Multiconfigurational Hartree-Fock calculations of hyperfine-induced transitions in heliumlike ions

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We are investigating the hyperfine quenching of $1s2p$ $^3P_0^o$ for the three heliumlike ions $^{19}F^{7+}$, $^{23}Na^{9+}$, and $^{27}Al^{11+}$ in the multiconfigurational Hartree-Fock-Breit-Pauli scheme. The configuration expansions are generated with the active-space method and are increased in a systematic way, allowing the convergence of the calculated parameters to be studied. A careful comparison is done with the pioneering work of Mohr using a perturbation approach [*Beam-Foil Spectroscopy, Atomic Structure and Lifetimes*, edited by I. Sellin and D. Pegg (Plenum, New York, 1976), Vol. 1, pp. 97–103]. In the present calculations the orbital and spin-dipole magnetic contributions, which were previously neglected, are added to the dominant Fermi contact interaction term and a detailed analysis of the hyperfine-induced transition rate is done in order to learn how to get an accurate description of the property in the multiconfiguration Hartree-Fock Breit-Pauli approximation.

I. INTRODUCTION

The importance of forbidden lines in both laboratory and astrophysical sources has been illustrated magnificently by Garstang [1]. A complete survey of forbidden decays in one- and two-electron atoms written by Marrus and Mohr [2] covers the literature up to the end of the 1970s. The role and interest of forbidden transitions in astrophysical and fusion studies has been renewed, as pointed out in the recent bibliography by Biémont and Zeippen [3] focusing on forbidden processes and in many proceedings on "atomic spectra and oscillator strengths for astrophysical and laboratory plasmas" [4–6].

Besides the usual class of "forbidden" processes (electric or magnetic multipole, spin-forbidden electric dipole, or multiphoton transitions), hyperfine-induced transitions can be very interesting. The $J = 0 \leftrightarrow J = 0$ transitions are forbidden by the rigorous selection rules of electric dipole, magnetic dipole, and electric quadrupole radiation. Lines in Mg I, Zn I and Hg I for these forbidden processes appear, however, in spectra of planetary nebulae [7]. They have been shown to be due to the hyperfine interaction between the nucleus and the orbital electrons for isotopes with nonzero nuclear spin. The same interaction can open new decay channels [8] or produce an F dependency in the lifetimes, as observed in neutral strontium [9] for a strong localized singlet-triplet mixing between the $n = 19$ members of the $5snd$ $^1D_2$ and $5snd$ $^3D_3$ series. The shortening of the $1s2p$ $^3P^o$

lifetimes because of hyperfine-induced transitions to the ground state was demonstrated experimentally for $^3P_2^o$ in V^{21+} by Gould *et al.* [10]. The nuclear spin-induced quenching of the $^3P_0^o$ state has been searched in F^{7+} by Mowat *et al.* [11], but not found due to the experimental uncertainties. More accurate lifetimes allowing experimental verification were reported by Engström *et al.* [12,13]. These measurements with those of Denne *et al.* [14] and Livingston and Hinterlong [15] for Al^{11+} and P^{13+} respectively, all confirmed the theoretical predictions of Mohr [8].

The hyperfine interaction can mix significantly levels which cross for some specific nuclear charge in an isoelectronic series for isotopes with nonzero nuclear spin ($I \neq 0$). Indelicato *et al.* [16] suggested a precise measurement of the $1s2p$ $^3P_{0,F=I}^o \rightarrow 1s^2$ $^1S_{0,F=I}$ lifetime in heliumlike ions to determine the fine structure splitting $^3P_{1-0}^o$ in situations for which the radiative width of the $^3P_1^o$ level is larger than the level separation. This has been done successfully for heliumlike ions, Ni^{26+} [17], Ag^{45+} [18,19] and Gd^{62+} [20]. Marques *et al.* [21,22] investigated theoretically the hyperfine quenching of $nsnp$ $^3P_0^o$ in berylliumlike ($n = 2$) and magnesium-like ($n = 3$) ions. As in the heliumlike case, they show that it is possible to estimate the $^3P_{1-0}^o$ energy separation through a measurement of the hyperfine-quenched $^3P_0^o$ lifetime for ions with nonzero nuclear spin. Unlike heliumlike ions, the unperturbed lifetimes are infinite and the perturbed ones are rather long, but could be measured by taking advantage of the recent progress in ion

trap techniques. Along this line, laser cooling techniques have been used recently to measure the radiative lifetime of the forbidden transition $5s5p$ $^3P_0^o \to 5s^2$ $^1S_0$ of In^+ ions stored in a radio frequency trap by Peik *et al.* [23], who point out the possible use of this hyperfine-induced transition as a frequency standard because of its insensitivity to external perturbations.

Very accurate *ab initio* calculations of hyperfine structures are now possible from variational wave functions [24–26] and can even compete in some cases with the many-body perturbation theory [27]. This, associated with the rebirth of the hyperfine quenching, motivated the present study. We extended the MCHF_ASP package [28–31], very well adapted for weakly to moderately ionized systems, to allow J-hyperfine mixing in the Breit-Pauli configuration-interaction program [32] and hyperfine-induced radiative decay rate calculations in the transition probability computer codes [33]. These new programs are tested by evaluating the hyperfine quenching of the $1s2p$ $^3P_0^o$ level of a few heliumlike ions ($Z = 9, 11, 13$) for which experimental lifetimes are available. The comparison between our configuration-interaction approach and the perturbation pioneer work of Mohr [8] on the hyperfine quenching in heliumlike systems provides excellent guidelines for capturing the various physical effects affecting the hyperfine-induced transition probability in the multiconfiguration Hartree-Fock-Breit-Pauli scheme.

II. HYPERFINE QUENCHING IN HELIUMLIKE IONS

For systems having a nonzero nuclear spin ($I \neq 0$), the lifetime of $1s2p$ $^3P_0^o$, which decays to $1s2s$ $^3S_1$ by an allowed electric dipole ($E1$) transition, is shortened by the opening of the new decay channel $1s2p$ $^3P_0^o \to 1s^2$ $^1S_0$. This new decay channel is due first to the mixing of $^3P_1^o$ and $^1P_1^o$ by the Breit-Pauli interaction resulting in mixed states

$$|2\ ^1P_1^{o*}\rangle = a|2\ ^1P_1^o\rangle - b|2\ ^3P_1^o\rangle\ ,$$
$$|2\ ^3P_1^{o*}\rangle = b|2\ ^1P_1^o\rangle + a|2\ ^3P_1^o\rangle \tag{1}$$

and the subsequent mixing of $^3P_0^o$ with the above $J = 1$ states due to the hyperfine interaction. To first-order this wave function may be expressed as

$$|1s2p\ ^3P_0^o IM\rangle^{(1)}$$

$$= |1s2p\ ^3P_0^o IM\rangle$$

$$+ \frac{\langle 2\ ^3P_1^{o*} IM|H^{hpf}|2\ ^3P_0^o IM\rangle}{E(2\ ^3P_0^o) - E(2\ ^3P_1^{o*})}|1s2p\ ^3P_1^{o*} IM\rangle$$

$$+ \frac{\langle 2\ ^1P_1^{o*} IM|H^{hpf}|2\ ^3P_0^o IM\rangle}{E(2\ ^3P_0^o) - E(2\ ^1P_1^{o*})}|1s2p\ ^1P_1^{o*} IM\rangle \tag{2}$$

where, in the present case ($J = 0$), I is the value of the total angular momentum F with $\mathbf{F} = \mathbf{J} + \mathbf{I}$ and $M = M_I = M_F$ its z component. Mohr [8] expressed

the transition probability to the ground state induced by this hyperfine mixing as

$$A^{hfs} = \frac{4\omega^3 e^2}{3\hbar c^3}|\epsilon|^2\ |\langle 1\ ^1S|z_1 + z_2|2\ ^1P^o\rangle|^2 \tag{3}$$

with

$$\epsilon = \left[\frac{b^2}{\Delta} + \frac{a^2}{\Delta'}\right]\langle 2\ ^1P_1^o IM|H^{hpf}|2\ ^3P_0^o IM\rangle$$
$$+ \left[\frac{ab}{\Delta} - \frac{ab}{\Delta'}\right]\langle 2\ ^3P_1^o IM|H^{hpf}|2\ ^3P_0^o IM\rangle\ , \tag{4}$$

where a and b are coefficients describing the mixing of the $J = 1$ states of Eq. 1 and Δ and Δ' the energy shifts for this mixing, namely,

$$\Delta = E(2\ ^3P_0^o) - E(2\ ^3P_1^{o*})\ ,$$
$$\Delta' = E(2\ ^3P_0^o) - E(2\ ^1P_1^{o*})\ .$$

In this scheme, ϵ represents the "pure" nonrelativistic $^1P_1^o$ character of the $1s2p$ $^3P_0^o$ state that includes hyperfine mixing directly and spin-orbit mixing indirectly.

III. COMPUTATIONAL METHODS

Unlike Mohr, who used Z^{-1} perturbation theory and $(Z\alpha)^2$ expansions of the different quantities involved in A^{hfs}, we adopt a configuration-interaction approach based on radial functions $\{P_{n\ell}(r)\}$ optimized using nonrelativistic multiconfiguration Hartree-Fock (MCHF) expansions:

$$\Psi^{MCHF}(\gamma LS\pi) = \sum_i c_i \Phi(\gamma_i LS\pi)\ . \tag{5}$$

In our specific case, we will use the concept of "complete active space" (CAS) by generating *all* the configuration state functions (CSF's) of a given $LS\pi$ symmetry which can be built by distributing the two electrons within a specified set of orbitals defining the *active set*. Separate active sets were optimized for both $1s^2$ ^1S and $1s2p$ $^3P^o$. When required, a hybrid optimization procedure is used to get a balanced description of both $1s2p$ $^3P^o$ and $^1P^o$ (see Sec. IV B).

The hyperfine program [31] has been reorganized to take the J mixing of states induced by the hyperfine operators into account [32]. In our approach, the wave function expansions

$$\Psi(\gamma IF\pi) = \sum_i c_i \Phi(\gamma_i L_i S_i J_i IF\pi) \tag{6}$$

are obtained by diagonalizing the Breit-Pauli matrix [34] corrected by the hyperfine Hamiltonian, which represents the interaction between the orbital electrons and the electromagnetic moments of the nucleus:

$$[\mathbf{H}^{BP} + \mathbf{H}^{hpf}]\mathbf{C} = E\mathbf{C}\ . \tag{7}$$

The lowest-order hyperfine interaction, i.e., the magnetic dipole and the electric quadrupole interactions

$$H^{hpf} = H_{dip} + H_{quadr} \qquad (8)$$

are represented by the operators [35]

$$H_{dip} = \mathbf{T}^{(1)} \cdot \mathbf{M}^{(1)} , \qquad (9)$$

$$H_{quadr} = \mathbf{T}^{(2)} \cdot \mathbf{M}^{(2)} . \qquad (10)$$

For an N-electron atom the electronic tensor operators are, in atomic units,

$$\mathbf{T}^{(1)} = \frac{\alpha^2}{2} \sum_{i=1}^{N} \left[2\, \mathbf{l}^{(1)}(i) r_i^{-3} - g_s \sqrt{10} [\mathbf{C}^{(2)}(i) \right.$$
$$\left. \otimes \mathbf{s}^{(1)}(i)]^{(1)} r_i^{-3} + g_s \frac{8}{3} \pi \delta(\mathbf{r}_i) \mathbf{s}^{(1)}(i) \right] \qquad (11)$$

and

$$\mathbf{T}^{(2)} = -\sum_{i=1}^{N} \mathbf{C}^{(2)}(i) r_i^{-3} , \qquad (12)$$

where $g_s = 2.002\,32$ is the electronic g-factor and $\delta(\mathbf{r})$ the three-dimensional delta function. The magnetic dipole operator gives the magnetic field due to the electrons at the nucleus. The first term of Eq. (11) represents the contribution to the magnetic field of the orbiting electric charges and is called the orbital term. The second term (spin dipole) represents the dipole field due to the spin motion of the electrons. The third term (Fermi contact) comes from the contact interaction between the nuclear magnetic dipole moment and the electron spin. The electric quadrupole operator (12) represents the electric field gradient at the nucleus. The required electronic matrix element expressions are given elsewhere [31].

The nuclear data, i.e., the nuclear spin I, the nuclear magnetic dipole moment μ_I (in nuclear magnetons)

$$\mu_I = \langle \gamma_I II | M_0^{(1)} | \gamma_I II \rangle , $$

and the electric quadrupole moment Q (in barns),

$$\frac{Q_I}{2} = \langle \gamma_I II | M_0^{(2)} | \gamma_I II \rangle,$$

which are the expectation values of the nuclear tensors $M_0^{(k)}$ appearing in (9) and (10) in the nuclear state $|\gamma_I I M_I = I\rangle$, have been taken from the compilation of Raghavan [36] and are given in Table I for the three nuclei (^{19}F, ^{23}Na, and ^{27}Al) considered in the present study. The transition programs [29,30] have been adapted for evaluating the electric dipole line strength between hyperfine components, taking the J mixing of the wave functions (6) into account:

$$S(\gamma F, \gamma' F') = e^2 \sum_{q, M_F, M_F'} \left| \left\langle \gamma F M_F \left| \sum_{k=1}^{N} r(k) C_q^{(1)}(k) \right| \gamma' F' M_F' \right\rangle \right|^2$$
$$= e^2 \sum_{q, M_F, M_F'} \left| \sum_{ij} c_i^* c_j \left\langle \gamma_i L_i S_i J_i I F M_F \left| \sum_{k=1}^{N} r(k) C_q^{(1)}(k) \right| \gamma_j L_j S_j J_j I F' M_F' \right\rangle \right|^2 \qquad (13)$$

and the corresponding transition rate [33]

$$A_{\gamma F, \gamma' F'} = \frac{4\omega^3}{3\hbar c^3} \frac{1}{2F + 1} S(\gamma F, \gamma' F') . \qquad (14)$$

In this approach, the ϵ value of Eq. (3) is merely the configuration-interaction coefficient of the nonrelativistic (i.e., pure LS) $|1s2p\ {}^1P_1^o\rangle$ component in the eigenvector

(6), which is dominant in $|1s2p\ {}^3P_0^o\rangle$ within the $F = I$ subspace.

IV. RESULTS AND DISCUSSION

A. The one-configuration approximation

The approximation that limits the superposition (6) to one configuration for describing the initial ($1s^2$) and final ($1s2p$) states, though basically too crude, gives us a qualitative picture of what is going on and can even provide some useful quantitative information. The three nuclei considered differ by their nuclear angular momentum values I. The hyperfine coupling between the four configuration states arising from $1s2p$, i.e., the ${}^3P_J^o$ ($J = 2, 1, 0$) and ${}^1P_1^o$ terms, differently affect the three ions F^{7+}, Na^{9+}, and Al^{11+}. Since we are more interested in the contamination of $|1s2p\ {}^3P_0^o\rangle$ by any symmetry that could open radiative channels, we can restrict ourselves to the final "good" quantum number $F = I$. The $I = \frac{1}{2}$ value

TABLE I. Nuclear data.

Nucleus	Z	I	μ (nm)[a]	Q (b)[a]
^{19}F	9	$\frac{1}{2}$	+2.628868(8)	0.
^{23}Na	11	$\frac{3}{2}$	+2.2176556(6)	+0.1006(20)
^{27}Al	13	$\frac{5}{2}$	+3.64150687(65)	+0.150(6)

[a]From Ref. [36].

of the ^{19}F nucleus is a natural constraint which block diagonalizes the (4×4) hyperfine interaction matrix into one (3×3) block spanned by $^3P_0^o$ and two $^{1,3}P_1^o$ components, uncoupling $1s2p\ ^3P_2^o$, which can never give rise to the wanted $F = \frac{1}{2}$ value. Furthermore, the $I = \frac{1}{2}$ value makes the ^{19}F nucleus undeformed $(Q = 0)$.

For the two other nuclei $(I = \frac{3}{2}$ for Na^{9+} and $I = \frac{5}{2}$ for Al^{11+}), $1s2p\ ^3P_2^o$ should (in principle) be included in the $F = I$ hyperfine interaction matrix, giving rise to the desired F value. However, from a practical point of view, as shown in our ϵ values deduced from the single-configuration approximation using Hartree-Fock radial distributions (see Table II), the magnetic dipole hyperfine interaction selection rule makes the $^3P_2^o - {}^3P_0^o$ coupling indirect and the contamination of $^3P_0^o$ by $^3P_2^o$ very small. The direct electric quadrupole interaction $(\Delta J = \pm 2)$ does exist but, as shown in Table II, turns out to be negligible.

More important is the effect of the orbital and spin-dipole terms of the magnetic dipole hyperfine interaction [see the first two terms of Eq. (11)], which were neglected in Mohr's calculations. They have been considered by Mowat *et al.* [11] in ^{19}F^{7+}, but the matrix elements reported in their paper are not reliable. For that reason, we give in the Appendix the required matrix elements using radial unscreened hydrogenic wave functions. In contrast to their results, we found that these two terms counteract the effect of the dominant spin-contact $^3P_0^o - {}^3P_1^o$ off-diagonal matrix element (opposite signs), reducing the ϵ value. The effect found in ϵ^2, which monitors the hyperfine-induced transition probability, lies around 6–7 % in our Hartree-Fock model.

B. The multiconfiguration approximation

In order to capture correlation effects beyond the Hartree-Fock approximation, we will describe both the $1s^2\ ^1S$ and $1s2p\ \ ^3P^o$ states by multiconfiguration Hartree-Fock expansions of increasing sizes in the CAS scheme.

The $n = 5\ (^3P^o)$ CAS expansion corresponds to the superposition (5) of the 40 $(^3P^o)$ CSF's which can be built from the 15 radial distributions $\{P_{n\ell}(r); n \leq 5, \ell < n\}$. In the MCHF method, the latter are the numerical solutions of the multiconfiguration Hartree-Fock radial equations, coupled to the (40×40) configuration- interaction problem [37].

The $n = 5\ (^1P^o)$ CAS eigenvector can be obtained by diagonalizing the nonrelativistic Hamiltonian in the basis of the 40 CSF's $|n\ell n'\ell'\ ^1P^o\rangle$ constructed from the $^3P^o$-optimized radial orbital active set. The singlet-triplet a and b mixing coefficients of Eq. (4) are simply the eigenvectors of the Breit-Pauli matrix in the basis of the two nonrelativistic MCHF wave functions describing $|1s2p\ ^3P^o\rangle$ and $|1s2p\ ^1P^o\rangle$. An independent $n = 5$ CAS multiconfiguration Hartree-Fock (35 CSF's) calculation is performed on the ground state $1s^2\ ^1S$. The hyperfine matrix elements, limited to the Fermi contact interaction term,

$$x = \langle 2\ ^1P_1^o IM|H_{dip}^{contact}|2\ ^3P_0^o IM\rangle,\qquad(15)$$

$$y = \langle 2\ ^3P_1^o IM|H_{dip}^{contact}|2\ ^3P_0^o IM\rangle\qquad(16)$$

and the nonrelativistic transition moment $S_{nr}^{\frac{1}{2}} = e\langle 1\ ^1S\|\sum_k r(k)\mathbf{C}^{(1)}(k)\|2\ ^1P^o\rangle$ can be evaluated from the nonrelativistic wave functions. The different contributions to the analytical expression of ϵ [see Eq. (3)] and to the hyperfine-induced transition rate [Eq. (2)] are reported in Table III for the ion ^{23}Na^{9+} and compared with those evaluated from the Z^{-1} and $(Z\alpha)^2$ expanded quantities given by Mohr [8]. The agreement between our results and Mohr's values is already very satisfactory.

Using the *same* nonrelativistic MCHF radial orbital basis sets, we can compare this perturbation approach

TABLE II. Effect of the orbital and spin-dipole terms on the ϵ value for different nuclei. The numbers in parentheses are computed by neglecting the hyperfine coupling with $1s2p\ ^3P_2^o$.

	Z	$H_{dip}^{contact}$	H_{dip}^{total}	$H_{dip+quadr}^{total}$
$|\epsilon|$	9	0.00170294	0.00164758	0.00164758
		(0.00170294)	(0.00164758)	(0.00164758)
	11	0.00097039	0.00093486	0.00093484
		(0.00097036)	(0.00093483)	(0.00093485)
	13	0.00165589	0.00159393	0.00159390
		(0.00165584)	(0.00159389)	(0.00159387)

TABLE III. Analysis of the contributions to the hyperfine-induced transition probability of $1s2p\ ^3P_0^o \rightarrow 1s^2\ ^1S_0$ in ^{23}Na^{9+} in the perturbation approach.

	MCHF[a]	Mohr[b]
a	0.9995100	0.9994990
b	0.0313152	0.0316492
Δ (cm^{-1})	-520	-532
Δ' (cm^{-1})	-67164	-66243
y (cm^{-1})	13.142	13.223
x (cm^{-1})	9.327	9.350
$|\epsilon|$	9.412×10^{-4}	9.382×10^{-4}
$S_{nr}^{\frac{1}{2}}$ (a.u.)	0.163598	0.163545
A^{hfs} (ns^{-1})	0.0118	0.0118

[a]This work.
[b]From Ref. [8].

with the more "direct" configuration-interaction method described in Sec. III, considering the hyperfine-induced transition rates. This is done in Table IV for two ions $^{19}F^{7+}$ and $^{23}Na^{9+}$, limiting the hyperfine interaction to the Fermi contact term to be consistent with Mohr's study. The comparison clearly illustrates that the excellent agreement between our results and Mohr's values found in the (2×2) perturbation model (Table III) is somewhat degraded (10–20%) when adopting the configuration interaction approach of Sec. III. One can therefore conclude that the coupling between the nonrelativistic wave functions through both relativistic and hyperfine interactions *cannot* be limited to the two lowest eigenvectors $|1s2p \, ^3P^o\rangle$ and $|1s2p \, ^1P^o\rangle$, as it is in the perturbation method.

Considering the *total* magnetic dipole hyperfine interaction, the multiconfiguration calculations corroborate the observation made in the one-configuration level of approximation that the orbital and spin-dipole terms reduce the ϵ^2 value by a factor of $\simeq 8\%$. As in the one-configuration approach, we checked in our $(n = 5)$ multiconfiguration calculations that the interaction with the $^3P_2^o$ configuration state functions can *definitely* be neglected.

On the basis of these observations, we can adopt the following systematic computational strategy for the odd parity.

(i) First, solve the nonrelativistic multiconfiguration problem with increasing active sets with the constraint that the intermediate coupling Breit-Pauli matrix, eventually corrected for hyperfine structure operators, will be built on a *common* one-electron orthonormal set describing all the configuration state functions appearing in (6). The analysis of the different contributions to the hyperfine-induced transition rate (see Table III) does not help in the delicate choice of targeting either the triplet or the singlet wave function in this nonrelativistic optimization procedure. *Both* spin symmetries' wave functions have to be described accurately and a judiciously balanced optimization procedure is prescribed to get simultaneously the correct singlet-triplet mixing and the spin-allowed $E1$ transition probability.

(ii) Second, diagonalize the Breit-Pauli matrix corrected by the hyperfine Hamiltonian [Eq. (7)] restricting the space to $LS = \, ^{1,3}P^o$ and $J = 0, 1$ and including the *total* magnetic dipole interaction for the odd parity.

Step (i) is also performed for the ground state, but hyperfine mixings are systematically neglected. No radial orthogonality constraints are imposed in these two *separate* optimizations.

The total nonrelativistic energies are reported for $1s2p \, ^3P^o$ and $1s2p \, ^1P^o$ in F^{7+} in Table V as a function of the increasing active set. The notation $9k$ means that for $n = 9$, the highest ℓ value considered is $\ell = 7$ (k electrons), the number of magnetic integrals occurring in configurations such as $nkn\ell$, becoming too large for the Breit-Pauli codes [34]. The total number of CSF's might be considered, at first sight, as relatively small in comparison to some now "routinely" performed large-scale atomic structure calculations for more complex systems. One should realize that the evaluation of the angular part of the Breit-Pauli Hamiltonian, consisting of a number of complex operators, is much more time consuming than the nonrelativistic Hamiltonian.

In a first approach ("$^3P^o$ optimized"), the radial orbitals are optimized on $1s2p \, ^3P^o$ and the corresponding $1s2p \, ^1P^o$ energy is calculated through configuration interaction. The convergence with the n-active set is much faster for $^3P^o$ than for $^1P^o$, as it should be. To avoid this unbalanced description, a *hybrid* optimization procedure is also used, consisting of optimizing the 28 radial orbitals belonging to the $(n = 7)$ active set on the $^3P^o$. The active set is then increased, optimizing the *new* orbitals on $^1P^o$ and keeping the first 28 orbitals frozen.

The total energies are compared with the nonrelativistic energies used in the unified method by Drake [38], who combines high precision nonrelativistic variational calculations with relativistic and quantum electrodynamic corrections. The results of the hybrid approach are rather good, within an accuracy somewhat less than (10^{-6}) for the $^1P^o$ state.

In Table VI, we report the $^3P^o$ fine structure splittings and the $^1P_1^o$-$^3P_0^o$ energy separation, obtained by diagonalizing the Breit-Pauli matrix in the LS basis for the largest active set $(9k)$, neglecting the orbit-orbit interaction. No LS mixing other than $^3P^o$-$^1P^o$ was considered, making the number of CSF's twice or identical

TABLE IV. Hyperfine-induced transition rates (ns^{-1}) of $1s2p \, ^3P_0^o \rightarrow 1s^2 \, ^1S_0$ in $^{19}F^{7+}$ and $^{23}Na^{9+}$.

| | $^{19}F^{7+}$ | | $^{23}Na^{9+}$ | |
	$H_{dip}^{contact}$	H_{dip}^{total}	$H_{dip}^{contact}$	H_{dip}^{total}
Mohr[a]	0.0127		0.0118	
MCHF $(n = 5)$/perturbation[b]	0.0125		0.0118	
MCHF $(n = 5)$/CI[b]	0.0151	0.0141	0.0130	0.0120

[a]From Ref. [8].
[b]This work.

TABLE V. Total nonrelativistic energies (a.u.) of $1s2p\ ^3P^o$ and $1s2p\ ^1P^o$ in F^{7+}.

n	$^3P^o$ optimized $E(^3P^o)$	$E(^1P^o)$	Hybrid $E(^3P^o)$	$E(^1P^o)$	No. of CSF's[a]
2	−48.6638979	−48.4153878			1
3	−48.6679420	−48.4207681			8
4	−48.6683215	−48.4375498			20
5	−48.6683939	−48.4387694			40
6	−48.6684143	−48.4393327			70
7	−48.6684214	−48.4396641			112
8	−48.6684243	−48.4398572	−48.6684238	−48.4401566	168
9k	−48.6684255	−48.4399768	−48.6684251	−48.4401777	238
theory[b]	−48.6684273			−48.4402443	

[a]Number of configuration state functions.
[b]From Ref. [38].

to the one reported in Table V for $J = 1$ or $J = 0, 2$, respectively. Mass-polarization corrections have been included, but Lamb-shift corrections, contributing for 9.5 cm^{-1} to the $^1P^o_1$-$^3P^o_0$ energy difference [38], were systematically neglected. The $^1P^o$-$^3P^o$ energy differences are systematically too large, due to the optimization procedure which remains a little unbalanced in favor of the

$^3P^o$ state, despite its hybrid character. The agreement with Drake's values is very satisfactory for our purposes and the wave functions are undoubtedly adequate for the accuracy of the present hyperfine-induced transition rate calculations.

The transition energies, line strengths, and hyperfine-induced transition rates (calculated with the theoretical

TABLE VI. Fine structures, $^1P^o - \ ^3P^o$ energy separations (cm^{-1}), transition energies, line strengths, and hyperfine-induced transition probabilities for $1s2p\ ^3P^o_0 \to 1s^2\ ^1S_0$ in $^{19}F^{7+}$.

	$\Delta E(^3P^o_2 - \ ^3P^o_1)$		$\Delta E(^3P^o_1 - \ ^3P^o_0)$		$\Delta E(^1P^o_1 - \ ^3P^o_0)$	
	$^3P^o$ optimized	hybrid	$^3P^o$ optimized	hybrid	$^3P^o$ optimized	hybrid
this work (9k)	960	960	151	151	50931	50890
AEL[a]					50750	
observed[b]	958		149			
unified theory[c]	957		150		50571	

	$\Delta E(1\ ^1S_0 - 2\ ^3P^o_0)$ (cm^{-1})		S (10^{-8} a.u.)		$A(2\ ^3P^o_0 \to 1\ ^1S_0)$ (ns^{-1})	
	$^3P^o$ optimized	hybrid	$^3P^o$ optimized	hybrid	$^3P^o$ optimized	hybrid
this work (9k)	5900921	5900893	6.82855	6.84353	0.01421	0.01424
unified theory[c]	5899553					
perturbation[d]					0.0130	
Expt.	5899150[a]				0.0142 ± 0.0020[e]	

[a]From Ref. [40].
[b]From Ref. [41].
[c]From Ref. [38].
[d]From Ref. [8].
[e]From Ref. [42].

energy differences) for $1s2p\,^3P_0^o \rightarrow 1s^2\,^1S_0$ in ^{19}F^{7+} are reported in the same table. The final theoretical transition energy remains 1000 wave numbers too large, after adding the 705 cm^{-1} Lamb-shift corrections calculated by Drake [38]. The effect of increasing the active set is obviously larger for low n, but the line strength rapidly stabilizes to the 1% level. Our final theoretical transition rate is in remarkably good agreement with the value of Engström et al. [12,13], deduced from the difference between the measured lifetimes of $^3P_2^o$ ($\tau = 10.44 \pm 0.15$ ns) and $^3P_0^o$ ($\tau = 9.48 \pm 0.20$ ns), assuming a wavelength scaling $\lambda^{-3}(2\,^3P_J^o - 2\,^3S_1)$ of the transition rates $A(2\,^3P_J^o \rightarrow 2\,^3S_1)$ for $J = 2$ and 0, respectively. The source of the 10% difference with Mohr's result has been discussed above (see Table IV).

The results of our most accurate complete calculations are presented in Table VII, using a hybrid wave function up to $n = 10k$ for Al^{13+}. Comments made above for our F^{7+} results remain relevant for the two other ions considered in our study. One should remember from the discussion relevant to Table IV that the very good agreement with Mohr's values found for Na^{9+} and Al^{11+} is accidental due to the cancellation between the transition amplitude reduction from the orbital and spin-dipole magnetic terms not considered in the hyperfine interaction by Mohr and the increasing effect found when going from the perturbation scheme to the more direct configuration-interaction approach.

There is no experimental value of the hyperfine quench-

ing in ^{23}Na^{9+}. Denne et al. [14] estimated, from their $1s2p\,^3P_0^o$ experimental value ($\tau = 4.8 \pm 0.2$ ns), the hyperfine-induced transition probability in ^{27}Al^{11+} to be $(6.1 \pm 1.7)10^7$ s^{-1} and $(6.9 \pm 1.7)10^7$ s^{-1}, using the theoretical rates of Lin et al. [39] and Mohr [8], respectively, for $2\,^3P_0^o \rightarrow 2\,^3S_1$. Our transition rate, in perfect agreement with the experimental value for ^{19}F^{7+} [12,13], falls within the (large) experimental error bounds for ^{27}Al^{11+} [14].

ACKNOWLEDGMENTS

APPENDIX: HYPERFINE MATRIX ELEMENTS

The hyperfine magnetic dipole matrix element can be written as

TABLE VII. Energy differences (cm^{-1}) and hyperfine-induced transition rates (ns^{-1}) for ^{19}F^{7+}, ^{23}Na^{9+}, and ^{27}Al^{11+}.

		$\Delta E(^3P_2^o - {}^3P_1^o)$	$\Delta E(^3P_1^o - {}^3P_0^o)$	$\Delta E(^1P_1^o - {}^3P_0^o)$	A^{hpf} (ns^{-1})
^{19}F^{7+}	9k-active set	960	151	50890	0.0142
	unified theory[a]	957	150	50571	-
	perturbation[b]				0.0127
	observed	958[c]	149[c]	50750[d]	0.0142(20)[e]
^{23}Na^{9+}	9k-active set	2418	525	66959	0.0122
	unified theory[a]	2406	520	66355	
	perturbation[b]				0.0117
	observed	2397[f]	522[f]	66347[f]	
^{27}Al^{11+}	10k-active set	5166	1256	84277	0.0760
	unified theory[a]	5124	1241	83233	
	perturbation[b]				0.0737
	observed	5100[g]	1240[g]	83240[g]	0.069(17)[h]
					0.061(17)[i]

[a]From Ref. [38].
[b]From Ref. [8].
[c]From Ref. [41].
[d]From Ref. [40].
[e]From Refs. [12,13].
[f]From Ref. [43].
[g]From Ref. [44].
[h]From Ref. [14] using the $2\,^3P_0^o \rightarrow 2\,^3S_1$ transition rate of Ref. [8].
[i]From Ref. [14] using the $2\,^3P_0^o \rightarrow 2\,^3S_1$ transition rate of Ref. [39].

$$\langle \gamma LSJIFM | \mathbf{T}^{(1)} \cdot \mathbf{M}^{(1)} | \gamma' L'S'J'IF'M' \rangle$$

$$= \delta_{FM,F'M'} (-1)^{J'+I+F} \begin{Bmatrix} J & I & F \\ I & J' & 1 \end{Bmatrix}$$

$$\times \langle \gamma LSJ || \mathbf{T}^{(1)} || \gamma' L'S'J' \rangle$$

$$\times \frac{\mu_I}{I} \sqrt{I(I+1)(2I+1)}. \tag{A1}$$

The electronic reduced matrix element is evaluated using expression (11). We will focus on the one-configuration case $\gamma = 1snl$ ($l \neq 0$) for which the orbital contribution is simply

$$\langle 1snl \ LSJ \left|\left| \sum_{i=1}^{2} \mathbf{1}^{(1)}(i) r_i^{-3} \right|\right| 1snl \ L'S'J' \rangle$$

$$= \delta_{SS'} (-1)^{S+J'+l} [J,J',L,L']^{1/2} \times \begin{Bmatrix} L & S & J \\ J' & 1 & L' \end{Bmatrix}$$

$$\times \begin{Bmatrix} 0 & l & L \\ 1 & L' & l \end{Bmatrix} \sqrt{l(l+1)(2l+1)} \langle r^{-3} \rangle_{nl}. \tag{A2}$$

The spin-dipole term can be evaluated as

$$\langle 1snl \ LSJ \left|\left| \sum_{i=1}^{2} [\mathbf{C}^{(2)}(i) \otimes \mathbf{s}^{(1)}(i)]^{(1)} r_i^{-3} \right|\right| 1snl \ L'S'J' \rangle$$

$$= (-1)^{l+L+S} \sqrt{3} [J,J',L,L',S,S']^{1/2} \begin{Bmatrix} L & S & J \\ L' & S' & J' \\ 2 & 1 & 1 \end{Bmatrix}$$

$$\times \begin{Bmatrix} 0 & l & L \\ 2 & L' & l \end{Bmatrix} \begin{Bmatrix} \frac{1}{2} & \frac{1}{2} & S \\ 1 & S' & \frac{1}{2} \end{Bmatrix}$$

$$\times \langle l || \mathbf{C}^{(2)} || l' \rangle \sqrt{\frac{3}{2}} \langle r^{-3} \rangle_{nl}. \tag{A3}$$

The matrix element of the contact term is given by

$$\langle 1snl \ LSJ \left|\left| \sum_{i} \delta(\mathbf{r}_i) \mathbf{s}^{(1)}(i) \right|\right| 1snl \ LSJ \rangle$$

$$= \delta_{LL'} (-1)^{L+J+1} [J,J',S,S']^{1/2}$$

$$\times \begin{Bmatrix} L & S & J \\ 1 & J' & S' \end{Bmatrix} \begin{Bmatrix} \frac{1}{2} & \frac{1}{2} & S \\ S' & 1 & \frac{1}{2} \end{Bmatrix} \sqrt{\frac{3}{2}} \langle \delta(\mathbf{r}) \rangle_{1s}. \tag{A4}$$

The ($l = L = 1$) $1snp$ $^{1,3}P_J^o$ hyperfine magnetic dipole interaction matrix can then be built from

$$\langle 1snp \ (L=1)SJIFM | \mathbf{T}^{(1)} \cdot \mathbf{M}^{(1)} | 1snp \ (L=1)S'J'IF'M' \rangle$$

$$= \frac{\alpha^2}{2} \frac{m}{M} g_I (-1)^{J'+I+F} \begin{Bmatrix} J & I & F \\ I & J' & 1 \end{Bmatrix} \sqrt{I(I+1)(2I+1)} \sqrt{6} [J,J']^{1/2}$$

$$\times \Bigg[(-1)^{S+J'} \delta_{SS'} \begin{Bmatrix} 1 & S & J \\ J' & 1 & 1 \end{Bmatrix} \langle r^{-3} \rangle_{np} + (-1)^S \frac{3}{2} g_s [S,S']^{1/2} \begin{Bmatrix} 1 & S & J \\ 1 & S' & J' \\ 2 & 1 & 1 \end{Bmatrix} \begin{Bmatrix} \frac{1}{2} & \frac{1}{2} & S \\ 1 & S' & \frac{1}{2} \end{Bmatrix} \langle r^{-3} \rangle_{np}$$

$$+ (-1)^J \frac{2\pi}{3} g_s [S,S']^{1/2} \begin{Bmatrix} 1 & S & J \\ 1 & J' & S' \end{Bmatrix} \begin{Bmatrix} \frac{1}{2} & \frac{1}{2} & S \\ S' & 1 & \frac{1}{2} \end{Bmatrix} \langle \delta(\mathbf{r}) \rangle_{1s} \Bigg]. \tag{A5}$$

The triplet ($S = 1$) matrix elements for the $I = 1/2$ case considered by Mowat et al. [11] using unscreened hydrogenic wave functions with $\langle r^{-3} \rangle_{2p} = \frac{Z^3}{24}$ and $\langle \delta(\mathbf{r}) \rangle_{1s} = \frac{Z^3}{\pi}$ are corrected as follows: for $F = 1/2$,

$$\langle 1s2p \ ^3P_1^o | \mathbf{T}^{(1)} \cdot \mathbf{M}^{(1)} | 1s2p \ ^3P_1^o \rangle = \frac{\alpha^2}{2} \frac{m}{M} g_I Z^3 \left[-\frac{1}{48} - \frac{1}{48} - \frac{2}{3} \right],$$

$$\langle 1s2p \ ^3P_1^o | \mathbf{T}^{(1)} \cdot \mathbf{M}^{(1)} | 1s2p \ ^3P_0^o \rangle = \frac{\alpha^2}{2} \frac{m}{M} g_I Z^3 \left[-\frac{1}{48} - \frac{1}{96} + \frac{2}{3} \right], \tag{A6}$$

and for $F = 3/2$,

$$\langle 1s2p \ ^3P_1^o | \mathbf{T}^{(1)} \cdot \mathbf{M}^{(1)} | 1s2p \ ^3P_1^o \rangle = \frac{\alpha^2}{2} \frac{m}{M} g_I Z^3 \left[\frac{1}{96} + \frac{1}{96} + \frac{1}{3} \right]. \tag{A7}$$

The three terms are the orbital, spin-dipole, and contact contributions, respectively.

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