6.5866     | 193                             | -1.5820 | -46                           | 147                           |
| $(^4P, ^4D)$         | 0.0804  | -3.4526    | -70                             | 0.1382 | 3                            | -67                           |
| $(^4F, ^4F)$         | 0.0145  | 5.5886     | 20                              | -1.6204 | -6                           | 14                            |
| $(^4D, ^4D)$         | 0.0748  | 1.8130     | 34                              | 1.2194 | 23                           | 57                            |
| $2 \times (^2D, ^2F)$ | 2x0.2831 | 1.2310 | 175                             | 1.9724 | 280                          | 455                           |
| $2 \times (^2P, ^2D)$ | 2x0.2346 | 00        | 00                              | -0.3794 | -45                          | -45                           |
| $2 \times (^2P, ^2D)$ | 2x0.0998 | 00        | 00                              | -1.2125 | 61                           | 61                            |
| $2 \times (^4P, ^4D)$ | 2x0.2263 | 00        | 00                              | 1.0475 | 119                          | 119                           |
| $2 \times (^4F, ^4F)$ | 2x0.0970 | 00        | 00                              | 0.4052 | 20                           | 20                            |
| $2 \times (^4F, ^4F)$ | 2x0.0413 | 00        | 00                              | -0.6195 | 13                           | 13                            |
| $2 \times (^2P, ^2D)$ | 2x0.0936 | 00        | 00                              | 0.1317 | 6                            | 6                             |
| $2 \times (^4P, ^4D)$ | 2x0.0775 | 3.0342    | 118                             | -1.0124 | -39                          | -79                           |
| $2 \times (^4P, ^4D)$ | 2x0.0330 | 2.3542    | -39                             | 1.1791 | -20                          | -59                           |
| $2 \times (^4P, ^4D)$ | 2x0.0342 | 00        | 00                              | 1.4495 | -25                          | -25                           |

$A^{orb}(2D_{5/2})$ $A^{sd}(2D_{5/2})$ $A(2D_{5/2})$

| HF | 827 | 186 | 1013 |
| MR-BP[9f] | 843 | 197 | 1067 |
| Exp [29] | 1046 ± 50 | | |

† These totals differ from $A^{orb}(2D_{5/2}) + A^{sd}(2D_{5/2})$ because they include the contact contribution which is not strictly zero in the HF and MR-BP[9f] calculations (see text for more details).
Table VII: Values of $A_{1/2}^{orb}(\gamma L_i S_i, \gamma L_j S_j) = orb$, $A_{1/2}^{sd}(\gamma L_i S_i, \gamma L_j S_j) = sd$, $A_{1/2}(\gamma L_i S_i, \gamma L_j S_j) = orb + sd$ for $^4D$, $^4P$ and $^3P$ states. At the bottom of the table we give the total values $A_{1/2}^{orb}$, $A_{1/2}^{sd}$ and $A_{1/2}$ corresponding to [9f] calculations, while the last row contains the experimental values.

| (LiSi, LjSj) | orb | sd | orb + sd | orb | sd | orb + sd | orb | sd | orb + sd |
|---------------|-----|----|----------|-----|----|----------|-----|----|----------|
| $^2P$,$^2P$   |     |    |          |     |    |          |     |    |          |
|               | −479| −64| −543     | −876| −117| −993     | −1449| −194| −1643    |
| $^4P$,$^4P$   |     |    |          |     |    |          |     |    |          |
|               | 164 | 11  | 175      | 958 | 64  | 1022     | 279  | 19  | 298      |
| $^4D$,$^4D$   |     |    |          |     |    |          |     |    |          |
|               | 1002| 1401| 2403     | 05  | 97  | 12       | 400  | 559| 959      |
| $2 \times ^2P$,$^2P$ |     |    |          |     |    |          |     |    |          |
|               | 0  | −19 | −19      | 0   | 61  | 61       | 0    | 457| 457      |
| $2 \times ^2P$,$^4P$ |     |    |          |     |    |          |     |    |          |
|               | 2431| 487 | 2918     | −430| −86 | −516     | −2003| −401| −2404    |
| $2 \times ^4P$,$^4P$ |     |    |          |     |    |          |     |    |          |
|               |     |    |          |     |    |          |     |    |          |
| $A_{1/2}^{orb}$ | 3318| 1400| 4518     | −343| −112| −455     | −2773| 397| −2376    |
| $A_{1/2}^{sd}$ |     |    |          |     |    |          |     |    |          |
| $A_{1/2}$      |     |    |          |     |    |          |     |    |          |
| MR-BP[9f]     | 3183| 1499| 4646†    | −351| −115| −462†    | −2824| 467| −2327†   |
| Exp [29]      |     |    |          |     |    |          |     |    |          |
|               | 4541±50 |     | −226±50  | −2378±80 |     |          |     |    |          |

† These totals differ from orb + sd because they include the contact contribution which is not zero in the MR-BP[9f] calculations (see text for more details).

Table VIII: Values of $A_{3/2}^{orb}(\gamma L_i S_i, \gamma L_j S_j) = orb$, $A_{3/2}^{sd}(\gamma L_i S_i, \gamma L_j S_j) = sd$, $A_{3/2}(\gamma L_i S_i, \gamma L_j S_j) = orb + sd$ for $^4D$, $^4F$, $^4P$ and $^3P$ states. At the bottom of the table we give the total values $A_{3/2}^{orb}$, $A_{3/2}^{sd}$ and $A_{3/2}$ corresponding to BP[9f] calculations, while the last row contains the experimental values.

| (LiSi, LjSj) | orb | sd | orb + sd | orb | sd | orb + sd | orb | sd | orb + sd |
|---------------|-----|----|----------|-----|----|----------|-----|----|----------|
| $^2D$,$^2D$   |     |    |          |     |    |          |     |    |          |
|               | 138 | 129 | 267      | 0   | 0  | 0        | 146 | 137| 283      |
| $^2P$,$^2P$   |     |    |          |     |    |          |     |    |          |
|               | −97 | 3   | −94      | −381| 10 | −371     | −78 | 2  | −76      |
| $^4P$,$^4P$   |     |    |          |     |    |          |     |    |          |
|               | −46 | −10| −56      | −19 | −4 | −23      | −335| −76| −411     |
| $^4F$,$^4F$   |     |    |          |     |    |          |     |    |          |
|               | 118 | −43| 75       | 1559| −561| 998     | 0   | 0  | 0        |
| $^4D$,$^4D$   |     |    |          |     |    |          |     |    |          |
|               | 355 | 498| 853      | 0   | 0  | 97 136   | 233 | 43 | 61 104   |
| $2 \times ^2D$,$^2P$ |     |    |          |     |    |          |     |    |          |
|               | 179 | −72| 107      | −18 | 7  | −11      | −165| 66 | −99      |
| $2 \times ^2D$,$^4P$ |     |    |          |     |    |          |     |    |          |
|               | 0   | −9 | −9       | 0   | 0  | 0        | 0   | −24| −24      |
| $2 \times ^2D$,$^4F$ |     |    |          |     |    |          |     |    |          |
|               | 0   | 105| 105      | 0   | 19 | 19       | 0   | 4  | 4        |
| $2 \times ^2D$,$^6D$ |     |    |          |     |    |          |     |    |          |
|               | 0   | −127| −127     | 0   | 0  | 0        | 0   | 68 | 68       |
| $2 \times ^2P$,$^4P$ |     |    |          |     |    |          |     |    |          |
|               | 0   | 8  | 8        | 0   | 11 | 11       | 0   | −20| −20      |
| $2 \times ^2P$,$^4F$ |     |    |          |     |    |          |     |    |          |
|               | 0   | 34 | 34       | 0   | 245| 245      | 0   | −1| −1       |
| $2 \times ^2P$,$^6F$ |     |    |          |     |    |          |     |    |          |
|               | 0   | −106| −106     | 0   | −3 | −3       | 0   | 50 | 50       |
| $2 \times ^4P$,$^4D$ |     |    |          |     |    |          |     |    |          |
|               | 686 | 0   | 686      | 7   | 0  | 7        | −968| 0  | −968     |
| $2 \times ^4P$,$^4F$ |     |    |          |     |    |          |     |    |          |
|               | 342 | 0   | 342      | −18 | 0  | −18      | −7  | 0  | −7       |
| $2 \times ^4P$,$^6F$ |     |    |          |     |    |          |     |    |          |
|               | 0   | 66 | 66       | 0   | −156| −156     | 0   | 7  | 7        |
| $A_{3/2}^{orb}$ | 1675| 476| 2151     | 1130| −922| 208      | −1310| 249| −1061    |
| $A_{3/2}^{sd}$ |     |    |          |     |    |          |     |    |          |
| $A_{3/2}$      |     |    |          |     |    |          |     |    |          |
| MR-BP[9f]     | 1706| 507| 2262†    | 1146| −1009| 122†     | −1333| 281| −1033†   |
| Exp [29]      |     |    |          |     |    |          |     |    |          |
|               | 2290±50|     | 110±10  | −1035±50|     | −498±80 |     |    |          |

† These totals differ from orb + sd because they include the contact contribution which is not zero in the MR-BP[9f] calculations (see text for more explanations).
Table IX: Values of $A^{orb}_{5/2}(\gamma L_i S_i, \gamma L_j S_j) = orb$, $A^{sd}_{5/2}(\gamma L_i S_i, \gamma L_j S_j) = sd$, $A^{orb}_{7/2}(\gamma L_i S_i, \gamma L_j S_j) = orb + sd$ for $^4D$, $^4F$, $^2F$ and $^4P$ states. At the bottom of the table we give the total values $A^{orb}_{5/2}$, $A^{sd}_{5/2}$ and $A^{orb}_{7/2}$ corresponding to BP[9f] calculations, while the last row contains the experimental values.

| $(L_i S_i, L_j S_j)$ | $^4D$ | $^4F$ | $^2F$ | $^4P$ |
|----------------------|-------|-------|-------|-------|
|                      | orb   | sd    | orb + sd | orb   | sd    | orb + sd | orb   | sd    | orb + sd |
| $(2D,2D)$            | 46    | −18   | 28     | 87    | −35   | 52     | 33    | −13   | 20     |
| $(2F,2F)$            | 11    | −3    | 8      | 531   | −128  | 403    | 323   | −77   | 246    |
| $(2P,2P)$            | −53   | −2    | −51    | −1    | 0     | −1     | −390  | 16    | −374   |
| $(2D,2F)$            | 149   | −43   | 106    | 647   | −187  | 460    | 184   | −53   | 131    |
| $(2D,2P)$            | 326   | 219   | 545    | 18    | 11    | 29     | 63    | 42    | 105    |
| $2\times(2D,2F)$     | 15    | 23    | 38     | −135  | −217  | −352   | −65   | −104  | −169   |
| $2\times(2D,2P)$     | 0     | 13    | 13     | 0     | −3    | −3     | 0     | 30    | 0      |
| $2\times(2F,2F)$     | 0     | 56    | 56     | 0     | −160  | −160   | 0     | 52    | 52     |
| $2\times(2F,2P)$     | 0     | −126  | −126   | 0     | −40   | −40    | 0     | 46    | 46     |
| $2\times(2P,2F)$     | 0     | −4    | −4     | 0     | −4    | −4     | 0     | 60    | 60     |
| $2\times(2P,2P)$     | 0     | 8     | 8      | 0     | 120   | 120    | 0     | 50    | −50    |
| $2\times(2F,4D)$     | 0     | 5     | 5      | 0     | 7     | 7      | 0     | 11    | −11    |
| $2\times(2P,4D)$     | 320   | −107  | 213    | −10   | 3     | −7     | −380  | 127   | −253   |
| $2\times(4F,4D)$     | 326   | 163   | 489    | −158  | −79   | −237   | −159  | −80   | −239   |
| $2\times(4P,4D)$     | 0     | 59    | 59     | 0     | 17    | 17     | 0     | 177   | 177    |
| $A^{orb}_{5/2}$      | 1140  | 237   | 1377   | 979   | −695  | 284    | −391  | 162   | −229   |
| $A^{sd}_{5/2}$       |       |       |        |       |       |        |       |       |        |
| $A^{orb}_{7/2}$      |       |       |        |       |       |        |       |       |        |
| $A^{sd}_{7/2}$       |       |       |        |       |       |        |       |       |        |
| MR-BP[9f]            | 1157  | 253   | 1461   | 990   | −764  | 252    | −400  | 180   | −202   |
|                      |       |       |        |       |       |        |       |       |        |
|                      |       |       |        |       |       |        |       |       |        |

† These totals differ from orb + sd because they include the contact contribution which is not zero in the MR-BP[9f] calculations (see text for more explanations).

Table X: Values of $A^{orb}_{7/2}(\gamma L_i S_i, \gamma L_j S_j) = orb$, $A^{sd}_{7/2}(\gamma L_i S_i, \gamma L_j S_j) = sd$, $A^{orb}_{7/2}(\gamma L_i S_i, \gamma L_j S_j) = orb + sd$ for $^4D$, $^4F$ and $^2F$ states. At the bottom of the table we give the total values $A^{orb}_{7/2}$, $A^{sd}_{7/2}$ and $A^{orb}_{7/2}$ corresponding to BP[9f] calculations, while the last row contains the experimental values.

| $(L_i S_i, L_j S_j)$ | $^4D$ | $^4F$ | $^2F$ |
|----------------------|-------|-------|-------|
|                      | orb   | sd    | orb + sd | orb   | sd    | orb + sd | orb   | sd    | orb + sd |
| $(2F,2F)$            | 127   | −13   | 114    | 673   | −67   | 606    | 270   | −27   | 243    |
| $(2D,2F)$            | 338   | −203  | 135    | 63    | −38   | 25     | 0     | 0     | 0      |
| $2\times(2F,2F)$     | 0     | −22   | −22    | 0     | −119  | −119   | 0     | 141   | 141    |
| $2\times(2D,2F)$     | 0     | 61    | 61     | 0     | −62   | −62    | 0     | 1     | 1      |
| $2\times(4F,4D)$     | 207   | 249   | 456    | −206  | −248  | −144   | −1    | −2    | −3     |
| $A^{orb}_{7/2}$      | 718   | 78    | 796    | 787   | −500  | 287    | 1170  | 233   | 1403   |
| $A^{sd}_{7/2}$       |       |       |        |       |       |        |       |       |        |
| $A^{orb}_{7/2}$      |       |       |        |       |       |        |       |       |        |
| $A^{sd}_{7/2}$       |       |       |        |       |       |        |       |       |        |
| MR-BP[9f]            | 729   | 82    | 852    | 799   | −553  | 263    | 1187  | 247   | 1480   |
|                      |       |       |        |       |       |        |       |       |        |
|                      |       |       |        |       |       |        |       |       |        |

† These totals are slightly different from orb + sd because they include the contact contribution which is not zero in the MR-BP[9f] calculations (see text for more explanations).
VI. CONCLUSION

In this work, we present the results of elaborate \textit{ab initio} variational calculations of hyperfine constants for 17 levels in fluorine, all arising from the 6 terms $2p^4(3P)3d\quad 4D,\quad 2^2D,\quad 4^2F,\quad 2^2F,\quad 4^2P$ and $2^3P$. The choice of these levels was guided and justified by the recent publication of experimental $A_J$ values for 15 of these 17 levels, extracted from concentration modulation spectroscopy experiments \textsuperscript{29}. The global theory-observation agreement is very good (\approx $3.5\%$) for 13 levels, taking into account of the relatively large experimental uncertainty of the order of 5%. The larger disagreement observed for $A(4P_{1/2})$ and $A(4P_{3/2})$ can be fully understood in terms of large cancellation and interference effects that make their estimation particularly challenging.

The present theoretical study is at first sight quite surprising, although some previous work on other levels of fluorine atom opened this perspective \textsuperscript{20, 28}. It indeed reveals, in contrast to what is a priori expected for light atoms, weak electron correlation effects on hyperfine structures, but large (if not huge) relativistic effects on hyperfine constants. To explain the latter observation, we investigated the matrix elements of the magnetic dipole hyperfine interaction Hamiltonian in the limited $\{2p^4(3P)3d\quad L_iS_i\}$ configuration space, extracting the weights from the eigenvectors of much larger CSF expansions. This detailed analysis, combining the Breit-Pauli wave function compositions, with the analytical Racah algebra ingredients, beautifully illustrates the crucial role of relativistic term-mixing in the theoretical estimation of the hyperfine constants. It also sheds invaluable light on the interference mechanism between the orbital and spin-dipole contributions, and between the relativistic coupling-term contributions to the hyperfine constant values, allowing to understand their relative magnitude.

Estimations and investigations of theoretical uncertainties of atomic properties should be systematically included, when possible. As observed by Drake \textsuperscript{49}, it is clear that the culture is changing within the theoretical computational community to make uncertainty quantification (UQ) the usual expectation when theoretical results are presented. The present work is one step in this direction, as a few others in the framework of multiconfiguration variational approaches \textsuperscript{51, 52}. It indeed illustrates how the details of the magnetic dipole hyperfine operators can be explored to point difficult cases in terms of cancellation, either between LS pairs for individual operators, or between the orbital and the spin-dipolar operators, and to assess the reliability of the theoretical hyperfine constants. As an example, the relative large uncertainty inferred from the observed differences between MCHF-BP and MCDHF-RCI, as well as from the theory-experiment differences for the two levels $2p^4(3P)3d\quad 4P_{1/2}$ and $4P_{3/2}$ can be explained by large interferences occurring in the amplitude of the observable.

Incidentally, the perfect consistency between the Breit-Pauli calculations and the RCI-P approaches was demonstrated. Orbital orthogonality constraints in the BP calculations forcing the use of a simultaneous optimization strategy in the MCHF approach, and the layer-by-layer approach used to solve convergence issues in the fully relativistic MCDHF scheme \textsuperscript{53}, are the current limiting factors to guarantee the consistency between the two approaches. The global agreement between the two methods is however good for similar configuration lists and orbital active sets used to build the variational spaces.

Acknowledgments

F.Z.B. and M.N. acknowledge financial support from the Direction Générale de la Recherche Scientifique et du Développement Technologique (DGRSDT) of Algeria. M.G. acknowledges support from the FWO & FNRS Excellence of Science Programme (EOS-O022818F). P.J. acknowledges support from the Swedish research council under contract and 2016-04185.

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