

Relativistic effects on the hyperfine structures of $2p^4(^3P)3p^2D^o$, $4D^o$, and $4P^o$ in $^{19}\text{F I}$

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The hyperfine interaction constants of the $2p^4(^3P)3p^2D_{3/2,5/2}^o$, $4D_{1/2-7/2}^o$, and $4P_{1/2-5/2}^o$ levels in neutral fluorine are investigated theoretically. Large-scale calculations are carried out using the multiconfiguration Hartree-Fock (MCHF) and Dirac-Hartree-Fock (MCDHF) methods. In the framework of the MCHF approach, the relativistic effects are taken into account in the Breit-Pauli approximation using nonrelativistic orbitals. In the fully relativistic approach, the orbitals are optimized using the Dirac-Coulomb Hamiltonian with correlation models inspired by the nonrelativistic calculations. Higher-order excitations are captured through multireference configuration interaction calculations including the Breit interaction. In a third (intermediate) approach, the Dirac-Coulomb-Breit Hamiltonian matrix is diagonalized in a relativistic configuration space built with nonrelativistic MCHF radial functions converted into Dirac spinors using the Pauli approximation. The magnetic dipole hyperfine-structure constants calculated with the three relativistic models are consistent and reveal unexpectedly large effects of relativity for $2D_{5/2}^o$, $4P_{3/2}^o$, and $4P_{5/2}^o$. The agreement with the few available experimental values is satisfactory. The strong J dependence of relativistic corrections on the hyperfine constants is investigated through the detailed analysis of the orbital, spin-dipole, and contact relative contributions calculated with the nonrelativistic magnetic dipole operator.

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I. INTRODUCTION

Atomic fluorine is a highly reactive free radical. Its natural state is molecular fluorine, a poisonous and corrosive material that makes experimental studies quite delicate and scarce [1,2]. The atomic resonance transitions lie in the ultraviolet region but many of the transitions between excited states lie in the visible and near-infrared and can be driven using diode lasers, as explored by Tate and Aturaliye [3] who reported for the first time high-resolution laser spectroscopy measurements of hyperfine structures. These authors used Doppler-free saturation absorption spectroscopy of excited states of atomic fluorine to measure and analyze the hyperfine-structure intervals of the $2p^4(^3P)3s^2P_J \rightarrow 2p^4(^3P)3p^2D_J^o$ fine-structure multiplet components. Using the observed hyperfine-structure splittings (hfs), the magnetic hyperfine constants A_J were determined for the levels involved in the transitions, with a higher accuracy than those determined earlier by Lidén [4] and Hocker [5]. The comparison of the experimental hfs reveals large discrepancies [3]. For instance, hfs values for the splittings of the $2p^4(^3P)3p^2D_{3/2}^o$ and $2D_{5/2}^o$ states have been found to be negative in [5] while positive in [4] and [3], with a large discrepancy (21%) between the two latter for the hfs values of $2p^4(^3P)3p^2D_{3/2}^o$, well outside the error bars. In contrast with the hyperfine study of the ground-state levels $2p^5^2P_{1/2,3/2}^o$ for which observation [6–8] and theory [9–11] have been compared, there is no theoretical prediction for the hyperfine structure of the excited levels considered in [3], except the pioneer work by Brown and Bartlett [12]. More

recently, in a feasibility study of in-beam polarization of fluorine, Levy *et al.* [13] measured the hyperfine structures of $2p^4(^3P)3s^2P_{5/2}$ and $2p^4(^3P)3p^4D_{5/2,7/2}^o$ states via laser-induced fluorescence and modulated optical depopulation pumping. As for $2p^4(^3P)3p^2D_{3/2}^o$ and $2D_{5/2}^o$, no theoretical values are available in the literature for these quartet levels, to the knowledge of the authors.

The present work was originally motivated by the following observation: On the one hand, a serious disagreement appeared when comparing our first theoretical estimation of the hyperfine constant of $2p^4(^3P)3p^2D_{5/2}^o$ based on robust nonrelativistic calculations with the Doppler-free spectroscopy value reported by Tate and Aturaliye [3]. On the other hand, *ab initio* calculations of hyperfine constants for ^{14}N and ^{15}N [14] were found to be in complete disagreement with the experimental values of Jenner *et al.* [15], also deduced from the analysis of the near-infrared Doppler-free saturated absorption spectra. This nitrogen theory-observation discrepancy problem was recently solved through a reinterpretation of the recorded weak spectral lines as crossover signals [16], leading to a new set of experimental hyperfine constants in very good agreement with the *ab initio* predictions [14]. Considering that the apparition of crossover signals in Doppler-free saturated absorption spectroscopy that has been used for both fluorine [3] and nitrogen [15] is helpful in some cases but also problematic in others, we investigate in the present work the relativistic corrections that could explain the nonrelativistic theory-observation discrepancy mentioned above for the $A_{5/2}$ value of $2p^4(^3P)3p^2D_{5/2}^o$.

For light atomic systems, the relativistic effects are usually included with success in the Breit-Pauli approximation [17,18] for fine-structure and transition probability calculations. In the

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case of fluorine, the relativistic corrections are expected to be relatively small. We expect therefore that relativity could be treated in a perturbation regime using either the Breit-Pauli approximation [19,20] or the relativistic configuration interaction approach in the Pauli approximation [21,22]. It is worthwhile to investigate if these methods lead to hyperfine-structure constants consistent with each other, with the fully relativistic approach and with observation, when available. The evaluation of hyperfine interaction structures for atomic states provides a good opportunity to study the interplay between the correlation and relativistic effects. Different theoretical approaches can be used for estimating hyperfine structures, with their advantages and disadvantages, depending on the size and complexity of the targeted atomic systems. Fluorine has a special place in this diversity. As a nine-electron atom, it definitely lies outside the “few”-electron systems domain for which the elaborate variational calculations in Hylleraas coordinates can be successfully applied, usually giving rise to the most reliable expectation values [23–25]. Moreover, taken in its $2p^4 3p$ excited configuration, neutral fluorine constitutes a difficult target for many-body approaches that are often restricted to single- or two-valence atoms or ions [26–28]. The coupled-cluster theory is promising [29–31] but investigation of hyperfine structures in more complex systems remains scarce [32]. Although further developments might be expected [33–36], the traditional multiconfiguration methods combined with configuration interaction in their nonrelativistic [14,37,38] and relativistic [39–43] versions keep a respectable place in the ranking of *ab initio* methods for hyperfine-structure calculations.

Section II describes the atomic state functions in the nonrelativistic multiconfiguration Hartree-Fock, relativistic Breit-Pauli, multiconfiguration Dirac-Hartree-Fock and Pauli approaches. The theoretical background needed for understanding the hyperfine interaction is given in Sec. III. The computational strategy is developed in Sec. IV. The theoretical hyperfine constants calculated using the different models are compared to each other and with observation in Sec. V.

II. ATOMIC STATE FUNCTION

A. Nonrelativistic approach

In the nonrelativistic multiconfiguration Hartree-Fock (MCHF) approximation [44], the atomic state function (ASF) is described as a linear combination of N_c configuration state functions (CSFs)

$$\Psi(\alpha LSM_L M_S \pi) = \sum_i^{N_c} c_i \Phi(\alpha_i LSM_L M_S \pi) \quad (1)$$

built on one-electron spin-orbitals

$$\phi_{nlm_l m_s}(\mathbf{r}, \sigma) = \frac{P_{nl}(r)}{r} Y_{lm_l}(\theta, \varphi) \chi_{m_s}(\sigma). \quad (2)$$

The MCHF equations are the system of coupled, nonlinear differential equations that arises when we require the energy to be stationary with respect to variations in the radial functions $\{P_{nl}(r)\}$. At the same time the energy must be stationary with respect to variations in the mixing coefficients $\{c_i\}$, leading to a system of secular equations [17]. Once a set of one-electron

orbitals is optimized, a larger system of secular equations can be solved for diagonalizing the nonrelativistic Hamiltonian in an enlarged CSF basis to get a better description of the desired eigenvector. In the present paper, we will refer to these calculations as configuration interaction (CI).

B. Relativistic approach

1. Breit-Pauli approximation

Relativistic corrections to the MCHF or CI wave functions can be included efficiently in the Breit-Pauli (BP) approximation [17] that consists in writing the ASF as the following expansion:

$$\Psi(\alpha JM_J \pi) = \sum_i^{N_c} c_i \Phi(\alpha_i L_i S_i JM_J \pi). \quad (3)$$

This wave function is the eigenvector of the Breit-Pauli Hamiltonian matrix corresponding to the desired root. Note that, opposite to Eq. (1), the ASF (3) allows LS mixing due to the fine-structure BP Hamiltonian terms that do not commute with \mathbf{L} and \mathbf{S} [17,45].

2. Multiconfiguration Dirac-Hartree-Fock approach

Starting from the Dirac-Coulomb Hamiltonian [22]

$$H_{\text{DC}} = \sum_i^N [c \boldsymbol{\alpha}_i \cdot \mathbf{p}_i + (\beta_i - 1)c^2 + V_i^{\text{nuc}}] + \sum_{i>j} 1/r_{ij}, \quad (4)$$

where V^{nuc} is the monopole part of the electron-nucleus Coulomb interaction, the atomic state function (ASF) of a specific fine-structure level is described by a linear combination of relativistic configuration state functions $\Phi(\gamma_i JM_J \pi)$

$$\Psi(\gamma JM_J \pi) = \sum_{i=1}^{N_c} c_i \Phi(\gamma_i JM_J \pi), \quad (5)$$

which are built on relativistic configurations γ_i involving the jj coupling of subshell Dirac spinors [22]

$$\phi_{\kappa m}(\mathbf{r}, \sigma) = \frac{1}{r} \begin{pmatrix} P_{\kappa m}(r) & \chi_{\kappa m}(\theta, \varphi) \\ iQ_{\kappa m}(r) & \chi_{-\kappa m}(\theta, \varphi) \end{pmatrix}, \quad (6)$$

where κ is defined as

$$\kappa = \begin{cases} -l - 1 & \text{when } j = l + 1/2, \\ l & \text{when } j = l - 1/2. \end{cases} \quad (7)$$

Applying the variational principle, the radial functions $\{P_{\kappa m}(r), Q_{\kappa m}(r)\}$ and the mixing coefficients c_i appearing in Eq. (5) are optimized by solving iteratively the self-consistent field (SCF) problem and the secular equations. Calculations can be performed not only for a single level, but also for a portion of a spectrum in an extended optimal level (EOL) scheme where optimization is applied on a weighted sum of energies. In the EOL optimization scheme [22,46] that we adopt for the present study (using the “standard” option of the GRASP2K [47] computer code), the functional has the form

$$\mathcal{F} = \sum_{r=1}^{N_c} \sum_{s=1}^{N_c} d_{rs} H_{rs} + \mathcal{L}, \quad (8)$$

where \mathcal{L} contains the Lagrange multipliers contributions and

$$d_{rs} = \left(\sum_{i=1}^{n_L} (2J_i + 1) c_{ri} c_{si} \right) / \left(\sum_{i=1}^{n_L} (2J_i + 1) \right). \quad (9)$$

n_L specifies the number of the targeted eigenvalues, each of them weighted by the $(2J_i + 1)$ degeneracy factor.

An extension of the MCDHF approach, allowing the mixing coefficients to be varied but keeping the one-electron orbitals frozen, is referred to in the present work as the relativistic configuration interaction (RCI) method. In the latter, the transverse photon interaction [48]

$$H_{\text{Transv}} = - \sum_{i < j}^N \left[\boldsymbol{\alpha}_i \cdot \boldsymbol{\alpha}_j \frac{\cos(\omega_{ij} r_{ij}/c)}{r_{ij}} + (\boldsymbol{\alpha} \cdot \nabla)_i (\boldsymbol{\alpha} \cdot \nabla)_j \frac{\cos(\omega_{ij} r_{ij}/c) - 1}{\omega_{ij}^2 r_{ij}/c^2} \right] \quad (10)$$

may be included in the Hamiltonian matrix. However ω_{ij} appearing in this equation is the energy of the exchanged photon between the two electrons (i, j), and is not well defined for correlation orbitals. Therefore, it is only possible to estimate the low-frequency ($\omega_{ij} \rightarrow 0$) limit of Eq. (10) by multiplying the computed photon frequency by a small number to get the Breit interaction [48,49]

$$H_{\text{Breit}} = - \sum_{i < j}^N \frac{1}{2r_{ij}} \left[\boldsymbol{\alpha}_i \cdot \boldsymbol{\alpha}_j + \frac{(\boldsymbol{\alpha}_i \cdot \mathbf{r}_{ij})(\boldsymbol{\alpha}_j \cdot \mathbf{r}_{ij})}{r_{ij}^2} \right]. \quad (11)$$

3. Pauli approximation

Another interesting way to estimate relativistic effects is to diagonalize the Dirac-Coulomb-Breit Hamiltonian ($H_{\text{DC}} + H_{\text{Breit}}$) matrix, in a relativistic CSF basis built on Dirac spinors whose large and small radial components are calculated from nonrelativistic MCHF radial functions, using the Pauli approximation [21,22,50]

$$P_{nk}(r) = P_{nl}^{\text{MCHF}}(r), \quad (12)$$

$$Q_{nk}(r) \approx \frac{\alpha}{2} \left(\frac{d}{dr} + \frac{\kappa}{r} \right) P_{nk}(r),$$

where α is the fine-structure constant. This method based on the use of the relativistic configuration interaction approach in the Pauli approximation is labeled RCI-P in the present work.

III. HYPERFINE INTERACTION

The hyperfine contribution to the Hamiltonian is represented by a multipole expansion

$$H_{\text{hfs}} = \sum_{k \geq 1} \mathbf{T}^{(k)} \cdot \mathbf{M}^{(k)}, \quad (13)$$

where $\mathbf{T}^{(k)}$ and $\mathbf{M}^{(k)}$ are spherical tensor operators of rank k in the electronic and nuclear space, respectively [51,52]. The $k = 1$ and $k = 2$ terms represent, respectively, the magnetic dipole interaction and the electric quadrupole interaction. The ^{19}F nucleus, the only stable fluorine isotope, has a nuclear spin $I = 1/2$ and a magnetic moment $\mu_I = 2.628868\mu_N$ [53–55] but no quadrupole moment ($Q = 0$). The hyperfine shifts of the

fine-structure levels may be expressed to first order in terms of the magnetic dipole A_J hyperfine interaction constant [56] that is proportional to the reduced matrix element of the electronic tensor operator of rank one

$$A_J = \frac{\mu_I}{I} \frac{1}{\sqrt{J(J+1)(2J+1)}} \langle \gamma J \| \mathbf{T}^{(1)} \| \gamma J \rangle. \quad (14)$$

In nonrelativistic calculations, the electronic matrix elements are obtained by integrating the irreducible spherical tensors [57,58]

$$\mathbf{T}^{(1)} = \frac{\alpha^2}{2} \sum_{i=1}^N \left\{ 2\mathbf{l}^{(1)}(i)r_i^{-3} - g_s \sqrt{10} [\mathbf{C}^{(2)}(i) \times \mathbf{s}^{(1)}(i)]^{(1)} r_i^{-3} + g_s \frac{8}{3} \pi \delta(\mathbf{r}_i) \mathbf{s}^{(1)}(i) \right\} \quad (15)$$

using the ASF of the form (1) adapted to the $\mathbf{J} = \mathbf{L} + \mathbf{S}$ symmetry

$$\Psi(\alpha LSJM_J\pi) = \sum_i^{N_e} a_i \Phi(\alpha_i LSJM_J\pi), \quad (16)$$

i.e., an expansion similar to Eq. (3), but restricted to the same LS values. For light atoms in which the LS coupling remains valid to a good approximation, relativistic corrections can be introduced in the BP approximation. The resulting wave functions (3) used to evaluate the matrix elements of the electronic tensor operator (15) allow LS mixing for a specific J value. In both cases, the hyperfine constant defined by Eq. (14) is composed of the orbital, spin-dipole, and contact contributions

$$A_J = A_J^{\text{orb}} + A_J^{\text{sd}} + A_J^{\text{c}}, \quad (17)$$

which are evaluated using the eigenvectors (1) or (3). In cases where LS coupling is strictly valid, i.e., omitting the ($L' \neq L$) and ($S' \neq S$) off-diagonal relativistic matrix elements, the three contributions to the hyperfine constant appearing in Eq. (17) take the form

$$A_J^{\text{orb}} = G_\mu \frac{\mu_I}{I} a_l \mathcal{F}^{\text{orb}}(L, S, J), \quad (18)$$

$$A_J^{\text{sd}} = \frac{1}{2} G_\mu g_s \frac{\mu_I}{I} a_{\text{sd}} \mathcal{F}^{\text{sd}}(L, S, J), \quad (19)$$

$$A_J^{\text{c}} = \frac{1}{6} G_\mu g_s \frac{\mu_I}{I} a_c \mathcal{F}^{\text{c}}(L, S, J), \quad (20)$$

where the J -independent orbital (a_l), spin-dipole (a_{sd}), and contact (a_c) electronic hyperfine parameters are defined as [57,58]

$$a_l \equiv \langle \alpha LSM_L M_S | \sum_{i=1}^N l_0^{(1)}(i) r_i^{-3} | \alpha LSM_L M_S \rangle, \quad (21)$$

$$a_{\text{sd}} \equiv \langle \alpha LSM_L M_S | \sum_{i=1}^N 2C_0^{(2)}(i) s_0^{(1)}(i) r_i^{-3} | \alpha LSM_L M_S \rangle, \quad (22)$$

$$a_c \equiv \langle \alpha LSM_L M_S | \sum_{i=1}^N 2s_0^{(1)}(i) r_i^{-2} \delta(r_i) | \alpha LSM_L M_S \rangle, \quad (23)$$

with $M_L = L$ and $M_S = S$. The dimensionless factors $\mathcal{F}^i(L, S, J)$ can be evaluated from the following expectation values:

$$\mathcal{F}^{\text{orb}}(L, S, J) = \frac{\langle \mathbf{L} \cdot \mathbf{J} \rangle}{LJ(J+1)}, \quad (24)$$

$$\mathcal{F}^{\text{sd}}(L, S, J) = \frac{3\langle \mathbf{L} \cdot \mathbf{S} \rangle \langle \mathbf{L} \cdot \mathbf{J} \rangle - L(L+1)\langle \mathbf{S} \cdot \mathbf{J} \rangle}{SL(2L-1)J(J+1)}, \quad (25)$$

$$\mathcal{F}^{\text{c}}(L, S, J) = \frac{\langle \mathbf{S} \cdot \mathbf{J} \rangle}{SJ(J+1)}. \quad (26)$$

Expressing the electronic parameters a_l , a_{sd} and a_c in atomic units (units of a_0^{-3}) and μ_l in nuclear magnetons (μ_N), the magnetic dipole hyperfine-structure constants A_J are calculated in units of frequency (MHz) by using $G_\mu = 95.41067$.

In fully relativistic calculations, the structure of the magnetic dipole electronic tensor is much simpler than the nonrelativistic form (15) [57,59]

$$\mathbf{T}^{(1)} = -i\alpha \sum_{j=1}^N [\boldsymbol{\alpha}_j \cdot \mathbf{l}_j \mathbf{C}^{(1)}(j)] \frac{1}{r_j^2}. \quad (27)$$

The hyperfine constant A_J is estimated from the expectation value of this operator, using Eq. (14) and the atomic state function (5).

IV. COMPUTATIONAL MODELS

A. Nonrelativistic calculations

We perform two types of nonrelativistic calculations. The first one is based on the multiconfiguration Hartree-Fock approach [17,60] with configuration expansions generated by single (S) and double (D) excitations from the single reference. For a given calculation, the orbital active space (AS) is characterized by $[n_{\text{max}}]$ when no angular limitation applies. The active set is specified by $[n_{\text{max}}l_{\text{max}}]$ when angular orbital limitation is introduced. We have performed systematic SD-MCHF calculations, considering angular momentum values up to $l = 5$ (h electrons), and concluded that truncating the AS at $l_{\text{max}} = 3$ is safe for getting hyperfine constants within 0.2%. These calculations are denoted SD-MCHF in Table I.

With these MCHF orbital sets, we investigate the use of SD-multireference expansions by performing configuration interaction calculations (MR-CI) based on expansions generated by allowing SD excitations from the three configurations $\{2s^22p^43p, 2s^22p^23p3d^2, 2s2p^43p3d\}$. To keep the size of the interaction matrices manageable, the three CSFs of the MR space are not treated identically in terms of SD excitations, considering a smaller orbital active set $[6f]$ for the two $\{2s^22p^23p3d^2, 2s2p^43p3d\}$ components than the one adopted $[10f]$ for the major $(2s^22p^43p)$ component. We observe that the use of a multireference space is worthwhile, bringing a 3.6% variation in the hyperfine constants of the $^4P_{1/2}^o$ level. For the $^4D^o$ symmetry, we test a ‘‘reduction strategy’’ that consists in limiting in the final expansions the excited CSFs that interact with at least one of the three

TABLE I. Hyperfine-structure constants A_J (in MHz) of $2p^4(^3P)3p^4D_J^o$, $^4P_J^o$, and $^2D_J^o$. Upper part: nonrelativistic values obtained with the multiconfiguration Hartree-Fock method using single- and double-monoreference expansions (SD-MCHF), and multireference configuration interaction (MR-CI) calculations. Lower part: relativistic values calculated in the Breit-Pauli (BP and MR-BP) and the Pauli (RCI-P) approximations.

| Method | AS | $^4D^o$ | | | | $^4P^o$ | | | $^2D^o$ | |
|-----------|----------------------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|
| | | $A_{1/2}$ | $A_{3/2}$ | $A_{5/2}$ | $A_{7/2}$ | $A_{1/2}$ | $A_{3/2}$ | $A_{5/2}$ | $A_{3/2}$ | $A_{5/2}$ |
| HF | | 2466 | 987 | 1109 | 1538 | -1991 | 1260 | 731 | 1862 | 2037 |
| SD-MCHF | [3] | 1535 | 1152 | 1433 | 1919 | -454 | 1935 | 1274 | 1509 | 2387 |
| | [4] | 2275 | 893 | 1033 | 1474 | -1961 | 1226 | 674 | 1768 | 1954 |
| | [5] | 2087 | 931 | 1113 | 1579 | -1820 | 1330 | 744 | 1705 | 2058 |
| | [6 <i>f</i>] | 2161 | 925 | 1093 | 1551 | -1712 | 1370 | 783 | 1733 | 2032 |
| | [7 <i>f</i>] | 2156 | 931 | 1098 | 1554 | -1739 | 1354 | 773 | 1731 | 2037 |
| | [8 <i>f</i>] | 2157 | 929 | 1096 | 1550 | -1738 | 1350 | 770 | 1730 | 2031 |
| | [9 <i>f</i>] | 2163 | 925 | 1091 | 1546 | -1759 | 1343 | 763 | 1732 | 2027 |
| | [10 <i>f</i>] | 2152 | 926 | 1094 | 1549 | -1743 | 1349 | 768 | 1727 | 2030 |
| MR-CI | [10 <i>f</i>] | 2114 | 930 | 1103 | 1561 | -1682 | 1374 | 788 | 1711 | 2041 |
| MR-CI-red | [10 <i>f</i>] | 2119 | 929 | 1102 | 1559 | | | | | |
| MR-MCHF | {10s9p8d4 <i>f</i> } | 2122 | 930 | 1102 | 1560 | -1697 | 1369 | 784 | 1715 | 2040 |
| BP | [8 <i>f</i>] | 2102 | 839 | 1099 | 1543 | -1616 | 1742 | 1007 | 1763 | 1685 |
| | [9 <i>f</i>] | 2110 | 835 | 1093 | 1538 | -1637 | 1737 | 1001 | 1772 | 1686 |
| | [10 <i>f</i>] | 2100 | 837 | 1095 | 1542 | -1620 | 1745 | 1007 | 1768 | 1691 |
| RCI-P | [8 <i>f</i>] | 2103 | 839 | 1097 | 1540 | -1615 | 1737 | 1005 | 1763 | 1686 |
| | [9 <i>f</i>] | 2112 | 835 | 1091 | 1536 | -1636 | 1732 | 999 | 1772 | 1686 |
| | [10 <i>f</i>] | 2101 | 836 | 1093 | 1540 | -1620 | 1740 | 1005 | 1768 | 1691 |
| MR-BP | [10 <i>f</i>] | 2073 | 846 | 1107 | 1553 | -1572 | 1762 | 1022 | 1759 | 1701 |

MR components. These calculations are performed using LSREDUCE, which is part of the utilities provided in the MCHF atomic-structure package [60], and are labeled MR-CI-red in the present work. While the number of CSFs is sensitively decreased by this reduction strategy (from 394 190 to 206 340), the hyperfine constants are not affected, as illustrated by Table I.

The use of the multireference is also tested in the orbital optimization by performing MR-MCHF calculations to capture higher-order correlation effects. For the latter, we use the above reduction strategy, adopting the reversed orbital order consisting in coupling sequentially the subshells by decreasing n and l . This technique indeed reduces substantially the size of the MCHF expansions while keeping the dominant correlation contributions [14]. For specifying the AS, it is sometimes more convenient to use another notation involving curly brackets instead of brackets, where the number of orbitals for each angular symmetry is specified, i.e., $\{10s9p8d7f\} = [10f]$. The $\{10s9p8d4f\}$ AS used for the MR-MCHF calculations means that for its three multireference components, the orbital angular momentum is limited to $l_{\max} = 3$ for $n \leq 7$ and $l_{\max} = 2$ for $n \geq 8$. As shown by Table I, the inclusion of the MR in the MCHF model reproduces the MR-CI results within less than 1%.

B. Relativistic calculations

In the Breit-Pauli (BP) approximation, the CSF expansions of the atomic state function (3) are constructed in the same way as in the SD-MCHF calculations, but including all possible symmetries $L_i S_i$ for a given J value. The radial functions spanning the CSFs are taken from the $[nf]$ SD-MCHF calculations. All the Breit-Pauli operators are taken into account.

Relativistic configuration interaction calculations are also performed in the Pauli approximation (RCI-P) by generating jj -coupled relativistic configuration state function expansions (5) from SD excitations of the monoreference configuration using the $[10f]$ active set. The radial functions are the non-

relativistic MCHF radial functions converted to approximate Dirac spinors according to Eq. (12).

Replacing the monoreference by a MR model in the nonrelativistic framework brings variations of a few percent in the hyperfine constants, as shown in the previous section. It is therefore worthwhile investigating the multireference approach in the Breit-Pauli approximation. For these calculations (denoted MR-BP), we build the CSF expansions by including SD excitations from the three-configuration $\{2s^2 2p^4 3p, 2s^2 2p^2 3p 3d^2, 2s 2p^4 3p 3d\}$ multireference, using respectively, the $[10f]$, $[5d]$, and $[5d]$ active space. For a given J value, all symmetries resulting from the main reference ($2s^2 2p^4 3p$) are included, while for the other two references $\{2s^2 2p^2 3p 3d^2, 2s 2p^4 3p 3d\}$ only the ${}^2(S, P, D)$ and ${}^4(S, P, D)$ symmetries are considered. The size of the spaces are reduced with LSREDUCE. The three sets of BP, RCI-P, and MR-BP results are presented in the second half of Table I.

In Table II, we report fully relativistic results. In the nonrelativistic approximation, the desired states $2p^4 3p^4 D^o$, ${}^4P^o$, ${}^2D^o$ are the lowest of their symmetry. This is not true anymore in the relativistic framework for the $J = 1/2, 3/2$ levels for which the interaction with the ground configuration $2p^5$ should be taken into account. The simplest model is therefore a two-configuration model $\{2p^4 3p + 2p^5\}$ for these J subspaces. MCDHF calculations are performed by using the active space approach inspired from the nonrelativistic SD-MCHF correlation models. Denoting the n th root of the J block by $E(n_J)$ and referring to Eqs. (8) and (9), the EOL strategy is applied to optimize separately three orbitals sets, using the following energy functionals: $[6E(1_{\frac{5}{2}}) + 4E(2_{\frac{3}{2}}) + 2E(2_{\frac{1}{2}})]/12$, $[8E(1_{\frac{7}{2}}) + 6E(2_{\frac{5}{2}}) + 4E(3_{\frac{3}{2}}) + 2E(3_{\frac{1}{2}})]/20$, and $[6E(3_{\frac{5}{2}}) + 4E(4_{\frac{3}{2}})]/10$, describing, respectively, the fine-structure levels J of the three terms $2p^4({}^3P)3p^4P^o$, ${}^4D^o$, and ${}^2D^o$.

The number of CSFs in SD-MCDHF expansions increases drastically with the extension of the AS compared to SD-MCHF ones. To keep the size of the multiconfiguration expansions manageable the reduction strategy, which has been proven to be efficient in the nonrelativistic MR-CI

TABLE II. Hyperfine-structure constants A_J (in MHz) of $2p^4({}^3P)3p^4D^o$, ${}^4P^o$, and ${}^2D^o$ obtained with the fully relativistic multiconfiguration-Dirac-Hartree-Fock method using single- and double-monoreference expansions (SD-MCDHF), and multireference relativistic configuration interaction (MR-RCI) calculations.

| Method | [AS] | ${}^4D^o$ | | | | ${}^4P^o$ | | | ${}^2D^o$ | |
|----------------------|------------------------------------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|
| | | $A_{1/2}$ | $A_{3/2}$ | $A_{5/2}$ | $A_{7/2}$ | $A_{1/2}$ | $A_{3/2}$ | $A_{5/2}$ | $A_{3/2}$ | $A_{5/2}$ |
| $\{2p^4 3p + 2p^5\}$ | | 2250 | 809 | 1125 | 1529 | -1772 | 1811 | 1045 | 1795 | 1633 |
| SD-MCDHF | [3] | 1380 | 1086 | 1532 | 1883 | -317 | 2418 | 1525 | 1362 | 1914 |
| | [4] | 2120 | 746 | 1035 | 1461 | -1769 | 1713 | 948 | 1783 | 1630 |
| | [5] | 2027 | 785 | 1109 | 1533 | -1708 | 1790 | 995 | 1748 | 1673 |
| | [6f] | 2087 | 782 | 1083 | 1511 | -1663 | 1777 | 992 | 1788 | 1650 |
| | [7f] | 2061 | 805 | 1131 | 1526 | -1601 | 1818 | 1023 | 1818 | 1739 |
| | $\{8s7p6d4f\}$ | 2037 | 814 | 1127 | 1529 | -1583 | 1807 | 1017 | 1814 | 1738 |
| | $\{9s8p7d4f\}$ | 2065 | 812 | 1109 | 1523 | -1624 | 1780 | 998 | 1784 | 1660 |
| | $\{10s9p8d4f\}$ | 2060 | 818 | 1111 | 1526 | -1606 | 1784 | 1002 | 1789 | 1666 |
| MR-RCI | $\{10s9p8d3f\}/[5d]$ (see text) | 2071 | 850 | 1127 | 1546 | -1555 | 1784 | 1028 | 1772 | 1700 |

calculations for the 4D symmetry, is applied by using the JJREDUCE code [61]. Moreover, the orbital active sets are restricted to $l_{\max} = 2$ from $n = 8$, as indicated by the curly bracket notation used in Table II. Another difference with the SD-MCHF strategy is that the calculations are carried out layer by layer, i.e., optimizing only the correlation orbitals of the added layer together with the mixing coefficients. The Breit interaction (11) is taken into account in the subsequent RCI computations. The configuration space is built by allowing SD excitations from the same multireference $\{2s^22p^43p, 2s^22p^23p3d^2, 2s2p^43p3d\}$ as the one used in the nonrelativistic calculations. To keep the configuration interaction problem tractable, we adopt two different active spaces: $\{10s9p8d3f\}$ for the major component $2s^22p^43p$ and $[5d]$ for the two others. Moreover, for $2s^22p^23p3d^2$, the excitations are restricted to the ones in which the $1s$ shell remains closed.

V. RESULTS AND DISCUSSION

The convergence of the hyperfine-structure constants with the progressive extension of the orbital active sets within a given correlation model is satisfactory, as illustrated by Tables I and II for the nonrelativistic SD-MCHF and relativistic SD-MCDHF results, respectively. The excellent agreement between the BP and the RCI-P results is rather comforting. Both sets arise from the same radial one-electron orbitals optimized through the nonrelativistic MCHF approach, but relativity is included not only through different approaches but also by using independent computational tools (ATSP2K [60] and GRASP2K [47] codes). The Breit-Pauli Hamiltonian is indeed a low-order approximation of the Dirac-Coulomb Hamiltonian and the expectation values of its operators are evaluated using nonrelativistic LSJ -basis functions, while the RCI-P method diagonalizes the Dirac-Coulomb-Breit Hamiltonian in a jjJ -CSF basis built on approximated Dirac spinors. Moreover the evaluation of the expectation values of the magnetic dipole electronic tensors (15) and (27) is done

within radically different frameworks. The effect of enlarging the reference set that can be estimated by comparing the MR-CI and SD-MCHF values for a given active set [10*f*] is coherent with the MR-BP and BP differences found in the Breit-Pauli approximation. This means that enlarging the multireference space mostly captures electron correlation. A detailed cross-comparison of the most elaborate calculations reported in Tables I and II shows that enlarging the reference space improves the agreement between the Breit-Pauli and fully relativistic values.

We present in Table III the magnetic dipole hyperfine constants corresponding to the largest AS for each theoretical model and compare them with experimental values when available. As already observed above, the two sets of non-relativistic MR-MCHF and MR-CI values are consistent with each other, but the comparison with the SD-MCHF values indicates the significant effect of higher-order excitations. In the monoreference model, the comparison between the SD-MCHF and BP values reveals the importance of the relativistic corrections for some levels. This is *a priori* unexpected for a light system such as neutral fluorine. Among the nine levels considered, the hyperfine constants of $^4P_{3/2}^o$ and $^4P_{5/2}^o$ are the most affected by relativity, the difference between the BP and SD-MCHF results reaching as much as 30%. This effect is less important but still quite large for $^2D_{5/2}^o$ (17%), $^4D_{3/2}^o$ (10%), and $^4P_{1/2}^o$ (7%). The same observation can be made from the relativistic configuration interaction calculations in the Pauli approximation (RCI-P).

The fully relativistic results (MCDHF) confirm the large relativity effects found in the Breit-Pauli approximation. The comparison between the MCDHF, BP and RCI-P values, all based on monoreference correlation models, is by itself interesting, illustrating the rather good coherence (within 2%) of the hyperfine constant values. The agreement between the Breit-Pauli and fully relativistic values is maintained when enlarging the reference space. The agreement between MR-BP and MR-RCI is indeed better than 1.8%. Going from MCDHF to MR-RCI, one takes into account, not only the higher-order

TABLE III. Comparison of the hyperfine constants A_J (in MHz) estimated from nonrelativistic (SD-MCHF, MR-MCHF, and MR-CI) and relativistic calculations. From the nonrelativistic MCHF orbitals, relativity is included in the Breit-Pauli approximation, monoreference (BP) and multireference (MR-BP), or through relativistic configuration interaction calculations using one-electron orbitals built in the Pauli approximation (RCI-P). Fully relativistic multiconfiguration Dirac-Hartree-Fock (MCDHF) and multireference relativistic configuration interaction (MR-RCI) are also reported and compared with observation.

| Term | A_J | Nonrelativistic | | | Relativistic | | | | | Observed |
|--------------------|-----------|------------------|----------------------------------|-------|--------------|----------------|-------|---------------------------------|-------|-----------------|
| | | Mono- SD-MCHF | Multi-reference MR-MCHF MR-CI | | BP | Mono- RCI-P | MCDHF | Multi-reference MR-BP MR-RCI | | |
| $2p^4(^3P)3p^4D^o$ | $A_{1/2}$ | 2152 | 2122 | 2114 | 2100 | 2101 | 2060 | 2073 | 2071 | |
| | $A_{3/2}$ | 926 | 930 | 930 | 837 | 836 | 818 | 846 | 850 | |
| | $A_{5/2}$ | 1094 | 1102 | 1103 | 1095 | 1093 | 1111 | 1107 | 1127 | 1148(1) [13] |
| | $A_{7/2}$ | 1549 | 1560 | 1561 | 1542 | 1540 | 1526 | 1553 | 1546 | 1564(1) [13] |
| $2p^4(^3P)3p^4P^o$ | $A_{1/2}$ | -1743 | -1697 | -1682 | -1620 | -1620 | -1606 | -1572 | -1555 | |
| | $A_{3/2}$ | 1349 | 1369 | 1374 | 1745 | 1735 | 1784 | 1762 | 1784 | |
| | $A_{5/2}$ | 768 | 784 | 788 | 1007 | 1004 | 1002 | 1022 | 1028 | |
| $2p^4(^3P)3p^2D^o$ | $A_{3/2}$ | 1727 | 1715 | 1711 | 1768 | 1768 | 1789 | 1759 | 1772 | 1857.1(2.1) [3] |
| | $A_{5/2}$ | 2030 | 2040 | 2040 | 1691 | 1691 | 1666 | 1701 | 1700 | 1746.5(1.5) [3] |

TABLE IV. Comparison of the orbital, spin-dipole, and contact contributions to the hyperfine-structure constants (all numbers in MHz) calculated with the nonrelativistic SD-MCHF method and including the relativistic Breit-Pauli corrections (BP). The $\Delta A_i/A_{\text{tot}}$ contributions are defined in the text [see Eq. (28)].

| | $J = 1/2$ | | | $J = 3/2$ | | | $J = 5/2$ | | | $J = 7/2$ | | |
|------------------|-----------|-------|-----------------------------|-----------|------|-----------------------------|-----------|------|-----------------------------|-----------|------|-----------------------------|
| | SD-MCHF | BP | $\Delta A_i/A_{\text{tot}}$ | SD-MCHF | BP | $\Delta A_i/A_{\text{tot}}$ | SD-MCHF | BP | $\Delta A_i/A_{\text{tot}}$ | SD-MCHF | BP | $\Delta A_i/A_{\text{tot}}$ |
| $4D^o$ | | | | | | | | | | | | |
| A_{orb} | 4360 | 4028 | -15.4% | 1744 | 1562 | -19.7% | 1370 | 1287 | -7.6% | 1246 | 1246 | 0% |
| A_{sd} | -2099 | -1821 | 12.9% | -840 | -759 | 8.7% | -317 | -244 | 6.7% | 257 | 248 | -0.6% |
| A_{c} | -109 | -107 | 0.1% | 22 | 34 | 1.3% | 40 | 52 | 1% | 47 | 47 | 0% |
| A_{tot} | 2152 | 2100 | -2.4% | 926 | 837 | -9.6% | 1094 | 1095 | 0% | 1549 | 1542 | -0.5% |
| $4P^o$ | | | | | | | | | | | | |
| A_{orb} | -1454 | -1159 | 16.9% | 582 | 1012 | 31.9% | 872 | 983 | 14.5% | | | |
| A_{sd} | -497 | -668 | -9.8% | 676 | 641 | -2.6% | -179 | -51 | 16.7% | | | |
| A_{c} | 208 | 207 | 0% | 91.5 | 92 | 0% | 75 | 75 | 0% | | | |
| A_{tot} | -1743 | -1620 | 7% | 1349 | 1745 | 29.3% | 768 | 1007 | 31.1% | | | |
| $2D^o$ | | | | | | | | | | | | |
| A_{orb} | | | | 2618 | 2657 | 2.2% | 1745 | 1691 | -2.7% | | | |
| A_{sd} | | | | -848 | -836 | 0.7% | 242 | -32 | -13.5% | | | |
| A_{c} | | | | -43 | -53 | -0.6% | 43 | 32 | -0.5% | | | |
| A_{tot} | | | | 1727 | 1768 | 2.4% | 2030 | 1691 | -16.7% | | | |

excitations beyond the monoreference model (including the interplay between electron correlation and relativity), but also the Breit interaction (11). The corresponding variation systematically improves the theory-observation agreement in the four A_J values for which experimental data are available [3,13]. The remaining discrepancies between experiment and theory arise most likely from higher-order electron correlation. Unfortunately, experimental values are limited to four levels among the nine considered. Taking these values as the truth, the uncertainty of the (MR-BP and MR-RCI) average values is estimated to be better than 3%. With this respect, the 5% difference between theory and observation for $2D_{3/2}^o$ is somewhat surprising, as suggested by the following detailed analysis.

To get some insight into the origin of the strong level dependence of relativistic effects, we report in Table IV the SD-MCHF and BP values of the three different hyperfine contributions A_i ($i = \text{orb}, \text{sd}, \text{c}$). The ratios of the SD-MCHF values, for a given contribution i , are strictly conditioned by the factors $\mathcal{F}^{\text{orb}}(L, S, J)$, $\mathcal{F}^{\text{sd}}(L, S, J)$, and $\mathcal{F}^{\text{c}}(L, S, J)$ defined in Eqs. (24), (25), and (26). These are explicitly reported in Table V. For instance, the first line numbers (4360 : 1744 :

1370 : 1246) appearing in Table IV and corresponding to the A_{orb} contributions of $4D_J^o$ are in the ratios (35 : 14 : 11 : 10) which can be found in the \mathcal{F}^{orb} column of Table V. Similarly, the sixth line numbers (-497 : 676 : -179) reporting the A_{sd} values for $4P_J^o$ in Table IV follow the \mathcal{F}^{sd} ratios (50 : -68 : 18) of Table V. As can be realized from the BP values reported in Table IV, these ratios are strongly affected by the relativistic corrections in the Breit-Pauli approximation due to the LS mixing in Eq. (3). For example, the ratios (35 : 14 : 11 : 10) and (50 : -68 : 18) calculated from the corresponding A_{orb} and A_{sd} MCHF values, respectively, become (32.3 : 12.5 : 10.3 : 10) and (70.9 : -68 : 5.4). Table V includes the LS composition of the BP wave functions. The strongest LS mixing appears for the $2D_{5/2}^o$ and $4D_{5/2}^o$ terms, but the purity of all $4P_J^o$ levels remains high. One can then conclude that there is no trivial correlation between the LS -mixing magnitude and the relativistic effect on the hyperfine constant value.

In the Table IV, we report the relative differences between the SD-MCHF and BP values

$$\frac{\Delta A_i}{A_{\text{tot}}} = \frac{A_i(\text{SD-MCHF}) - A_i(\text{BP})}{A_{\text{tot}}(\text{SD-MCHF})} \quad (28)$$

TABLE V. J -dependent factors of the orbital [$\mathcal{F}^{\text{orb}}(L, S, J)$], spin-dipole [$\mathcal{F}^{\text{sd}}(L, S, J)$], and contact [$\mathcal{F}^{\text{c}}(L, S, J)$] contributions to the hyperfine constant A_J [see Eqs. (24)–(26)]. LS eigenvector compositions are given in %.

| LS term | J | \mathcal{F}^{orb} | \mathcal{F}^{sd} | \mathcal{F}^{c} | Composition (%) |
|-----------------|-----|----------------------------|---------------------------|--------------------------|--|
| $2p^4 3p^4 D^o$ | 1/2 | +35/35 | -245/105 | -70/105 | 99.6($4D$), 0.3($4P$), 0.1($2P$) |
| | 3/2 | +14/35 | -98/105 | +14/105 | 96.9($4D$), 2.2($2D$), 0.8($4P$) |
| | 5/2 | +11/35 | -37/105 | +26/105 | 92.5($4D$), 6.5($2D$), 0.9($4P$) |
| | 7/2 | +10/35 | +30/105 | +30/105 | 100.0($4D$) |
| $2p^4 3p^4 P^o$ | 1/2 | -10/15 | +50/45 | +50/45 | 99.6($4P$), 0.2($4D$), 0.2($2S$) |
| | 3/2 | +4/15 | -68/45 | +22/45 | 98.8($4P$), 0.7($4D$), 0.5($4S$) |
| | 5/2 | +6/15 | +18/45 | +18/45 | 98.9($4P$), 1.0($4D$), 0.1($2D$) |
| $2p^4 3p^2 D^o$ | 3/2 | +3/5 | -7/5 | -2/5 | 96.9($2D$), 2.7($4D$), 0.3($2P$) |
| | 5/2 | +2/5 | +2/5 | +2/5 | 91.4($2D$), 8.1($4D$), 0.5($4P$) |

for the three different hyperfine contributions, using $A_{\text{tot}}(\text{SD-MCHF})$ as the reference value. The analysis of these relative contributions sheds some light on the J -level dependence of relativistic effects for a given LS term. The 31% found for the relativistic effect on $A_{5/2}$ of $2p^4(^3P)3p^4P_{5/2}^o$ is due to the cumulative effects of +14.5% and +16.7% relativistic contributions to the orbital and spin-dipole contributions, while the very small impact of relativity (−2.4%) found on $A_{1/2}$ of $2p^4(^3P)3p^4D_{1/2}^o$ is explained by the strong cancellation of the (still large in absolute value) −15.4% and +12.9% relativistic contributions to the orbital and spin-dipole contributions.

VI. CONCLUSION

Relativistic effects on the hyperfine structures of heavy elements are well known. Woodgate showed that a calculation of the breakdown of the LS coupling and of second-order corrections, off-diagonal in J , is necessary for an interpretation of the spectrum of samarium [62]. It has been shown independently by Sandars and Beck [63] that hyperfine-structure calculations can often be made more conveniently by using effective operators between nonrelativistic LS basis states. This approach has been used for instance by Childs [64] for studying relativistic effects in the hyperfine structure of the tin isotopes. A critical analysis of the methods used to interpret the hyperfine structure in complex free atoms and ions can be found in [65]. The investigation of relativity on hyperfine parameters in light systems is less common. In the present work, robust correlation models are built in the nonrelativistic approach, to investigate hyperfine-structure parameters in fluorine. The reliability of these models is assessed by comparing single- and double-, mono- and multi-reference MCHF and CI calculations that all agree with each other within, at most, 3.5%. For some levels— $2p^4(^3P)3p^2D_{5/2}^o$ is a nice example—all nonrelativistic correlation models perfectly agree with each other but differ quite substantially ($\simeq 17\%$) from observation. It is well known that relativistic corrections on the electronic atomic structures grow with the nuclear charge [21,22] but are expected to be smaller than the electron correlation effects for neutral and light atomic systems. In neutral fluorine, yet a very light element ($Z = 9$), we show that relativistic corrections to the nonrelativistic hyperfine parameters can be large for some low-lying levels, reaching around 30% for the A values of $2p^4(^3P)3p^4P_{3/2}^o$ and $4P_{5/2}^o$. While nonrelativistic approaches are often successful in computing hyperfine constants with good accuracy, even in heavier systems [38], we see here that it is necessary to systematically estimate relativistic corrections.

In this context, BPCI and RCI-P methods stand as valuable tools since they are computationally cheap compared to fully relativistic calculations.

Core-orbital contraction and charge-density rearrangement due to relativity can be very important [57] and are *a priori* poorly described in the MCHF-BP approximation [42]. For fluorine, however, the hyperfine structure parameters estimated with the MCHF-BP method are nicely coherent with the results obtained from the fully relativistic MCDHF method, suggesting that the orbital contraction effects are minor in comparison to the LS term relativistic mixing. When both methods produce similar results, the first approach (MCHF-BP) offers some advantages compared with the second one (MCDHF). The analysis of the relative orbital, spin-dipole, and contact contributions, which is difficult in the MCDHF framework [66,67] and becomes impossible when using the simple form of the magnetic dipole operator (27), sheds indeed some light in the origin of the large J dependency of relativistic effects, as we explicitly illustrate in the present work.

Refining our preliminary nonrelativistic results by introducing relativity through the Breit-Pauli Hamiltonian, we find large unexpected variations in the hyperfine structure constants that evidently bring the theoretical estimations closer to the experimental values of Tate and Aturaliye [3]. While it has been clearly demonstrated that the theory-observation disagreement was due to a wrong interpretation of the Doppler-free saturated absorption spectroscopy signals in nitrogen [3], a good agreement is found with the fluorine experimental values obtained with the same technique if the relativistic corrections are included. This observation excludes any misinterpretation of the crossover signals in fluorine. We identify in the present work the origin of the relativistic effects on the hyperfine constants for specific levels and expect them to be even larger for levels that are not yet considered experimentally. We strongly encourage the performance of experimental studies of the hyperfine structures in fluorine to confirm our theoretical estimation of the crucial role of relativity, in particular for the $4P_{3/2,5/2}^o$ levels.

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