Ab initio calculations of the $^{33}\text{S} \, 3p^4 \, ^3P_J$ and $^{33}\text{S}^-/^{37,35}\text{Cl} \, 3p^5 \, ^2P^o_J$ hyperfine structures

T Carette and M R Godefroid

Chimie Quantique et Photophysique, CP160/09, Université Libre de Bruxelles, Avenue FD Roosevelt 50, B-1050 Brussels, Belgium
E-mail: tcarette@ulb.ac.be and mrgodef@ulb.ac.be

Received 8 February 2011, in final form 27 March 2011
Published 27 April 2011
Online at stacks.iop.org/JPhysB/44/105001

Abstract
We present highly correlated multi-configuration Hartree–Fock (MCHF) calculations of the hyperfine structure of the $3p^5 \, ^2P^o_J$ levels of $^{33}\text{S}^-$ and $^{35,37}\text{Cl}$. We obtain good agreement with observation. The hyperfine structure of the neutral sulphur $^{33}\text{S} \, 3p^4 \, ^3P_J$ lowest multiplet that has never been measured to the knowledge of the authors is also estimated theoretically. We discuss some interesting observations made on the description of the atomic core in MCHF theory.

1. Introduction

As the experimental techniques evolve, the window of isotope effects in negative ions is becoming wider and wider [1–7]. It offers new possibilities for understanding negative ions, correlation effects and the effect of nuclear properties on the electronic structure. In order to keep to this agenda, we need accurate models.

The hyperfine interaction, as arising mainly from the non-spherical nature of the electronic wavefunction near the nucleus, is an operator that is particularly sensitive to both core and valence correlation effects. It is also sensitive to contributions that do not affect the energy much. When trying to calculate it, we face the difficulty of getting simultaneously a good description of the valence correlation—crucial for negative ions—, core–valence and core correlation. It is therefore a useful tool for testing new approaches.

Experimental studies of the hyperfine interaction in atomic negative ions are scarce. A pioneering study was made by Mader and Novick on the $^3\text{He}^- \, 1s2s2p \, ^4P^o$ metastable state [8]. Much more recently, the hyperfine structure of the only known E1 transition between bound states of a negative ion, the Os$^-$, was studied [9]. In between, Trainham et al [1] performed a study of the $^{33}\text{S}^- \, 3p^5 \, ^2P^o_{3/2}$ hyperfine structure. The S$^-$ ion offers a good possibility for testing the methods on a mediumweight system.

Recently, the isotope shift on the electron affinity of sulphur between the zero-spin isotopes 32 and 34 was measured and calculated [6]. A similar study involving the isotope 33 of sulphur, of spin $I = 3/2$, would require the knowledge of the hyperfine structure of the involved states [5]. However, if the $^{33}\text{S}^-$ ground state hyperfine structure is known, the one of the $^{33}\text{S} \, 3p^4 \, ^3P_J$ lowest multiplet is not, to the knowledge of the authors.

In section 3, we present large scale multi-configuration Hartree–Fock (MCHF) calculations on the iso-electronic systems S$^-$ and Cl, testing the possibility of using the valence correlation orbitals [10] for describing core effects. This choice of orbital set was successfully adopted for including a core–valence contribution in the calculation of the isotope shift on the electron affinity of sulphur [6] and chlorine [7]. In section 4, we calculate the hyperfine structure of the neutral sulphur lowest multiplet and point out a remarkable interplay of core and valence correlation in a MCHF description. We compare our theoretical results with experiment in section 5 and conclude in section 6 that some computational strategies provide a better definition for the core region.

2. Theory

2.1. The MCHF/CI approach

The MCHF variational approach is based on the following ansatz

$$
\Psi(\gamma L S M_L M_S) = \sum_i c_i \Phi(\gamma_i L S M_L M_S)
$$

(1)
where the $\Phi(\gamma L S M_L M_S)$ are configuration state functions (CSF) that are built on a single orthonormal basis set [11]. A CSF is a symmetry-adapted linear combination of Slater determinants corresponding to a given term with its own coupling tree. Energy functionals integrated on the electron angular coordinates for an ansatz of type (1) are efficiently obtained using Racah algebra [12]. Large expansions of CSFs can automatically be generated using existing programs [13], allowing the considered excitations of the main configuration to the classes of states to be reduced. In MCHF theory, all $c_i$ are optimized and some—if not all—orbital radial functions are varied until self-consistency. We use the ATSP2K implementation of this method [14].

In this work, we first perform MCHF calculations to determine the set of spectroscopic and virtual one-electron states in the MCHF expansion. We then do subsequent larger configuration interaction (CI) calculations, i.e. optimizing only the $\{c_i\}$ mixing coefficients in (1). At all stages, the variational principle is applied using the non-relativistic isotope-independent Hamiltonian. An orbital active set is defined as the set of all orbitals characterized by quantum numbers with $n \leq n_{\text{max}}$ and $l \leq l_{\text{max}}$, and is denoted $[n_{\text{max}} l_{\text{max}}]$. Our scheme is based on the concept of the ‘multi-reference-interacting’ (MR-I) set of CSFs detailed elsewhere [6]. It is defined as the set of all CSFs that interact to first order with at least one component of a small set of configurations, the multi-reference (MR). The $LS$ angular momenta of the occupied sub-shells are coupled by decreasing $n$ and $l$. For a given orbital basis set, a MR-I space is a subset of all single and double (SD) excitations of the MR. Even though this scheme is largely optimized for having the fastest convergence of the energy, it also allows one to efficiently obtain accurate wavefunctions [15]. Using this strategy, the most important components of the MCHF expansion (1) contributing to the state’s hyperfine structure are included with the right mixing coefficient.

### 2.2. Hyperfine interaction

The hyperfine structure of a $LSJ$ level is caused by the magnetic and electric interaction of the electrons with the atomic nucleus of the angular momentum quantum number $I$ [16]. The total atomic angular momentum quantum number is denoted $F$. To first order, the hyperfine energy correction has the form

$$W(J, J) = A_J \frac{C}{2} + B_J \frac{3C(C + 1) - 4I(I + 1)J(J + 1)}{8I(2I - 1)J(2J - 1)},$$

where $A_J$ and $B_J$ are respectively the magnetic dipole (M1) and electric quadrupole (E2) hyperfine constants and $C = F(F + 1) - J(J + 1) - I(I + 1)$. The theory underlying the computation of hyperfine structures using multi-configuration wavefunctions can be found in [17, 18] in which the non-relativistic hyperfine interaction is expressed in terms of the $J$-independent orbital ($a_i$), spin-dipole ($a_{\text{sd}}$), contact ($a_c$) and electric quadrupole ($b$) electronic hyperfine parameters:

$$a_{\text{sd}} \equiv \langle \Gamma L S M_L M_S \rangle \sum_{i=1}^{N} l_0^{(2)}(i) r_i^{-3} \langle \Gamma L S M_L M_S \rangle,$$  

$$a_c \equiv \langle \Gamma L S M_L M_S \rangle \sum_{i=1}^{N} 2s_0^{(1)}(i) r_i^{-2} \delta(r_i) \langle \Gamma L S M_L M_S \rangle,$$  

$$b \equiv \langle \Gamma L S M_L M_S \rangle \sum_{i=1}^{N} 2c_0^{(2)}(i) r_i^{-3} \langle \Gamma L S M_L M_S \rangle,$$

and calculated for the magnetic component $M_L = L$ and $M_S = S$ [17]. The first three parameters (3), (4) and (5) contribute to the magnetic dipole hyperfine interaction constant through

$$A_J = A'_J + A''_{\text{sd}} + A'_{\text{c}},$$

with

$$A'_J = G_{\mu} \frac{H_J}{I} K'_J a_i,$$  

$$A''_{\text{sd}} = \frac{1}{2} G_{\mu} g_{\text{sd}} \frac{H_J}{I} K''_{\text{sd}} a_{\text{sd}},$$  

$$A'_{\text{c}} = \frac{1}{6} G_{\mu} g_{\text{c}} \frac{H_J}{I} K'_{\text{c}} a_c,$$

where the $K_J$'s are the appropriate non-relativistic angular factors [19]. The last one ($b$) constitutes the electronic contribution to the electric quadrupole hyperfine interaction

$$B_J = -G_q Q K''_J b.$$  

Expressing the electronic parameters $a_i$, $a_{\text{sd}}$ and $a_c$ in atomic units (units of $a_0^{-3}$) and $\mu_J$ in nuclear magnetons (units of $\mu_N$), the magnetic dipole hyperfine structure constants $A_J$ are calculated in units of frequency (MHz) by using $G_{\mu} = 95.41067$. Similarly, the electric quadrupole hyperfine structure constants $B_J$ are expressed in MHz when adopting atomic units (units of $a_0^{-3}$) for $b$, barns for $Q$ and $G_q = 234.964 75$.

### 2.3. The distinction between core and valence electrons

When studying an atomic system, it is common to distinguish core and valence electrons based on the mono-configuration approximation. This separation can usually be made quite efficiently by choosing a rare-gas-like core. In our case, the core is neon-like $(1s^22s^22p^6)$ and the valence is composed of $3s^23p^5$ for $S^-$ and Cl, and $3s^23p^4$ for $S$. From that distinction, a lot of concepts based on a first-order picture of the correlation arise: core polarization, valence, core–valence and core–core correlation (V, CV, CC), etc. This terminology remains vague and the contributions those terms refer to often depend on the method [10, 20–22]. In MCHF theory it is in general impossible to have a clean partition of those different contributions due to systematic rearrangements of the $\{c_i\}$ MCHF eigenvector and orbital shapes from one model to another. The variational procedure is not perturbative and the core–valence distinction is based on a perturbative picture of the correlation. Still, the core–valence separation has a physical background so that it should not be discarded.
In this notation, distinct sets of electrons are dispatched in series of shells and/or subshells. Here, all ten slots of the \( n = 1, 2 \) shells are filled, five electrons are shared between the spectroscopic orbitals 3s and 3p and the two remaining electrons occupy either the spectroscopic orbitals or the virtual 3d subshell. After having generated the CSF list, we perform HF frozen-core MCHF calculations on the SR-I and MR-I sets obtained by activating all the electrons in orbital basis sets ranging from \( \ell = 4f \) to \( \ell = 13h \) and \( \ell = 10h \) for SR and MR, respectively. The so-obtained one-electron radial functions are denoted SR-I-C and MR-I-C. In addition, we perform valence MCHF calculations on the MR-I \( \ell = 4n \), \( n = 4 - 13 \), \( l \leq 5 \) (h orbitals). The resulting basis set is denoted MR-I-V. In all calculations, the [Ne] core is frozen to its HF shape.

Tables 1 and 2 display, respectively for Cl and S\(^{-}\), the weights of the first configurations in the various MCHF}

Table 1. Sorted weights of the first configurations in the SR-I-C, MR-I-C and MR-I-V wavefunctions of Cl. The active set is [(10h)]. The 1s and 2s sub-shells are closed in all those configurations.

| Configurations          | SR-I-C | MR-I-C | MR-I-V |
|-------------------------|--------|--------|--------|
| Configurations          | Configurations | Configurations | Configurations |
| w                       | w      | w      |
| 2p^63s^23p^5           | 0.9712 | 0.9584 | 0.9567 |
| 2p^63s^3p^33d^1       | 0.1413 | 0.1877 | 0.1905 |
| 2p^63s^3p^33d^1       | 0.0806 | 0.1121 | 0.1145 |
| 2p^63s^3p^4p^1       | 0.0649 | 0.0653 | 0.0786 |
| 2p^63s^3p^33d^4f^1   | 0.0527 | 0.0538 | 0.0691 |
| 2p^63s^3p^34p^1      | 0.0411 | 0.0416 | 0.0584 |
| 2p^63s^3p^34p^1      | 0.0403 | 0.0407 | 0.0537 |
| 2p^63s^3p^5           | 0.0346 | 0.0407 | 0.0475 |
| 2p^63s^3p^4f^1        | 0.0311 | 0.0323 | 0.0417 |
| 2p^63s^3p^4f^1        | 0.0310 | 0.0311 | 0.0370 |
| 2p^63s^3p^4f^1        | 0.0269 | 0.0273 | 0.0322 |
| 2p^63s^3p^4f^1        | 0.0268 | 0.0267 | 0.0306 |
| 2p^63s^3p^35d^1       | 0.0257 | 0.0253 | 0.0292 |
| 2p^63s^3p^4p^15s^1   | 0.0328 | 0.0328 | 0.0357 |
| 2p^63s^3p^4p^15s^1   | 0.0328 | 0.0328 | 0.0357 |
| 2p^63s^3p^35p^1       | 0.0329 | 0.0329 | 0.0357 |
| 2p^63s^3p^4p^15s^1   | 0.0328 | 0.0328 | 0.0357 |
| 2p^63s^3p^35p^1       | 0.0329 | 0.0329 | 0.0357 |
| 2p^63s^3p^4p^15s^1   | 0.0328 | 0.0328 | 0.0357 |
| 2p^63s^3p^35p^1       | 0.0329 | 0.0329 | 0.0357 |

Hence, we need a reliable definition of the core in order to interpret the so-called ‘core effects’.

In this work, the uncorrelated core is defined as being the \( N_c \)-electron core state built on the Hartree–Fock orbital set optimized for the total system. In the case of multiple solutions in the HF model, we select the one satisfying the Koopmans requirement [12].

3. Hyperfine structures of the 3p\(^5\) 2P\(^o\) J levels of S\(^{-}\) and Cl

3.1. Definition of the orbital set: MCHF calculations

To explore the impact of the choice of the MCHF model defining the orbital set on the results of the open-core CI models, we use two references: the single main configuration, denoted SR, and the set of all valence SD excitations in the \( n = 3 \) shell, denoted MR. The latter is formally written as

\[
\text{MR} = \{1, 2\}^{10} \{3s, 3p^5\}^3. \tag{12}
\]

In this notation, distinct sets of electrons are dispatched in series of shells and/or subshells. Here, all ten slots of the \( n = 1, 2 \) shells are filled, five electrons are shared between the spectroscopic orbitals 3s and 3p and the two remaining electrons occupy either the spectroscopic orbitals or the virtual 3d subshell. After having generated the CSF list, we perform HF frozen-core MCHF calculations on the SR-I and MR-I sets obtained by activating all the electrons in orbital basis sets ranging from [4f] to [13h] and [10h] for SR and MR, respectively. The so-obtained one-electron radial functions are denoted SR-I-C and MR-I-C. In addition, we perform valence MCHF calculations on the MR-I [(nl)], \( n = 4 - 13 \), \( l \leq 5 \) (h orbitals). The resulting basis set is denoted MR-I-V. In all calculations, the [Ne] core is frozen to its HF shape.

Tables 1 and 2 display, respectively for Cl and S\(^{-}\), the weights of the first configurations in the various MCHF
calculations with \( n_{\text{max}}^{\text{nl}} = 10h \). The weight of a configuration is defined as
\[
w = \left( \sum_i c_i^2 \right)^{1/2},
\]
where the sum runs over the CSFs belonging to the configuration. We observe that the order of the few most important configurations is very similar in all cases. Still, some differences appear mainly due to the fact that some radial functions \( P_{\alpha l}(r) \) become inner orbitals in the MR-I-C and SR-I-C models. This is illustrated in the first four columns of table 3 in which we compare the mean radius of the MR-I-C model with the ones of the MR-I-V model for both Cl and S\(^-\). In open-core calculations, most of the \( n = 5 \) orbitals become inner orbitals and \( P_{\alpha l}, P_{\beta l} \) contract significantly. The SR-I-C orbitals do not differ strongly from the MR-I-C ones and are therefore not presented here.

### 3.2. Fully correlated CI calculations

The results of tables 1 and 2 indicate that, even if the variational contents of open- and closed-core calculations are \textit{a priori} very different [23], it is here possible to find extensions of the models developed above that remain comparable. Indeed, if we choose as MR the five or nine first configurations in the sorted lists
\[
\text{MR}_5 = \{3s^23p^5, 3s^23p^33d^2, 3s^13p^33d^4, 3s^33p^44p^2, 3s^13p^33d^14f^1\}
\]
\[
\text{MR}_9 = \text{MR}_5 \cup \{3s^13p^44s^14p^1, 3s^13p^34d^14p^1, 3p^3d^2, 3s^33p^4f^1\}
\]
for both systems, the selected MRs account for approximately the same correlation effects in all S\(^-\) and Cl orbital sets. It allows a significant comparison between the CI calculations performed on the MR\(_5\)- and MR\(_9\)-I-C multi-reference-interacting sets performed with the orbital sets arising from either the SR-I-C, MR-I-C or MR-I-V MCHF calculations.

### 3.3. Behavior of \( a_0, a_\gamma, \delta_\gamma, \delta_\gamma \) parameters

Figure 1 and the top two plots of figure 2 present the convergence of the \( a_0, a_\gamma, \delta_\gamma \), and \( b \) hyperfine parameters (3)–(6) calculated with the MR\(_9\)-I-C model in the three orbital basis sets (SR-I-C, MR-I-C and MR-I-V). All parameters are given in atomic units \((a_0^{-1})\). In all cases the MR-I-V \((13h)\) and SR-I-C \((13h)\) results differ by about \( 2^{-1}a_0^3 \), the final \( A_j \) constants themselves differing by less than half a per cent. The convergence of the calculations with the orbital sets obtained from the MR-I-V model is slow compared to the one where the calculations are based on the SR- and MR-I-C orbital sets. It is remarkable to note that, to the contrary of the magnetic dipole parameters \((a_0\), the electric quadrupole parameter \((b) \) converges as rapidly in the SR-I-C and MR-I-V basis sets.

Comparing the S\(^-\) and Cl trends, it is the similarities that strike first. However, the \( y \)-axis scales being the same between the left (S\(^-\)) and corresponding right (Cl) plots, we observe easily that (i) the S\(^-\) hyperfine parameters are shifted to smaller values compared to the Cl parameters, and (ii) the S\(^-\) hyperfine structure calculations converge slightly faster that the Cl ones. These two observations can easily be understood by the mere diffuseness of the negative ion electron charge distribution. Indeed, when an electron attaches to a neutral atom, the valence shells spread and the core–valence separation becomes larger. Then, even though the negative ion has more electrons, the core–valence overlap is only slightly larger in the negative ion than in the neutral, even if there are more valence electrons in the former than in the latter [7, 24]. Hence, the negative ion core is more spherical and the hyperfine constants tend to be smaller than in comparable systems. Consequently, even if negative ions are highly correlated systems, they are characterized by a comparatively smaller core–valence correlation. In particular, the hyperfine structure of negative ions is slightly less sensitive to correlation effects than one would first expect.

Even though the MR\(_5\) and MR\(_9\) sets do not account for exactly the same correlation effects depending on the active set, the approach based on the orbitals obtained at the SR-I-C \((13h)\) level is superior. Tables 4 and 5 show the total

### Table 3. Mean radius \((a_0)\) of the \( n = 1–5 \) orbitals of Cl, S\(^-\) and S in the MR-I-V \((10h)\) (valence) and MR-I-C \((10h)\) (open-core) models.

| \(nl\) | Valence | Open-core | Valence | Open-core | Valence | Open-core |
|-------|---------|-----------|---------|-----------|---------|-----------|
| 1s    | 0.09130 | 0.09130   | 0.09715 | 0.09715   | 0.09715 | 0.09715   |
| 2s    | 0.44171 | 0.44171   | 0.47585 | 0.47585   | 0.47577 | 0.47577   |
| 2p    | 0.40572 | 0.40572   | 0.44106 | 0.44106   | 0.44104 | 0.44104   |
| 3s    | 1.54735 | 1.55045   | 1.76214 | 1.76836   | 1.71095 | 1.71268   |
| 3p    | 1.82220 | 1.82778   | 2.28135 | 2.29572   | 2.02884 | 2.03898   |
| 3d    | 1.76250 | 1.75997   | 2.1597 | 2.16075   | 1.95878 | 1.96343   |
| 4s    | 2.03477 | 1.92840   | 2.44030 | 2.39304   | 2.40713 | 0.71754   |
| 4p    | 2.41053 | 2.13745   | 3.34104 | 2.80812   | 2.81064 | 0.70561   |
| 4d    | 2.23120 | 1.35932   | 2.86818 | 1.64193   | 2.45573 | 1.42118   |
| 4f    | 1.82616 | 1.30900   | 3.03237 | 1.17530   | 2.98537 | 1.20579   |
| 5s    | 2.14697 | 0.69456   | 2.71559 | 0.74676   | 2.28372 | 2.13212   |
| 5p    | 2.16166 | 0.68502   | 2.81873 | 0.75013   | 2.42314 | 2.38464   |
| 5d    | 2.08468 | 0.54938   | 2.04493 | 0.76611   | 1.70728 | 0.60688   |
| 5f    | 2.06913 | 0.65051   | 2.31986 | 1.55795   | 2.31174 | 0.63876   |
| 5g    | 1.85751 | 1.78797   | 3.40818 | 2.12699   | 3.83176 | 1.94307   |
energies and $\alpha_t$, $\alpha_{sd}$, $\alpha_c$ and $b$ parameters deduced from the MR$_5$-, MR$_9$-I-C[12h] and MR$_9$-I-C[13h] models using the SR-I-C orbitals. The final results are obtained by reporting the impact of the 13th shell on the MR$_5$-I-C model on the MR$_9$-based values.

4. Hyperfine structures of the $3p^4\,^3P_J$ levels of S

4.1. Definition of the orbital set: MCHF calculations

For the $3p^4\,^3P$ state of neutral sulphur, we first select the references from which the MCHF expansions are generated.
Figure 2. For both S⁻ (left plots) and Cl (right plots), values of non-relativistic electric quadrupole hyperfine interaction parameter \(b\) (in \(a_\text{u}^{-3}\)) and energy \(E\) (in \(E_\text{h}\)) obtained by CI calculations in the MR5-I-C model with the three explored orbital basis sets SR-I-C, MR-I-C and MR-I-V, as a function of the active space \(\left\{nl\right\}_l \leq 5\).

Table 4. Best estimates of the energy (in \(E_\text{h}\)) and hyperfine parameters (in \(a_\text{u}^{-3}\)) of Cl (see the text). The final values are the results of the MR9-I-C model with the 13th correlation shell on the MR5-I-C model is reported.

|          | MR5       | MR9       |
|----------|-----------|-----------|
|          | 12h       | 13h       | 12h       | final     |
| \(E\)    | -460.12061| -460.12145| -460.12315|
| \(a_L\)  | 7.157 68  | 7.157 24  | 7.140 14  | 7.139 71  |
| \(a_{sd}\)| -1.504 71 | -1.505 41 | -1.503 69 | -1.504 39|
| \(a_c\)  | 0.490 79  | 0.487 33  | 0.528 70  | 0.525 25  |
| \(b\)    | 2.847 68  | 2.847 38  | 2.839 12  | 2.838 82  |

Similar to Cl and S⁻, we use the mono-reference (SR) and a MR

\[
\text{MR} = \{1, 2\}\{3s, 3p\}^4(3)\text{.} 
\]

The weights of the most important configurations in the SR-I-C, MR-I-C and MR-I-V calculations using the active set \([10h]\) are presented in table 6. The corresponding mean radii of the orbitals are shown in the fifth and sixth columns of table 3. We observe that the eigenvector composition differences between the open-core and valence calculations are much more pronounced than in the S⁻ and Cl cases. For instance, the 1s²2s²2p⁴3s²3p⁴4p² configuration gains a significant weight in both open-core calculations (SR- and MR-I-C), the 4p orbital being localized in the inner region of the atom. This important core reorganization is accompanied by the extinction of the closed-core configuration 3s²3p²4p² in comparison with the MR-I-V eigenvector composition, counterbalanced by the turning on of another closed-core configuration, 3s²3p²5p². In the open-core models, the
cumulative weight of these two configurations $2p^63s^23p^24p^2$ and $2p^63s^23p^25p^2$ reaches 0.055, which is comparable to the weight of the $3s^23p^24p^2$ in the closed core model ($= 0.068$). It indicates that the correlation of the $3p^2$ and $2p^6$ electrons is similar so that, even if we fix the core to its HF shape, high-order correlation effects mix the core and valence electrons through the $2p^63s^23p^24p^2$ configuration, $(3p, 4p)$ being variational. Similar observations are made in the context of the calculation of the electron affinity of chlorine [7], in which case the negative ion neon-like core can strongly mix with the valence $3p^6$ electrons compared to the neutral MCHF solution.

4.2. Fully correlated CI calculations

The large differences between the roles played by each correlation orbital in the open-core and valence calculations prevent us from comparing the two models as in the cases of $\text{S}^-$ and Cl. Although the results of the different open-core CI models are coherent, we limit our discussion to the SR-I-C and MR-I-C models.

Driven by the eigenvector composition analysis presented in table 6, we choose the MR
\[
\text{MR}_5 = \{3s^23p^4, 3s^23p^3d^2, 3s^13p^4d^l, 3s^13p^3d^l4f^l, 3p^3d^2\},
\]
and finally we define
\[
\text{MR}_6 = \text{MR}_5 \cup \{2s^22p^43s^23p^44s^44p^1\},
\]
\[
\text{MR}_7 = \text{MR}_6 \cup \{2s^22p^43s^23p^44p^2, 2s^22p^63s^13p^3d^15p^1\}.
\]

We show in table 7 the hyperfine parameters for the sulphur $3p^3\text{P}$ ground state using these MR-P-I-C models ($p = 5, 6, 8$) for the largest possible active set and using the SR-I-C radial functions. The final results are obtained by reporting the impacts of the 13th correlation shell on the MR-P-I-C model and the impacts of the extension of the MR$_8$ reference to the MR$_9$ reference using the active set [9h], on the hyperfine parameter values obtained in the MR$_8$-I-C[12h] calculation.

5. Comparison with experiment

The three considered isotopes, $^{33}\text{S}$, $^{35}\text{Cl}$ and $^{37}\text{Cl}$, have a spin $I = 3/2$ and respectively a magnetic dipole moment of $+0.643\,8212(14)\mu_N$, $+0.821\,8743(4)\mu_N$ and $+0.684\,1236(4)\mu_N$ [25]. Their nuclear quadrupole moments are still best determined through theoretical inputs [26], as we will see below.

The non-relativistic $A_J$ constants computed using the final set of hyperfine parameters of tables 4, 5 and 7 are shown in table 8. We estimate the relativistic corrections by running mono-reference non-relativistic and corresponding relativistic CI calculations using the Pauli approximation with the SR-I-C[9h] orbital set, as described in [15, 19].

At the non-relativistic level, the neutral sulphur $A_1(3\text{P})$ hyperfine constant is characterized by a strong cancellation between the spin-dipole ($A_{sd}$) and orbit ($A_{orb}$) contributions. Indeed, in the MR$_8$-I-C[12h] CI calculation performed with the SR-I-C orbitals, we find
\[
A_l = 105.04 \text{ MHz} \quad A_{sd} = -110.74 \text{ MHz}
\]
\[
A_c = 6.28 \text{ MHz}.
\]

We realize from table 4, 5 and 7 that the contact term ($A_c$) is by far the less converged contribution, bringing the largest source of uncertainty ($\sim 1$ MHz). It is unclear to what extent the $^{33}\text{S}^-$ theory–experiment excellent agreement is accidental.

As far as the $B_I$ constants are concerned, it is more relevant to tabulate the electric quadrupole moments ($Q$) obtained for $\text{S}^-$ and Cl from the formula [17]
\[
Q = \frac{(B^2/2)_{\text{exp}}}{(b)_{\text{exp}} G_q}
\]
Table 7. Best estimates of the energy (in $E_a$) and hyperfine parameters (in $a_o$) of the neutral sulphur $^3P$ state. The final results are obtained by reporting the impacts of the 13th correlation shell on the MR3-I-C model and the impacts of the extension of the MR4 to reference the MR8 reference using the active set $[9h]$, on the values of hyperfine parameters obtained in the MR6-I-C $[12h]$ calculation.

|      | $E_a$ | $a_o$ | $a_{o0}$ | $b$ |
|------|------|------|--------|-----|
| MR4 | -398.07547 | 5.13968 | 1.08020 | -2.05860 |
| MR6 | -398.08254 | 5.12937 | 1.07860 | -2.05035 |
| MR8 | -398.08289 | 5.12869 | 1.07918 | -2.04957 |

Table 8. Comparison of theoretical and experimental $A_J$ hyperfine constants (in MHz) for the lowest multiplet of $^{33}S$, $^{35}Cl$ and $^{37}Cl$. Non-relativistic estimations (NR) computed from the final results of tables 4, 5 and 7. Relativistic corrections estimated with a CI-RCI approach [15, 19].

|      | $^{33}S$ | $^{35}Cl$ | $^{37}Cl$ |
|------|---------|---------|---------|
| $A_J$ | $A_J$ | $A_J$ | $A_J$ |
| Non-relativistic | 133.58 | 92.48 | 202.45 |
| +relativistic corrections | 130.09 | 91.43 | 201.25 |
| Experiment | 91.49 | 170.69 | 205.05 |

Table 9. Nuclear electric quadrupole moments ($Q$, in barns) estimated with equation (21) for $^{33}S^-$, $^{35}Cl$ and $^{37}Cl$. From those $Q$, we calculate the $B_J$ constants of the $^{33}S$ lower multiplet with our value of $b(S^3P)$. Non-relativistic estimations (NR) computed from the final values of tables 4, 5 and 7. Relativistic corrections estimated with a CI-RCI approach [15, 19].

|      | $^{33}S$ | $^{35}Cl$ | $^{37}Cl$ |
|------|---------|---------|---------|
| $Q$  | $B_J(33S^-)$ | $B_J(33S^-)$ | $Q$ |
| Non-relativistic | -0.0655(6) | -31.49 | -0.082265 |
| +rel. corrections | -0.0657(6) | -31.60 | -0.081764 |
| Sundholm and Olsen* | -0.0678(13) | -32.60 | -0.08165(80) |
| Alonso et al* | -0.0850(11) | -0.08435(64) |
| Yakobi et al* | -0.0811(12) |

* Reference [2] for $^{33}S$ and [28] for the chlorine isotopes.

** Reference [29].

† Reference [30].

(see section 2.2). The available experimental data are

$$B_{3/2}(33S^-) = 26.24(23) \text{ MHz} \ [1]$$

$$B_{3/2}(35Cl) = 54.872 905(55) \text{ MHz} \ [27]$$

$$B_{3/2}(37Cl) = 43.245 245(55) \text{ MHz} \ [27].$$

We compare our $Q$ values with previous works in table 9. Since, to our knowledge, there is no measurement of the neutral sulphur hyperfine structure, we use our value for the $b(S^3P)$ parameter for estimating the $B_J$ constants of $^{33}S$ with each $Q(33S^-)$ value.

6. Conclusion

We perform MCHF-CI and RCI calculations of the hyperfine constants of the $3p^5 2P^o_J$ multiplet of $^{33}S^-$ and $^{35,37}Cl$ and the $3p^4 3P_J$ multiplet of $^{33}S$. We obtain good agreement with previous theoretical works [2, 28] for the nuclear electric quadrupole moments of $^{33}S$ and $^{35,37}Cl$, and with the $A(3p^5 2P^o_J)$ experimental values [1, 27]. It appears that the contact contribution, the main source of uncertainty in our non-relativistic calculations, is ten times smaller in $S^-$ than in $Cl$. We interpret this as an effect of an increased separation of the core and valence regions in negative ions.

We show that, for sufficiently large active sets, orbitals optimized in closed-core MCHF calculations reproduce the results of proper open-core MCHF calculations. This approach has a significant advantage: the core–valence distinction in frozen and closed-core MCHF calculations is much cleaner. It allows us to minimize the high-order core and valence mixing and hence get a better comparison between calculations performed on different systems (e.g. $S$ and $S^-$).

Acknowledgments

T Carette is grateful to the ‘Fonds pour la formation à la Recherche dans l’Industrie et dans l’Agriculture’ of Belgium for a PhD Grant (Boursier F.R.S.-FNRS). M Godefroid thanks
the Communauté française of Belgium (Action de Recherche Concertée) and the Belgian National Fund for Scientific Research (FRFC/IISN Convention) for financial support.

References

[1] Trainham R, Jopson R M and Larson D J 1989 *Phys. Rev. A* **39** 3223
[2] Sundholm D and Olsen J 1990 *Phys. Rev. A* **42** 1160
[3] Berzinsh U, Gustafsson M, Hanstorp D, Klinkmüller A, Ljungblad U and Mårtensson-Pendrill A M 1995 *Phys. Rev. A* **51** 231
[4] Godefroid M R and Froese Fischer C 1999 *Phys. Rev. A* **60** R2640
[5] Blondel C, Delsart C, Valli C, You S, Godefroid M R and Van Eck S 2001 *Phys. Rev. A* **64** 052504
[6] Carette T, Drag C, Scharf O, Blondel C, Delsart C, Fischer C, Froese and Godefroid M R 2010 *Phys. Rev. A* **81** 042522
[7] Carette T and Godefroid M 2011 *J. Phys. B: At. Mol. Opt. Phys.* to be submitted
[8] Mader D L and Novick R 1974 *Phys. Rev. Lett.* **32** 185–8
[9] Fischer A, Canali C, Warring U, Kellerbaer A and Fritzsche S 2010 *Phys. Rev. Lett.* **104** 073004
[10] Verdebout S, Jönsson P, Gaigalas G, Godefroid M and Froese Fischer C 2010 *J. Phys. B: At. Mol. Opt. Phys.* **43** 074017
[11] Froese Fischer C, Brage T and Jönsson P 1997 *Computational Atomic Structure: An MCHF Approach* 1st edn (London: Taylor and Francis)
[12] Froese Fischer C 1977 *Hartree–Fock Method for Atoms. A Numerical Approach* (New York: Wiley)
[13] Sturesson L and Froese Fischer C 1993 *Comput. Phys. Commun.* **74** 432
[14] Froese Fischer C, Tachiev G, Gaigalas G and Godefroid M R 2007 *Comput. Phys. Commun.* **176** 559
[15] Carette T and Godefroid M 2011 *Phys. Rev. A* at press
[16] Lindgren I and Rosén A 1974 *Chem. Stud. At. Phys.* **4** 93–196
[17] Hibbert A 1975 *Rep. Prog. Phys.* **38** 1217
[18] Jönsson P, Wahlström C-G and Froese Fischer C 1993 *Comput. Phys. Commun.* **74** 399
[19] Jönsson P, Carette T, Nemouchi M and Godefroid M 2010 *J. Phys. B: At. Mol. Opt. Phys.* **43** 115006
[20] Froese Fischer C and Saxena K M S 1974 *Phys. Rev. A* **9** 1498
[21] Lindgren I and Morrison J 1986 *Atomic Many-Body Theory* (Springer Series on Atoms and Plasmas vol 3) 2nd edn (Berlin: Springer)
[22] Migdalek J and Kim Y K 1998 *J. Phys. B: At. Mol. Opt. Phys.* **31** 1947
[23] Godefroid M R, Jönsson P and Froese Fischer C 1998 *Phys. Scr.* **T78** 33
[24] Carette T 2010 Isotope effects in atomic spectroscopy of negative ions and neutral atoms: a theoretical contribution PhD Thesis Université Libre de Bruxelles http://theses.ulb.ac.be/ETD-db/collection/available/ULBetd-12132010-195-442/
[25] Stone N J 2005 *At. Data Nucl. Data Tables* **90** 75
[26] Pyykkö P 2008 *Mol. Phys. 106* 1965
[27] Fuller G H 1976 *J. Phys. Chem. Ref. Data* **5** 835
[28] Sundholm D and Olsen J 1993 *J. Chem. Phys.* **98** 7152
[29] Alonso R E, Svane A, Rodríguez C O and Christensen N E 2004 *Phys. Rev. B* **69** 125101
[30] Yakobi H, Eliav E, Visscher L and Kaldor U 2007 *J. Chem. Phys.* **126** 054501