Ab initio calculations of hyperfine structures of zinc and evaluation of the nuclear quadrupole moment \(Q^{(67} \text{Zn)}\)

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The relativistic multiconfiguration Dirac-Hartree-Fock (MCDHF) and the non-relativistic multiconfiguration Hartree-Fock (MCHF) methods have been employed to calculate the magnetic dipole and electric quadrupole hyperfine structure constants of zinc. The calculated electric field gradients for the \(4s4p\) \(^3P_0\) and \(4s4p\) \(^3P_1\) states, together with experimental values of the electric quadrupole hyperfine structure constants, made it possible to extract a nuclear electric quadrupole moment \(Q^{(67} \text{Zn)} = 0.122(10)\) b. The error bar has been evaluated in a quasi-statistical approach — the calculations had been carried out with eleven different methods, and then the error bar has been estimated from the differences between the results obtained with those methods.

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I. INTRODUCTION

One of the most accurate methods to determine nuclear quadrupole moments, \(Q\), is to combine measured nuclear quadrupole coupling constants, \(B\), with calculated or deduced electric field gradients (EFG), \(q\). The aim of the present work is to apply this method to determine improved nuclear quadrupole moments of zinc, the second most abundant essential trace element in the human body, after iron.

For zinc, the standard value cited in the 2008 review of Pyykkö \cite{12} and the 2016 review of Stone \cite{13} is still the 1969 value obtained by Laulainen and McDermott \cite{5}: \(Q^{(67} \text{Zn)} = 0.150(15)\) b (1 barn = 1 b = \(10^{-28}\) m\(^2\)).

This value is based on the experimental \(B_{63}/B_{67} = 1.8347(13)\) of Laulainen and McDermott \cite{5} and the 2016 review of Stone \cite{13} is still the 1969 value obtained by Laulainen and McDermott \cite{5}: \(Q^{(67} \text{Zn)} = 0.150(15)\) b (1 barn = 1 b = \(10^{-28}\) m\(^2\)). The experimental ratio \(B_{63}/B_{67} = 1.8347(13)\) of Laulainen and McDermott \cite{5} corresponds to \(Q^{(63} \text{Zn)} = +0.275(30)\) b (incidentally, Laulainen and McDermott \cite{5} arrived at \(Q^{(63} \text{Zn)} = +0.29(3)\) b). Potential improvements could be obtained by using the measurement of Byron et al \cite{14} of \(B_{63}^{(3P_1)} = -18.782(8)\) MHZ for the same \(4s4p\) \(^3P_1\) state of \(67\) \text{Zn}. Their \(65/67\) ratio was \(-0.1528(3)\) which, combined with their \(Q^{(65} \text{Zn)} = 0.024(2)\) b, corresponds to \(Q^{(67} \text{Zn)} = 0.157\) b. More recently the EFGs of \text{Zn} in solid \text{Zn} have been calculated in a series of papers by Haas and collaborators \cite{8–10}, who employed the Density Functional Theory. In their latest paper \cite{10} using a recently developed hybrid Density Functional Theory approach, combined with the experimental quadrupole coupling constants measured by Potzel et al \cite{11}, and corrected for thermal effects, they obtained a considerably smaller value of the quadrupole moment \(Q^{(67} \text{Zn)} = 0.125(5)\) b. The 5 mb error limit is considered as “may be optimistic” in the 2017 compilation of Pyykkö \cite{12}.

In the present work magnetic hyperfine interaction constants, \(A\), and electric field gradients, \(q\), necessary for an atomic evaluation of the quadrupole moments, were calculated for the \(4s4p\) \(^3P_0\) and \(4s4p\) \(^3P_1\) atomic states of the stable \(67\) \text{Zn} isotope using both the non-relativistic multiconfiguration Hartree-Fock (MCHF) method \cite{13–15} and the fully relativistic multiconfiguration Dirac-Hartree-Fock (MCDHF) method \cite{10–12}. MCHF is efficient in capturing electron correlation effects while MCDHF is necessary for correctly describing relativistic contraction due to the mass variation, influencing the wave function close to the nucleus. With this respect, the two methods were complementary: a ‘DHF/HF factor’ was used to correct the non-relativistic results for the relativistic effects and a ‘triples correction’ was used to correct the relativistic results for the electron correlation effects arising from triple substitutions, a calculation that became unfeasible in the fully relativistic scheme. The present work is the follow-up of the recent measurement of the hyperfine resonances of the \(4s4p\) \(^3P_2\) \(\rightarrow\) \(4s5s\) \(^3S_1\) transition by Wraith et al \cite{10}, as a detailed exposition of theoretical tools and computational approaches, employed to calculate magnetic fields and electric field gradients necessary for the evaluation of nuclear multipole moments.

The paper is divided into six sections. Section \cite{11} introduces the essential elements of the multiconfiguration methods, as well as of the theory of the hyperfine struc-
ture in the non-relativistic and relativistic frameworks. Non-relativistic calculations are presented in section III while section IV focuses on relativistic calculations. In section V we summarize the calculations, and we evaluate the nuclear quadrupole moment $Q(67\text{Zn})$ on the basis of eleven independent determinations of the electric field gradients. Section VI concludes the paper.

II. THEORY

A. Multiconfiguration methods

In multiconfiguration methods [15], the wave function, $\Psi$, for an atomic state is determined as an expansion over configuration state functions (CSFs)

$$\Psi = \sum_{i=1}^{N_{\text{CSFs}}} c_i \Phi_i,$$

where $N_{\text{CSFs}}$ is the number of CSFs in the expansion. The CSFs are coupled anti-symmetric products of one-electron orbitals. The expansion coefficients $c_i$ and the radial parts of the one-electron orbitals are determined in a self-consistent procedure by finding stationary states of an energy functional based on a given Hamiltonian. Once a radial orbital set has been determined, configuration interaction (CI) calculations can be performed in which the expansion coefficients only are determined by diagonalizing the Hamiltonian matrix. CI calculations are simpler and faster than the self-consistent calculations and, for this reason, the number of CSFs can be extended.

Fully relativistic MCDHF calculations give wave functions for fine-structure states and are based on the Dirac-Coulomb Hamiltonian [16, 17]. The CSFs are obtained as $jj$-coupled and anti-symmetric products of Dirac-orbitals. The wave function representation in $jj$-coupling is transformed to an approximate representation in $LSJ$-coupling, using the methods and program developed by Gaigalas and co-workers [20, 21]. The non-relativistic MCHF calculations give wave functions for $LS$ terms, and are based on the Schrödinger Hamiltonian [13, 15]. The CSFs are obtained as $LS$-coupled and anti-symmetric products of non-relativistic spin-orbitals.

The two methods have different strengths and weaknesses relative to the atomic system at hand. Zinc is a fairly relativistic system for which relativistic contraction due to the mass variation starts to get important, especially for the calculated hyperfine constants. These effects are captured very efficiently in the MCDHF method by the shape of the radial orbitals. Although the MCHF method corrected for relativistic effects through the Breit-Pauli approximation produces reliable atomic data for systems with relatively large nuclear charges [22], it will never fully account for these corrections at the level of orbital optimisation [23]. At the same time zinc is a large system with many subshells, and electron correlation effects captured by extended CSFs expansions are important for all computed properties. Due to the restriction to $LS$ symmetry, the sizes of the CSF expansions for MCHF calculations grow less rapidly than do the corresponding expansions for the MCDHF calculations. As a consequence it is possible to include more electron correlation excitations in MCHF calculations.

B. Hyperfine structure

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

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

where $\mathbf{T}^{(k)}$ and $\mathbf{M}^{(k)}$ are spherical tensor operators of rank $k$ in the electronic and nuclear spaces. The $k = 1$ and $k = 2$ terms represent, respectively, the magnetic dipole ($M1$) and the electric quadrupole ($E2$) interactions. In non-relativistic calculations for an $N$-electron system the electronic contributions are obtained from the expectation values of the irreducible spherical tensors [24, 25].

$$\mathbf{T}^{(1)} = \frac{\alpha^2}{2} \sum_{j=1}^{N} \left\{ 2 \mathcal{T}^{(1)}(j) \frac{1}{r_j^2} - g_s \sqrt{10} \mathbf{C}^{(2)}(j) \times \mathbf{s}^{(1)}(j) \right\},$$

$$\mathbf{T}^{(2)} = -\sum_{j=1}^{N} \mathbf{C}^{(2)}(j) \frac{1}{r_j^2},$$

and

$$\mathbf{T}^{(1)} = -i \alpha \sum_{j=1}^{N} \left( \alpha_j \cdot \mathbf{l}_j \mathbf{C}^{(1)}(j) \right) \frac{1}{r_j^2}.$$
The electronic contribution for the magnetic dipole interaction is combined with the nuclear spin $I = 5/2$ and the measured magnetic dipole moment $\mu = 0.875479 \mu_N$ [4] to give the magnetic dipole hyperfine interaction constant, $A$, for the $4s4p^3P_0^o$ states in $^{67}$Zn. The electric field gradient (EFG), also denoted $q$ [28], is obtained from the reduced matrix element of the operator $\hat{q}$ using the electronic wave function of the considered electronic state (see [24, 29] for details). It corresponds to the electronic part of the electric quadrupole hyperfine interaction constant, $B$. The latter, expressed in MHz, can be calculated using the following equation

$$B/\text{MHz} = 234.9646 (q/a_0^{-3})(Q/b),$$

(6)

where the EFG ($q$) and the nuclear quadrupole moment ($Q$) are expressed in $a_0^{-3}$ and barns, respectively. Instead of reporting $q$, we will monitor in the present work the related $B/Q \propto q$ ratio values (in MHz/b).

III. NON-RELATIVISTIC CALCULATIONS

A. MCHF calculations

The MCHF calculations were performed using the Atomic Structure Package (ATSP2K) [30]. As a starting point a Hartree-Fock (HF) calculation was performed for $4s4p^3P^o$. The HF calculation was followed by a sequence of calculations describing valence-valence and core-valence electron correlation effects. The CSF expansions for these calculations were obtained by allowing single (S) and double (D) substitutions from $2s^22p^53s^23p^63d^{10}4s4p^3P^o$ to increasing active sets of orbitals with the restriction that there is at most one substitution from the core shells. The 1s-shell is kept closed in all calculations. These expansions are referred to as singles and restricted doubles (SrD) expansions. The active sets are denoted by giving the highest orbital of each symmetry. For example, $\{5s5p4d4f\}$ denotes the orbital set that includes the orbitals $1s, 2s, 3s, 4s, 5s, 2p, 3p, 4p, 5p, 3d, 4d, 4f$. In the MCHF calculations the HF orbitals were kept frozen and the remaining orbitals were optimized together. The MCHF calculations were followed by a CI calculation based on the largest orbital set. The CI calculation describes valence-valence (VV), core-valence (CV) and core-core (CC) correlation effects and includes CSFs obtained by all single and double (SD) substitutions. Whereas SD expansions describe the major corrections to the wave function, it is known that CSFs obtained from triple (T) substitutions are important for hyperfine structures [31]. The effects of the T substitutions were accounted for in CI, by augmenting the largest SD expansion with expansions obtained by T substitutions to increasing orbital sets. All calculations are summarized in Table I.

To correct for the relativistic contraction due to the mass variation, Dirac-Hartree-Fock (DHF) calculations were also performed and the final SD+T values were multiplied with the DHF/HF ratio. This correction will be discussed in more detail in the next section. From Table II we see that valence-valence and core-valence effects, as described by SrD expansions, increase the absolute values of all computed hyperfine parameters. The increase is around 30% for the $A$ constant and 60% for the electric field gradient $q \propto B/Q$. The changes are well converged and are consistent with a contraction of the wave function when accounting for core-valence correlation as observed in [32, 33]. The effect of unrestricted D substitutions, resulting in CSFs describing also core-core correlation, is to decrease the absolute values of the computed hyperfine parameters. The CSFs resulting from the unrestricted double substitutions can be shown to have small effects on the hyperfine parameters by themselves. Instead the effects are indirect, changing or effectively diluting the mixing coefficients of the more important CSFs describing core-valence effects [34, 35].

Finally, the effect of the T substitutions is to increase the absolute values of the hyperfine constants. Again, the effect is mainly indirect, affecting the expansion coefficients of the important singly excited CSFs: $2s^22p^53s3p3d104s4p^3P^o$ and $2s^22p^53s^23p^53d104s4p^3P^o$, describing spin-polarization; $2s^22p^53s3p^3nl3d104s4p^3P^o$ and $2s^22p^53s2p^53p^53d104s4p^3P^o$, the last two describing orbital-polarization [37, 38]. The latter effects will be analyzed in more detail in the section III-C below. The general convergence trends and behavior with respect to different correlation effects are consistent with the ones found for other similar systems [30]. It is interesting to note that the effects discussed above are partly canceling. Thus it is better to include only the valence-valence and core-valence effects than the valence-valence, core-valence and core-core effects. If the core-core effects are included, then also the effects of the T substitutions should be accounted for. The final $A$ constants for the $4s4p^3P_{1,2}^o$ states differ from the experimental values by 1.8% and 5.2%, respectively.

B. DHF/HF correction

Table II presents expectation values $\langle r \rangle_{nl}$ and $\langle r \rangle_{n\kappa}$ of spectroscopic orbitals obtained in zeroth-order (no electron correlation) non-relativistic Hartree-Fock (HF) and relativistic Dirac-Hartree-Fock (DHF) approximations, where $\kappa = -(l+1)$ for $j = l+1/2$ and $\kappa = +l$ for $j = l-1/2$. For all spectroscopic orbitals but 3d, the direct relativistic contraction due to the mass variation dominates the indirect one, induced by the relativistic charge redistribution [39]. The differences in radii of correlation orbitals are more complex. They usually reflect specific correlation effects, targeted in the self-consistent-field optimisation strategies [13]. For the M1 hyperfine interaction, a detailed comparison of the non-relativistic expectation values of eq. 4 and of the relativistic ones...
ratios of $M_1$ and $E_2$ hyperfine constants, as illustrated the corresponding relativistic expression of eq. (5). Quadrupole couplings have been investigated by Pyykkö are the most important. Relativistic effects in nuclear to the nucleus where the relativistic contraction effects allow the inclusion of valence (VV) and core-valence (CV) effects (see text). Core-core correlation (CC) is included through unrestricted D substitutions. SD+T denote expansions where the largest SD expansion has been augmented by expansions from T substitutions to increasing active orbital sets. The largest SD+T results were scaled by the DHF/HF ratio factor in the line labeled MCHF×DHF/HF. HF = uncorrelated Hartree-Fock values; DHF = uncorrelated Dirac-Hartree-Fock values. $N_{\text{CSFs}}$ is the number of CSFs in the expansion.

| Label | $N_{\text{CSFs}}$ | $A$ (MHz) | $B/Q$ (MHz/b) | $A$ (MHz) | $B/Q$ (MHz/b) |
|-------|------------------|-----------|---------------|-----------|---------------|
| HF    |                  | 412.72451 | −109.033      | 373.00296 | 186.0866      |
| DHF   |                  | 473.40239 | −100.373      | 419.93437 | 192.924       |

SD (VV+CV)
- 5s5p4d4f: 404 471.978 −120.16 429.223 240.33
- 6s6p5d5f5g: 1593 507.266 −136.52 459.667 273.04
- 7s7p6d6f6g6h: 3872 526.518 −142.07 476.132 284.15
- 8s8p7d7f7g7h: 7232 536.870 −146.85 484.970 293.70
- 9s9p8d8f8g8h: 11673 541.017 −148.95 488.430 297.90
- 10s10p9d9f9g9h: 17195 542.624 −148.27 489.789 296.55
- 11s11p10d10f10g10h: 23798 542.926 −148.44 490.022 296.89

SD+T (VV+CV+CC)
- 5s5p4d4f: 92810 533.150 −141.59 481.192 283.18
- 6s6p5d5f5g: 225457 540.485 −143.86 487.481 289.73
- 7s7p6d6f6g6h: 446457 544.960 −147.53 491.050 295.06
- 8s8p7d7f7g7h: 761267 551.678 −151.68 496.389 303.36
- 9s9p8d8f8g8h: 1175344 553.437 −152.988 497.691 305.976
- MCHF×DHF/HF: 634.802 −165.058 560.310 317.254

Expt: 609.086$^a$ 531.987$^b$

$^a$Byron et al [28].
$^b$Lurio [29].

of eq. (5) in terms of single-electron orbitals contributions is not easy. The global effect in the single configuration approximation is to produce large DHF/HF ratios of $M_1$ and $E_2$ hyperfine constants, as illustrated by the first two lines of Table II. As can be seen, the relativistic effect is much larger for the $A$ constants than for the EFG values, which can be explained by the contact interaction that appears in the non-relativistic expression for the $M_1$ interaction with the three-dimensional delta function (see the last term of eq. (5)). Although the corresponding relativistic expression of eq. (5) does not contain a contact operator, the tensorial structure of the relativistic operator indicates that it is highly biased towards the behavior of the wave function close to the nucleus where the relativistic contraction effects are the most important. Relativistic effects in nuclear quadrupole couplings have been investigated by Pyykkö and Seth [28] who estimated relativistic correction factors $C$ for EFGs due to valence $p$ electrons from one-electron matrix elements $q_{+,+}$, $q_{+,−}$ and $q_{−−}$. The $q_{−−}$ combination has $j = 1/2$ for $l = 1$ and corresponds to a spherical charge distribution. It will therefore not contribute to the EFG, oppositely to $q_{++,}$ and $q_{+−}$. These $C$ factors can be used to scale the non-relativistic EFG values. They have been estimated in the quasirelativistic (QR) approximation (no fine-structure splitting), using hydrogen-like (H) and Dirac-Fock (DF) expectation values, or the Casimir’s $n$-independent formulae (Cas). They are reported in the first three lines of Table III. Beyond the QR approximation, correction factors can be estimated for the fine-structure levels of light atoms by taking the right combination of the $C$ coefficients, $1/3 (C_{++} + 4/3 C_{−−})$ and $C_{−−}$ for $J = 1$ and $J = 2$, respectively, with $C_{++} = 1.02556$ and $C_{−−} = 1.06177$ [28]. These factors are also reported in the Table III and compared with the DHF/HF ratios estimated from the EFG values reported in Table II.

These ratios, obtained in the single configuration picture, may be used to scale the multiconfiguration results, as it is done in the line MCHF×DHF/HF of Table II with the underlying assumption that cross terms between relativistic contraction and electron correlation are negligible. Looking at the differences in ratios between different methods, we infer that application of the DHF/HF correction ratio induces an uncertainty of at most 2-3% for the electric field gradient $q$ of the $J = 1$ state. The un-
Table II. HF \(\langle r\rangle_{nl}\) vs DHF \(\langle r\rangle_{nl}\) orbital radii (\(a_0\)). HF calculation for the 4s4p \(^3P^o\) term. DHF calculation optimised on the 4s4p \(^3P^o_{0,1,2}\) states together. Notation: \(\langle n\rangle\) = HF orbital; \(\langle n\rangle^+\) = DHF orbital with negative \(\kappa\) (1s, 2s, 3s, 4s, 2p, 3p, 3d, 4p); \(\langle n\rangle^-\) = DHF orbital with positive \(\kappa\) (2p\(\rightarrow\), 3p\(\rightarrow\), 3d\(\rightarrow\), 4p\(\rightarrow\)). The table illustrates the direct relativistic contraction of \(s\) orbitals due to mass variation.

| \(\langle r\rangle_{nl}\) (\(a_0\)) | 1s | 2s | 3s | 3p | 4s | 4p |
|-----------------------------|-----|-----|-----|-----|-----|-----|
| \(nl\)                      | 0.05108 | 0.22878 | 0.19951 | 0.69107 | 0.71948 | 0.87132 | 2.77730 | 3.80035 |
| \(nl^+\)                    | 0.05028 | 0.22498 | 0.19912 | 0.68907 | 0.71824 | 0.87909 | 2.72995 | 3.79473 |
| \(nl^-\)                    | 0.19578 | 0.70820 | 0.87169 | 3.76246 |       |       |       |       |

C. Contributions to \(A\) and EFG from different classes of orbital substitutions

The uncertainties of the computed \(A\) constants and electric field gradients \(q\) are to a large extent determined by the size of the cancellation effects [40] [41]. In the non-relativistic formalism the \(A\) constants are computed based on the operator in eq. (3) and are the sums of three terms \(A_t\), \(A_{sd}\), \(A_c\), orbital, spin-dipolar, and Fermi contact term, respectively. At the HF level we have (in MHz): \(A_t = 33.06\), \(\sim A_{sd} \approx 33.10\), \(\sim A_c \approx 346.56\), and \(A_t = 33.06\), \(\sim A_{sd} \approx -6.62\), \(\sim A_c \approx 346.56\), for 4s4p \(^3P^o\) and 4s4p \(^3P^o_2\), respectively. It is seen that the Fermi contact term dominates, but this part is largely canceled by the spin-dipolar contribution for the \(J = 2\) state. Based on this simple observation we may expect that the computed \(A\) constant is less accurate for the \(J = 2\) state. To shed light on the sensitivity of \(A\) and \(B/\)Q to electron correlation effects we analyze the contributions to these parameters from different classes of orbital substitutions. Given the \{1s1p10d10f10g10h\} orbital set, the \(A\) constants and \(B/\)Q ratio values are computed from accumulated CSF expansions that result from allowing single and double substitutions from deeper and deeper lying orbitals of the 2s2p\(^6\)3s\(^3\)p\(^3\)d\(^{10}\)4s4p reference configuration. The results are presented in Table IV. The accumulated CSF expansions are denoted by the innermost orbitals from which the substitutions are allowed. For example, \(3d3d\) denotes the accumulated CSF expansion that is obtained by allowing the substitutions

\[vv \rightarrow nln'\ell', \ 3dv \rightarrow nln'\ell', \ 3d \rightarrow nl, \ 3d3d \rightarrow nln'\ell'\]

whereas \(3pv\) denotes the accumulated CSF expansion obtained from the substitutions

\[vv \rightarrow nln'\ell', \ 3dv \rightarrow nln'\ell', \ 3d \rightarrow nl, \ 3d3d \rightarrow nln'\ell', \ 3pv \rightarrow nln'\ell'\]

where \(nl, \ n\ell' \in \{1s1p10d10f10g10h\}\). By comparing the results for \(3d3d\) and \(3pv\) we can infer how large are the contributions from CSFs obtained from the \(3pv \rightarrow nln'\ell'\) substitutions. From Table IV one can see that CSFs obtained from \(3dv \rightarrow nln'\ell'\) substitutions describing core-valence correlation are very important for both \(A\) and \(B/\)Q. One can also see that CSFs obtained from \(3s, 2s \rightarrow nl\) substitutions describing spin-polarization are important for the \(A\) parameters whereas CSFs obtained from \(3d, 3p, 2p \rightarrow nl\) substitutions describing orbital-polarization are important for the \(q\) parameters. One further notes that the effects of CSFs from single substitutions are often canceled by those of CSFs from double substitutions. Of particular importance are the effects from \(3d3d \rightarrow nln'\ell'\). The corresponding CSFs do not directly contribute to the hyperfine parameters but they are important for the total wave function, lowering, or diluting, the effects of the other CSFs (compare the discussion in the previous section). The accuracy of the calculated \(A\) constant and \((B/\)Q) ratio values is to a large extent determined by the fact that they result from a summation of a number of canceling contributions. We refer to chapter 8 of [14] for a general discussion about spin- and orbital-polarization effects.

IV. MULTICONFIGURATION DIRAC-HARTREE-FOCK/RCI CALCULATIONS

Two different approaches were used for the 4s4p \(^3P^o_2\) states. In the first approach, called OLI (Optimal Level 1) the wave functions for the 4s4p \(^3P^o_2\) state were optimised for a single state, i.e. the 4s4p \(^3P^o_2\) level itself. In the second approach (called OLI4) the wave functions were generated with the Extended Optimal Level 12 form of the variational functional, built from all 4 states of the 4s4p configuration (4s4p \(^3P^o_0, \ ^3P^o_1, \ ^3P^o_2, \ ^1P^o_1\)). The full description of numerical methods, virtual orbital sets, electron substitutions, and other details of the computations, can be found in [15, 18, 29, 42] [46].

A. Optimal Level calculations for the 4s4p \(^3P^o_2\) state

As mentioned above, the first approach (OLL1) targets the optimisation of the single state 4s4p \(^3P^o_2\) wave function. The spectroscopic orbitals 1s2s3sp3dp4sp were generated in Dirac-Hartree-Fock (DHF) mode, i.e. without correlation (virtual) orbitals, and were frozen through all further steps. Five layers of virtual orbitals [15] of \(s,p,d,f,g,h\) angular symmetries were sequentially gener-
Table III. Relativistic correction factors for EFG estimated with different methods. Quasirelativistic correction factors reported are taken from Ref. [28] using Dirac-Fock (DF), Hydrogen-like (H) expectation values or the Casimir’s n-independent formulae (Cas) (see Ref. [28] for more details.) The $J$-dependent correction factors are either calculated following the procedure outlined in the conclusion section of Ref. [28], or from the DHF/HF ratio of EFG values (this work). $”^+” = p_{3/2}$ orbital; $”^−” = p_{1/2}$ orbital.

| QR approach | $C_{QR}$(Cas) : Casimir’s n-independent formula [28] | $C_{QR}$(H) : H-like [28] | $C_{QR}$(DF) : DHF [28] |
|-------------|---------------------------------|-----------------|-----------------|
| $J = 1$     | 1.05468                         | 1.05776         | 1.04970         |
| $J = 2$     | 1.07384                         | calculated from [28] $(-1/3 C_{++} + 4/3 C_{+0})$ | 1.07890 DHF/HF ratio, this work (1st line of Table I). |

Table IV. The effect on $A$ and $B/Q$ ($\propto$ EFG) of $4s4p \,^3P_0^0$ from different classes of orbital substitutions. Analysis for the final SD calculation. See text for details of the notation and for a discussion about the importance of different classes.

| Label | $A$ (MHz) | $B/Q$ (MHz/b) | $A$ (MHz) | $B/Q$ (MHz/b) |
|-------|-----------|--------------|-----------|--------------|
| HF    | 412.72    | -93.033      | 373.00    | 186.06       |
| vv    | 411.07    | -92.28       | 371.67    | 184.56       |
| 3dv   | 479.96    | -109.23      | 433.48    | 218.46       |
| 3d    | 479.93    | -112.88      | 434.33    | 225.76       |
| 3d3d  | 459.77    | -106.35      | 416.60    | 212.71       |
| 3pv   | 470.26    | -109.49      | 425.92    | 218.98       |
| 3p3d  | 469.76    | -109.55      | 425.52    | 219.10       |
| 3p    | 477.31    | -133.89      | 428.89    | 267.78       |
| 3p3p  | 475.54    | -133.21      | 427.30    | 266.43       |
| 3sv   | 479.38    | -133.58      | 429.93    | 267.16       |
| 3s3d  | 479.19    | -133.96      | 430.54    | 267.92       |
| 3s3p  | 479.35    | -134.17      | 430.60    | 268.34       |
| 3s    | 506.62    | -134.16      | 457.86    | 268.32       |
| 3s3s  | 506.11    | -134.07      | 457.38    | 268.15       |
| 2pv   | 509.65    | -135.20      | 460.48    | 270.40       |
| 2p3d  | 509.88    | -135.52      | 460.61    | 271.05       |
| 2p3p  | 509.72    | -135.34      | 460.47    | 270.68       |
| 2p3s  | 509.71    | -135.44      | 460.41    | 270.89       |
| 2p    | 512.05    | -139.21      | 461.24    | 278.43       |
| 2p2p  | 509.03    | -137.95      | 458.45    | 275.90       |
| 2sv   | 510.21    | -138.12      | 459.55    | 276.25       |
| 2s3d  | 510.53    | -138.08      | 459.86    | 276.16       |
| 2s3p  | 510.91    | -138.08      | 460.24    | 276.16       |
| 2s3s  | 511.00    | -138.06      | 460.33    | 276.13       |
| 2s2p  | 511.36    | -138.15      | 460.66    | 276.30       |
| 2s    | 521.91    | -137.89      | 471.20    | 275.78       |
| 2s2s  | 521.47    | -137.73      | 470.79    | 275.47       |

Table IV. The effect on $A$ and $B/Q$ ($\propto$ EFG) of $4s4p \,^3P_0^0$ from different classes of orbital substitutions. Analysis for the final SD calculation. See text for details of the notation and for a discussion about the importance of different classes.

Appended with configurations arising from subsets of unrestricted single and double (SD) substitutions, or with (subsets of) unrestricted single, double, and triple (SDT) substitutions.

Figure I shows the dependence of the magnetic dipole hyperfine constant $A$ (MHz), (curves in the upper graph of the figure), and the $B/Q$ ratio (MHz/b), proportional to EFG, of the $4s4p \,^3P_0^0$ state (curves in the lower graph of the figure), on the size of the multiconfiguration expansion. All lines in both graphs are drawn only for the guidance of the eyes. The results of the calculations are represented by several symbols described in the following paragraph. Each integer value on the abscissa represents the maximal principal quantum number of the virtual orbital set for a particular multiconfiguration expansion. The fractional values represent approximations, where CSF expansions were appended with subsets of SD or SDT expansions. In these configuration interaction calculations, these subsets were generated in the following ways: the occupied orbitals were systematically opened for SD and SDT substitutions; the size of the virtual orbital set was systematically increased for SD substitutions, until the expectation values saturated with respect to the size of the virtual orbital set; then the size of the virtual orbital set was systematically increased for SDT substitutions. The convergence of the SDT results was not reached since larger SDT multiconfiguration expansions would exceed the capacity of the computer systems at our disposal (6x96 CPU @ 2.4GHz with 6x256 GB RAM).

A stepwise, systematic increase of different classes of substitutions makes it possible to identify those classes which bring about considerable contributions to the expectation value(s), as well as to quantify these contributions. Those with sizeable contributions were later included in the final configuration interaction calculations. Four curves in Figure I represent the following correlation models:

- circles (black online) = single and restricted double substitutions (SrD);
- squares (green online) = unrestricted single and double (SD) substitutions;
The results were not corrected for unrestricted double (SD), or substitutions from 3s,3p,3d,4s,4p occupied orbitals to two layers of virtual orbitals. The oscillations of the blue curves is a clear evidence that the triple substitutions were not saturated in these calculations.

The SD and OL4 curves, with squares (green online) and crosses (magenta online) in both upper and lower graphs, respectively, in Figure 1 represent the values corrected for the triple substitutions in a systematic manner: the triple substitutions were accounted for with an additive correction computed with the non-relativistic Hartree-Fock program ATSP2K [30] (see section IV.B below).

The straight horizontal line (red online) across the upper part of the upper graph in Figure 1 represents the experimental magnetic dipole hyperfine constant $A = 531.987(5)$ MHz for the $4s4p^3P_2$ state of the $^{67}$Zn isotope [6].

The end products of the calculations described in the present section are the magnetic dipole hyperfine constant, $A = 509.861$ MHz and the $B/Q = 281.799$ MHz/b ratio represented in Figure 1 by the points at the right hand side ends of the curve with squares (green online) on the upper and lower graphs, respectively. These values were obtained from the configuration interaction calculation with single and double substitutions from $2sp3spd4sp$ occupied orbitals to five layers of virtual orbitals (the largest size of the virtual orbital set generated in this approximation). These results, corrected for triple substitutions as described in the section IV.B below, were considered final in the single-reference calculations described in the present section. They are quoted in Table IV in marked ‘MCDHF-SD-SR-OL1+t(MCHF)’.

The scatter of points at the right hand side end of the four curves presented in the Figure 1 and the oscillations of the individual curves could serve as a guideline for estimating the error bars of the theoretical EFG contribution to $B$, and indirectly to $Q \propto B/q$. In the present paper however, the error bars have been estimated with a somewhat more reliable procedure described in the section IV below.

B. Additive corrections for triple substitutions

If the contribution of triple substitutions is small, it may be approximately assumed as an additive correction, approximately independent of relativity, and may be computed in the non-relativistic framework as the difference between the values obtained with and without triple substitutions, respectively. As an example, the correction (31.96 MHz) for the magnetic dipole hyperfine constant $A(4s4p^3P_2)$ in Table IV was evaluated as

- triangles (blue online) = single and double and triple (SDT) substitutions;
- crosses (magenta online) = results of the OL4 calculation, described in section IV.C below.

The curves with circles (black online) represent the initial phase of the calculations, where the third, fourth, and fifth layers of virtual orbitals were generated with single and restricted double substitutions (SrD). These results were not corrected for unrestricted double (SD), nor for triple (SDT) substitutions. The curves with triangles (blue online) represent the configuration interaction calculations, where unrestricted double and triple (SDT) substitutions were included. However, due to the limitations of available computer resources the triple substitutions were limited to substitutions from $4s4p$ occupied orbitals to one layer of virtual orbitals, or substitutions from $3s,3p,3d,4s,4p$ occupied orbitals to two layers of virtual orbitals. The oscillations of the blue curves is a clear evidence that the triple substitutions were not saturated in these calculations.

Figure 1. (Color online) Hyperfine constant $A(4s4p^3P_2)$ (MHz) (curves in the upper graph of the figure) and $B/Q$ ratio (MHz/b) of the $4s4p^3P_2$ state (curves in the lower graph of the figure), obtained in several approximations. Each integer value on the abscissa axis represents the maximal principal quantum number of the virtual orbital set for a particular multiconfiguration expansion. The fractional values represent approximations, where multiconfiguration expansions were appended with subsets of SD or SDT expansions. The straight horizontal line (red online) represents the experimental value $A(3P_2) = 531.987(5)$ MHz. More details are provided in text.

The curves with circles (black online) represent the initial phase of the calculations, where the third, fourth, and fifth layers of virtual orbitals were generated with single and restricted double substitutions (SrD). These results were not corrected for unrestricted double (SD), nor for triple (SDT) substitutions. The curves with triangles (blue online) represent the configuration interaction calculations, where unrestricted double and triple (SDT) substitutions were included. However, due to the limitations of available computer resources the triple substitutions were limited to substitutions from $4s4p$ occupied orbitals to one layer of virtual orbitals, or substitutions from $3s,3p,3d,4s,4p$ occupied orbitals to two layers of virtual orbitals. The oscillations of the blue curves is a clear evidence that the triple substitutions were not saturated in these calculations.

The SD and OL4 curves, with squares (green online) and crosses (magenta online) in both upper and lower graphs, respectively, in Figure 1 represent the values corrected for the triple substitutions in a systematic manner: the triple substitutions were accounted for with an additive correction computed with the non-relativistic Hartree-Fock program ATSP2K [30] (see section IV.B below).

The straight horizontal line (red online) across the upper part of the upper graph in Figure 1 represents the experimental magnetic dipole hyperfine constant $A = 531.987(5)$ MHz for the $4s4p^3P_2$ state of the $^{67}$Zn isotope [6].

The end products of the calculations described in the present section are the magnetic dipole hyperfine constant, $A = 509.861$ MHz and the $B/Q = 281.799$ MHz/b ratio represented in Figure 1 by the points at the right hand side ends of the curve with squares (green online) on the upper and lower graphs, respectively. These values were obtained from the configuration interaction calculation with single and double substitutions from $2sp3spd4sp$ occupied orbitals to five layers of virtual orbitals (the largest size of the virtual orbital set generated in this approximation). These results, corrected for triple substitutions as described in the section IV.B below, were considered final in the single-reference calculations described in the present section. They are quoted in Table IV in marked ‘MCDHF-SD-SR-OL1+t(MCHF)’.

The scatter of points at the right hand side end of the four curves presented in the Figure 1 and the oscillations of the individual curves could serve as a guideline for estimating the error bars of the theoretical EFG contribution to $B$, and indirectly to $Q \propto B/q$. In the present paper however, the error bars have been estimated with a somewhat more reliable procedure described in the section IV below.
the difference between the value calculated in the SD+T approximation \((A = 553.4370 \text{ MHz})\) and the value calculated in the SD approximation \((A = 521.4771 \text{ MHz})\). Analogous differences were assumed as triple contributions for the \(A(4s4p \ 3P^o_0)\) constant, as well as for the \(B/Q\) ratio-values for both states.

### C. Extended Optimal Level calculations for the \(4s4p \ 3P^o_1\) and \(4s4p \ 3P^o_2\) states

The calculations described in this section were performed in a similar manner as those presented in section \(\text{\[V\]A}\) with one significant difference: wave functions were optimised for all four states of \(4s4p\) configuration \((4s4p \ 3P^o_0, \ 3P^o_1, \ 3P^o_2, \ 1P^o_1)\) in the Extended Optimal Level (OL4) approach \([42]\), with equal weights. The calculations of hyperfine \(A\) and EFG factors for \(4s4p \ 3P^o_2\) states presented in this section are computationally more demanding than those for \(4s4p \ 3P^o_2\) state presented in section \(\text{\[V\]A}\). The \(4s4p\) configuration splits into four levels \((3P^o_0, \ 3P^o_1, \ 3P^o_2, \ 1P^o_1)\) and there are two levels of \(J = 1\) symmetry. The singlet \(1P^o_1\) state interacts considerably with the triplet \(3P^o_1\) state, and in such situations optimisation on all close lying levels often yields a better balance of states involved in configuration mixings. However, the multiconfiguration expansions are larger, and self-consistent-field process requires considerably more computer resources. The end products of the calculations described in the present section are the hyperfine \(A\) constants and \(B/Q\) ratios for the \(4s4p \ 3P^o_2\) states, obtained from the configuration interaction calculation with single and double substitutions from \(2s3p3d4sp\) occupied orbitals to five layers of virtual orbitals (the largest size of the virtual orbital set generated in this approximation).

These results, corrected for triple substitutions as described in the section \(\text{\[V\]B}\) above, were considered final in the Extended Optimal Level calculations and they are quoted in Table \(\text{\[X\]}\) in lines marked ‘MCDHF-SD-SR-OL4+1(t(MCHF))’ (separately for \(4s4p \ 3P^o_2\) state and \(4s4p \ 3P^o_1\) state). The results of these calculations for the \(4s4p \ 3P^o_2\) state are also represented by (magenta online) curves with crosses in Figure \(\text{\[I\]}\).

### D. Liu et al’s approach

Other computation strategies have been attempted and it is worthwhile to test their coherence. Liu et al \([47]\) focused on the spin-forbidden transition \(4s^2 \ 1S^o_0 - 4s4p \ 3P^o_0\) and the hyperfine-induced transition \(4s^2 \ 1S^o_0 - 4s4p \ 3P^o_0\) for ions between \(Z = 30\) (Zn) and \(Z = 47\) (Ag). These authors considered the following active set sequence

\[
\begin{align*}
\text{AS1} &= \{4s, 4p, 4d, 4f\}, \\
\text{AS2} &= \text{AS1} + \{5s, 5p, 5d, 5f, 5g\}, \\
\text{AS3} &= \text{AS2} + \{6s, 6p, 6d, 6f, 6g\}, \\
\text{AS4} &= \text{AS3} + \{7s, 7p, 7d, 7f, 7g\}, \\
\text{AS5} &= \text{AS4} + \{8s, 8p, 8d, 8f, 8g\}. \\
\end{align*}
\]

Their electron correlation model took into account the VV correlation, CV correlation through excitations of maximum one core electron from the 3d, 3p and 3s subshells, as well as spin-polarization (SP) effects by including CSFs of the forms \(1s^2 2s^2 2p^6 3s(3p)^3 3d^{10}, 1s^2 2s(3p)^3 2p^6 3s^2 3p^3 3d^{10}\) and \(1s(3p)^2 2s^2 2p^6 3s^2 3p^6 3d^{10}\). CC correlation was systematically neglected. The \(A\) and \(B\) values that they obtained for the \(4s4p \ 3P^o_1\) level of \(^{67}\text{Zn}\) are respectively \(A = 20.21 \text{ mK}\) and \(B = -0.7539 \text{ mK}\), to be compared with the two experimental results \(A = 20.317(7) \text{ mK} (609.086(2) \text{ MHz})\) and \(B = -0.6265(3) \text{ mK} (-18.782(8) \text{ MHz})\) from Byron et al \([7]\). The corresponding results are denoted as MCDHF-SrDT-SP-Liu.

### E. Wave functions optimised for isotope shifts

Relativistic MCDHF wave functions have been recently optimised for estimating the electronic isotope shift parameters of \(4s^2 \ 1S^o_0 - 4s4p \ 3P^o_1\) and \(4s4p \ 3P^o_0 - 4s5s \ 3S^o_1\) by Filippin et al \([35]\). Oppositely to hyperfine parameters, a reliable calculation of transition isotope shifts requires a correct balance of electron correlation effects between the levels involved. These authors attempted three different strategies, systematically omitting core-core correlation in the variational process of orbital optimisation. It is indeed well-known that CC correlation effects are better balanced with the use of a common orbital basis for describing both states involved in a given transition. Neglecting CC enables to get separate orbital basis sets to allow orbital relaxation. It is interesting to investigate the hyperfine constants calculated with these computational strategies. In the present work, we estimate the hyperfine structure parameters using three approaches labelled hereafter M1, M2 and M3.

The first approach (M1) was inspired by the strategy of Liu et al \([47]\), also omitting core-core correlation. Single (S) and double (D) substitutions were performed

---

**Table V.** Corrections for triple substitutions, (SDT–SD), calculated for hyperfine constant \(A\) (MHz) and \(B/Q\) (MHz/b) in \(4s4p \ 3P^o_{2,2}\) states.

|   | \(A(J = 1)\) | \(B/Q(J = 1)\) | \(A(J = 2)\) | \(B/Q(J = 2)\) |
|---|--------------|----------------|--------------|----------------|
| SD | 521.4771     | -137.7380      | 476.7987     | 275.4760       |
| SD+T | 553.4370     | -152.9882      | 497.6906     | 305.9764       |
| SD–SD | 31.96        | -15.25         | 26.89        | 30.50          |
on a single-reference (SR) set. These SD-SR substitutions take into account valence-valence (VV) and core-valence (CV) correlations. A VV correlation model only allows SD substitutions from valence orbitals, while the VV+C

| Active space | 4s4p \(^3\Pi^o\) | 4s4p \(^3\Pi^o\) |
|-------------|----------------|----------------|
|             | NCSFs | A (MHz) | \(B/Q\) (MHz/b) | Q (b) | NCSFs | A (MHz) | \(B/Q\) (MHz/b) | Q (b) |
|             |       |         |                |       |         |         |                |       |
| 5s5p4d4f    | 1592  | 558.02  | -131.036       | 0.1433| 2122    | 483.71   | 254.975       | 0.1404|
| 6s6p5d5f5g  | 11932 | 590.45  | -146.084       | 0.1286| 16961   | 507.74   | 280.708       | 0.1276|
| 7s7p6d6f6g6h| 48574 | 610.80  | -150.997       | 0.1244| 71610   | 529.87   | 290.233       | 0.1234|
| 8s8p7d7f7g7h| 128264| 613.17  | -152.617       | 0.1231| 191495 | 532.46   | 292.535       | 0.1220|
| 9s9p8d8f8g8h| 267998| 617.02  | -154.391       | 0.1217| 402586 | 536.97   | 296.441       | 0.1208|
| 10s10p9d9f9g9h| 484772| 618.47  | -154.071       | 0.1219| 730853 | 537.48   | 294.773       | 0.1215|

Expt. | 609.086(2)\(^a\) | 531.987(5)\(^b\)

\(^a\)Byron et al [17].
\(^b\)Lurio [20].

Table VI. A (MHz), B/Q (MHz/b), and Q (b) values calculated with method M1 (see section [IV E]), as functions of the increasing active space for the 4s4p \(^3\Pi^o\) and 4s4p \(^3\Pi^o\) states in \(^{67}\)Zn \(1^+\), \(I^+ = 5/2^-\) and \(\mu_{\text{expt}} = 0.875479(9) \mu_N\). The Q-values are extracted from the relation \(Q = B_{\text{expt}}/(B/Q)\), where the experimental values are \(B_{\text{expt}}(\Pi^o) = -18.782(8)\) MHz and \(B_{\text{expt}}(\Pi^o) = 35.806(5)\) MHz.

The corresponding results are presented in Table VI. The MCDHF-SrDT-SP-Liu active space expansion used in [17] optimised simultaneously the \(\Pi^o\) and \(\Pi^o\) levels. Therefore the A, B/Q and Q results obtained in the present work slightly differ from those reported in [17] for \(J = 1\).

The second approach (M2) considered single and restricted double substitutions performed on a single-reference (SR) set (MCDHF-SrD-SR). The VV correlation model only allows SD substitutions from valence orbitals, while the VV+C

(1) Run a calculation using SR set consisting of CSF(s) of the form \(2s^22p^63s^23p^63d^{10}1s4p\) \(J^\Pi\).
(2) Keep the orbitals fixed from step (1), and optimise an orbital basis layer by layer up to an active space equal to \(11s11p10d10f10g10h\), described by CSFs with the \(J^\Pi\) symmetry of the state. These CSFs are obtained by SrD-SR substitutions (at most one substitution from the \(2s^22p^63s^23p^63d^{10}\) core).
(3) Perform a CI calculation on the CSFs expansion with the \(J^\Pi\) symmetry of the state, describing VV, CV and CC correlation obtained by SD-SR substitutions to the orbital basis from step (2).
(4) Add a correction to the A and EFG values from step (3), accounting for triple (t) substitutions and obtained from a non-relativistic MCHF computation.

Step (3), allowing the inclusion of core-core correlation through CI, and step (4) specific to hyperfine constants, were not considered in [17]. The corresponding results are denoted MCDHF-SrD-SR/CI-SD-SR+t(MCHF) in...
Table VII. MR configurations for the $4s4p\ ^3P_0$ and $4s4p\ ^3P_2$ states in $^{67}$Zn. The MR-cutoff value, $\varepsilon_{MR}$, determines the set of CSFs in the MR space. $N_{CSFs}$ is the number of CSFs describing each MR space.

| State | $\varepsilon_{MR}$ | MR configurations | $N_{CSFs}$ |
|-------|------------------|-------------------|-------------|
| 4s4p$\ ^3P_0$ | 0.01 | $[\text{Ar}]3d^{10}\{4s4p, 4p4d\}, [\text{Ar}]3d^9\{4s4p4d, 4s4d4f, 4p^2, 4p^3, 4f, 4s^24p\}$ | 31 |
| 4s4p$\ ^3P_2$ | 0.01 | $[\text{Ar}]3d^{10}\{4s4p, 4p4d\}, [\text{Ar}]3d^9\{4s4p4d, 4s4d4f, 4p^2, 4f, 4s^24p\}$ | 31 |

Table VIII. $A$ (MHz), $B/Q$ (MHz/b), and $Q$ (b) values calculated with methods M2 (upper part) and M3 (lower part) - see section [IV.E], as functions of the increasing active space for the $4s4p\ ^3P_0$ and $4s4p\ ^3P_2$ states in $^{67}$Zn. $I^+ = 5/2^-$ and $\mu_{exp} = 0.875479(9)\mu_N$. The $Q$-values are extracted from the relation $Q = B_{exp}/EFG$, where the experimental values are $B_{exp}(^3P_1) = -18.782(8)^a$ MHz and $B_{exp}(^3P_2) = 35.806(5)^b$ MHz.

| Active space | $N_{CSFs}$ | $A$ (MHz) | $B/Q$ (MHz/b) | $Q$ (b) |
|--------------|-----------|-----------|---------------|--------|
| 4s4p3d (DHF) | 2 | 475.27 | -100.43 | 0.1870 |
|              | MCDHF-SrD-SR (VV+CV) |               |             |        |
| 5s5p4d4f     | 1454 | 554.21 | -129.614 | 0.1449 | 2108 | 483.74 | 253.875 | 0.1410 |
| 6s6p5d5f5g   | 5857 | 590.45 | -145.650 | 0.1290 | 5790 | 509.32 | 280.362 | 0.1277 |
| 7s7p6d6f6g6h | 14381 | 617.54 | -152.198 | 0.1234 | 14467 | 534.86 | 292.975 | 0.1222 |
| 8s8p7d7f7g7h | 27052 | 627.21 | -157.702 | 0.1191 | 27426 | 542.93 | 303.008 | 0.1182 |
| 9s9p8d8f8g8h | 43870 | 627.36 | -159.448 | 0.1178 | 44667 | 547.10 | 305.735 | 0.1171 |
| 10s10p9d9f9g9h | 64835 | 631.06 | -159.859 | 0.1175 | 66190 | 550.27 | 306.528 | 0.1168 |
| 11s11p10d10f10g10h | 89947 | 632.63 | -159.987 | 0.1174 | 91995 | 550.84 | 306.521 | 0.1168 |
| + 1s open    | 95907 | 638.82 | -159.974 | 0.1174 | 97610 | 556.64 | 306.592 | 0.1168 |
|              | CI-SD-DR (VV+CC) |               |             |        |
|              | 1236101 | 546.09 | -129.845 | 0.1446 | 1243611 | 479.14 | 249.303 | 0.1436 |
| + t(MCHF) 9s9p8d8f8g | 578.05 | -145.095 | 0.1294 | 506.03 | 279.803 | 0.1280 |

| Active space | $N_{CSFs}$ | $A$ (MHz) | $B/Q$ (MHz/b) | $Q$ (b) |
|--------------|-----------|-----------|---------------|--------|
| 4s4p3d (MR)  | 903 | 541.40 | -112.267 | 0.1673 | 1231 | 414.61 | 198.252 | 0.1806 |
|              | MCDHF-SrD-MR (VV+CV) |               |             |        |
| 6s6p5d5f5g   | 12015 | 595.05 | -148.023 | 0.1269 | 16521 | 511.98 | 284.444 | 0.1259 |
| 7s7p6d6f6g6h | 32172 | 621.07 | -153.354 | 0.1225 | 45722 | 535.07 | 294.919 | 0.1214 |
| 8s8p7d7f7g7h | 62730 | 631.14 | -159.206 | 0.1180 | 90401 | 544.19 | 306.010 | 0.1170 |
| 9s9p8d8f8g8h | 103689 | 630.28 | -160.573 | 0.1170 | 150558 | 548.36 | 308.353 | 0.1161 |
| 10s10p9d9f9g9h | 155049 | 633.80 | -160.991 | 0.1167 | 226193 | 551.29 | 300.010 | 0.1159 |
| 11s11p10d10f10g10h | 216810 | 635.32 | -161.806 | 0.1167 | 317306 | 551.96 | 308.985 | 0.1159 |
| + 1s open    | 232877 | 641.60 | -161.025 | 0.1167 | 339230 | 557.60 | 300.005 | 0.1159 |

| Multireference calculations |
|-----------------------------|
| Expt.                       |
| 609.086(2)$^a$              |
| 531.987(5)$^b$              |

$^a$Byron et al.$^a$.

$^b$Lario.$^b$.

the upper part of Table VIII. The final line shows that opening 1s brings a non-negligible contribution to the $A$-values, which become approximately 6 MHz larger for both states. This approach is very similar to the method described in section [V.A]. However, the advantage of the M2 calculations is in the simultaneous generation of both $4s4p\ ^3P_2$ and $4s4p\ ^3P_1$ states, at the Optimal Level (OL) of the variational functional. For $4s4p\ ^3P_2$, the results are indeed very similar to the MCDHF-SR-OL-1+t(MCHF) values already reported in Table IX and discussed in section [V.A] dedicated to that level. For these M2 results, only the $4s4p\ ^3P^2$ values are therefore reported in the final summary in Table X.

The third approach (M3) considered SrD substitutions performed on a multi-reference (MR) set. The latter contains the CSFs that have large expansion coefficients and account for the major correlation effects. For building this MR set, a MCDHF calculation is first performed using a CSF expansion based on SrDT substitutions from the 3d and the occupied valence orbitals towards the 5s, 5p and $n = 4$ valence orbitals (maximum of one hole in the 3d orbital).
Due to limited computer resources, such an MR set would be too large for subsequent calculations. Hence, only the CSFs whose expansion coefficients are, in absolute value, larger than a given MR cutoff are kept, i.e., |c_ρ| > ε_{MR}. The resulting MR sets are outlined in Tables VII, VIII and IX. Only orbitals occupied in the single configuration DHF approximation are treated as spectroscopic, and the occupied reference orbitals are kept frozen in the subsequent calculations.

The M3 procedure consists in the following sequence:

(1) Perform a calculation using an MR set consisting of CSFs with two forms:
\[ 2s^22p^63s^23p^63d^{10}nln'l' J^{\Pi} \] with \( n, n' = 4 \) and \( l, l' = s, p, d, f + 5s \) and \( 5p \), and
\[ 2s^22p^63s^23p^63d^{10}nln'l'n''l'' J^{\Pi} \] with \( n, n', n'' = 4 \) and \( l, l', l'' = s, p, d, f + 5s \) and \( 5p \). These CSFs account for a fair amount of the VV correlation, and for CV correlations between the 3d core orbital and the 5s, 5p and \( n = 4 \) valence orbitals. Keep in the MR set the CSF whose expansion coefficients are, in absolute value, larger than \( \epsilon_{MR} = 0.01 \).

(2) Keep the orbitals fixed from step (1), and optimise an orbital basis layer by layer up to an active space equal to 1s11p10d10f10g10h, described by CSFs with the \( J^{\Pi} \) symmetry of the state. These CSFs are obtained by SrD-MR substitutions (at most one substitution from the 2s^22p^63s^23p^63d^{10} \) core). As observed for M2, spin-polarisation of the 1s shell is not negligible. The results of these calculations are presented in the lower part of Tables VIII and IX and labeled MCDHF-SrD-MR in Table IX.

V. EVALUATION OF THE NUCLEAR QUADRUPOLE MOMENT OF \( ^{67}\text{Zn} \)

| State | \( A \) (MHz) | \( B/Q \) (MHz/b) | \( Q \) (b) | Method |
|-------|--------------|-----------------|--------|--------|
| 4s4p \( \text{3P}_o^0 \) | 634.802 | -165.058 | 0.113790 | MCHF-SD(T) |
| 605.9 | -150.7 | 0.1247 | MCDHF-SrD-SP-Liu |
| 618.47 | -154.071 | 0.121905 | MCDHF-SrD-SP |
| 641.60 | -161.025 | 0.116640 | MCDHF-SrD-MR |
| 578.05 | -145.095 | 0.129446 | MCDHF-SrD-SP-Liu |
| 577.886 | -142.579 | 0.131730 | MCDHF-SrD-OL4+t(MCHF) |
| 609.086(2)^a | 670.387 | 317.254 | 0.121862 | MCHF-SD(T) |
| 557.48 | 294.773 | 0.121470 | MCDHF-SrD-SP |
| 557.60 | 309.005 | 0.115875 | MCDHF-SrD-MR |
| 509.861 | 281.799 | 0.127062 | MCDHF-SrD-OL4+t(MCHF) |
| 513.200 | 271.989 | 0.131645 | MCDHF-SrD-OL4+t(MCHF) |
| 531.987b | 531.987b | | | \( ^{67}\text{Zn} \) |

aByron et al. \[7\]

\( ^{67}\text{Zn} \). We report in the present section eleven calculated \( Q \) (and \( A \)) values, obtained with the following approaches:

- MCHF-SD/CI-SDT+DHF/HF correction \( (3\text{P}_o^0, 2 \) levels), under label MCHF-SD(T), - see sections III A and III E
- MCDHF-SrD-SP-Liu: from Liu et al. \[47\] (only \( 3\text{P}_o^0 \) level), - see section IV D
- MCDHF-SrD-SP: calculation based on Liu et al.’s strategy \( (3\text{P}_o^0, 2 \) levels) - see method M1 in section IV E
- MCDHF-SrD-SP: single-reference + MCHF triples correction \( (3\text{P}_o^0 \) level \[50\] - see method M2 in section IV E
- MCDHF-SrD-MR: multi-reference \( (3\text{P}_o^0, 2 \) levels), - see method M3 in section IV E
- MCDHF-SD-OL1+t(MCHF): OL1 \( (J = 2 \) single reference + MCHF triples correction (only \( 3\text{P}_o^0 \) level) - see section IV A
- MCDHF-SD-OL4+t(MCHF): OL4 \( (J = 0, 1, 1, 2 \) single reference + MCHF triples correction \( (3\text{P}_o^0, 2 \) levels) - see section IV C
where the shorthand notations above represent the following computational methods:

**MCHF**  MultiConfiguration Hartree-Fock (non-relativistic)

**CI-SDT** Configuration Interaction Hartree-Fock (non-relativistic)

**DHF/HF** multiplicative relativistic correction described in section [III]

**MCDHF** MultiConfiguration Dirac-Hartree-Fock (relativistic)

**SD** Single and Double substitutions in the SCF process

**SrD** Single and restricted Double substitutions in the SCF process

**t(MCHF)** additive correction for triple substitutions estimated from MCHF calculation (see section [IVB]).

**SP** Spin Polarisation (method described in Liu et al [47])

**SR** Single-Reference

**MR** Multi-Reference

**OL1** Optimal Level calculation with optimisation on one level (J=2)

**OL4** Optimal Level calculation with optimisation on four levels

We adopted a convention used by chemists, where T in parentheses (T) implies that triple substitutions are included in a post-SCF approach (Møller-Plesset or CI or another method). In our notation t(MCHF) means an additive correction for triple substitutions evaluated with the ATSP code [30]. The calculated EFGs were combined with the measured B values for the 4s4p 3P  \text{ state} \[ \text{[8]}; \text{ and for the 4s4p 3P}_2 \text{ state} \[ \text{[8]} \text{ of the neutral Zn atom, to yield eleven calculated values of } Q^{(67}\text{Zn)} \text{, presented in the fourth column of Table IX.}

Although these eleven values do not represent the sample in the statistical sense, the scatter of the values gives us an information about the dependence of the calculated values of EFG on the choice of the method of calculation, and provides a basis for an estimate of the error bar for the determination of the quadrupole moment \(Q^{(67}\text{Zn)}\). We assumed that the error bar should at least overlap with all eleven results. For computing the final value of \(Q^{(67}\text{Zn)}\) one might consider taking the average of the results of the eleven calculations \((Q = 0.1208 \text{ b})\), or the median value thereof \((Q = 0.1223 \text{ b})\); both methods yield very close results, the difference being negligible compared to the error bar resulting from the arguments presented above. Assuming the above procedures and estimates, we arrived at \(Q^{(67}\text{Zn)} = 0.12 \pm 0.01 \text{ b}\), obtained from the 4s4p 3P \text{ states} of zinc. The relative error bar \((8 \%)\) is of the same order as the error bar \((10 \% )\) associated with the previous standard value, \(Q^{(67}\text{Zn)} = 0.150(0.015) \text{ b}\), quoted by Stone \[3\] and by Pyykkö \[3\], and based on measurements performed by Laulainen and McDermott \[5\], but the \(Q^{(67}\text{Zn)}\) value itself is now downshifted by 20 \%. On the other hand, our value is in very good agreement with \(Q^{(67}\text{Zn)} = 0.125(5) \text{ b}\), of Haas et al \[10\], who used a hybrid Density Functional Theory approach.

An inspection of the results presented in the Table IX leads to the conclusions, that the multi-reference MCDHF-SrD-MR calculations overshoot the values of the magnetic dipole hyperfine constant \(A\) by about 20 – 25 MHz, while single reference MCDHF-SD-SR-OL1+t(MCHF) and MCDHF-SD-SR-OL4+t(MCHF) results for \(A\) are too small by nearly the same amount. The best agreement with the experimental \(A\) value was obtained in the calculation of Liu et al [17], which is understandable, since, as mentioned in section [IVD], the main objective of Liu et al was the magnetic dipole hyperfine structure, therefore they carefully treated the spin-polarization effects. Incidentally, the nuclear quadrupole moment \(Q^{(67}\text{Zn)}\) calculated from their EFG value is in fact quite close to the median value \(Q = 0.1223 \text{ b}\), mentioned above. The abovementioned discrepancies may be assumed as another tool to estimate the error bar for determination of \(Q\). The error bar estimate from \(A\) is of the order of 4 \%, smaller than that obtained from the sample of eleven values. We assumed the larger of the two error bar estimates, and finally we propose

\[
Q^{(67}\text{Zn)} = 0.122(10) \text{ b}.
\]  

This value has been utilized to extract electric quadrupole moments of odd-A nuclei in the range \(A=63–79\) across the isotopic chain of zinc, following the measurements of electromagnetic moments by Wraith et al [10].

**VI. CONCLUSIONS**

The calculations of hyperfine shifts are inherently inaccurate (or accurate to a few percent). We do have computational tools to estimate accuracy of expectation values \([29, 44, 45]\), but they are more expensive computationally than the calculations of expectation values themselves. Therefore we rarely *compute* accuracy, because normally we compute the expectation values themselves at the limits of our computing resources, and this does not leave enough resources for computing accuracy. Then we *estimate* the accuracy. Estimating the accuracy of a single calculation of an EFG for a single level is in fact not much more than guesswork. If magnetic dipole hyperfine coupling constant \(A\) is known (i.e. measured \(A_{\text{expt}}\) exists) then accuracy of EFG is sometimes assumed from the difference \(A_{\text{expt}} - A_{\text{calc}}\). Another method is to carry out calculations with several different methods and evaluate the accuracy from differences between the results obtained with those methods. In the present paper the
The latter approach yields the larger error bar. The optimal method would be to carry out measurements and calculations for several levels. From this point of view having hyperfine structure data for several levels would give us a benefit of more tools to estimate accuracy. Combined with measured values of \( A \) and \( B \) for these levels, we would obtain a statistical sample for both \( A \) and \( EFG \). It is not exactly statistical because calculations are in principle not fully independent, but several levels is still better than one or two levels.

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[49] The original notation adopted in [48] was (SrDT-SS) where the ‘SS’ stands for “single s substitutions” describing spin-polarisation (SP) of the core s subshells.

[50] The corresponding $^3P_2^o$ results are not reported in Table IX since the strategy is similar to the MCDHF-SD-OL1+t(MCHF) method (see sectionIVA), with consistent results.