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Study of the Hyperfine Structure of the Low-Lying Ca II and Ra I–II Levels: Applying the MCDHF Models Developed for Ba I–II

Lorenzo Nezosi ¹ , Patrick Palmeri ^{1,*}  and Per Jönsson ² 

¹ Physique Atomique et Astrophysique, Université de Mons—UMONS, B-7000 Mons, Belgium; lorenzo.nezosi@student.umons.ac.be

² Materials Science and Applied Mathematics, Malmö University, SE-205 06 Malmö, Sweden; per.jonsson@mau.se

* Correspondence: patrick.palmeri@umons.ac.be

Abstract

Building on our previous multi-configuration Dirac–Hartree–Fock (MCDHF) computational strategies tailored for the hyperfine structure (HFS) of low-lying levels in one-valence electron Sr II and Ba II ions and in two-valence electrons in a Ba I atom, we successfully extend these methodologies along the alkaline-earth elements to the lighter Ca II and heavier Ra I–II ions. MCDHF-recommended HFS constants, along with their uncertainty estimates, are reported for the first time and critically discussed. Where applicable, the Bohr–Weisskopf correction is applied to the HFS constants, and its effects are analyzed. This is particularly valuable for cases where no measurement is available such as for the $[Rn]6d\ ^2D_{3/2,5/2}$ levels in $^{223,225}\text{Ra II}$, for the $[Rn]7s6d\ ^3D_{1,2,3}$ and $^1D_2$ levels in $^{223}\text{Ra I}$, for the $[Rn]7s6d\ ^3D_{2,3}$ and $^1D_2$ levels in $^{223}\text{Ra I}$, and for the $[Rn]7s7p\ ^3P_2^o$ level in $^{225}\text{Ra I}$. In all cases, our MCDHF values agree with the ones found in the literature within our error bars. For the $^2D_{5/2}$ levels in Ca II and Ra II, the discrepancies with the experiment observed in Sr II and Ba II for the HFS A constant are not seen.

Keywords: atomic structure; hyperfine structure; MCDHF method; GRASP package; calcium; radium

1. Introduction

Alkaline-earth metals from Mg to Ra, particularly in their singly ionized forms (e.g., Ca II and Ra II), are ideal for high-precision calculations and measurements in astrophysics and metrology due to their simple electronic structures [1]. Neutral radium (Ra I) is also crucial for beyond-standard-model (BSM) physics.

In astrophysics, Ca II infrared triplet lines (8498, 8542, and 8665 Å) serve as key calcium abundance indicators in stellar atmospheres, detectable even at extremely low metallicities ($[\text{Fe}/\text{H}] \leq -3.0$) [2], enabling studies of metal-poor stars [3] and galactic chemical evolution [4]. Ra II UV–Vis lines (3814, 4682, and 6705 Å) can be used to probe r-process nucleosynthesis, as Ra is produced exclusively by neutron capture in neutron-rich environments where the s-process ends at bismuth ($Z = 83$) [5,6]. Its likely production in neutron star mergers makes Ra’s detection in kilonova spectra a direct indicator of such events [7].

In fundamental physics, Ca II and Ra II are crucial for frequency standards and precision measurements. Quadrupole moments in metastable atomic ions introduce systematic



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energy shifts in such systems [8]. High theoretical precision ($<1\%$) is required for meaningful comparisons with parity non-conservation (PNC) experiments [9]. While heavier atoms like Ra offer more favorable PNC conditions, lighter elements such as Ca II serve as essential test cases for validating theoretical methods before tackling heavier systems.

Neutral radium (Ra I) offers unique opportunities for fundamental physics tests. The search for a permanent electron electric dipole moment (EDM) is among the most stringent BSM tests, with polar molecules like RaF serving as exceptionally sensitive probes due to their large internal electric fields and Ra's heavy, octupole-deformed nucleus [10]. Precise ab initio calculations for Ra are essential, providing wavefunctions needed to interpret molecular EDM measurements and constrain CP -violating interactions. Multi-configuration Dirac–Hartree–Fock (MCDHF) calculations for Ra I address this by capturing critical enhancement mechanisms, notably the $[Rn]7s7p\ ^3P_1^o$ and $[Rn]7s6d\ ^3D_2$ levels, separated by only 5.41 cm^{-1} . Combined with Ra high-atomic-number ($Z = 88$) and nuclear octupole deformation, this yields P - and T -reversal-odd effect enhancements up to five orders of magnitude greater than in other systems [11,12]. Electron correlation effects, which dominate the atomic EDM signal, are systematically accounted for in combination of MCDHF and relativistic configuration interaction (MCDHF + RCI) calculations. Ra II, with its 8230 Å clock transition and narrow linewidth, is also a candidate for optical atomic clocks. The low-cost diode lasers required for Ra II, relative to expensive UV lasers, make it attractive for both laboratory and transportable applications [13].

Accounting for the hyperfine structure (HFS) of the levels is essential. In astrophysics and atomic clock applications, HFS broadening and the resulting asymmetries in line profiles introduce inaccuracies in line positions and strengths. For BSM research, HFS constants enable extraction of electric field gradients that can be used to calibrate molecular theory against high-resolution RaF spectroscopy at ISOLDE (CERN), where 14 excited states have been characterized with 99.6% theory–experiment agreement and laser-coolable transitions have been identified [10]. Accurate ab initio atomic wavefunctions and correlation energies could enhance RaF's sensitivity to e-EDM searches, wherein experimental data are scarce.

For Ca II and Ra I–II, the HFSs of certain levels remain experimentally unstudied, including the $[Rn]6d\ ^2D_{3/2,5/2}$ levels in $^{223,225}\text{Ra II}$ and the $[Rn]7s6d\ ^3D_{1,2,3}$ and $[Rn]7s7p\ ^3P_2^o$ levels in Ra I. While extensive MCDHF calculations are available for Mg II [14], Ca II [8], Sr II, and Ba II [15], comprehensive calculations for Ra II remain limited.

In this work, we present theoretical calculations of magnetic dipole (A) and electric quadrupole (B) hyperfine structure constants for low-lying levels of Ca II and Ra I–II. Using the MCDHF method with Relativistic Configuration Interaction (RCI) within the GRASP framework [16], we extend our previously validated computational strategies from Sr II and Ba I–II [15] to the lighter Ca II and the heavier Ra I–II systems, employing, for the first time, a natural orbital basis transformation [17] approach for HFS calculations in heavy Ra I–II. Particular attention is paid to the Bohr–Weisskopf (BW) effect, which is systematically accounted for in our calculations. By providing theoretical values for levels where experimental data are unavailable and demonstrating agreement with existing measurements within our uncertainty estimates, we enable refined tests of atomic structure and nuclear effects. These results offer essential theoretical input for astrophysical abundance studies via Ca II infrared triplet lines, precision metrology using Ra II clock transitions, and searches for physics beyond the standard model through Ra I molecular and atomic electric dipole moment investigations.

This paper extends the work presented in the poster at the 1st International Online Conference on Atoms (IOCAT2026), held 29–30 January 2026, titled “Study of the hyperfine structure of Ba-like elements: an MCDHF approach for modeling the first excited levels” [15]. It is organized as follows: Section 2 describes the MCDHF and RCI methods

for calculating HFS constants and provides details about the transformation into natural orbitals. Section 3 presents Ca II calculations to validate the theoretical method from the earlier Sr II/Ba II study [15], followed by Ra II and Ra I HFS studies. Section 4 concludes with an outlook.

2. Method and Computational Details

2.1. The MCDHF Method

The multi-configuration Dirac–Hartree–Fock (MCDHF) method, described in [18], is a fully relativistic approach to atomic structure calculation. It is particularly well suited for the study of medium- and high- Z elements as well as highly charged ions. Within this framework, an atomic state characterized by the quantum numbers Γ , J , M_J , and parity π is represented by an Atomic State Function (ASF), denoted by $\Psi(\Gamma\pi JM_J)$. The ASF is expressed as a linear combination of Configuration State Functions (CSFs) $\Phi(\gamma_i\pi JM_J)$,

$$\Psi(\Gamma\pi JM_J) = \sum_{i=1}^{N_{\text{CSFs}}} c_i^{\Gamma\pi J} \Phi(\gamma_i\pi JM_J), \quad (1)$$

where the label γ_i specifies the electronic configuration, the angular momentum coupling scheme, and any additional quantum numbers required to uniquely identify the CSF. The expansion coefficients $\{c_i^{\Gamma\pi J}\}$, together with the corresponding atomic-state energy E , are obtained by solving the secular equation

$$Hc = Ec, \quad (2)$$

where H denotes the Hamiltonian matrix.

Applying the variational principle to the total energy functional leads to the MCDHF equations, a set of coupled integro-differential equations that are solved self-consistently for the radial components of the one-electron spin-orbitals.

Subsequent Relativistic Configuration Interaction (RCI) calculations are performed by solving Equation (2) using an enlarged CSF expansion, if desired, while keeping the orbitals obtained from the preceding MCDHF optimization fixed. At this stage, additional relativistic contributions may be incorporated into the Hamiltonian, including the Breit interaction and quantum electrodynamic (QED) corrections, thereby improving the accuracy of the calculated atomic properties.

2.2. Natural Orbitals

Due to numerical convergence challenges, and to reduce computation time, the MCDHF method employs a layer-by-layer (LBL) [19] approach in which only the newly introduced orbitals for the layer considered are optimized while the remaining ones are kept frozen. Therefore, the frozen orbitals, especially the spectroscopic reference orbitals, cannot react to the addition of the newly introduced layer. Natural orbitals (NOs) provide an alternative orbital basis, first introduced in quantum chemistry, that addresses this limitation. They modify the orbitals of the reference states in a way that partly captures the response to the new layers. The NOs are obtained by diagonalizing the density matrix, which provides a more natural description of the electron correlation. One of the first applications to atomic physics was performed by Lindgren et al. [20] in order to evaluate hyperfine interactions in alkali atoms in many-body perturbation calculations. Schiffmann et al. [17] developed the NO formalism in the MCDHF framework and applied it in the hyperfine structure calculation of Na I [21], exhibiting results in better agreement with experiments than those obtained using the traditional LBL approach. Transformation into NOs was also found

to considerably improve the hyperfine interaction constants and transition rates in other systems, e.g., In I [22].

For each value of κ , the relativistic angular quantum number, the density matrix is built as follows:

$$\rho^\kappa = \rho_{nn'}^\kappa, \quad (3)$$

with

$$\rho_{nn'}^\kappa = \sum_{ij} c_i^* v_{nn'}^{ij,\kappa} c_j, \quad (4)$$

where $v_{nn'\kappa}^{ij}$ denotes the spin-angular coefficients. The NOs $\tilde{\phi} = \tilde{\phi}_{n\kappa}$ are obtained from the eigenvectors $\mathbf{U}^\kappa$ of the density matrix diagonalizing it:

$$\mathbf{U}^{\kappa\dagger} \rho^\kappa \mathbf{U}^\kappa = \tilde{\rho}^\kappa, \quad (5)$$

$$\tilde{\phi}^\kappa = \phi^\kappa \mathbf{U}^\kappa, \quad (6)$$

where the eigenvalues are the occupation numbers $\eta_{n'}^\kappa$ of the NOs

$$\sum_\kappa \sum_{n'} \eta_{n'}^\kappa = N_e, \quad 0 \leq \eta_{n'}^\kappa \leq 1, \quad (7)$$

with N_e denoting the number of electrons. The large and small components of the radial function of the NOs are therefore

$$\begin{aligned} \tilde{P}_{n'\kappa}(r) &= \sum_n u_{nn'}^\kappa P_{n\kappa}(r), \\ \tilde{Q}_{n'\kappa}(r) &= \sum_n u_{nn'}^\kappa Q_{n\kappa}(r), \end{aligned} \quad (8)$$

with the coefficients $u_{nn'}^\kappa$ the matrix elements of the unitary matrix $\mathbf{U}^\kappa$ in Equation (5), and $P_{n\kappa}(r)$ and $Q_{n\kappa}(r)$ —the large and the small components of the radial function in the MCDHF equations [18].

2.3. Hyperfine Structure

The hyperfine structure (HFS) of an atomic fine-structure level arises from the interaction between the atomic electrons and the electromagnetic multipole moments of the nucleus. This interaction can be described through the multipole expansion

$$H_{\text{HFS}} = \sum_{k \geq 1} \mathbf{T}^{(k)} \cdot \mathbf{M}^{(k)}, \quad (9)$$

where $\mathbf{T}^{(k)}$ and $\mathbf{M}^{(k)}$ are spherical tensor operators of rank k acting in the electronic and nuclear spaces, respectively. The terms corresponding to $k = 1$ and $k = 2$ represent the magnetic dipole (M1) and electric quadrupole (E2) interactions.

For an atom containing N_e electrons, the electronic tensor operators are expressed as

$$\mathbf{T}^{(1)} = \sum_{j=1}^{N_e} \mathbf{t}^{(1)}(j) = \sum_{j=1}^{N_e} -i\sqrt{2}\alpha r_j^{-2} (\boldsymbol{\alpha} j \cdot \mathbf{C}^{(1)}(\theta_j, \varphi_j)), \quad (10)$$

$$\mathbf{T}^{(2)} = \sum_{j=1}^{N_e} \mathbf{t}^{(2)}(j) = \sum_{j=1}^{N_e} -r_j^{-3} \mathbf{C}^{(2)}(\theta_j, \varphi_j), \quad (11)$$

where $i^2 = -1$, α is the fine-structure constant, and $\boldsymbol{\alpha}$ denotes the vector of Dirac matrices related to the Pauli matrices.

The nuclear magnetic dipole moment, denoted by μ_I , and the electric quadrupole moment, denoted by Q , are determined from the matrix elements of the nuclear tensor operators,

$$\mu_I = \langle II | M^{(1)} | II \rangle, \quad (12)$$

$$Q = 2 \langle II | M^{(2)} | II \rangle, \quad (13)$$

where $|II\rangle$ denotes the nuclear state with maximal spin projection— $M_I = I$ [23]. The operators $M^{(1)}$ and $M^{(2)}$ correspond to the magnetic dipole and electric quadrupole moments of the nucleus, respectively.

Since the hyperfine interaction is generally much weaker than the fine-structure splitting, it can be treated within first-order perturbation theory. The corresponding hyperfine energy shift is given by

$$E_{\text{HFS}} = \langle \Gamma J I F M_F | H_{\text{HFS}} | \Gamma J I F M_F \rangle = E_{\text{HFS}}^{\text{M1}} + E_{\text{HFS}}^{\text{E2}}, \quad (14)$$

where $|\Gamma J I F M_F\rangle$ is the zeroth-order wave function of the coupled electron–nucleus system [19], with F and M_F denoting the total hyperfine angular momentum and its projection on the quantization axis, respectively.

One can express the hyperfine energy shifts in terms of the magnetic dipole (A) and electric quadrupole (B) hyperfine constants:

$$E_{\text{HFS}}^{\text{M1}} = \frac{1}{2} A_{\Gamma J} K, \quad (15)$$

$$E_{\text{HFS}}^{\text{E2}} = B_{\Gamma J} \frac{\frac{3}{4} K(K+1) - I(I+1)J(J+1)}{2I(2I-1)J(2J-1)}, \quad (16)$$

where

$$A_{\Gamma J} = \frac{\mu_I}{I} \frac{1}{\sqrt{J(J+1)(2J+1)}} \langle \Gamma J || \mathbf{T}^{(1)} || \Gamma J \rangle, \quad (17)$$

$$B_{\Gamma J} = 2Q \sqrt{\frac{J(2J-1)}{(J+1)(2J+1)(2J+3)}} \langle \Gamma J || \mathbf{T}^{(2)} || \Gamma J \rangle, \quad (18)$$

and

$$K = F(F+1) - J(J+1) - I(I+1). \quad (19)$$

The reduced matrix elements that appear in Equations (17) and (18) are evaluated with the atomic state functions (ASFs) defined in Equation (1).

2.4. Computational Details

The MCDHF calculations and the evaluation of the hyperfine structure (HFS) constants were performed by employing GRASP2018 [16,24]. To improve computational efficiency, the GRASPG package recently developed by Si et al. [25], which exploits Configuration State Function Generators (CSFGs), was used for the RCI calculations.

Following the methodology introduced by Papoulia et al. [26], the final HFS constants are reported as recommended values derived from the largest RCI calculations obtained with different orbital optimization strategies. The results of these calculations are treated as independent estimates, allowing the determination of both an average value and a standard deviation for each constant. This procedure provides a reliable prediction of the HFS constants together with a quantitative uncertainty assessment, which is particularly valuable in the absence of experimental data. In what follows, we will express our recommended values as $\mu \pm 2\sigma$, which corresponds to a 95% confidence interval.

3. Results and Discussion

3.1. Ca II

Calcium (Ca) has 26 known isotopes, of which 5 are stable [27]. ^{43}Ca has an abundance of only 0.135% but is the only stable isotope that has a hyperfine structure due to its non-zero nuclear spin ($I = 7/2$). The levels of interest in ^{43}Ca II are the even $[\text{Ar}]4s\ ^2S_{1/2}$ and $[\text{Ar}]3d\ ^2D_{3/2,5/2}$ as well as the odd $[\text{Ar}]4p\ ^2P_{1/2,3/2}^o$.

Due to its relatively simple electronic structure, ^{43}Ca II has already been studied in depth theoretically by Silverans et al. [28] and Yu et al. [29] using the Relativistic Many-Body Perturbation Theory (RMBPT) approach, Itano [8] with the MCDHF method, Chakraborty et al. [30] with the Relativistic Coupled Cluster (RCC) method, and Safronova et al. [31] using the relativistic all-order method, where all single, double, and partial-triple (SDpT) excitations of the wavefunctions are included to all orders of perturbation theory. Goble et al. [9] and Nortershauser et al. [1] performed optical spectroscopy experiments using hollow cathode discharge and fast ion beam collinear laser spectroscopy, whereas Garcia Ruiz et al. [32] adopted bunched-beam collinear laser spectroscopy.

The MCDHF method used in this paper relies on the AS [19] and LBL [24] approaches, which enable the optimization of only a subset of orbitals in each calculation step. For example, for the ground $^2S_{1/2}$ level, an initial Dirac–Hartree–Fock (DHF) layer is considered. This layer is built using the $\{4s, 3p\}$ spectroscopic orbitals in nonrelativistic notation, where the highest n quantum number is quoted for each l -symmetry, and no electron correlation is included at this stage. The ASs are then expanded with correlation orbitals up to $l_{\text{max}} = 4$ (g -orbitals) to directly apply the Ba/Sr model [15] and achieve high precision in the calculations [33]. For each AS given in Table 1, only the newly introduced orbitals are optimized, while the remaining orbitals are kept frozen. The mixing coefficients of the ASFs are then determined, and Quantum Electrodynamics (QED) corrections are included during the RCI step. Finally, the HFS constants are computed.

Table 1. Considered active sets used for the levels studied in ^{43}Ca II.

Correlation Layer	$^2S_{1/2}$	$^2D_{3/2,5/2}$	$^2P_{1/2,3/2}^o$
DHF	$\{4s, 3p\}$	$\{3s, 3p, 3d\}$	$\{3s, 4p\}$
AS1	$\{5s, 4p, 3d\}$	$\{4s, 4p, 4d, 4f\}$	$\{4s, 5p, 3d\}$
AS2	$\{6s, 5p, 4d, 4f\}$	$\{5s, 5p, 5d, 5f, 5g\}$	$\{5s, 6p, 4d, 4f\}$
AS3	$\{7s, 6p, 5d, 5f, 5g\}$	$\{6s, 6p, 6d, 6f, 6g\}$	$\{6s, 7p, 5d, 5f, 5g\}$
AS4	$\{8s, 7p, 6d, 6f, 6g\}$	$\{7s, 7p, 7d, 7f, 7g\}$	$\{7s, 8p, 6d, 6f, 6g\}$
AS5	$\{9s, 8p, 7d, 7f, 7g\}$	$\{8s, 8p, 8d, 8f, 8g\}$	$\{8s, 9p, 7d, 7f, 7g\}$
AS6	$\{10s, 9p, 8d, 8f, 8g\}$	$\{9s, 9p, 9d, 9f, 9g\}$	$\{9s, 10p, 8d, 8f, 8g\}$
AS7	$\{11s, 10p, 9d, 9f, 9g\}$	$\{10s, 10p, 10d, 10f, 10g\}$	$\{10s, 11p, 9d, 9f, 9g\}$

Following Bieroń et al.’s approach [34], we investigated the impact of different classes of orbital substitutions. Via an DHF orbital basis, more correlations were accumulated by allowing single and double (SD) substitutions from deeper orbitals employing Single References (SRs) for each level using the fourth correlation layer (AS4) given in Table 1.

In Table 2, the individual contribution of single (S) orbital substitution to the magnetic dipole HFS constant of the ground level, $A(^2S_{1/2})$, is presented. Figure 1 gives a more visual representation of these contributions.

While the contribution of the $3p$ orbital is negligible, namely, $+0.08$ MHz, the s orbital substitutions dominate, with the $3s$ orbital contributing -81.54 MHz. This highlights the critical role of s single substitutions in the HFS. To align with the Ba/Sr methodology [15], the $2p$ and $2s$ orbitals are included in the optimization step, even though the $2s$ substitution contributes less than one percent. Consequently, $1s$ correlations are excluded from the optimization.

Table 2. Contributions of occupied orbitals to the calculated values of A hyperfine constant for the $^2S_{1/2}$ level of $^{43}\text{Ca II}$. ΔA shows the individual contributions coming from the single (S) orbital substitutions.

Orbital	N_{CSFs}	A (MHz)	ΔA
	1	−606.08	
3p	32	−604.24	+0.08
3s	2377	−685.78	−81.54
2p	4303	−669.77	+15.79
2s	12,455	−679.77	−9.78
1s	16,468	−687.26	−7.49

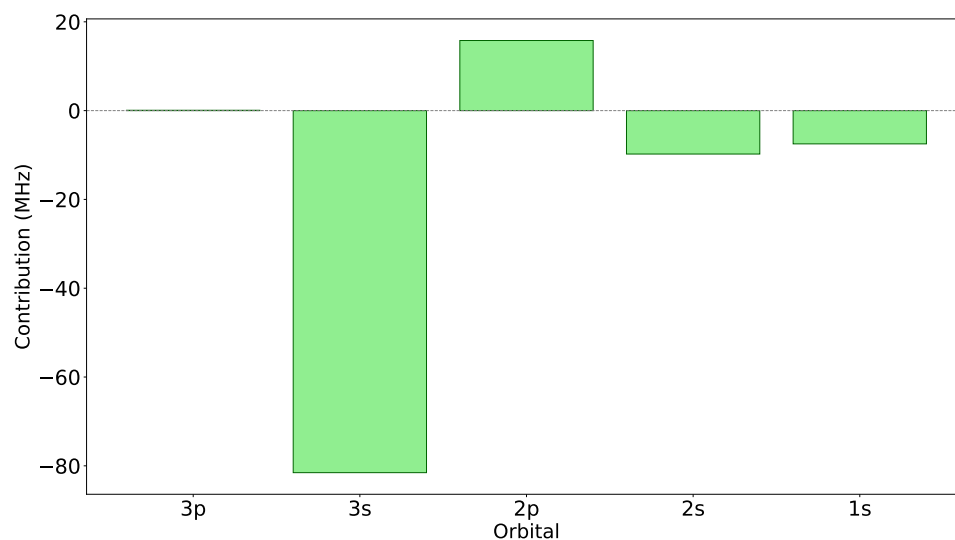


Figure 1. Contributions of single (S) orbital substitutions relative to the DHF $A(^2S_{1/2})$ constant in $^{43}\text{Ca II}$.

As shown in Table 3 and Figure 2, the contributions for the excited states are similar, with the 3p contribution being negligible compared to those of 3s, 2p and 2s. The contributions for the B hyperfine constants indicate that the most important contribution comes from 2p correlations, which is mainly due to the orbital polarization or Sternheimer effect [23]. The trends above are also observed in the $^2D_{5/2}$ and the odd P levels.

Table 3. Contributions of occupied orbitals to the calculated values of A and B hyperfine constants for the $^2D_{3/2}$ level of $^{43}\text{Ca II}$. Δ columns show the individual contributions to the HFS constant coming from the single (S) orbital substitutions.

Orbital	N_{CSFs}	A (MHz)	ΔA	B (MHz)	ΔB
	1	−34.31		−2.67	
3p	153	−33.96	+0.36	−2.63	+0.03
3s	8201	−41.78	−7.82	−2.52	+0.12
2p	14,737	−37.33	+4.45	−3.22	+0.71
2s	44,884	−39.56	−2.23	−3.07	+0.15
1s	58,688	−39.96	−0.40	−3.07	+0.00

Thanks to this analysis, the optimization of the radial orbitals can be targeted for relevant correlations for the hyperfine structure. The GRASP package [16] considers spectroscopic orbitals in two ways. Let us take the example of the ground $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2$ $^2S_{1/2}$ (or $[\text{Ar}]4s^2$ $^2S_{1/2}$) level. The core orbitals are $1s^2 2s^2 2p^6 3s^2 3p^6$, while the valence orbital is 4s. We can therefore build our MCDHF optimizations on core–valence (CV) correlations.

To directly apply the MCDHF + RCI model developed for ^{87}Sr II and ^{137}Ba II [15], we used the equivalent CV single and restricted double (SrD) orbital optimization strategy with $nl \geq 3s$ substitutions. Here, “restricted” means at most one hole per active core orbital, i.e., allowing substitutions from $3s^2$ and $3p^6$ to $4s$, with a maximum of one substitution from each core orbital to the valence one [35]. A second optimization strategy (MCDHF CV SrD $nl \geq 2s$) addressing the $2s$ and $2p$ core orbitals important for correctly describing the HFS for the excited levels was also considered. With the ASs described in Table 1, seven layers of correlation orbitals were considered in order to achieve convergence in our results. The latter is obtained when the HFS constants do not vary within some a priori-accepted variation interval. The results for the HFS constants in each optimization step are given in Table 4.

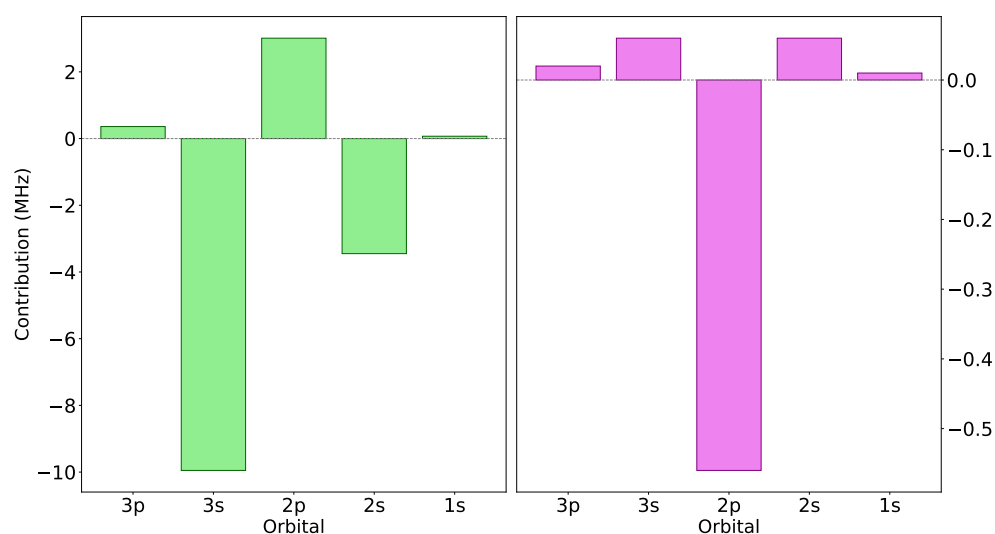


Figure 2. Contributions of single (S) orbital substitutions relative to the DHF $A(^2D_{3/2})$ (left, in light green) and $B(^2D_{3/2})$ (right, in violet) constants in ^{43}Ca II.

As expected, CV correlations are crucial for describing the hyperfine interaction. The MCDHF CV SrD $nl \geq 3s$ shows a stable value that was achieved for the fourth active set (AS4). The ground-level results already agree with the experimental results to within ≈ 7 MHz (0.5%). This agreement was observed for each HFS constant except the $A(^2D_{5/2})$ value with a persistent ≈ 9 MHz difference (223%). This behavior is well known from the Sr/Ba study [15]. To try to overcome this discrepancy, the second orbital set, MCDHF CV SrD $nl \geq 2s$, is considered. The agreement worsened for all HFS constants but improved for the $A(^2D_{5/2})$ constant, which still shows a ≈ 3 MHz ($\approx 89\%$) difference.

After the MCDHF calculations are performed, deeper core–core (CC) correlations are added in the RCI step. The first RCI CC SD $nl \geq 3s$ model allows SD substitutions from $3p$ and $3s$ orbitals to the valence orbital, with no substitutions between the core orbitals in order to save computational time by decreasing the number of CSFs by a factor of two. As we want to account for as much correlation as possible, a second RCI strategy based on CC SD $nl \in \{3p, 3s, 2p, 2s\}$ substitutions is considered. Adding correlations from the $1s$ core orbital was shown to have a negligible effect, with a less-than-one-percent-change in the values for the ground level. Therefore, they were also omitted. Using the MCDHF CV SrD $nl \geq 3s$ optimization, the extended RCI CC SD $nl \in \{3p, 3s, 2p, 2s\}$ model modifies the electric quadrupole A hyperfine constants by $\approx 5\%$ for the ground level. The largest change appears for $A(^2D_{5/2})$, which varies by $\approx 60\%$. For the magnetic dipole B constant, we observed shifts of ≈ 1 MHz for the D levels, while $B(^2P_{3/2}^o)$ remained unchanged. The second MCDHF CV SrD $nl \geq 2s$ optimization yielded identical results with the same RCI approach.

Table 4. Magnetic dipole A and electric quadrupole B hyperfine structure constants (in MHz) of $^{43}\text{Ca II}$ ($I = 7/2, \mu = -1.31833\mu_N, Q = -0.0473\text{b}$) [36] obtained in this work along with other theoretical and experimental data available in the literature. The recommended values are presented in the form $\mu \pm 2\sigma$, with a 95% confidence level. *: Number of CSFs retained after reduction employing the rcsfginteract_csfg code. ^a: Th. Silverans et al. (RMBPT) [28]; ^b: Th. Yu et al. (RMBPT) [29]; ^c: Th. Itano (MCDHF) [8]; ^d: Th. Chakraborty et al. (RCC) [30]; ^e: Th. Safronova et al. (SDpT) [31]; ^f: Expt. Goble et al. [9]; ^g: Expt. Nortershauser et al. [1]; ^h: Expt. Garcia Ruiz et al. [32]; ⁱ: Expt. Silverans et al. [28].

Step	$^2S_{1/2}$		$^2D_{3/2}$			$^2D_{5/2}$			$^2P_{1/2}^o$		$^2P_{3/2}^o$		
	N _{CSFs}	A	N _{CSFs}	A	B	N _{CSFs}	A	B	N _{CSFs}	A	N _{CSFs}	A	B
Optimization CV SrD $nl \geq 3s$													
DHF	1	−606.08	1	−34.31	−2.67	1	−14.61	−3.77	1	−108.90	1	−21.11	−4.93
MCDHF (+AS1)	37	−740.61	120	−45.94	−1.92	130	−11.57	−2.74	53	−133.06	74	−25.64	−6.75
MCDHF (+AS2)	152	−774.30	433	−48.78	−2.67	496	−12.32	−3.79	181	−142.25	278	−32.92	−7.19
MCDHF (+AS3)	380	−802.39	944	−50.54	−2.65	1100	−12.12	−3.77	423	−145.46	688	−34.14	−7.29
MCDHF (+AS4)	722	−796.91	1653	−50.63	−2.78	1942	−12.52	−3.94	781	−146.26	1300	−33.58	−7.33
MCDHF (+AS5)	1178	−800.83	2560	−50.81	−2.72	3022	−12.20	−3.87	1255	−147.96	2114	−33.77	−7.36
MCDHF (+AS6)	1748	−800.26	3665	−50.93	−2.76	4340	−12.33	−3.92	1845	−147.82	3130	−33.76	−7.35
MCDHF (+AS7)	2432	−801.87	4968	−50.91	−2.75	5896	−12.26	−3.90	2551	−146.87	4348	−33.79	−7.35
RCI CC SD $nl \geq 3s$ (+AS7)	9407 *	−737.72	27,462 *	−44.88	−2.75	38,541 *	−9.50	−3.91	9825 *	−125.47	23,013 *	−28.59	−6.33
RCI CC SD $nl \in \{3p, 3s, 2p, 2s\}$ (+AS7)	18,806 *	−763.60	54,916 *	−44.63	−4.64	77,074 *	−4.94	−4.00	19,642 *	−131.02	46,018 *	−30.50	−6.68
RCI CC SD $nl \geq 3s$ (+AS7, NO)	9407 *	−764.91	27,462 *	−46.83	−2.85	38,541 *	−10.47	−4.06	9825 *	−126.58	23,013 *	−28.81	−6.35
RCI CC SD $nl \in \{3p, 3s, 2p, 2s\}$ (+AS7, NO)	18,806 *	−810.51	54,916 *	−48.34	−3.48	77,074 *	−5.23	−4.95	19,642 *	−133.17	46,018 *	−31.30	−6.76
Optimization CV SrD $nl \geq 2s$													
DHF	1	−606.08	1	−34.31	−2.67	1	−14.61	−3.77	1	−108.90	1	−21.11	−4.93
MCDHF (+AS1)	72	−745.89	238	−46.16	−2.05	258	−9.52	−2.90	104	−135.35	146	−25.82	−6.89
MCDHF (+AS2)	301	−782.91	863	−49.68	−3.11	989	−8.55	−4.42	359	−145.30	553	−33.02	−7.37
MCDHF (+AS3)	756	−841.46	1884	−52.18	−3.19	2196	−7.10	−4.54	842	−155.70	1372	−35.74	−7.89
MCDHF (+AS4)	1439	−845.50	3301	−53.03	−3.47	3879	−7.34	−4.94	1557	−157.58	2595	−36.59	−8.00
MCDHF (+AS5)	2350	−854.23	5114	−53.21	−3.36	6038	−7.08	−4.79	2504	−158.81	4222	−37.50	−8.02
MCDHF (+AS6)	3489	−854.63	7323	−53.33	−3.41	8673	−7.26	−4.86	3682	−159.24	6253	−37.52	−8.00
MCDHF (+AS7)	4856	−854.43	9928	−53.33	−3.39	11,784	−7.18	−4.81	5094	−159.55	8688	−37.51	−8.02
RCI CC SD $nl \geq 3s$ (+AS7)	11,831 *	−782.79	32,422 *	−46.82	−3.29	44,429 *	−5.30	−4.70	12,368 *	−135.67	27,353 *	−31.58	−6.87
RCI CC SD $nl \in \{3p, 3s, 2p, 2s\}$ (+AS7)	18,806 *	−760.96	54,916 *	−44.42	−3.25	77,074 *	−4.61	−3.98	19,642 *	−130.84	46,018 *	−30.35	−6.61
RCI CC SD $nl \geq 3s$ (+AS7, NO)	11,831 *	−815.92	32,422 *	−49.24	−3.42	44,429 *	−5.29	−4.88	12,368 *	−136.23	27,353 *	−32.12	−6.64
RCI CC SD $nl \in \{3p, 3s, 2p, 2s\}$ (+AS7, NO)	18,806 *	−810.50	54,916 *	−48.34	−3.48	77,074 *	−5.23	−4.95	19,642 *	−133.17	46,018 *	−31.30	−6.76
This work (LBL)		−763.16 ± 2.85		−44.51 ± 0.32	−2.81 ± 0.02		−4.91 ± 0.12	−3.99 ± 0.03		−130.93 ± 0.25		−30.43 ± 0.21	−5.73 ± 0.10
This work (NO), recommended		−811.38		−48.32	−3.00		−5.24	−4.27		−133.17		−31.30	−5.83
Th. ^a		−819								−148		−30.9	−6.7
Th. ^b		−805.35		−47.82	−3.0		−3.55	−4.4		−143.07		−30.49	−6.7
Th. ^c				−47.27	−2.94		−4.84	−4.18					
Th. ^d		−806 ± 3		−47.8 ± 0.3	−3.06 ± 0.07		−3.30 ± 0.04	−4.24 ± 0.09					
Th. ^e		−801.28		−47.63	−2.87		−4.24	−4.08		−144.96		−30.34	−6.64
Expt. ^f		−797.5 ± 2.4								−158.0 ± 3.3		−29.7 ± 1.6	
Expt. ^g				−47.3 ± 0.2	−3.7 ± 1.9		−3.8 ± 0.6	−3.9 ± 6.0		−145.4 ± 0.1		−31.0 ± 0.2	−6.9 ± 1.7
Expt. ^h		−806.87 ± 0.42										−31.10 ± 0.30	−4.2 ± 1.3
Expt. ⁱ		−805 ± 2								−145.5 ± 1.0		−31.9 ± 0.2	−6.7 ± 1.4

The uncertainty in the theoretical HFS values can be evaluated through multiple approaches. One method involves treating the largest RCI calculations derived from distinct MCDHF optimizations as independent values. A mean value and standard deviation are then calculated from this set. The final result is expressed as $\mu \pm 2\sigma$, which corresponds to a 95% confidence interval.

However, this uncertainty estimation could only be applied to the layer-by-layer (LBL) calculation. The presented MCDHF + RCI methods were originally developed for barium (Ba) [15], which has a larger electronic core including *d* orbitals. When directly applied to lighter elements (such as calcium, with a lower atomic number *Z*), the largest MCDHF + RCI method encountered limitations. Specifically, for calculations using the Natural Orbital (NO) basis, single (S) substitutions from all orbitals were included. In this case, both RCI calculations produced identical results. As a consequence, no uncertainty estimate could be obtained. This highlights a limitation of the model when applied to lighter elements.

Recent studies by Sahoo et al. [14] and Atalay [22] suggested a different approach for the use of an NO basis for HFS calculations. In contrast to Nezosi et al.'s approach [15], wherein the biggest optimized MCDHF orbitals resulting from traditional single and restricted double (SrD) substitutions are transformed into NOs using the rdensity program [17], here, the NO basis is obtained via S substitutions (with a maximum of one substitution from all core orbitals) from a multi-reference (MR) for the *S*, *D* and *P* levels studied in this paper. The largest MCDHF optimization calculation following this approach is then transformed into natural orbitals and then used in RCI calculations. This new approach is appealing, as it can relax all orbitals in a single, compact calculation, as only a total of 4196 CSFs were needed, which can be compared to the 4858 CSFs required for the MCDHF CV $nl \geq 2s$ optimization just for the $^2S_{1/2}$ HFS calculations at AS7. This approach is especially suitable for a high *Z*, as the number of CSFs grows rapidly with the number of active orbitals.

At first glance, Equations (17) and (18) show that $A \propto \langle r^{-2} \rangle$ and $B \propto \langle r^{-3} \rangle$. Johnson [37] showed, in the Pauli approximation where the small $Q_{n\kappa}(r)$ and the large $P_{n\kappa}(r)$ can be linked by

$$Q_{n\kappa}(r) \approx -\frac{1}{2c} \left(\frac{d}{dr} + \frac{\kappa}{r} \right) P_{n\kappa}(r), \quad (20)$$

that $\langle r^{-2} \rangle$ is linked to $\langle r^{-3} \rangle$, indicating that the *A* and *B* HFS constants are both $\propto \langle r^{-3} \rangle$ in the Pauli approximation.

Any modification in $\langle r \rangle$ caused by the transformation into NOs could result in a modification in $\langle r^{-3} \rangle$. Table 5 compares the change in these expectation values for each *d*-subshell for a layer-by-layer (LBL) calculation and after transformation into NOs. The spectroscopic 3*d* orbital is highlighted. Even the smallest change in $\langle r \rangle$ induces variation in $\langle r^{-3} \rangle$, as can be seen for the 3*d* valence orbital

$$\begin{aligned} \langle r \rangle_{3d}^{\text{LBL}} &= 2.5227 a_0 \rightarrow \langle r \rangle_{3d}^{\text{NO}} = 2.3033 a_0, \\ \langle r^{-3} \rangle_{3d}^{\text{LBL}} &= 0.5937 a_0^{-3} \rightarrow \langle r^{-3} \rangle_{3d}^{\text{NO}} = 0.6947 a_0^{-3}, \end{aligned} \quad (21)$$

inducing a direct change in $A(^2D_{3/2})$ and $A(^2D_{5/2})$:

$$\begin{aligned} A(^2D_{3/2})^{\text{LBL}} &= -51 \text{ MHz} \rightarrow A(^2D_{3/2})^{\text{NO}} = -49 \text{ MHz}, \\ A(^2D_{5/2})^{\text{LBL}} &= -12 \text{ MHz} \rightarrow A(^2D_{5/2})^{\text{NO}} = -11 \text{ MHz}. \end{aligned} \quad (22)$$

The orbital contraction is more visible in Figure 3 between 3 and $6a_0$. The top-left graph shows the large component $P_{3d}(r)$ of the valence orbital as a function of *r* for the LBL calculation (in blue) and the transformed NO (in dashed red) obtained from the S substitution MR calculation. The bottom-left graph shows the absolute difference between

these two orbital bases. There are multiple zones where the NO valence orbital is more contracted than the LBL one. On the right-hand side, the $[3;6]a_0$ region is magnified, where the contraction is clearly denoted by the red arrow. Even this small contraction (about 3% in this region) can cause a difference in the A HFS constants. The same behavior applies for the valence orbitals of the ground and the P excited levels, as well as in the B HFS constants.

Table 5. Comparison of $\langle r \rangle$ (in a_0) and $\langle r^{-3} \rangle$ (in a_0^{-3}) for the $^2D_{3/2,5/2}$ levels of $^{43}\text{Ca II}$ between layer-by-layer (LBL) (MCDHF CV $nl \geq 3s$) and natural orbital (NO) calculations. The $3d$ spectroscopic orbital is highlighted in grey.

Subshell	$\langle r \rangle$		$\langle r^{-3} \rangle$	
	LBL	NO	LBL	NO
$3d$	2.5227	2.3033	0.5937	0.6947
$4d$	2.3718	2.3325	1.7532	1.5547
$5d$	2.4586	2.9116	2.4162	1.9883
$6d$	2.5629	3.0360	4.7478	5.5875
$7d$	3.0079	3.1761	6.3437	7.0810
$8d$	2.2484	3.8998	12.0424	5.4211
$9d$	5.2031	1.8125	2.4986	23.4276
$10d$	1.5182	5.1953	20.3480	6.1427

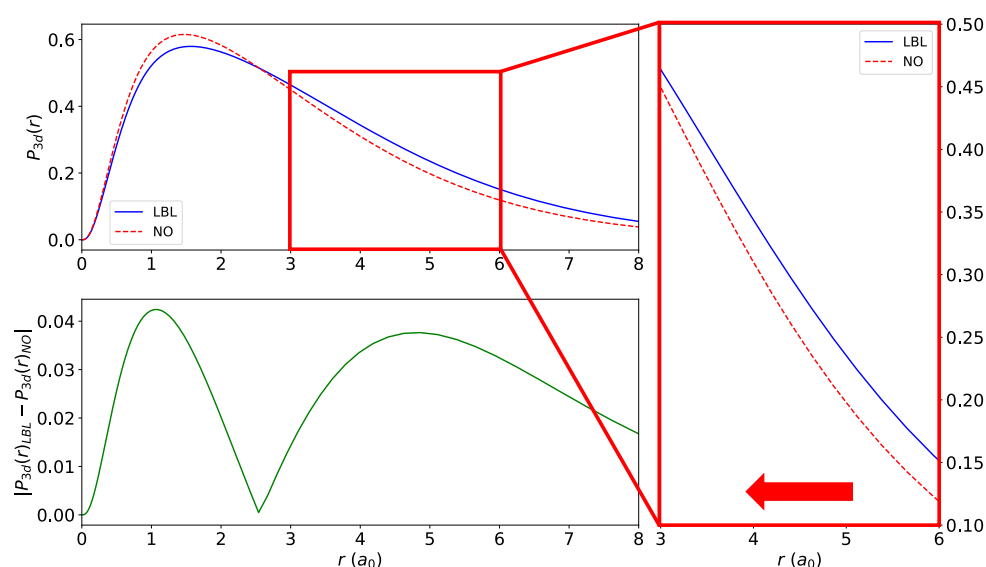


Figure 3. Comparison between the large $P_{3d}(r)$ valence orbital component of the $^{43}\text{Ca II}$ MCDHF CV $\text{SrD } nl \geq 3s$ LBL calculation in solid blue and multi-reference (MR) with allowed single (S) substitutions from all core orbitals transformed into natural orbitals (NOs) in dashed red (top-left corner). The absolute difference $|P_{3d}(r)_{\text{LBL}} - P_{3d}(r)_{\text{NO}}|$, given in green (bottom-left corner), shows the NO contraction in multiple areas between 0 and $8a_0$. A magnified view is given on the right-hand side; it provides a clearer image of the orbital contraction with the red arrow in the $[3;6]a_0$ region.

Using the NO basis, we repeated all RCI calculations (labeled NO in Table 4). The results for both optimizations differ by only a few MHz. We recommend the final NO values, as they account for orbital contraction and show better agreement with experimental values, except for $A(^2P_{1/2}^o)$.

For an accurate theoretical determination of the HFS constants, one should account for the Bohr–Weisskopf (BW) effect [38], a correction of the finite nuclear magnetization distribution of the nucleus, making a contribution to the HFS. Chakraborty et al. [30] studied the effect of BW correction on the calculated HFS constants in $^{43}\text{Ca II}$, with limited correction (at most 0.30% for the $^2D_{5/2}$ level). The BW-corrected A HFS constants for the

$^2S_{1/2}$ and $^2D_{3/2,5/2}$ levels are given in Table 6, but the BW effect could not correct the fact that the values calculated with the LBL orbital basis are closer to the experimental values than the ones calculated with the NO orbitals.

Table 6. Bohr–Weisskopf (BW)-corrected magnetic dipole A hyperfine structure constants (in MHz) of $^{43}\text{Ca II}$ ($I = 7/2$, $\mu = -1.31833\mu_N$ [39], $Q = -0.0473$ b [36]), using the extracted relative BW corrections of Chakraborty et al. [30], obtained in this work alongside other theoretical and experimental data available in the literature. The recommended values are presented in the form of $\mu \pm 2\sigma$, with a 95% confidence level. ^a: Th. Silverans et al. (RMBPT) [28]; ^b: Th. Yu et al. (RMBPT) [29]; ^c: Th. Itano (MCDHF) [8]; ^d: Th. Chakraborty et al. (RCC) [30]; ^e: Th. Safronova et al. (SDpT) [31]; ^f: Expt. Goble et al. [9]; ^g: Expt. Nortershauser et al. [1]; ^h: Expt. Garcia Ruiz et al. [32]; ⁱ: Expt. Silverans et al. [28].

Reference	$^2S_{1/2}$	$^2D_{3/2}$	$^2D_{5/2}$
	$^{43}\text{Ca II}$		
This work (LBL)	-762.29 ± 3.73	-44.51 ± 0.34	-4.89 ± 0.11
This work (NO)	-810.49	-48.30	-5.22
Th. ^a	-819		
Th. ^b	-805.35	-47.82	-3.55
Th. ^c		-47.27	-4.84
Th. ^d	-806 ± 3	-47.8 ± 0.3	-3.30 ± 0.04
Th. ^e	-801.28	-47.63	-4.24
Expt. ^f	-795.5 ± 2.4		
Expt. ^g		-47.3 ± 0.2	-3.8 ± 0.6
Expt. ^h	-806.87 ± 0.42		
Expt. ⁱ	-805 ± 2		

3.2. Ra II

Radium (Ra) is the heaviest alkaline earth metal, with 34 known radioactive isotopes. The most stable, ^{226}Ra , has a half-life of 1600 years [27]. The isotopes ^{223}Ra and ^{225}Ra , with nuclear spin $I = 3/2$ and half-lives of 11.44 and 14.82 days, respectively, only exist in trace amounts. Their short half-lives make experiments challenging, so theoretical hyperfine structure calculations are needed to provide experimental bounds. The levels of interest are the even $[\text{Rn}]7s\ ^2S_{1/2}$ and $[\text{Rn}]6d\ ^2D_{3/2,5/2}$ levels, as well as the odd $[\text{Rn}]7p\ ^2P_{1/2,3/2}^o$ levels, for which only a few experimental values are available. Using collinear fast-beam laser spectroscopy, Wendt et al. [40] determined the HFSs of both $J = 1/2$ levels, while Neu et al. [41] studied both the ground $^2S_{1/2}$ and $^2P_{3/2}^o$ levels. Theoretical values were obtained using RCC [42,43], Atomic Many-Body Perturbation Theory in the Screened Coulomb Interaction (AMPSCI) [44], or the relativistic all-order SDpT method [45]. This is the first paper to compute HFS constants using the MCDHF and RCI methods and to benchmark the new GRASPG [25] package for high- Z ions.

With the AS given in Table 7, the code limited the investigation of orbital substitutions to those no higher than $3d$. Table 8 and Figure 4 show that, for the ground level, the highest contribution comes from $6s$ substitutions. $5d$ and $5p$ substitutions can be added to the optimization model in order to follow the Ba/Sr [15] strategies.

Table 7. Considered active sets used for the levels studied in $^{223}\text{Ra II}$.

Correlation Layer	$^2S_{1/2}$	$^2D_{3/2,5/2}$	$^2P_{1/2,3/2}^o$
DHF	$\{7s, 6p, 5d, 4f\}$	$\{6s, 6p, 6d, 4f\}$	$\{6s, 7p, 5d, 4f\}$
AS1	$\{8s, 7p, 6d, 5f, 5g\}$	$\{7s, 7p, 7d, 5f, 5g\}$	$\{7s, 8p, 6d, 5f, 5g\}$
AS2	$\{9s, 8p, 7d, 6f, 6g\}$	$\{8s, 8p, 8d, 6f, 6g\}$	$\{8s, 9p, 7d, 6f, 6g\}$
AS3	$\{10s, 9p, 8d, 7f, 7g\}$	$\{9s, 9p, 9d, 7f, 7g\}$	$\{9s, 10p, 8d, 7f, 7g\}$
AS4	$\{11s, 10p, 9d, 8f, 8g\}$	$\{10s, 10p, 10d, 8f, 8g\}$	$\{10s, 11p, 9d, 8f, 8g\}$
AS5	$\{12s, 11p, 10d, 9f, 9g\}$	$\{11s, 11p, 11d, 9f, 9g\}$	$\{11s, 12p, 10d, 9f, 9g\}$
AS6	$\{13s, 12p, 11d, 10f, 10g\}$	$\{12s, 12p, 12d, 10f, 10g\}$	$\{12s, 13p, 11d, 10f, 10g\}$
AS7	$\{14s, 13p, 12d, 11f, 11g\}$	$\{13s, 13p, 13d, 11f, 11g\}$	$\{13s, 14p, 12d, 11f, 11g\}$

Table 8. Contributions from occupied orbitals to the calculated values of A hyperfine constant for the $^2S_{1/2}$ level of $^{223}\text{Ra II}$. ΔA shows the individual contributions coming from the single (S) orbital substitutions.

Orbital	N_{CSFs}	A (MHz)	ΔA
	1	2811.00	
6p	33	2810.67	−0.13
6s	3321	2973.83	+163.16
5d	5914	2941.59	−32.24
5p	25,194	2918.51	−23.08
5s	45,642	2924.92	+6.41
4f	54,323	2927.97	+3.05
4d	105,167	2909.87	−18.10
4p	163,867	2900.49	−9.38
4s	211,495	2900.20	−0.29
3d	229,830	2922.14	+21.94

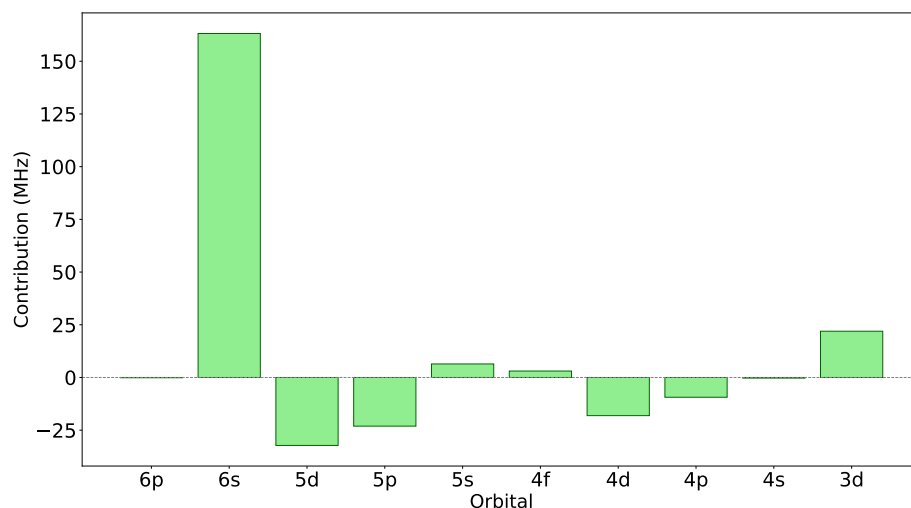


Figure 4. Contributions of single (S) orbital substitutions relative to the DHF $A(^2S_{1/2})$ constant in $^{223}\text{Ra II}$.

With this understanding, the first MCDHF CV $\text{SrD } nl \geq 6s$ is already able to give electric quadrupole A HFS constants that are near the values in the literature, with a maximum difference of 14% for $A(^2D_{5/2})$. However, more correlations are needed for the magnetic dipole B constants to be accurately determined, as shown by the discrepancies in the D levels ($\approx 50\%$). However, when an experimental value exists, the calculated value agrees with only $\approx 9\%$ difference for the $B(^2P_{3/2}^o)$ constant. Adding deeper correlations with the second MCDHF CV $\text{SrD } nl \geq 5p$ deteriorates the agreement with the experimental values [40,41] and the other theoretical values [42–44] for all the A HFS constants except

$A(^2D_{5/2})$. The B HFS constants are 40% closer to the calculated theoretical values reported by Sahoo et al. [42] (RCC). The agreement is preserved for the $B(^2P_{3/2}^o)$ constant ($\approx 9\%$) but is now too large compared to the experiment value. We are still convinced that adding correlation orbitals with higher l encapsulates the orbital polarization that was neglected in the first MCDHF CV SrD $nl \geq 6s$ strategy and is important for reliable determination of the B hyperfine constant [23].

After the MCDHF calculations, higher-order core–core (CC) correlations are added using RCI. Like in the Ca II case, two models are considered for each optimization strategy by allowing single and double (SD) substitutions. For all A HFS constants and for each orbital basis, both RCI models (RCI CC SD $nl \geq 6s$ and RCI CC SD $nl \in \{6p, 6s, 5p, 5s\}$) lower the positive values and increase the negative values. However, the added CC correlations are not sufficient to yield a significantly better agreement for the B HFS constants for the D levels while using the MCDHF CV SrD $nl \geq 6s$ orbital basis. The agreement even worsened for the $^2P_{3/2}^o$ level, with nearly a 100 MHz difference with respect to the experimental value. Overall, the best agreement was obtained with the MCDHF CV SrD $nl \geq 5p +$ RCI CC SD $nl \in \{6p, 6s, 5p, 5s\}$ strategy. The agreement between the calculated value and RCC value [42] is still satisfactory for the $A(^2D_{5/2})$ constant.

We recall that, for Sr ($Z = 38$) and Ba ($Z = 56$), the $A(^2D_{5/2})$ HFS constant was problematic, with an opposite sign between calculated values and those from the literature [15]. For Ra ($Z = 88$), the HFS constant does not show the same behavior. To understand this more clearly, we again move to the non-relativistic formalism, where the magnetic dipole HFS constant A is given as a sum of orbital, spin-dipole, and Fermi contact terms [46]. Table 9 shows the contribution of the different nonrelativistic hyperfine factors to the total A constant. For the Hartree–Fock (HF) calculation, the contact term is zero. Adding core–valence (CV) correlations by opening $6p$ and $6s$ for substitutions to one layer of correlation orbitals $\{7s, 7p, 7d\}$, we see positive interference for the $^2D_{3/2}$ level and negative interference for the $^2D_{5/2}$ level. Compared with Sr and Ba, the negative interference between the different terms is less pronounced for Ra, making it less sensitive to neglected higher-order correlation effects derived from triple (T) and quadruple (Q) substitutions, which are the likely cause of the lack of agreement with the experiment for the former elements.

Table 9. Magnetic dipole A hyperfine constant (in MHz) for $6d\ ^2D_{3/2,5/2}$ in $^{223}\text{Ra II}$. The results at the top are from an HF calculation, and the individual contributions from the orbital, spin-dipolar, and Fermi contact terms are shown along with the total value. The results at the bottom are the corresponding values from an MCHF calculation, including CV correlation based on one layer of correlation orbitals.

Level	Orbital	Term Contribution		Total A
		Spin-Dipolar	Contact	
HF				
$^2D_{3/2}$	46.42	15.49	0.0	61.91
$^2D_{5/2}$	30.95	−4.43	0.0	26.52
MCHF CV SrD $nl \geq 6s$				
$^2D_{3/2}$	34.26	6.11	30.86	71.23
$^2D_{5/2}$	22.84	−1.75	−30.86	−9.76

In Ca II, the recommended values for this work were obtained using an NO basis. Following the same approach for Ra II, RCI calculations were repeated, with the results presented in Table 10. While the LBL orbital basis remains suitable for the ground level, the NO basis provides better agreement for all excited levels, with an outstanding $<1\%$ difference with an experimental value of $A(^2P_{3/2}^o)$. Nevertheless, the uncertainty calculation for $A(^2S_{1/2})$ encompasses both the NO result and the experimental value.

Table 10. Magnetic dipole A and electric quadrupole B hyperfine structure constants (in MHz) of $^{223}\text{Ra II}$ ($I = 3/2, \mu = +0.2692\mu_N, Q = 1.22 \text{ b}$ [39]) obtained in this work along with other theoretical and experimental data available in the literature. The recommended values are presented in the form of $\mu \pm 2\sigma$, with a 95% confidence level. *: Number of CSFs obtained after reduction using the rcsfginteract_csfg code; ^a: Th. Sahoo et al. (RCC) [42]; ^b: Th. Cserveny et al. (AMPSCI) [44]; ^c: Th. Li et al. (RCC) [43]; ^d: Th. Pal et al. (SDpT) [45]; ^e: Expt. Wendt et al. [40]; ^f: Expt. Neu et al. [41].

Step	$^2S_{1/2}$		$^2D_{3/2}$			$^2D_{5/2}$			$^2P_{1/2}^o$		$^2P_{3/2}^o$		
	N _{CSFs}	A	N _{CSFs}	A	B	N _{CSFs}	A	B	N _{CSFs}	A	N _{CSFs}	A	B
Optimization CV SrD $nl \geq 6s$													
DHF	1	2811	1	55	272	1	20	288	1	490	1	39	562
MCDHF (+AS1)	70	3335	156	76	129	184	−35	157	90	620	150	51	732
MCDHF (+AS2)	252	3408	505	72	194	601	−29	251	289	618	493	61	773
MCDHF (+AS3)	548	3514	1052	73	185	1256	−30	235	604	642	1038	53	789
MCDHF (+AS4)	958	3487	1797	72	185	2149	−28	238	1035	640	1785	50	787
MCDHF (+AS5)	1482	3492	2740	72	184	3280	−28	235	1582	642	2734	52	791
MCDHF (+AS6)	2120	3480	3881	72	184	4649	−28	235	2245	638	3885	52	787
MCDHF (+AS7)	2872	3481	5220	72	185	6256	−28	236	3024	638	5238	52	787
RCI CC SD $nl \geq 6s$ (+AS7)	11,391 *	3222	29,379 *	65	234	41,692 *	−21	295	11,861 *	570	28,513 *	47	706
RCI CC SD $nl \in \{6p, 6s, 5p, 5s\}$ (+AS7)	22,774 *	3349	58,750 *	66	247	83,376 *	−23	379	23,714 *	589	57,018 *	51	754
RCI CC SD $nl \geq 6s$ (+AS7, NO)	11,391 *	3336	29,379 *	67	231	41,692 *	−26	297	11,861 *	606	28,513 *	50	747
RCI CC SD $nl \in \{6p, 6s, 5p, 5s\}$ (+AS7, NO)	22,774 *	3477	58,750 *	69	317	83,376 *	−26	405	23,714 *	627	57,018 *	55	806
Optimization CV SrD $nl \geq 5p$													
DHF	1	2811	1	55	272	1	20	288	1	490	1	39	562
MCDHF (+AS1)	184	3424	440	80	190	526	−34	234	236	645	404	50	766
MCDHF (+AS2)	680	3685	1415	81	328	1705	−27	418	775	655	1347	62	836
MCDHF (+AS3)	1490	3877	2944	85	327	3558	−26	406	1630	730	2846	58	922
MCDHF (+AS4)	2614	3850	5027	84	338	6085	−24	523	2801	737	4801	57	932
MCDHF (+AS5)	4052	3877	7664	84	336	9286	−24	419	4288	747	7512	59	942
MCDHF (+AS6)	5804	3867	10,855	84	338	13,161	−24	423	6091	743	10,679	58	937
MCDHF (+AS7)	7870	3871	14,600	84	338	17,710	−24	423	8210	745	14,402	58	940
RCI CC SD $nl \geq 6s$ (+AS7)	16,389 *	3522	38,759 *	74	366	53,146 *	−18	455	17,047 *	650	37,677 *	51	823
RCI CC SD $nl \in \{6p, 6s, 5p, 5s\}$ (+AS7)	25,714 *	3583	64,343 *	76	365	90,280 *	−21	454	26,668 *	632	62,303 *	54	808
RCI CC SD $nl \geq 6s$ (+AS7, NO)	16,389 *	3583	38,759 *	81	396	53,146 *	−22	494	17,047 *	678	37,677 *	54	869
RCI CC SD $nl \in \{6p, 6s, 5p, 5s\}$ (+AS7, NO)	25,714 *	3709	64,343 *	81	393	90,280 *	−23	492	26,668 *	669	62,303 *	57	864
This work (LBL)		3466 ± 331		71 ± 14	306 ± 167		−22 ± 3	417 ± 106		611 ± 61		53 ± 4	781 ± 76
This work (NO), recommended		3593 ± 328		75 ± 17	355 ± 107		−25 ± 4	449 ± 123		648 ± 59		56 ± 3	835 ± 82
Th. ^a		3567.26		77.08	383.88		−23.90	477.09					
Th. ^b		3424 ± 71		95 ± 20			−29 ± 10			675 ± 13		57.7 ± 60	
Th. ^c		3426 ± 82		79.7 ± 1.7			−21.8 ± 2.3			660 ± 11.4		56.5 ± 1.2	
Th. ^d		3450		79.56			−24.08			671.5		54.40	
Expt. ^e		3398.3 ± 2.9								667.1 ± 2.1			
Expt. ^f		3404 ± 1.9										56.5 ± 8	864.8 ± 1.9

The Bohr–Weisskopf (BW) effect could significantly affect our HFS A constants in heavy elements such as radium [43,44]. Table 11 reports and compares our BW-corrected values, as determined by using the extracted relative BW corrections reported by Cserveny et al. [44], with the available theoretical and experimental data. These corrections are more important for the S and D states than for the P states [44]. It can be seen that our BW-corrected NO values are now closer to the experimental values than our LBL ones, as expected.

Nuclear physicists are also interested in ^{225}Ra . As $I(^{225}\text{Ra}) = 1/2$ strictly implies that $Q(^{225}\text{Ra}) = 0$ according to the Wigner–Eckart theorem [23], only the A hyperfine structure constant can be evaluated for this isotope. Using ^{223}Ra II hyperfine constants in Table 10, the ^{225}Ra II constants were determined via the HFS electronic constants [26]:

$$A_{\text{el.}} = A \left(\frac{I}{\mu_I} \right). \quad (23)$$

Table 11 reports the BW-corrected values for the A HFS constants of ^{225}Ra II, obtained through the use of the extracted relative BW corrections reported by Cserveny et al. [44], compared with the data from the literature. It shows the overall better agreement of the HFS constants calculated with the transformed NO basis, with the notable exception of the $^2S_{1/2}$ ground level, where our LBL value is closer to the experimental results. This exception remains unexplained, as it was not the case for ^{223}Ra II and as these values were calculated using Equation (23).

Table 11. Bohr–Weisskopf (BW)-corrected magnetic dipole A hyperfine structure constants (in MHz) of ^{223}Ra II and ^{225}Ra II ($I_{223} = 3/2, \mu_{223} = +0.2692\mu_N, Q_{223} = 1.22\text{ b}$ and $I_{225} = 1/2, \mu_{225} = -0.730\mu_N$, respectively [39]), determined using the extracted relative BW corrections reported by Cserveny et al. [44], obtained in this work along with theoretical and experimental data available in the literature. The recommended values are presented in the form of $\mu \pm 2\sigma$, with a 95% confidence level. ^a: Th. Sahoo et al. (RCC) [42]; ^b: Th. Cserveny et al. (AMPSCI) [44]; ^c: Th. Li et al. (RCC) [43]; ^d: Th. Pal et al. (SDpT) [45]; ^e: Th. Skripnikov et al. (RCC) [47]; ^f: Expt. Wendt et al. [40]; ^g: Expt. Neu et al. [41].

Reference	$^2S_{1/2}$	$^2D_{3/2}$	$^2D_{5/2}$	$^2P_{1/2}$	$^2P_{3/2}$
	$^{223}\text{Ra II}$				
This work (LBL)	3329 ± 359	68 ± 15	-21 ± 4	603 ± 63	52 ± 4
This work (NO)	3451 ± 331	72 ± 18	-24 ± 4	640 ± 61	55 ± 3
Th. ^a	3567	77	−24		
Th. ^b	3424 ± 71	95 ± 20	-29 ± 10	675 ± 13	57.7 ± 60
Th. ^c	3426 ± 82	79.9 ± 1.7	-21.8 ± 2.3	660 ± 11.4	56.5 ± 1.2
Th. ^d	3450	80	−24	672	54
Expt. ^f	3398.3 ± 2.9			667 ± 2.1	
Expt. ^g	3404 ± 1.9				56.5 ± 8
$^{225}\text{Ra II}$					
This work (LBL)	$-27,424 \pm 3038$	-560 ± 110	158 ± 37	-4984 ± 534	-442 ± 24
This work (NO)	$-29,233 \pm 4193$	-612 ± 144	166 ± 37	-5478 ± 823	-487 ± 59
Th. ^a	−28,978	−626	194		
Th. ^e	−27,731			−5451	−461
Expt. ^f				-5446 ± 7	
Expt. ^g	$-27,731 \pm 13$				-466.4 ± 4.6

3.3. Ra I

Neutral radium (Ra I) has two valence electrons. Only a few levels have had their HFSs experimentally studied. The odd $[\text{Rn}]7s7p\ ^3P_1^o$ was studied by Lynch et al. [48] at the ISOLDE facility, and $[\text{Rn}]7s7p\ ^3P_2^o, ^1P_1^o$ were studied by Wendt et al. [40]. The HFSs of the even $[\text{Rn}]7s6d\ ^1D_2, ^3D_{1,2,3}$ levels are only known theoretically. Hassounah et al. [49] and Bieroń et al. [50] studied them using the MCDHF method, while Dzuba et al. [51] used a Relativistic Hartree–Fock + Configuration Interaction (RHF + CI) method to determine the HFS of $^{213}\text{Ra I}$ ($I = 1/2$, $\mu = 0.6133\ \mu_N$). Their values were used to compute the HFS constants for $^{225}\text{Ra II}$ using Equation (23). The latter two were computationally limited by the number of CSFs or by using a pseudo-relativistic Schrödinger Hamiltonian that would not be sufficient for studying the intense relativistic effects of electrons in heavy atoms.

Nezosi et al.'s [15] Ba I HFS study highlighted that a multi-reference (MR) is needed for heavy neutral elements such as Ra I when using the MCDHF method. As the main goal of this paper is mainly to transpose Sr II/Ba I–II MCDHF strategies, the configuration that interacts the most with the reference is added for both studied parities. The even $[\text{Rn}]7s6d\ ^1D_2, ^3D_{1,2,3}$ levels were augmented by a $[\text{Rn}]6d^2$ configuration, while the odd $[\text{Rn}]7s7p\ ^3P_{1,2}^o, ^1P_1^o$ levels were augmented by a $[\text{Rn}]7p6d$ configuration. Seven correlation layers were considered, as shown in Table 12, for the optimization of the MR formed by the two parity configurations.

Table 12. Considered active sets used for the levels studied in $^{223}\text{Ra I}$.

Correlation Layer	$^1D_2, ^3D_{1,2,3}, ^1P_1^o, ^3P_{1,2}^o$
DHF	$\{7s, 7p, 6d, 4f\}$
AS1	$\{8s, 8p, 7d, 5f, 5g\}$
AS2	$\{9s, 9p, 8d, 6f, 6g\}$
AS3	$\{10s, 10p, 9d, 7f, 7g\}$
AS4	$\{11s, 11p, 10d, 8f, 8g\}$
AS5	$\{12s, 12p, 11d, 9f, 9g\}$
AS6	$\{13s, 13p, 12d, 10f, 10g\}$
AS7	$\{14s, 14p, 13d, 11f, 11g\}$

The first calculations were performed using the layer-by-layer (LBL) approach, and the results are displayed in Table 13. Due to the two-valence-electron structure of Ra I, an additional optimization strategy could be considered based on valence–valence (VV) correlations. Computations showed that the MCDHF VV SrD optimization strategy is not sufficient to account for the core polarization needed for an accurate determination of the hyperfine structure, with differences ranging from ≈ 40 MHz for $B(^3D_1)$ to ≈ 260 MHz for $B(^3P_2^o)$. Adding core–valence (CV) correlations in the MCDHF VV SrD + CV SrD $nl \geq 6s$ strategy adds the important polarization of the core caused by the valence electrons with already satisfactory agreement with values from the literature for the A constants. The cost of including these important correlations is an increase in the number of CSFs by nearly 70-fold for the even levels and 100-fold for the odd levels. One final layer of optimization in MCDHF VV SrD + CV SrD $nl \geq 5d$ was added to match the Ba I [15] model. It again shows that the more correlations there are, the better the outcome, especially for the B hyperfine constants, when asymmetrical d ($5d$) core orbital substitutions are allowed. This behavior was already observed in Ba, and it reinforces the idea that substitutions from orbitals with a higher l take into account the orbital polarization that was previously neglected and are therefore important for reliable determination of B [23]. This third layer of optimization increases the HFS constants for all the levels in terms of the absolute values.

Adding higher-order correlations with SD substitutions in an RCI step greatly increases the number of CSFs to a total of 2,933,035 for the biggest MCDHF VV SrD + CV SrD $nl \geq 5d$ + RCI CC SD $nl \in \{6s, 6p, 5s, 5p\}$ step. Therefore, even if T substitutions are known, in Na I, to correct CC correlations with the HFS [21], they could not be added in Ra I. Nevertheless, the largest model shows the best agreement for this approach, with a discrepancy of only 1 MHz for $B(^3D_2)$, but can still under-perform for $B(^3D_2)$ or $B(^3P_{1,2}^o)$, with ≈ 60 and $\approx 20\%$ differences with respect to values from the literature, respectively.

Taking the LBL picture as a whole when determining the final values in the $\mu \pm 2\sigma$ format yields satisfactory results for $A(^3D_1)$, with an only 2% difference with respect to the latest available MCDHF values [49]. Our calculations are in agreement with the available experimental value for $A(^3P_2^o)$ [40], with an $\approx 2\%$ discrepancy, and out-perform Hassouneh et al.'s [49] MCDHF calculations for this level while giving an uncertainty estimation.

Moving to the NO basis allows us to attain overall better agreement than the LBL calculation, as was already the case for ^{43}Ca II and ^{223}Ra II. The final values with uncertainty estimates cover other theoretical calculations. When the NO basis degrades the values relative to the LBL basis, it is always only by a few percentage points.

Using the correction factor reported by Bieroń [50], our results for ^{223}Ra I in Table 13 now include the BW effect. A rescaling of the A hyperfine constants using Equation (23) for ^{225}Ra I was also done. The corrected results are shown in Table 14. The situation is less clear than in the case of Ra II. There is no evidence of a quasi-systematic improvement in the agreement with the measurements when one transforms LBL orbitals into NO orbitals. Now, one can see from Table 14 that the BW-corrected MCDHF-RCI calculations reported by both Hassouneh and Salah [49] and Bieroń [50] show better general agreement with experimental results than our BW-corrected values. There are still two exceptions: the $^3P_2^o$ level in ^{223}Ra I and the $^3D_1$ level in ^{225}Ra I. For these levels, our BW-corrected NO and LBL HFS A constants are in better agreement with the measurements reported by Wendt et al. [40] and Guest et al. [52], respectively. This shows that the differences seen here in Ra I are more due to the correlation model adopted than the BW effect. However, this BW correction factor (≈ 0.96) reported by Bieroń [50], when applied to each level, is a limited approach, as [30,43,44] showed the dependence of the BW effect on the level studied.

Table 13. Magnetic dipole A and electric quadrupole B hyperfine structure constants (in MHz) of $^{223}\text{Ra I}$ ($I = 3/2, \mu = +0.2692\mu_N, Q = 1.22 \text{ b}$ [39]) compared to available theoretical and experimental data. The recommended values are given in the form of $\mu \pm 2\sigma$, exhibiting a 95% confidence level. *: Number of CSFs obtained after reduction using the rcsfginteract_csfg code; ^a: Th. Hassouneh et al. (MCDHF) [49]; ^b: Th. Bieroń et al. (MCDHF) [50]; ^c: Th. Calculated from Dzuba et al. (RHF + RCI) [51]; ^d: Expt. Lynch et al. [48]; ^e: Expt. Wendt et al. [40].

Strategy	³ D ₁			³ D ₂			¹ D ₂		³ D ₃			³ P ₁ ^o			¹ P ₁ ^o		³ P ₂ ^o		
	N _{CSFs}	A	B	N _{CSFs}	A	B	A	B	N _{CSFs}	A	B	N _{CSFs}	A	B	A	B	N _{CSFs}	A	B
Layer-by-layer (LBL)																			
MCDHF VV SrD	626	−458	91	910	292	135	−81	303	898	350	199	635	896	−323	−225	228	852	565	425
RCI CC SD <i>nl</i> ≥ 6 <i>s</i>	85,320 *	−559	78	266,206 *	272	133	−75	272	189,081 *	382	211	172,279 *	963	−322	−219	353	320,622 *	637	447
RCI CC SD <i>nl</i> ∈ {6 <i>s</i> , 6 <i>p</i> , 5 <i>s</i> , 5 <i>p</i> }	170,014 *	−567	98	531,502 *	273	162	−73	320	377,264 *	388	264	353,923 *	976	−327	−220	375	640,392 *	646	459
MCDHF VV SrD + CV SrD <i>nl</i> ≥ 6 <i>s</i>	41,956	−596	70	59,801	367	127	−136	285	65,843	425	188	64,276	1221	−421	−362	395	91,187	717	625
RCI CC SD <i>nl</i> ≥ 6 <i>s</i>	123,653 *	−572	79	322,284 *	320	134	−100	250	248,578 *	404	209	237,283 *	1059	−344	−274	347	404,447 *	666	477
RCI CC SD <i>nl</i> ∈ {6 <i>s</i> , 6 <i>p</i> , 5 <i>s</i> , 5 <i>p</i> }	208,347 *	−583	101	587,580 *	320	166	−98	302	436,761 *	410	267	413,927 *	1070	−345	−274	371	724,217 *	675	483
MCDHF VV SrD + CV SrD <i>nl</i> ≥ 5 <i>d</i>	116,496	−658	129	167,242	421	212	212	396	186,546	477	328	177,207	1385	−477	−416	464	253,427	805	719
RCI CC SD <i>nl</i> ≥ 6 <i>s</i>	197,118 *	−623	129	429,417 *	364	206	−116	357	355,757 *	447	330	349,045 *	1180	−389	−311	404	563,936 *	735	548
RCI CC SD <i>nl</i> ∈ {6 <i>s</i> , 6 <i>p</i> , 5 <i>s</i> , 5 <i>p</i> }	280,602 *	−628	129	693,084 *	362	204	−113	343	553,300 *	449	330	524,247 *	1179	−372	−309	397	881,802 *	738	523
Natural orbitals (NOs)																			
MCDHF VV SrD	626	−458	91	910	292	135	−81	303	898	350	199	635	896	−323	−225	228	852	565	425
RCI CC SD <i>nl</i> ≥ 6 <i>s</i>	85,320 *	−581	77	266,206 *	280	134	−76	278	189,081 *	398	210	172,279 *	1000	−384	−202	444	320,622 *	657	554
RCI CC SD <i>nl</i> ∈ {6 <i>s</i> , 6 <i>p</i> , 5 <i>s</i> , 5 <i>p</i> }	170,014 *	−607	112	531,502 *	291	184	−79	369	377,264 *	416	298	353,923 *	1048	−407	−208	480	640,392 *	691	600
MCDHF VV SrD + CV SrD <i>nl</i> ≥ 6 <i>s</i>	41,956	−599	72	59,801	369	129	−135	290	65,843	427	192	64,276	1216	−429	−353	410	91,187	714	639
RCI CC SD <i>nl</i> ≥ 6 <i>s</i>	123,653 *	−595	80	322,284 *	331	136	−104	257	248,578 *	420	212	237,283 *	1093	−400	−256	422	404,447 *	686	569
RCI CC SD <i>nl</i> ∈ {6 <i>s</i> , 6 <i>p</i> , 5 <i>s</i> , 5 <i>p</i> }	208,347 *	−621	117	587,580 *	342	189	−107	354	436,761 *	437	305	413,927 *	1138	−421	−262	480	724,217 *	718	613
MCDHF VV SrD + CV SrD <i>nl</i> ≥ 5 <i>d</i>	116,496	−664	132	167,242	425	216	−157	403	186,546	481	334	177,207	1377	−492	−400	494	253,427	800	746
RCI CC SD <i>nl</i> ≥ 6 <i>s</i>	197,118 *	−638	147	429,417 *	374	231	−119	409	355,757 *	459	370	349,045 *	1202	−458	−284	505	563,936 *	748	668
RCI CC SD <i>nl</i> ∈ {6 <i>s</i> , 6 <i>p</i> , 5 <i>s</i> , 5 <i>p</i> }	280,602 *	−662	147	693,084 *	385	231	−123	400	553,300 *	474	370	524,247 *	1237	−450	−292	506	881,802 *	776	658
This work (LBL)	−593 ± 63	109 ± 35		318 ± 89	177 ± 46	−95 ± 40	322 ± 41		416 ± 62	287 ± 74		1075 ± 203	−348 ± 45	−267 ± 89	381 ± 28		686 ± 94	488 ± 65	
This work (NO), recommended	−630 ± 57	125 ± 38		339 ± 94	201 ± 52	−103 ± 45	374 ± 47		442 ± 59	324 ± 79		1141 ± 189	−426 ± 44	−254 ± 85	489 ± 29		728 ± 87	624 ± 61	
Th. ^a	−607	130		218	213	−143	388		428	346		1207	−468	−341	419		622	655	
Th. ^b	−612	125		382	210	−140	382		428	346		1252	−476	−330	419				
Th. ^c	−604			257		−47			403			1185		−242.3					
Expt. ^d												1202.5 ± 3.0	−472.1 ± 2.0						
Expt. ^e												1202.1 ± 0.6	−470.2 ± 1.2	−344.5 ± 0.9	421.5 ± 1.6		699.6 ± 3.3	688.5 ± 4.0	

Table 14. Bohr–Weisskopf (BW)-corrected magnetic dipole A hyperfine structure constants (in MHz) of $^{223}\text{Ra I}$ and $^{225}\text{Ra I}$ ($I_{223} = 3/2$, $\mu_{223} = +0.2692\mu_N$, $Q_{223} = 1.22$ b and $I_{225} = 1/2$, $\mu_{225} = -0.730\mu_N$, respectively [39]), determined using the relative BW correction factor reported by Bieroń [50], i.e., 0.96, compared to available theoretical and experimental data. The recommended values are given in the form of $\mu \pm 2\sigma$, exhibiting a 95% confidence level. ^a: Th. Hassouneh et al. (MCDHF) [49]; ^b: Th. Bieroń et al. (MCDHF) [50]; ^c: Th. Calculated from Dzuba et al. (RHF + RCI) [51]; ^d: Expt. Lynch et al. [48]; ^e: Expt. Wendt et al. [40]; ^f: Expt. Guest et al. [52].

Reference	$^3D_1$	$^3D_2$	$^1D_2$	$^3D_3$	$^3P_1^o$	$^1P_1^o$	$^3P_2^o$
$^{223}\text{Ra I}$							
This work (LBL)	-569 ± 63	305 ± 89	-91 ± 40	399 ± 62	1032 ± 203	-256 ± 89	659 ± 94
This work (NO)	-605 ± 57	325 ± 94	-99 ± 45	424 ± 59	1095 ± 189	-244 ± 85	699 ± 87
Th. ^a	−607	218	−143	428	1207	−341	622
Th. ^b	−612	382	−140	428	1252	−330	
Th. ^c	−604	257	−47	403	1185	−243.3	
Expt. ^d					1202 ± 3.0		
Expt. ^e					1202.1 ± 0.6	-344.5 ± 0.9	699.6 ± 3.3
$^{225}\text{Ra I}$							
This work (LBL)	4654 ± 519	-2500 ± 726	743 ± 330	-3265 ± 509	-8439 ± 1661	2099 ± 730	-5388 ± 771
This work (NO)	4946 ± 463	-2665 ± 767	808 ± 364	-3471 ± 482	-8957 ± 1546	1994 ± 692	-5717 ± 713
Th. ^a	4905	−1763	1153	−3455	−9751	2757	−5027
Th. ^b	4955	−3093	1133	−3465	−10,137	2672	
Th. ^c	4890	−2082	381	−3266	−9591	1962	−5519
Expt. ^f	4687.70 ± 1.5					2796.5 ± 1.5	
Expt. ^e					-9793.9 ± 4.3		

4. Conclusions

This work presents a comprehensive computational study of the hyperfine structures (HFSs) of low-lying levels in Ca II and Ra I–II, employing the MCDHF and RCI method [8] within the GRASP framework [53] enhanced with Configuration State Function Generators (CSFGs) [25].

Building upon our established models for strontium (Sr) and barium (Ba) [15], we successfully extended this methodology to both a lighter alkaline-earth ion, calcium (Ca), and the heavy radioactive element radium (Ra). The implementation of a natural orbital (NO) basis for HFS calculations in heavy elements represents a significant methodological advancement, accounting for orbital relaxation and systematically improving accuracy. Furthermore, we introduced a robust statistical approach for uncertainty estimation, providing experimenters with reliable theoretical bounds for their measurements.

The calcium ion (Ca II) served as a crucial validation case, allowing us to refine our computational approach through detailed analysis of orbital substitution contributions. This investigation revealed the dominant electron correlations influencing HFSs and demonstrated that an NO basis induces valence orbital contraction, consistent with observations in lighter elements [21]. Our final values for Ca II exhibited excellent agreement with experimental data while offering precise theoretical uncertainty estimates, thereby confirming the reliability of our method for subsequent application to more complex systems. However, the application of the theoretical uncertainty determination approach within the new NO transformation framework yielded MCDHF + RCI calculations identical to those performed with the LBL orbital set, preventing estimation of uncertainty bars. This limitation was caused by the direct adoption of MCDHF models originally developed for Ba II [15], which incorporate a larger electronic core. Furthermore, the inclusion of the

Bohr–Weisskopf (BW) effect using the extracted values reported by Chakraborty et al. [30] did not improve our results.

For singly ionized radium (Ra II), we present the first MCDHF calculations of HFS constants for the $[\text{Rn}]6d\ ^2D_{3/2,5/2}$ levels, supplementing existing data for the ground and excited P levels. Despite computational limitations that restricted our correlation analysis to the $3d$ core orbital, we found that $6s$ substitutions make the most significant contributions. The NO basis yielded the best agreement with experimental values for the $[\text{Rn}]7p\ ^2P_{3/2}^o$ level, with discrepancies below one percent. Our recommended values, complete with uncertainty estimates, encompass existing theoretical predictions and established essential reference data for future spectroscopic studies. However, unlike other one-valence atomic structures like Sr II and Ba II, the sign change between the final and experimental values for $A(^2D_{5/2})$ did not appear, and, instead, good agreement was seen with other accurate calculations [42–44]. A succinct MCHF calculation for the $[\text{Rn}]6d\ ^2D_{3/2,5/2}$ levels still showed that this constant might be sensitive to interference in the CSF expansion with cancellation between the non-relativistic orbital and Fermi contact terms.

The neutral radium (Ra I) atom was examined to provide HFS constants critical for determining electric field gradients and interpreting molecular spectra, particularly for RaF. Our calculations for ^{223}Ra I produced electric quadrupole B constants that aligned well with values from the literature while incorporating uncertainty quantification. The $[\text{Rn}]7s6d\ ^3D_2$ and $[\text{Rn}]7s7p\ ^3P_1^o$ levels, which are separated by merely 5.41 cm^{-1} and are of particular importance in BSM physics due to their enhanced sensitivity to parity and time-reversal (PT) violating effects, were also studied. The theoretical bounds we provided will guide future experimental and theoretical investigations in this domain.

This HFS investigation marks the first successful application of the newly developed GRASPG [25] code to high- Z elements, demonstrating its capacity to efficiently handle complex atomic systems. Future enhancements, including the integration of partitioned correlation function interaction (PCFI) [54], promise to further improve the precision of hyperfine structure calculations by directly targeting the most significant orbital correlations. Experimental validation of our theoretical models would enable more refined uncertainty estimates. While higher-order substitutions remain computationally intensive, with configuration state function counts already approaching three million for Ra I, natural orbitals emerge as a particularly promising approach. A dedicated study exploring various natural orbital methodologies for second-row elements is currently in progress, highlighting the potential of this approach for atomic structure calculations. In addition, it would be interesting to test the accuracy of our methods for higher excited states, as they may be needed in astrophysical applications.

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Abbreviations

The following abbreviations are used in this manuscript:

AMPSCI	Atomic Many-Body Perturbation Theory in the Screened Coulomb Interaction
AS	Active Set
ASF	Atomic State Function
CC	Core–Core
CSF	Configuration State Function
CSFG	Configuration State Function Generator
CV	Core–Valence
D	Double
DHF	Dirac–Hartree–Fock
GRASP	General Relativistic Atomic Structure Package
HF	Hartree–Fock
HFS	Hyperfine Structure
IS	Isotope Shift
MCDHF	Multi-Configuration Dirac–Hartree–Fock
MCHF	Multi-Configuration Hartree–Fock
MR	Multi-Reference
NO	Natural Orbital
PCFI	Partitioned Correlation Function Interaction
RCC	Relativistic Coupled Cluster
RCI	Relativistic Configuration Interaction
RHF + CI	Relativistic Hartree–Fock + Configuration Interaction
RMBPT	Relativistic Many-Body Perturbation Theory
S	Single
SD	Single and Double
SrD	Single and Restricted Double
SR	Single Reference
VV	Valence–Valence

References

1. Nörtershäuser, W.; Blaum, K.; Icker, K.; Müller, P.; Schmitt, A.; Wendt, K.; Wiche, B. Isotope shifts and hyperfine structure in the $3d\ ^2D_J \rightarrow 4p\ ^2P_J$ transitions in calcium II. *Eur. Phys. J. D-At. Mol. Opt. Phys.* **1998**, *2*, 33–39. [[CrossRef](#)]
2. Frebel, A. Observing the r-Process Signature in the Oldest Stars. *arXiv* **2008**. [[CrossRef](#)]
3. Osorio, Y.; Aguado, D.S.; Prieto, C.A.; Hubeny, I.; González Hernández, J.I. Accurate Metallicities for Very Metal-poor Stars from the Ca II Infrared Triplet. *Astrophys. J.* **2022**, *928*, 173. [[CrossRef](#)]
4. Murga, M.; Zhu, G.; Ménard, B.; Lan, T.W. Calcium H & K and sodium D absorption induced by the interstellar and circumgalactic media of the Milky Way. *Mon. Not. R. Astron. Soc.* **2015**, *452*, 511–519. [[CrossRef](#)]
5. Burbidge, E.M.; Burbidge, G.R.; Fowler, W.A.; Hoyle, F. Synthesis of the Elements in Stars. *Rev. Mod. Phys.* **1957**, *29*, 547–650. [[CrossRef](#)]
6. Quinet, P.; Argante, C.; Fivet, V.; Terranova, C.; Yushchenko, A.V.; Biřmont, E. Atomic data for radioactive elements Ra I, Ra II, Ac I and Ac II and application to their detection in HD 101065 and HR 465. *Astron. Astrophys.* **2007**, *474*, 307–314. [[CrossRef](#)]
7. Pian, E.; D’Avanzo, P.; Benetti, S.; Branchesi, M.; Brocato, E.; Campana, S.; Cappellaro, E.; Covino, S.; D’Elia, V.; Fynbo, J.P.U.; et al. Spectroscopic identification of r-process nucleosynthesis in a double neutron-star merger. *Nature* **2017**, *551*, 67–70. [[CrossRef](#)]

8. Itano, W. Quadrupole moments and hyperfine constants of metastable states of Ca^+ , Sr^+ , Ba^+ , Yb^+ , Hg^+ and Au. *Phys. Rev. A* **2006**, *73*, 022510. [\[CrossRef\]](#)
9. Goble, A.T.; Maleki, S. Measurements of hyperfine constants in Ca^+ . *Phys. Rev. A* **1990**, *42*, 649–650. [\[CrossRef\]](#)
10. Neyens, G. (KU Leuven, Leuven, Belgium). Private communication, 2026.
11. Bieroń, J.; Gaigalas, G.; Gaidamauskas, E.; Fritzsche, S.; Indelicato, P.; Jönsson, P. Multi-configuration Dirac–Hartree–Fock calculations of the electric dipole moment of radium induced by the nuclear Schiff moment. *Phys. Rev. A* **2009**, *80*, 012513. [\[CrossRef\]](#)
12. Flambaum, V.V. Enhancement of parity and time invariance violation in the radium atom. *Phys. Rev. A* **1999**, *60*, R2611–R2613. [\[CrossRef\]](#)
13. Versolato, O.O.; Wansbeek, L.W.; Jungmann, K.; Timmermans, R.G.E.; Willmann, L.; Wilschut, H.W. Potential of electric quadrupole transitions in radium isotopes for single-ion optical frequency standards. *Phys. Rev. A* **2011**, *83*, 043829. [\[CrossRef\]](#)
14. Sahoo, B.K.; Jönsson, P.; Gaigalas, G. Comparative Analysis of Mg^+ Properties using Multiconfiguration Dirac–Hartree–Fock and Relativistic Coupled-Cluster Methods. *Phys. Rev. A* **2025**, *112*, 012809. [\[CrossRef\]](#)
15. Nezosi, L.; Maison, L.; Palmeri, P.; Jönsson, P.; Godefroid, M. Study of the Hyperfine Structure of Sr II, Ba I and Ba II: An MCDHF Approach for Modeling the Low-Lying Levels. *Atoms* **2026**, *14*, 17. [\[CrossRef\]](#)
16. Froese Fischer, C.; Gaigalas, G.; Jönsson, P.; Bieroń, J. GRASP2018—A Fortran 95 version of the General Relativistic Atomic Structure Package. *Comput. Phys. Commun.* **2019**, *237*, 184–187. [\[CrossRef\]](#)
17. Schiffmann, S.; Li, J.; Ekman, J.; Gaigalas, G.; Godefroid, M.; Jönsson, P.; Bieroń, J. Relativistic radial electron density functions and natural orbitals from GRASP2018. *Comput. Phys. Commun.* **2022**, *278*, 108403. [\[CrossRef\]](#)
18. Grant, I.P. *Relativistic Quantum Theory of Atoms and Molecules*; Springer Series on Atomic, Optical, and Plasma Physics; Springer: Berlin/Heidelberg, Germany, 2007.
19. Jönsson, P.; Godefroid, M.; Gaigalas, G.; Ekman, J.; Grumer, J.; Li, W.; Li, J.; Brage, T.; Grant, I.P.; Bieroń, J.; et al. An Introduction to Relativistic Theory as Implemented in GRASP. *Atoms* **2022**, *11*, 7. [\[CrossRef\]](#)
20. Lindgren, I.; Lindgren, J.; Mårtensson, A.M. Many-body calculations of the hyperfine interaction of some excited states of alkali atoms, using approximate Brueckner or natural orbitals. *Z. Phys. A At. Nucl.* **1976**, *279*, 113–125. [\[CrossRef\]](#)
21. Schiffmann, S.; Godefroid, M.; Ekman, J.; Jönsson, P.; Fischer, C.F. Natural orbitals in multiconfiguration calculations of hyperfine-structure parameters. *Phys. Rev. A* **2020**, *101*, 062510. [\[CrossRef\]](#)
22. Atalay, B. Relativistic multiconfiguration calculations of energy levels, transition rates and hyperfine constants in neutral indium. *J. Quant. Spectrosc. Radiat. Transf.* **2026**, *352*, 109812. [\[CrossRef\]](#)
23. Lindgren, I.; Morrison, J. *Atomic Many-Body Theory*; Springer: Berlin/Heidelberg, Germany, 1986. [\[CrossRef\]](#)
24. Jönsson, P.; Gaigalas, G.; Fischer, C.F.; Bieroń, J.; Grant, I.P.; Brage, T.; Ekman, J.; Godefroid, M.; Grumer, J.; Li, J.; et al. GRASP Manual for Users. *Atoms* **2023**, *11*, 68. [\[CrossRef\]](#)
25. Si, R.; Li, Y.; Wang, K.; Chen, C.; Gaigalas, G.; Godefroid, M.; Jönsson, P. GRASPG—An extension to GRASP2018 based on configuration state function generators. *Comput. Phys. Commun.* **2025**, *312*, 109604. [\[CrossRef\]](#)
26. Papoulia, A.; Schiffmann, S.; Bieroń, J.; Gaigalas, G.; Godefroid, M.; Harman, Z.; Jönsson, P.; Oreshkina, N.S.; Pyykkö, P.; Tupitsyn, I.I. Ab initio electronic factors of the $5s^2 5p 6s\ ^{1,3}P^o_1$ states in Sn I. *Phys. Rev. A* **2021**, *103*, 022815. [\[CrossRef\]](#)
27. Kondev, F.; Wang, M.; Huang, W.; Naimi, S.; Audi, G. The NUBASE2020 evaluation of nuclear physics properties. *Chin. Phys. C* **2021**, *45*, 030001. [\[CrossRef\]](#)
28. Silverans, R.E.; Vermeeren, L.; Neugart, R.; Lievens, P. Hyperfine structure constants of the CaII states $4s\ ^2S_{1/2}$ and $4p\ ^2P_{1/2,3/2}$ and the nuclear quadrupole moment of ^{43}Ca . *Z. Phys. D At. Mol. Clust.* **1991**, *18*, 351–356. [\[CrossRef\]](#)
29. Yu, K.-z.; Wu, L.-j.; Gou, B.-c.; Shi, T.-y. Calculation of the hyperfine structure constants in $^{43}\text{Ca}^+$ and $^{87}\text{Sr}^+$. *Phys. Rev. A* **2004**, *70*, 012506. [\[CrossRef\]](#)
30. Chakraborty, A.; Katyal, V.; Sahoo, B.K. Investigating roles of triple excitations for high-precision determination of clock properties of alkaline-earth-metal singly charged ions. *Phys. Rev. A* **2026**, *113*, L011101. [\[CrossRef\]](#)
31. Safronova, M.S.; Safronova, U.I. Blackbody radiation shift, multipole polarizabilities, oscillator strengths, lifetimes, hyperfine constants, and excitation energies in Ca^+ . *Phys. Rev. A* **2011**, *83*, 012503. [\[CrossRef\]](#)
32. Ruiz, R.F.G.; Bissell, M.L.; Blaum, K.; Frömmgen, N.; Hammen, M.; Holt, J.D.; Kowalska, M.; Kreim, K.; Menéndez, J.; Neugart, R.; et al. Ground-state electromagnetic moments of calcium isotopes. *Phys. Rev. C* **2015**, *91*, 041304. [\[CrossRef\]](#)
33. Sahoo, B.K.; Das, B.P.; Chaudhuri, R.K.; Mukherjee, D. Theoretical studies of the $6s\ ^2S_{1/2} \rightarrow 5d\ ^2D_{3/2}$ parity-nonconserving transition amplitude in Ba^+ and associated properties. *Phys. Rev. A* **2007**, *75*, 032507. [\[CrossRef\]](#)
34. Bieroń, J.; Filippin, L.; Gaigalas, G.; Godefroid, M.; Jönsson, P.; Pyykkö, P. Ab initio calculations of the hyperfine structure of zinc and evaluation of the nuclear quadrupole moment $Q(^{67}\text{Zn})$. *Phys. Rev. A* **2018**, *97*, 062505. [\[CrossRef\]](#)
35. Bieroń, J.; Froese Fischer, C.; Indelicato, P.; Jönsson, P.; Pyykkö, P. Complete-active-space multiconfiguration Dirac–Hartree–Fock calculations of hyperfine-structure constants of the gold atom. *Phys. Rev. A* **2009**, *79*, 052502. [\[CrossRef\]](#)

36. Tang, Y.B. Precision calculation of hyperfine-structure constants for extracting the nuclear quadrupole moment of ^{43}Ca . *Phys. Rev. A* **2025**, *112*, 042814. [[CrossRef](#)]
37. Jonhson, W.R. *Atomic Structure Theory*; Springer: Berlin/Heidelberg, Germany, 2007. [[CrossRef](#)]
38. Bohr, A.; Weisskopf, V.F. The Influence of Nuclear Structure on the Hyperfine Structure of Heavy Elements. *Phys. Rev.* **1950**, *77*, 94–98. [[CrossRef](#)]
39. Stone, N.J. *Table of Nuclear Magnetic Dipole and Electric Quadrupole Moments*; IAEA Nuclear Data Section: Vienna, Austria, 2014 [[CrossRef](#)]
40. Wendt, K.; Ahmad, S.A.; Klempt, W.; Neugart, R.; Otten, E.W.; Stroke, H.H. On the Hyperfine Structure and Isotope Shift of Radium. *Z. Phys. D At. Mol. Clust.* **1987**, *4*, 227–241. [[CrossRef](#)]
41. Neu, W.; Neugart, R.; Otten, E.W.; Passler, G.; Wendt, K.; Fricke, B.; Arnold, E.; Kluge, H.J.; Ulm, G. Quadrupole moments of radium isotopes from the $7p\ ^2P_{3/2}$ hyperfine structure in Ra II. *Z. Phys. D At. Mol. Clust.* **1988**, *11*, 105–111. [[CrossRef](#)]
42. Sahoo, B.K.; Das, B.P.; Chaudhuri, R.K.; Mukherjee, D.; Timmermans, R.G.E.; Jungmann, K. Investigations of Ra^+ properties to test possibilities of new optical frequency standards. *Phys. Rev. A* **2007**, *76*, 040504. [[CrossRef](#)]
43. Li, F.C.; Tang, Y.B.; Qiao, H.X.; Shi, T.Y. Ab initio calculations of the hyperfine structure of Ra^+ and evaluations of the electric quadrupole moment Q of $^{209,211,221,223}\text{Ra}$ nuclei. *J. Phys. B At. Mol. Opt. Phys.* **2021**, *54*, 145004. [[CrossRef](#)]
44. Cserveny, R.B.; Roberts, B.M. Theoretical characterization of the barium ii and radium ii ions. *Phys. Rev. A* **2025**, *112*, 032816. [[CrossRef](#)]
45. Pal, R.; Jiang, D.; Safronova, M.S.; Safronova, U.I. Calculation of parity-nonconserving amplitude and other properties of Ra^+ . *Phys. Rev. A* **2009**, *79*, 062505. [[CrossRef](#)]
46. Froese Fischer, C. *The Hartree-Fock Method for Atoms: A Numerical Approach*; John Wiley and Sons: Hoboken, NJ, USA, 1977.
47. Skripnikov, L.V. Nuclear magnetization distribution effect in molecules: Ra^+ and RaF hyperfine structure. *J. Chem. Phys.* **2020**, *153*, 0024103. [[CrossRef](#)]
48. Lynch, K.M.; Wilkins, S.G.; Billowes, J.; Binnersley, C.L.; Bissell, M.L.; Chrysalidis, K.; Cocolios, T.E.; Goodacre, T.D.; de Groote, R.P.; Farooq-Smith, G.J.; et al. Laser-spectroscopy studies of the nuclear structure of neutron-rich radium. *Phys. Rev. C* **2018**, *97*, 024309. [[CrossRef](#)]
49. Hassouneh, O.; Salah, W. Relativistic calculations of the Landé g_J -factors, and hyperfine parameters in Ra-223 isotope. *Eur. Phys. J. Plus* **2022**, *137*, 426. [[CrossRef](#)]
50. Bieroń, J. Multiconfiguration Dirac–Hartree–Fock calculations of the hyperfine structures of radium. *J. Phys. B At. Mol. Opt. Phys.* **2005**, *38*, 2221–2228. [[CrossRef](#)]
51. Dzuba, V.A.; Flambaum, V.V.; Ginges, J.S.M. Calculation of parity and time invariance violation in the radium atom. *Phys. Rev. A* **2000**, *61*, 062509. [[CrossRef](#)]
52. Guest, J.R.; Scielzo, N.D.; Ahmad, I.; Bailey, K.; Greene, J.P.; Holt, R.J.; Lu, Z.T.; O'Connor, T.P.; Potterveld, D.H. Laser Trapping of ^{225}Ra and ^{226}Ra with Repumping by Room-Temperature Blackbody Radiation. *Phys. Rev. Lett.* **2007**, *98*, 093001. [[CrossRef](#)]
53. Dylla, K.; Grant, I.; Johnson, C.; Parpia, F.; Plummer, E. GRASP: A general-purpose relativistic atomic structure program. *Comput. Phys. Commun.* **1989**, *55*, 425–456. [[CrossRef](#)]
54. Wu, S. (Fudan University, Shanghai, China); Si, R. (Fudan University, Shanghai, China); Chen, C. (Fudan University, Shanghai, China); Gaigalas, G. (Vilnius University, Vilnius, Lithuania); Godefroid, M. (ULB, Brussels, Belgium); Jönsson, P. (Malmö University, Malmö, Sweden). Private communication, 2026.

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