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 sizable 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 levels belonging to the spectroscopic terms $2p^4(^3P)3d\ ^{2,4}(P, D, F)$ 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. Multiconfiguration Dirac-Hartree-Fock calculations are performed to support the Breit-Pauli analysis.

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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 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 the MCHF+BP and MCDHF+Breit+QED approaches, respectively.

Correlation effects are traditionally presented as being dominant in light atoms, on the basis of the Z-dependent perturbation approach of the nonrelativistic 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 [9]: "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 [15,16]. 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, which 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 expanded outward. 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 $1s^22s^22p^43d$ configuration of fluorine ($Z = 9$), the mean radii of Dirac-Hartree-Fock and Hartree-Fock (HF) orbitals $\langle r\rangle_{1s}^{\mathrm{DHF}} = 0.175\,43$ and $\langle r\rangle_{1s}^{\mathrm{HF}} = 0.175\,67$, respectively, 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 nonrelativistic configuration interaction calculations of hyperfine parameters have been performed successfully in light atoms [19–23]. In some studies, relativity was included to improve the agreement with observation, either through the Breit-Pauli approximation or using the relativistic configuration interaction 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 which the relativistic effects on the hyperfine constants $A_{3/2}$ and $A_{5/2}$ of the $2p^4 3p\,^4P^o_{3/2,5/2}$ 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 $A(2p^4 3s\,^4P_{1/2})$ and, even more spectacular, reaching 182% for $A(2p^4 3p\,^4S^o_{3/2})$. Aourir *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.* [28] for $A_{3/2}$ and $A_{5/2}$ of the $2p^4 3p\,^4P^o_{3/2,5/2}$ levels, both strongly affected by relativity, were confirmed experimentally [29], while there are no experimental values available to compare with for the other two constants $A(2p^4 3s\,^4P_{1/2})$ and $A(2p^4 3p\,^4S^o_{3/2})$.

Hyperfine constant values for the $2p^4(^3P)3d\,^{2S+1}L_J$ 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 hundred 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 110 ± 10, 304 ± 50, and 276 ± 10 MHz, respectively.

In this work we investigate and explain the origin of the relativistic effects on the calculated hyperfine constants. We use the MCHF method to estimate the hyperfine constants of the $2p^4(^3P)3d\,^{2S+1}L_J$ levels, within the framework of a nonrelativistic approach for the optimization of the zeroth-order wave functions. A simultaneous optimization scheme is 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 perform fully relativistic MCDHF and 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 Sec. II. The simultaneous optimization strategy, used to get a common set of orbitals for the $2p^4(^3P)3d\,^{2S+1}L_J$ targeted levels, is described in Sec. III. The hyperfine constants calculated using the nonrelativistic and relativistic models are reported in Sec. IV for different correlation models and orbital active sets. The expressions of the matrix elements of the hyperfine operators in the configuration state function space limited to the [1/2, 9/2] range of J values arising from $2p^4(^3P)3d\,^{4,2}(F, D, P)$ terms are fully detailed in Sec. V A. The theoretical results are analyzed through a detailed comparison with observation in Sec. V B. The main conclusions are summarized in Sec. VI.

II. THEORY

A. Variational methods

In order to investigate the effects of electronic correlation and relativity on the magnetic dipole hyperfine constant, we use the MCHF approach with BP corrections and the RCI method in the framework of the Pauli approximation (RCI-P). We also used the 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) $\Phi(\gamma_i\pi LS)$ having the same parity π, L, and S quantum numbers

$$\Psi(\gamma\pi LS) = \sum_i c_i \Phi(\gamma_i \pi LS), \tag{1}$$

where the CSFs are spin-angular-coupled antisymmetric products of one-electron spin orbitals ϕ:

$$\phi_{nlm_lm_s}(\mathbf{r}) = \frac{1}{r} P_{nl}(r) Y_{lm_l}(\theta, \phi) \chi_{m_s}. \tag{2}$$

The radial functions $\{P_{n_il_i}(r)\}$ 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 $2p^4 3d$ 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 to 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 are optimized for the selected states, the BP Hamiltonian matrix is built and diagonalized in the basis of LSJ configuration states belonging to a given parity π. The resulting eigenvectors define the intermediate-coupling wave functions

$$\Psi(\gamma\pi J) = \sum_k c_k \Phi(\gamma_k \pi L_k S_k J), \tag{3}$$

which explicitly illustrates the possible LS mixing for the selected J value.

We also perform 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 $\Phi(\gamma_i\pi J)$,

$$\Psi(\gamma\pi J) = \sum_i c_i \Phi(\gamma_i \pi J), \tag{4}$$

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

$$\phi_{n\kappa m}(\mathbf{r}) = \frac{1}{r} \begin{pmatrix} P_{n\kappa}(r)\chi_{\kappa m}(\theta, \phi) \\ iQ_{n\kappa}(r)\chi_{-\kappa m}(\theta, \phi) \end{pmatrix}. \tag{5}$$

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

$$Q_{n\kappa}(r) \simeq \frac{\alpha}{2}\left(\frac{d}{dr} + \frac{\kappa}{r}\right) P_{n\kappa}(r), \tag{6}$$

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 optimize 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.

$$H_{\text{hfs}} = \boldsymbol{T}^{(1)} \cdot \boldsymbol{M}^{(1)}, \tag{7}$$

where $\boldsymbol{M}^{(1)}$ is the magnetic nuclear moment operator,

$$\boldsymbol{M}^{(1)} = \mu_N \sum_{i}^{\text{nucleons}} \nabla[r_i \boldsymbol{C}^{(1)}(i)][g_l \boldsymbol{l}^{(1)}(i) + g_s \boldsymbol{s}^{(1)}(i)],$$

μ_N is the nuclear magneton, and g_l and g_s are the nucleon orbital and spin gyromagnetic g factors, respectively. The z component of this irreducible tensorial operator $\boldsymbol{M}^{(1)}$ is related to the conventional nuclear magnetic moment μ_I through its nuclear matrix element

$$\mu_I = \langle \gamma_I I I | M_0^{(1)} | \gamma_I I I \rangle .$$

In addition, $\boldsymbol{T}^{(1)}$ is the dipolar magnetic operator tensor which, in the nonrelativistic framework, is the sum of three terms [31–33]

$$\boldsymbol{T}^{(1)} = \frac{\alpha^2}{2} \sum_{i=1}^{N} \{ 2\boldsymbol{l}^{(1)}(i) r_i^{-3} - g_s \sqrt{10} [\boldsymbol{C}^{(2)}(i) \times \boldsymbol{s}^{(1)}(i)]^{(1)} r_i^{-3} + g_s \tfrac{8}{3}\pi \delta(\boldsymbol{r}_i) \boldsymbol{s}^{(1)}(i) \} \tag{8}$$

corresponding to the orbital, spin dipole, and contact contributions, which we will denote by $\boldsymbol{T}^{(1)}_{\text{orb}}$, $\boldsymbol{T}^{(1)}_{\text{sd}}$, and $\boldsymbol{T}^{(1)}_{\text{con}}$, respectively, i.e.,

$$\boldsymbol{T}^{(1)} = \boldsymbol{T}^{(1)}_{\text{orb}} + \boldsymbol{T}^{(1)}_{\text{sd}} + \boldsymbol{T}^{(1)}_{\text{con}}. \tag{9}$$

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 $\boldsymbol{T}^{(1)}$,

$$A_J = \frac{\mu_I}{I} \frac{1}{\sqrt{J(J+1)(2J+1)}} \langle \gamma J \| \boldsymbol{T}^{(1)} \| \gamma J \rangle . \tag{10}$$

As suggested by Eq. (9), A_J can be written as

$$A_J = A_J^{\text{orb}} + A_J^{\text{sd}} + A_J^{c}, \tag{11}$$

where the orbital (A_J^{orb}), spin dipolar (A_J^{sd}), and contact (A_J^{c}) hyperfine constants can be evaluated using (1) when omitting relativistic corrections and with (3) 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 [31,34]

$$\boldsymbol{T}^{(1)} = -i\alpha \sum_{i=1}^{N} [\boldsymbol{\alpha}_i \cdot \boldsymbol{l}_i \boldsymbol{C}^{(1)}(i)] r_i^{-2} \tag{12}$$

and the A_J hyperfine constant (10) is evaluated using (4).

III. SIMULTANEOUS OPTIMIZATION STRATEGY

According to the NIST Atomic Spectra Database [35], the 17 levels of even parity of interest, $2p^4(^3P)3d\,^4D_{7/2,5/2,3/2,1/2}$, $^2D_{5/2,3/2}$, $^4F_{9/2,7/2,5/2,3/2}$, $^2F_{7/2,5/2}$, $^4P_{5/2,3/2,1/2}$, and $^2P_{3/2,1/2}$, arising from the six terms $2p^4(^3P)3d\ LS$, all lie in the narrow spectral window of 128 064.10–128 712.30 cm^{-1}, above the levels arising from the five terms $2p^4(^3P)3s\,^4P$, $2p^4(^3P)3s\,^2P$, $2p^4(^1D)3s\,^2D$, $2p^4(^3P)4s\,^4P$, and $2p^4(^3P)4s\,^2P$ of the same parity. To satisfy the Hylleraas-Undheim-MacDonald theorem [36,37] 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 [5], 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 [38,39] 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 HF calculation is done based on the 11 LS terms arising from the $\{2p^4 3d, 2p^4 3s, 2p^4 4s\}$ configuration and results in a common orthonormal set of spectroscopic orbitals $(1s, 2s, 2p, 3s, 3d, 4s)$.

Electron correlation is included by taking the $\{2p^4 3d, 2p^4 3s, 2p^4 4s\}$ 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 by SD-MR-MCHF[AS], although the latter acronym will be shortened in 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 Ref. [14]. We recall only that the orbital active set is denoted by $[n]$ when no angular limitation applies and $[nl]$ when angular orbital limitation $l_{\max} = l$ 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 with each other for a given J value. The corresponding notation SD-MR-BP[AS] will be used in the following.

Table I reports the excitation energies of the $2p^4(^3P)3d\ ^{2S+1}L_J$ 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 52 cm^{-1}, is observed between $^2D_{5/2}$ and $^4D_{5/2}$.

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 $\{2p^4(^3P)3d\ L_iS_i\}$ space. We

TABLE I. Excitation energies according to the NIST Atomic Spectra Database [35], fine structures ΔE_{NIST} and $\Delta E_{\text{SD-MR-BP}}$ in cm^{-1} for $2p^4(^3P)3d\ ^{2S+1}L_J$ levels, and mixing coefficients of the corresponding SD-MR-BP[$9f$] eigenvectors.

Term	J	Level (cm^{-1})	ΔE_{NIST}	$\Delta E_{\text{SD-MR-BP}}$	Mixing coefficients								
^4D	7/2	128 064.10	0	0	$0.905\,^4D_{7/2}$	+	$0.340\,^4F_{7/2}$	+	$0.193\,^2F_{7/2}$				
^4D	5/2	128 087.83	23.7	22.6	$0.847\,^4D_{5/2}$	+	$0.326\,^4F_{5/2}$	+	$0.248\,^4P_{5/2}$	−	$0.283\,^2D_{5/2}$	−	$0.083\,^2F_{5/2}$
^4D	3/2	128 122.72	58.6	56.4	$0.784\,^4D_{3/2}$	−	$0.399\,^2D_{3/2}$	+	$0.282\,^4P_{3/2}$	−	$0.259\,^2P_{3/2}$	+	$0.226\,^4F_{3/2}$
^4D	1/2	128 184.99	120.9	118.6	$-0.831\,^4D_{1/2}$	+	$0.407\,^2P_{1/2}$	−	$0.338\,^4P_{1/2}$				
^2D	5/2	128 140.48	0	0	$0.827\,^2D_{5/2}$	+	$0.342\,^2F_{5/2}$	+	$0.283\,^4P_{5/2}$	+	$0.273\,^4D_{5/2}$	−	$0.121\,^4F_{5/2}$
^2D	3/2	128 219.83	79.4	78.1	$-0.717\,^2D_{3/2}$	−	$0.345\,^2P_{3/2}$	−	$0.464\,^4P_{3/2}$	−	$0.338\,^4D_{3/2}$	+	$0.090\,^4F_{3/2}$
^4F	9/2	128 219.13	0	0	$^4F_{9/2}$								
^4F	7/2	128 514.75	295.6	299.2	$0.782\,^4F_{7/2}$	+	$0.455\,^2F_{7/2}$	−	$0.391\,^4D_{7/2}$				
^4F	5/2	128 525.35	306.2	309.3	$-0.679\,^4F_{5/2}$	+	$0.567\,^2F_{5/2}$	−	$0.387\,^2D_{5/2}$	+	$0.198\,^4D_{5/2}$	−	$0.034\,^4P_{5/2}$
^4F	3/2	128 611.92	392.8	393.6	$0.821\,^4F_{3/2}$	+	$0.514\,^2P_{3/2}$	−	$0.183\,^4P_{3/2}$	−	$0.020\,^2D_{3/2}$	−	$0.012\,^4D_{3/2}$
^2F	7/2	128 220.36	0	0	$0.853\,^2F_{7/2}$	−	$0.495\,^4F_{7/2}$	+	$0.004\,^4D_{7/2}$				
^2F	5/2	128 697.89	477.5	478.9	$-0.442\,^2F_{5/2}$	−	$0.671\,^4P_{5/2}$	−	$0.362\,^4F_{5/2}$	+	$0.372\,^4D_{5/2}$	+	$0.237\,^2D_{5/2}$
^4P	1/2	128 338.72	0	0	$0.815\,^4P_{1/2}$	+	$0.551\,^2P_{1/2}$	−	$0.061\,^4D_{1/2}$				
^4P	3/2	128 523.28	184.6	189.7	$0.762\,^4P_{3/2}$	−	$0.410\,^4D_{3/2}$	−	$0.412\,^2D_{3/2}$	+	$0.232\,^2P_{3/2}$	+	$0.008\,^4F_{3/2}$
^4P	5/2	128 606.09	267.4	271.4	$-0.614\,^4P_{5/2}$	+	$0.575\,^2F_{5/2}$	+	$0.509\,^4F_{5/2}$	+	$0.051\,^4D_{5/2}$	+	$0.030\,^2D_{5/2}$
^2P	1/2	128 712.30	0	0	$-0.708\,^2P_{1/2}$	−	$0.525\,^4D_{1/2}$	+	$0.440\,^4P_{1/2}$				
^2P	3/2	128 520.22	192.1	192.0	$-0.684\,^2P_{3/2}$	+	$0.489\,^4F_{3/2}$	+	$0.358\,^2D_{3/2}$	−	$0.274\,^4D_{3/2}$	+	$0.249\,^4P_{3/2}$

notice that for all 17 levels, $\sum_i c_i^2 \approx 0.97$, illustrating the fact that the CSFs produced by the single and double 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 $\{2p^4(^3P)3d\ L_iS_i\}$ space. For example, the contribution of the $2p^4(^3P)3d\ ^4F_{3/2}$, $^2D_{3/2}$, $^4D_{3/2}$, and $^4P_{3/2}$ states in the composition of $^2P_{3/2}$ level reaches $\sum c_i^2 - c_1^2 = 50.4\%$. It is interesting to cite the case of the $^2F_{5/2}$ level, which loses its dominant character to the detriment of the $^4P_{5/2}$ state with which it strongly interacts. A similar situation has been reported in the case of the $3p^54p$ configuration of the argon atom between the $^1D_2$ and $^3P_2$ states on the one hand and the $^3D_1$ and $^1P_1$ states on the other [40,41].

A similar simultaneous optimization scheme was used for the MCDHF calculations, called extended optimal level [42], in which the energy functional is built as the weighted sum of a set of targeted atomic states. With these MCDHF orbital sets, we performed RCI calculations that we denote by MR-MCDHF-RCI[AS].

IV. HYPERFINE CONSTANTS CALCULATIONS

^{19}F has a nuclear spin $I = 1/2$ and a nuclear magnetic moment $\mu_I = 2.628\,868\mu_{\text{N}}$ [43]. The magnetic dipole hyperfine constants A_J for all 17 $2p^4(^3P)3d\ ^{2S+1}L_J$ levels, calculated using the 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 introduces an estimated uncertainty contribution of less than 1% for the hyperfine constants, deduced by comparing similar calculations performed with the [ng] 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 [44,45]. 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% and 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 [29], 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 other than in electron correlation. The comparison of the hyperfine constants between BP[HF] and HF (see Table IV) 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%, 614%, 300%, and 316% for $A(^4P_{5/2})$, $A(^2F_{5/2})$, $A(^4F_{3/2})$, $A(^4F_{5/2})$, and $A(^4P_{1/2})$, respectively. In the same table we also report the relative differences between (SD)-MR-BP[$9f$] and BP[HF] hyperfine constants values, which illustrate how much electron excitations beyond the $\{2p^4(^3P)3d\ L_iS_i\}$ space model affect the hyperfine constants. Except for the four constants $A(^4P_{1/2})$, $A(^2F_{5/2})$, $A(^4P_{5/2})$, 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 radically 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

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.

	^2D		^4D				^2P	
AS	$A_{3/2}$	$A_{5/2}$	$A_{1/2}$	$A_{3/2}$	$A_{5/2}$	$A_{7/2}$	$A_{1/2}$	$A_{3/2}$
HF								
	1734	373	3554	1422	778	169	−3346	−1435
MR-MCHF								
[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
BP[HF]								
	1574	1066	4860	2304	1474	865	−2354	−565
MR-BP								
[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
MR-RCI-P								
[9f]	1652	1065	4640	2258	1458	850	−2326	−497
MR-MCDHF-RCI								
[9f]	1649	1066	4608	2257	1463	855	−2312	−463
Expt. [29]	1582 ± 50	1046 ± 50	4541 ± 50	2290 ± 50	1481 ± 20	793 ± 20	−2378 ± 80	−498 ± 80

GRASP2018 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 $A(^2P_{3/2})$, $A(^2F_{5/2})$, $A(^4F_{3/2})$, and $A(^4P_{5/2})$ with relative deviations of 6.8%, 9.4%, 19.7%, and 33.3%, respectively.

However, the values obtained in the two approaches lie within the uncertainty interval of the experimental values for the first constant $A(^2P_{3/2})$. This is almost the case for $A(^2F_{5/2})$ and $A(^4F_{3/2})$, while the case of the very small $A(^4P_{5/2})$ value is more problematic, as it will be further discussed below. The global agreement of the averaged MR-BP[9f] and MR-MCDHF-RCI[9f] hyperfine constant values with the 15 available measured hyperfine constants is around 20%. The largest discrepancies are found for $A(^4P_{1/2})$ and $A(^4P_{5/2})$. Excluding the last two from this sample, the global theory-observation agreement drops to 3.5%.

Large differences between the nonrelativistic and Breit-Pauli results are most likely due to the strong relativistic interaction between the terms. In order to verify this conjecture, we analyze in full detail the matrix elements of the different operators of the hyperfine interaction [see Eqs. (9) and (11)] in the $\{2p^4(^3P)3d\ L_iS_i\}$ space model. It should be noted that the contact hyperfine interaction is zero within this configuration space in which we keep the $1s$ and $2s$ shells closed in the CSF lists. That occupation restriction allows us to limit this detailed analysis to the orbital and spin dipole contributions to the A_J constants, as done in the next section. However, the complete hyperfine interaction Hamiltonian is used, including the contact contribution, in the more elaborate calculations based on larger configuration spaces and orbital active sets.

V. MAGNETIC DIPOLE HYPERFINE INTERACTION IN THE $\{2p^4(^3P)3d\ L_iS_i\}$ SPACE

A. Matrix elements

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

$$\Psi(\gamma\ ^{2S+1}L_J) = \sum_i c_i \phi(\gamma L_i S_i J), \tag{13}$$

TABLE III. Hyperfine-structure constants in (MHz) of $2p^4(^3P)3d\ ^4P$, ^2F, and ^4F 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.

	^4P			^2F		^4F			
AS	$A_{1/2}$	$A_{3/2}$	$A_{5/2}$	$A_{5/2}$	$A_{7/2}$	$A_{3/2}$	$A_{5/2}$	$A_{7/2}$	$A_{9/2}$
HF									
	1574	− 724	−848	1285	1437	1515	1021	1015	1184
MR-MCHF									
[4]	1823	− 565	−699	1156	1439	1295	962	1010	1207
[5f]	2667	− 206	−406	1017	1594	995	978	1135	1384
[6f]	1460	− 741	−841	1218	1390	1416	950	961	1146
[7f]	1694	− 634	−755	1178	1427	1334	956	994	1190
[8f]	1693	− 634	−755	1180	1427	1337	957	994	1189
[9f]	1699	− 632	−753	1178	1428	1333	956	995	1191
BP[HF]									
	−730	−1029	−43	−161	1457	212	255	282	1176
MR-BP									
[4]	−530	− 995	−30	−174	1494	149	267	280	1201
[5f]	−491	−910	−39	− 93	1716	48	383	353	1377
[6f]	−509	−1048	−41	−220	1420	146	201	230	1139
[7f]	−482	−1028	−34	−203	1477	130	244	258	1184
[8f]	−469	−1033	−32	−205	1477	129	250	262	1184
[9f]	−462	−1033	−36	−202	1480	122	252	263	1185
MR-RCI-P									
[9f]	−461	−1033	−34	−202	1478	124	252	263	1183
MR-MCDHF-RCI									
[9f]	−445	−1026	−48	−183	1483	98	259	266	1188
Expt. [29]	−226 ± 50	−1035 ± 50	−17 ± 10	−190 ± 10		110 ± 10	304 ± 50	276 ± 10	

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

$$A(^{2S+1}L_J) = A^{\text{orb}}(^{2S+1}L_J) + A^{\text{sd}}(^{2S+1}L_J), \tag{14}$$

where

$$A^{\text{orb}}(^{2S+1}L_J) = \sum_{ij} A_J^{\text{orb}}(\gamma L_iS_i, \gamma L_jS_j), \quad A^{\text{sd}}(^{2S+1}L_J) = \sum_{ij} A_J^{\text{sd}}(\gamma L_iS_i, \gamma L_jS_j) \tag{15}$$

are made of the diagonal ($i = j$) and off-diagonal ($i \neq j$) hyperfine interaction matrix elements coupling the CSFs in the basis. Here $A_J^{\text{orb}}(\gamma L_iS_i, \gamma L_jS_j)$ and $A_J^{\text{sd}}(\gamma L_iS_i, \gamma L_jS_j)$ are proportional to the reduced matrix elements $\langle \gamma L_iS_iJ \| \boldsymbol{T}^{(1)}_{\text{orb}} \| \gamma L_jS_jJ \rangle$ and $\langle \gamma L_iS_iJ \| \boldsymbol{T}^{(1)}_{\text{sd}} \| \gamma L_jS_jJ \rangle$, respectively, and to the relevant eigenvector coefficient products c_ic_j. They can be written as

$$A_J^{\text{orb}}(\gamma L_iS_i, \gamma L_jS_j) = \frac{1}{2}c_ic_jG_\mu \frac{\mu_I}{I} M^{\text{orb}}, \quad A_J^{\text{sd}}(\gamma L_iS_i, \gamma L_jS_j) = \frac{1}{2}c_ic_jG_\mu \frac{\mu_I}{I} M^{\text{sd}}, \tag{16}$$

with [33,46]

$$\begin{aligned} M^{\text{orb}} &= \delta_{S_iS_j}(-1)^{L_i+S_i+J+L_j+1} 2\sqrt{\frac{(2L_i+1)(2L_j+1)(2J+1)}{J(J+1)}} \begin{Bmatrix} L_i & S_i & J \\ J & 1 & L_j \end{Bmatrix} \\ &\times \left[\begin{Bmatrix} 1 & 2 & L_i \\ L_j & 1 & 1 \end{Bmatrix} \sqrt{6} \langle 2p^4\ ^3P \| \mathbf{U}^{(1)} \| 2p^4\ ^3P \rangle \langle 2p | r^{-3} | 2p \rangle + \begin{Bmatrix} 2 & 1 & L_i \\ L_j & 1 & 2 \end{Bmatrix} \sqrt{30} \langle 3d\ ^2D \| \mathbf{U}^{(1)} \| 3d\ ^2D \rangle \langle 3d | r^{-3} | 3d \rangle \right] \end{aligned} \tag{17}$$

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

^2D		^4D				^2P		^4P			^2F		^4F			
$A_{3/2}$	$A_{5/2}$	$A_{1/2}$	$A_{3/2}$	$A_{5/2}$	$A_{7/2}$	$A_{1/2}$	$A_{3/2}$	$A_{1/2}$	$A_{3/2}$	$A_{5/2}$	$A_{5/2}$	$A_{7/2}$	$A_{3/2}$	$A_{5/2}$	$A_{7/2}$	$A_{9/2}$
$\frac{\lvert\text{MR-MCHF}[9f]-\text{HF}\rvert}{\lvert\text{MR-MCHF}[9f]\rvert}$																
3.5	0.8	2.4	2.1	4.3	11	0.8	9.3	7.3	14.5	12.6	9.0	0.6	13.6	6.7	2.0	0.5
$\frac{\lvert\text{BP[HF]}-\text{HF}\rvert}{\lvert\text{BP[HF]}\rvert}$																
10.1	65.0	26.8	38.2	47.2	80.4	42.1	153.9	315.6	29.6	1872	898.1	1.3	614	300.3	259.9	0.6
$\frac{\lvert\text{MR-BP}[9f]-\text{BP[HF]}\rvert}{\lvert\text{MR-BP}[9f]\rvert}$																
4.8	0.0	4.6	1.8	0.9	1.5	1.2	13.9	58.0	0.4	19.4	20.2	1.5	73.7	1.2	7.2	0.7

and

$$M^{\mathrm{sd}} = (-1)^{S_j+L_j+1/2}\sqrt{\frac{(2S_i+1)(2S_j+1)(2L_i+1)(2L_j+1)(2J+1)}{J(J+1)}}\,g_s\sqrt{30}\begin{Bmatrix} L_i & S_i & J \\ L_j & S_j & J \\ 2 & 1 & 1 \end{Bmatrix}$$
$$\times\Bigg[-\sqrt{\frac{6}{5}}\begin{Bmatrix} 1 & \frac{1}{2} & S_i \\ S_j & 1 & 1 \end{Bmatrix}\begin{Bmatrix} 1 & 2 & L_i \\ L_j & 2 & 1 \end{Bmatrix}\langle 2p^4\,{}^3P\|\mathbf{V}^{(21)}\|2p^4\,{}^3P\rangle\langle 2p|r^{-3}|2p\rangle$$
$$-\sqrt{\frac{10}{7}}\begin{Bmatrix} \frac{1}{2} & 1 & S_i \\ S_j & 1 & \frac{1}{2} \end{Bmatrix}\begin{Bmatrix} 2 & 1 & L_i \\ L_j & 2 & 1 \end{Bmatrix}\langle 3d\,{}^2D\|\mathbf{V}^{(21)}\|3d\,{}^2D\rangle\langle 3d|r^{-3}|3d\rangle\Bigg]. \tag{18}$$

Here $G_\mu = 95.410\,68$ is the numerical factor to be used when expressing the matrix elements M^{orb} and M^{sd} in atomic units (a_0^{-3}), μ_I in nuclear magnetons (μ_{N}), and A_J in units of frequency (MHz), while $g_s = 2.002\,319\,3$ is the electronic g factor corrected for the quantum electrodynamic effects. In addition, $\mathbf{U}^{(1)}$ is the unit tensor operator acting only in the L space and $\mathbf{V}^{(21)}$ is the unit double tensor operator [47]. Further, $\langle nl|r^{-3}|nl\rangle$ 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 $\langle l\|\mathbf{l}^{(1)}\|l\rangle$ for $l = 1$ and 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 $\langle l\|\mathbf{C}^{(2)}\|l\rangle$ 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 M^{orb} [Eq. (17)] and M^{sd} [Eq. (18)], and the results of the formulas (14)–(16) are reported in Tables V and VI for $2p^4(^3P)3d\,^2D_{3/2}$ and $2p^4(^3P)3d\,^2D_{5/2}$, respectively. The mixing coefficients of the corresponding eigenvectors are taken from the MR-BP[9f] calculations (see Table I). The resulting $A_J^{\mathrm{orb}}(\gamma L_i S_i, \gamma L_j S_j)$ and $A_J^{\mathrm{sd}}(\gamma L_i S_i, \gamma L_j S_j)$ 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 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, 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, respectively. As previously indicated, 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 optimization scheme for $2p^4(^3P)3d\ ^2P$, ^4P, and ^2D states, which 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 Tables V and VI, 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 row.

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 nondiagonal matrix elements (^2D,^2P) and (^4P,^4D), which are equal to 428 and 487 MHz, respectively, 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 $A^{\mathrm{orb}}(^2D_{3/2})$ 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 $A^{\mathrm{sd}}(^2D_{3/2})$ 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 depends 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

TABLE V. Values of $A^{\rm orb}_{3/2}(\gamma L_iS_i, \gamma L_jS_j)$, $A^{\rm orb}({}^2D_{3/2})$, $A^{\rm sd}_{3/2}(\gamma L_iS_i, \gamma L_jS_j)$, $A^{\rm sd}({}^2D_{3/2})$, $A_{3/2}(\gamma L_iS_i, \gamma L_jS_j)$, and $A({}^2D_{3/2})$ in MHz according to the formulas (14)–(16).

(L_iS_i, L_jS_j)	c_ic_j	$M^{\rm orb}$	$A^{\rm orb}_{3/2}(\gamma L_iS_i, \gamma L_jS_j)$	$M^{\rm sd}$	$A^{\rm sd}_{3/2}(\gamma L_iS_i, \gamma L_jS_j)$	$A_{3/2}(\gamma L_iS_i, \gamma L_jS_j)$
$({}^2D, {}^2D)$	0.5145	3.4612	447	3.2288	417	864
$({}^2P, {}^2P)$	0.1187	−5.7542	−171	0.1539	5	−166
$({}^4P, {}^4P)$	0.2156	−2.3016	−124	−0.5220	−28	−152
$({}^4F, {}^4F)$	0.0081	9.2212	19	−3.3199	−7	12
$({}^4D, {}^4D)$	0.1143	2.3074	66	3.2298	93	159
$2 \times ({}^2D, {}^2P)$	2 × 0.2472	3.4540	428	−1.3844	−172	256
$2 \times ({}^2D, {}^4P)$	2 × 0.3330	00	00	0.1549	26	26
$2 \times ({}^2D, {}^4F)$	2 × −0.0645	00	00	−2.3147	75	75
$2 \times ({}^2D, {}^4D)$	2 × 0.2425	00	00	0.8069	98	98
$2 \times ({}^2P, {}^4P)$	2 × 0.1600	00	00	−0.2242	−18	−18
$2 \times ({}^2P, {}^4F)$	2 × −0.0310	00	00	−1.1580	18	18
$2 \times ({}^2P, {}^4D)$	2 × 0.1165	00	00	1.0390	61	61
$2 \times ({}^4P, {}^4D)$	2 × 0.1570	6.1800	487	00	00	487
$2 \times ({}^4F, {}^4D)$	2 × −0.0304	3.8538	−59	00	00	−59
$2 \times ({}^4P, {}^4F)$	2 × −0.0417	00	00	2.0711	−43	−43
			$A^{\rm orb}({}^2D_{3/2})$		$A^{\rm sd}({}^2D_{3/2})$	$A({}^2D_{3/2})$
			1093		525	1618
HF			910		825	1734[a]
MR-BP[9f]			1118		563	1654[a]
Expt. [29]						1582 ± 50

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

of the relativistic effects due to mixing effects are captured by the single $\{2p^4({}^3P)3d\ L_iS_i\}$ 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 VI), the HF hyperfine constants values $A^{\rm orb}_{5/2}$ and $A^{\rm sd}_{5/2}$ change from 607 to 827 MHz and from −236 to 186 MHz, respectively, when using the BP[HF] model, which is equivalent to a variation of the total $A({}^2D_{5/2})$

TABLE VI. Values of $A^{\rm orb}_{5/2}(\gamma L_iS_i, \gamma L_jS_j)$, $A^{\rm orb}({}^2D_{5/2})$, $A^{\rm sd}_{5/2}(\gamma L_iS_i, \gamma L_jS_j)$, $A^{\rm sd}({}^2D_{5/2})$, $A_{5/2}(\gamma L_iS_i, \gamma L_jS_j)$, and $A({}^2D_{5/2})$ in MHz according to the formulas (14)–(16).

(L_iS_i, L_jS_j)	c_ic_j	$M^{\rm orb}$	$A^{\rm orb}_{5/2}(\gamma L_iS_i, \gamma L_jS_j)$	$M^{\rm sd}$	$A^{\rm sd}_{5/2}(\gamma L_iS_i, \gamma L_jS_j)$	$A_{5/2}(\gamma L_iS_i, \gamma L_jS_j)$
$({}^2D, {}^2D)$	0.6846	2.3074	396	−0.9225	−158	238
$({}^2F, {}^2F)$	0.1170	6.5866	193	−1.5820	−46	147
$({}^4P, {}^4P)$	0.0804	−3.4526	−70	0.1382	3	−67
$({}^4F, {}^4F)$	0.0145	5.5986	20	−1.6204	−6	14
$({}^4D, {}^4D)$	0.0748	1.8130	34	1.2194	23	57
$2 \times ({}^2D, {}^2F)$	2 × 0.2831	1.2310	175	1.9724	280	455
$2 \times ({}^2D, {}^4P)$	2 × 0.2346	00	00	−0.3794	−45	−45
$2 \times ({}^2D, {}^4F)$	2 × −0.0998	00	00	−1.2125	61	61
$2 \times ({}^2D, {}^4D)$	2 × 0.2263	00	00	1.0475	119	119
$2 \times ({}^2F, {}^4P)$	2 × 0.0970	00	00	0.4052	20	20
$2 \times ({}^2F, {}^4F)$	2 × −0.0413	00	00	−0.6195	13	13
$2 \times ({}^2F, {}^4D$	2 × 0.0936	00	00	0.1317	6	6
$2 \times ({}^4P, {}^4D)$	2 × 0.0775	3.0342	118	−1.0124	−39	79
$2 \times ({}^4F, {}^4D)$	2 × −0.0330	2.3542	−39	1.1791	−20	−59
$2 \times ({}^4P, {}^4F)$	2 × −0.0342	00	00	1.4495	−25	−25
			$A^{orb}({}^2D_{5/2})$		$A^{sd}({}^2D_{5/2})$	$A({}^2D_{5/2})$
			827		186	1013
HF			607		−236	373[a]
MR-BP[9f]			843		197	1067[a]
Expt. [29]						1046 ± 50

[a]These totals differ from $A^{\rm orb}({}^2D_{5/2}) + A^{\rm sd}({}^2D_{5/2})$ because they include the contact contribution which is not strictly zero in the HF and MR-BP[9f] calculations (see the text for more details).

TABLE VII. Values of $A^{\mathrm{orb}}_{3/2}(\gamma L_iS_i,\gamma L_jS_j)=\mathrm{orb}$, $A^{\mathrm{sd}}_{3/2}(\gamma L_iS_i,\gamma L_jS_j)=\mathrm{sd}$, $A_{3/2}(\gamma L_iS_i,\gamma L_jS_j)=\mathrm{orb}+\mathrm{sd}$ for ^4D, ^4F, ^4P, and ^2P states. At the bottom of the table we give the total values $A^{\mathrm{orb}}_{3/2}$, $A^{\mathrm{sd}}_{3/2}$, and $A_{3/2}$ corresponding to BP[$9f$] calculations, while the last row contains the experimental values.

	^4D			^4F			^4P			^2P		
(L_iS_i, L_jS_j)	orb	sd	orb + sd	orb	sd	orb + sd	orb	sd	orb + sd	orb	sd	orb + sd
$(^2D,^2D)$	138	129	267	0	0	0	146	137	283	111	104	215
$(^2P,^2P)$	−97	3	−94	−381	10	−371	−78	2	−76	−675	18	−657
$(^4P,^4P)$	−46	−10	−56	−19	−4	−23	−335	−76	−411	−36	−8	−44
$(^4F,^4F)$	118	−43	75	1559	−561	998	0	0	0	552	−199	353
$(^4D,^4D)$	355	498	853	0	0	0	97	136	233	43	61	104
$2\times(^2D,^2P)$	179	−72	107	−18	7	−11	−165	66	− 99	−424	170	−254
$2\times(^2D,^4P)$	0	−9	−9	0	0	0	0	−24	−24	0	7	7
$2\times(^2D,^4F)$	0	105	105	0	19	19	0	4	4	0	− 203	−203
$2\times(^2D,^4D)$	0	−127	−127	0	0	0	0	68	68	0	−40	−40
$2\times(^2P,^4P)$	0	8	8	0	11	11	0	−20	−20	0	19	19
$2\times(^2P,^4F)$	0	34	34	0	−245	−245	0	−1	−1	0	194	194
$2\times(^2P,^4D)$	0	−106	−106	0	−3	−3	0	−50	−50	0	98	98
$2\times(^4P,^4D)$	686	0	686	7	0	7	−968	0	−968	−211	0	−211
$2\times(^4F,^4D)$	342	0	342	−18	0	−18	−7	0	−7	−259	0	−259
$2\times(^4P,^4F)$	0	66	66	0	−156	−156	0	7	7	0	126	126
	$A^{\mathrm{orb}}_{3/2}$	$A^{\mathrm{sd}}_{3/2}$	$A_{3/2}$	$A^{\mathrm{orb}}_{3/2}$	$A^{\mathrm{sd}}_{3/2}$	$A_{3/2}$	$A^{\mathrm{orb}}_{3/2}$	$A^{\mathrm{sd}}_{3/2}$	$A_{3/2}$	$A^{\mathrm{orb}}_{3/2}$	$A^{\mathrm{sd}}_{3/2}$	$A_{3/2}$
	1675	476	2151	1130	−922	208	−1310	249	−1061	−899	347	−552
MR-BP[$9f$]	1706	507	2262[a]	1146	−1009	122[a]	−1333	281	−1033[a]	−916	382	−496[a]
Expt. [29]			2290±50			110 ± 10			−1035 ± 50			−498 ± 80

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

constant from 371 to 1013 MHz. We notice a particularly important effect on the spin dipole interaction. This effect is mainly due to the two matrix elements $(^2D,^2F)$ and $(^2D,^4D)$ of the spin dipole operator, which increase the spin dipole contribution by 280 and 119 MHz, respectively. Note that among the $^2D_{5/2}$ eigenvector LS composition, the contribution of $^2F_{5/2}$ to the constant $A_{5/2}$ is 641 MHz, which corresponds to 63% of the total value.

In Tables VII–X, we report in detail, 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, and the totals A^{orb}_J, A^{sd}_J, and A_J. In the penultimate row we report the MR-BP[$9f$] values, which 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 $\{2p^4(^3P)3d\ L_iS_i\}$ space such that $\sum_i c_i^2=1$, the weight c_1^2 can be written as

$$c_1^2=\frac{A^{\mathrm{orb}}_J(LS,LS)}{A^{\mathrm{orb}}(^{2S+1}L_J)[\mathrm{HF}]}=\frac{A^{\mathrm{sd}}_J(LS,LS)}{A^{\mathrm{sd}}(^{2S+1}L_J)[\mathrm{HF}]}=\frac{A_J(LS,LS)}{A(^{2S+1}L_J)[\mathrm{HF}]},\tag{19}$$

where $c_1^2=1$ would correspond to a Hartree-Fock calculation. When $|c_1|$ decreases, the relative difference between $A_J(LS,LS)$ and $A(^{2S+1}L_J)[\mathrm{HF}]$ increases, which reveals large term-mixing effects. This can be illustrated in the case of $^2F_{5/2}$ for which $|c_1|=0.442$ (see Table I), with the following values: $A^{\mathrm{orb}}_{5/2}(^2F,^2F)=323$ MHz, $A^{\mathrm{sd}}_{5/2}(^2F,^2F)=-77$ MHz, $A_{5/2}(^2F,^2F)=246$ MHz, $A^{\mathrm{orb}}(^2F_{5/2})[\mathrm{HF}]=1691$ MHz, $A^{\mathrm{sd}}(^2F_{5/2})[\mathrm{HF}]=-406$ MHz, and $A(^2F_{5/2})[\mathrm{HF}]=1285$ MHz (see Table VIII). 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 $\sum_i c_i^2=1$. The large difference between the two values of $A_{5/2}(^2F,^2F)$ and $A(^2F_{5/2})[\mathrm{HF}]$ indicates a significant contribution from the other matrix elements, as it can be seen in Table VIII (column 10, labeled "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 $A(^4P_{1/2})$ and $A(^4P_{5/2})$, as already noted at the end of Sec. IV. For the first case [$A(^4P_{1/2})$], Table X 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 for the off-diagonal coupling matrix element $A_{1/2}(^4P,^4D)=-516$ MHz. For the second case [$A(^4P_{5/2})$], the fact that this hyperfine constant is the smallest one (in absolute value) among the 15 experimental values can be easily understood from the very large cancellation between the orbital and spin dipole contributions, as demonstrated in Table VIII. The use of the $\{2p^4(^3P)3d\ L_iS_i\}$ space combined with the c_i coefficients of the MR-BP[$9f$] eigenvector makes it possible to demonstrate very clearly the effects of the term mixing on the hyperfine constants. In some cases, for example, $^4F_{3/2}$ and $^4P_{3/2}$, the $\{2p^4(^3P)3d\ L_iS_i\}$ limited space is not large enough to obtain good agreement with the $[9f]$-space result, but is sufficient to demonstrate the importance of the mixtures.

TABLE VIII. Values of $A^{\rm orb}_{5/2}(\gamma L_iS_i, \gamma L_jS_j) = \text{orb}$, $A^{\rm sd}_{5/2}(\gamma L_iS_i, \gamma L_jS_j) = \text{sd}$, and $A_{5/2}(\gamma L_iS_i, \gamma L_jS_j) = \text{orb} + \text{sd}$ for ^4D, ^4F, ^2F, and ^4P states. At the bottom of the table we give the total values $A^{\rm orb}_{5/2}$, $A^{\rm sd}_{5/2}$, and $A_{5/2}$ corresponding to BP[9f] calculations, while the last row contains the experimental values.

	^4D			^4F			^2F			^4P		
(L_iS_i, L_jS_j)	orb	sd	orb + sd	orb	sd	orb + sd	orb	sd	orb + sd	orb	sd	orb + sd
$(^2D,^2D)$	46	−18	28	87	−35	52	33	−13	20	1	0	1
$(^2F,^2F)$	11	−3	8	531	−128	403	323	−77	246	547	−131	416
$(^4P,^4P)$	−53	2	−51	−1	0	−1	−390	16	−374	−327	13	−314
$(^4F,^4F)$	149	−43	106	647	−187	460	184	−53	131	364	−105	259
$(^4D,^4D)$	326	219	545	18	11	29	63	42	105	1	1	2
$2 \times (^2D,^2F)$	15	23	38	−135	−217	−352	−65	−104	−169	11	17	28
$2 \times (^2D,^4P)$	0	13	13	0	−3	−3	0	30	30	0	4	4
$2 \times (^2D,^4F)$	0	56	56	0	−160	−160	0	52	52	0	−9	−9
$2 \times (^2D,^4D)$	0	−126	−126	0	−40	−40	0	46	46	0	1	1
$2 \times (^2F,^4P)$	0	−4	−4	0	−4	−4	0	60	60	0	−72	−72
$2 \times (^2F,^4F)$	0	8	8	0	120	120	0	−50	−50	0	−91	−91
$2 \times (^2F,^4D)$	0	−5	−5	0	7	7	0	−11	−11	0	2	2
$2 \times (^4P,^4D)$	320	−107	213	−10	3	−7	−380	127	−253	−47	16	−31
$2 \times (^4F,^4D)$	326	163	489	−158	−79	−237	−159	−80	−239	31	15	46
$2 \times (^4P,^4F)$	0	59	59	0	17	17	0	177	177	0	−228	−228
	$A^{\rm orb}_{5/2}$	$A^{\rm sd}_{5/2}$	$A_{5/2}$	$A^{\rm orb}_{5/2}$	$A^{\rm sd}_{5/2}$	$A_{5/2}$	$A^{\rm orb}_{5/2}$	$A^{\rm sd}_{5/2}$	$A_{5/2}$	$A^{\rm orb}_{5/2}$	$A^{\rm sd}_{5/2}$	$A_{5/2}$
	1140	237	1377	979	−695	284	−391	162	−229	581	−567	14
MR-BP[9f]	1157	253	1461[a]	990	−764	252[a]	−400	180	−202[a]	589	−622	−36[a]
Expt. [29]			1481 ± 20			304 ± 50			−190 ± 10			−17 ± 10

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

VI. CONCLUSION

In this work we have presented the results of elaborate *ab initio* variational calculations of hyperfine constants for 17 levels in fluorine, all arising from the six terms $2p^4(^3P)3d$ ^4D, ^2D, ^4F, ^2F, ^4P, and ^2P. 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 [29]. The global theory-observation agreement is very good (of the order of 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 $A(^4P_{5/2})$ 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 [14,28]. It indeed reveals, in contrast to what is *a priori* expected for light atoms, weak electron

TABLE IX. Values of $A^{\rm orb}_{7/2}(\gamma L_iS_i, \gamma L_jS_j) = \text{orb}$, $A^{\rm sd}_{7/2}(\gamma L_iS_i, \gamma L_jS_j) = \text{sd}$, and $A_{7/2}(\gamma L_iS_i, \gamma L_jS_j) = \text{orb} + \text{sd}$ for ^4D, ^4F, and ^2F states. At the bottom of the table we give the total values $A^{\rm orb}_{7/2}$, $A^{\rm sd}_{7/2}$, and $A_{7/2}$ corresponding to BP[9f] calculations, while the last row contains the experimental values.

	^4D			^4F			^2F		
(L_iS_i, L_jS_j)	orb	sd	orb + sd	orb	sd	orb + sd	orb	sd	orb + sd
$(^2F,^2F)$	46	6	52	257	34	291	901	120	1021
$(^4F,^4F)$	127	−13	114	673	−67	606	270	−27	243
$(^4D,^4D)$	338	−203	135	63	−38	25	0	0	0
$2 \times (^2F,^4F)$	0	−22	−22	0	−119	−119	0	141	141
$2 \times (^2F,^4D)$	0	61	61	0	−62	−62	0	1	1
$2 \times (^4F,^4D)$	207	249	456	−206	−248	−454	−1	−2	−3
	$A^{\rm orb}_{7/2}$	$A^{\rm sd}_{7/2}$	$A_{7/2}$	$A^{\rm orb}_{7/2}$	$A^{\rm sd}_{7/2}$	$A_{7/2}$	$A^{\rm orb}_{7/2}$	$A^{\rm sd}_{7/2}$	$A_{7/2}$
	718	78	796	787	−500	287	1170	233	1403
MR-BP[9f]	729	82	852[a]	799	−553	263[a]	1187	247	1480[a]
Expt. [29]			793 ± 20			276 ± 10			

[a] 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 the text for further explanation).

TABLE X. Values of $A^{\mathrm{orb}}_{1/2}(\gamma L_i S_i, \gamma L_j S_j) = \mathrm{orb}$, $A^{\mathrm{sd}}_{1/2}(\gamma L_i S_i, \gamma L_j S_j) = \mathrm{sd}$, and $A_{1/2}(\gamma L_i S_i, \gamma L_j S_j) = \mathrm{orb} + \mathrm{sd}$ for ^4D, ^4P, and ^2P states. At the bottom of the table we give the total values $A^{\mathrm{orb}}_{1/2}$, $A^{\mathrm{sd}}_{1/2}$, and $A_{1/2}$ corresponding to $[9f]$ calculations, while the last row contains the experimental values.

	^4D			^4P			^2P		
(L_iS_i, L_jS_j)	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	07	12	400	559	959
$2 \times (^2P,^4P)$	0	−19	−19	0	61	61	0	−43	−43
$2 \times (^2P,^4D)$	0	−416	−416	0	−41	−41	0	457	457
$2 \times (^4P,^4D)$	2431	487	2918	−430	−86	−516	−2003	−401	−2404
	$A^{\mathrm{orb}}_{1/2}$	$A^{\mathrm{sd}}_{1/2}$	$A_{1/2}$	$A^{\mathrm{orb}}_{1/2}$	$A^{\mathrm{sd}}_{1/2}$	$A_{1/2}$	$A^{\mathrm{orb}}_{1/2}$	$A^{\mathrm{sd}}_{1/2}$	$A_{1/2}$
	3118	1400	4518	−343	−112	−455	−2773	397	−2376
MR-BP[$9f$]	3183	1499	4646[a]	−351	−115	−462[a]	−2824	467	−2327[a]
Expt. [29]			4541 ± 50			−226 ± 50			−2378 ± 80

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

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 $\{2p^4(^3P)3d\ L_iS_i\}$ 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 illustrated the crucial role of relativistic term mixing in the theoretical estimation of the hyperfine constants. It also shed 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 us to understand their relative magnitude.

Estimations and investigations of theoretical uncertainties of atomic properties should be systematically included, when possible. As observed by Drake [49], it is clear that the culture is changing within the theoretical computational community to make uncertainty quantification the usual expectation when theoretical results are presented. The present work is one step in this direction, among a few others in the framework of multiconfiguration variational approaches [50–52]. It indeed illustrates how the details of the magnetic dipole hyperfine operators can be explored to highlight 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 relatively 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 $2p^4(^3P)3d\ ^4P_{1/2}$ and $^4P_{5/2}$ can be explained by large interferences occurring in the amplitude of the observable.

Relativistic corrections should be systematically considered in hyperfine-structure calculations of close-lying levels that can interact with each other through the relativistic Hamiltonian, even in light atomic systems. This observation is particular relevant for excited regions of the spectrum for which the energy-level density is expected to increase. For nonrelativistic atomic systems, so qualified since the Schrödinger picture holds as a good zeroth-order approximation, the Breit-Pauli approximation remains an excellent approach to unravel the complex interference mechanisms involved in the theoretical *A* values, reproducing satisfactorily the four-component relativistic MCDHF results. 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 [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.

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