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Rajat K. Chaudhuri[1,a) and **Sudip Chattopadhyay**[2,b)

AFFILIATIONS

[1] Indian Institute of Astrophysics, Bangalore 560034, India
[2] Department of Chemistry, Indian Institute of Engineering Science and Technology, Shibpur, Howrah 711103, India

[a)] **Electronic mail:** rkchaudh@iiap.res.in. Formerly Associated with Indian Institute of Astrophysics.
[b)] sudip@chem.iiests.ac.in

ABSTRACT

Exploration of the tractable size basis set that can provide reliable estimates of computed properties for systems containing heavy elements has been the subject of interest in quantum chemistry over many decades. In this connection, the recently developed segmented all-electron relativistically contracted (SARC) basis set proposed by Rolfes *et al.* [J. Comput. Chem. **41**, 1842 (2020)] appears to be worth studying. In the present attempt, ground and excited state properties of the Ag atom is computed on this basis at the Fock-space multi-reference coupled cluster (FSMRCC) level of theory with four-component relativistic spinors. The computed quantities resulting from the SARC basis are subsequently compared with those obtained using an *even-tempered* basis to assess the efficacy of the SARC basis. Computations have also been performed with the extended SARC basis to improve the quality of the property of interest. The accuracy of the computed quantities such ionization energy, electron affinity, excitation energies, etc., obtained using the SARC basis at the FSMRCC level of theory demonstrates that the SARC basis (particularly the extended one), which is primarily designed for quantum chemical calculations at the two-component scalar relativistic level for systems containing heavy atoms, can be used for fully relativistic calculations. The magnetic dipole hyperfine structure constant $\mathcal{A}$, oscillator strengths f and transition rates A_{fi} calculated using the SARC basis also agree well with the experiment and with the available theoretical estimates.

I. INTRODUCTION

Despite immense methodological and numerical developments, relativistic calculations for heavy elements find it difficult to achieve the same level of precision as the non-relativistic ones for light elements due to the unavailability of a suitable basis set for heavy atoms. It is well known that the relativistic and electron correlation effects in systems containing heavy elements are often of the same order of magnitude, in which the former one increases with increasing nuclear charge. Not only that, the size of the single particle basis that needs to be used for reliable description of the system under investigation also increases as the atom gets heavier. For instance, the scaling of the second-order many-body perturbation theory (MBPT), the coupled-cluster method with single and double (CCSD) excitation, and CCSD with triple excitation (CCSDT) are of the order O^2V^3, O^2V^4, and O^3V^5, respectively, where O and V represent the numbers of occupied and virtual orbitals (N=O + V, with N being the total number of one-particle orbitals). As a result, full-blown correlated relativistic calculations of heavy atomic and molecular systems become highly prohibitive (computationally intensive) and almost unattainable. This is also true in non-relativistic situations where it limits the applications of reliable and accurate wave function based methods to moderate-size systems. Several schemes have been proposed to reduce the computational costs, such as excluding the core and high-lying virtual orbitals from the correlation calculations. It was also shown that larger computational savings can, in principle, be achieved by freezing a significant fraction of the virtual space based on their occupation numbers in natural orbital basis.[1–3] Despite all these developments, the basis set aspect still remains crucial because the relativistic calculations on heavy elements, till date, primarily rely on a large number of uncontracted bases due to the unavailability of an appropriate basis for heavy atoms. Several types of all-electron basis sets (both in contracted and uncontracted forms) have been put forward over the years by various research groups to address these requirements in an optimal and balanced way. Probably the earliest attempt in this direction was initiated by Raffenetti and Ruedenberg[4] who proposed the so-called *even-tempered* (ET) basis set where the name *even-tempered* comes from the constraint imposed on the choice of exponents used in generating the one-electron basis. In a subsequent publication, Bardo and Ruedenberg[5] explored the possibility of using a common set of exponent parameters, which are independent of orbital angular momentum. In order to attain high accuracy with a smaller basis size, Huzinaga *et al.*[6] proposed a generalized formula [the so-called *well-tempered* basis (WTB)] in generating the orbital exponent, which is a function of four parameters (orbital angular momentum dependent). In recent years, Rolfes *et al.*[7] developed a family of segmented all-electron relativistically contracted (SARC)[8–11] basis sets for routine calculations, chiefly based on density functional theory (DFT),[12,13] in combination with two widely available scalar relativistic Hamiltonian, viz., the second-order Douglas–Kroll–Hess (DKH),[14–25] the zeroth-order regular approximation (ZORA).[26,27] The SARC basis has also been successfully applied by Alizadeh and co-workers in their DKH based multi-reference configuration interaction (MRCI) on bimetallic clusters of Group XI elements.[28–30] The construction of the SARC basis follows simple rules and strives to provide a reasonable compromise between accuracy and efficiency. The SARC family basis sets have been developed for a wide range of moderate to heavy atoms, including the elements of the 6p-block of the Periodic Table.

To analyze the usefulness of the SARC basis set in a relativistic context, we have carried out Fock-space multi-reference coupled cluster (FSMRCC) calculation on the Ag atom using four-component relativistic spinors with the SARC basis of Rolfes *et al.*[7] Calculations have also been performed with the ET basis (Bardo and Ruedenberg[5] type) using the same number of basis functions to assess the relative performance of these two basis sets. With the system being moderately heavy, the relativistic effect will be non-negligible, and at the same time, it can be studied with a reasonable number of polarization functions without much computational complexity. This system is interesting from an application point of view as the relativistic contraction and stabilization of the *ns* valence shell ($n = 4$–6) of Group XI elements is known to undergo a local maximum. This phenomenon is known as "Gold maximum" as Gold exhibits pronounced relativistic effects. The theoretically predicted relative position of the low-lying excited states of Group XI elements is also quite interesting. For instance, the non-relativistic calculations predict the first excited ^{2}P ([Xe]$4f^{14}5d^{10}6p$) state of Gold to be energetically lower than the first excited ^{2}D ([Xe]$4f^{14}5d^{9}5s^{2}$) state whereas experimental values are in reverse order. It was subsequently shown that the inclusion of relativistic terms in the Hamiltonian (*at least the leading one*) is necessary to obviate this problem. The relative stability of the low-lying excited states of the Ag atom is also unique compared to Cu and Au atoms. To be more specific, the relative energy of the low-lying excited states of Cu and Au atoms are in the order ${}^2D_{\frac{5}{2}} < {}^2D_{\frac{3}{2}} < {}^2P_{\frac{1}{2}} < {}^2P_{\frac{3}{2}}$, whereas those in the Ag atom appear as ${}^2P_{\frac{1}{2}} < {}^2D_{\frac{5}{2}} < {}^2P_{\frac{3}{2}} < {}^2D_{\frac{3}{2}}$. The present work characterizes the ground and excited states of the Ag atom and its ions by computing their energies using the Fock-space multi-reference coupled cluster (FSMRCC) method.[31–39] It is well known that the non-uniqueness of the exponential nature of the wave operator employed in the CC method diversifies this method to a host of MRCC strategies. The traditional MRCC methods hinge on the effective Hamiltonian approach and work within the complete model space (CMS), although they are rather more varied in their scope of applications.[40] The effective Hamiltonian based MRCC strategies fall into two broad classes: (i) state-universal, a Hilbert-space approach[41] and (ii) valence-universal, a Fock-space approach.[31–39] The Hilbert space based method highlights only one valence sector at a time, where the cluster operators are defined with respect to each reference function. The Fock space approach, on the contrary, uses a single wave operator that not only correlates the reference functions of interest but also correlates all the lower valence (or the so-called *subduced*) sectors, obtained by deleting the occupancy systematically. At this juncture, we recall that the cluster amplitudes in Fock-space MRCC are generated hierarchically through the *subsystem embedding condition* (SEC),[34,37] which is equivalent to the *valence universality* condition used by Lindgren[32] in his formulation. We reiterate that FSMRCC is an ideal candidate for the characterization of the states with varying numbers of valence electrons through the use of a single "valence universal" wave operator and hence is very useful for estimating the energy differences of spectroscopic interest. The FSMRCC method, an all-order, size-extensive, and multi-root method, has already been used to estimate transition energies, providing satisfactory accordance with experiments in general.[42]

II. COMPUTATIONAL DETAILS

We are not going to discuss or provide theoretical details of the Dirac–Fock and Fock-space multi-reference coupled cluster methods as these are well documented in the literature. We shall rather concentrate on the computational aspects of these methods relevant to the present work. Here, the Dirac–Coulomb equations are first solved, assuming the nucleus size to be finite and imposing a *kinetic balance*[43] condition. The solution of the Dirac–Fock equations provides the single-particle orbitals and orbital energies, which are subsequently used to incorporate the electron correlation in the FSMRCC calculations of ionization potential, electron affinity, excitation energy, etc., by projecting out the negative energy states to avoid *continuum dissolution*.[44,45]

Since the ground state of Ag is an open-shell doublet (${}^2S_{1/2}$) with one electron in its outermost 5s orbital, we begin with Ag^+ ion. which defines the (0h, 0p) valence sector (Fermi vacuum) of the Fock-space. The ground and excited state energies of Ag are then computed employing the (0h, 1p) FSMRCC method for one-electron attachment process. Following this strategy, the ground ${}^2S_{\frac{1}{2}}$ ($4d^{10}5s$) and excited ${}^2P_{(\frac{1}{2},\frac{3}{2})}$ ($4d^{10}5p$), ${}^2S_{\frac{1}{2}}$ ($4d^{10}6s$), ${}^2P_{(\frac{1}{2},\frac{3}{2})}$ ($4d^{10}6p$), and ${}^2D_{(\frac{3}{2},\frac{5}{2})}$ ($4d^{10}5d$) state energies of Ag are obtained by adding an electron to the 5s, 5p, 6s, 6p, and 5d unoccupied (virtual) orbitals of Ag. It is observed that while the FSMRCC for one-electron attachment process offers reasonably accurate estimates of ${}^2S_{\frac{1}{2}}$ and ${}^2P_{\frac{1}{2},\frac{3}{2}}$, as well as $^2\mathrm{D}_{\frac{3}{2},\frac{5}{2}}$ excited state energies of configurations $4\mathrm{d}^{10}5\mathrm{s}$, $4\mathrm{d}^{10}6\mathrm{s}$, $4\mathrm{d}^{10}5\mathrm{p}$, $4\mathrm{d}^{10}6\mathrm{p}$, and $4\mathrm{d}^{10}5\mathrm{d}$, it fails to provide correct estimates for the second $^2\mathrm{D}_{\frac{5}{2}}$ and fourth excited $^2\mathrm{D}_{\frac{3}{2}}$ state energies of the configuration $4\mathrm{d}^9 5\mathrm{s}^2$. It further shows that the $^2\mathrm{D}_{\frac{5}{2}}$ ($4\mathrm{d}^9 5\mathrm{s}^2$) state is energetically lower but quite close to the $^2\mathrm{D}_{\frac{5}{2}}$ ($4\mathrm{d}^{10}5\mathrm{d}$) state. This is also true for $^2\mathrm{D}_{\frac{3}{2}}$ states arising from configurations $4\mathrm{d}^9 5\mathrm{s}^2$ and $4\mathrm{d}^{10}5\mathrm{d}$. This problem, most likely, arises due to the highly bound character of the single-particle orbitals 4d and 5s resulting from the Dirac–Fock self-consistent field (SCF) calculations with Ag^+ as the reference state. Also note that the low-lying $^2\mathrm{D}$ excited states of the electronic configuration $4\mathrm{d}^9 5\mathrm{s}^2$ are 1h–2p states (shake-off state) whereas $^2\mathrm{D}$ states with completely filled 4d orbitals are 0h–1p states with respect to Fermi vacuum. This incorrect ordering issue between $^2\mathrm{P}_{(\frac{1}{2},\frac{3}{2})}$ ($4\mathrm{d}^{10}5\mathrm{p}$) and $^2\mathrm{D}_{(\frac{3}{2},\frac{5}{2})}$ ($4\mathrm{d}^9 5\mathrm{s}^2$) states can be partly mitigated by choosing the unperturbed reference function of Ag^- ($4\mathrm{d}^{10}5\mathrm{s}^2$) as the Fermi vacuum, i.e., the (0h–0p) valence sector. With this particular choice of Fermi vacuum, ground $^2\mathrm{S}_{\frac{1}{2}}$ ($4\mathrm{d}^{10}5\mathrm{s}$), low-lying second $^2\mathrm{D}_{\frac{5}{2}}$ ($4\mathrm{d}^9 5\mathrm{s}^2$) ,and fourth excited $^2\mathrm{D}_{\frac{3}{2}}$ ($4\mathrm{d}^9 5\mathrm{s}^2$) states become the 1h–0p particle states (w.r.t. Fermi vacuum) whose energies can be computed using FSMRCC for one-electron detachment process. The same problem also exists in Cu and Au where these $^2\mathrm{D}_{\frac{5}{2}}$ and $^2\mathrm{D}_{\frac{3}{2}}$ states are the first and second excited states of these atoms. In fact, Eliav *et al.*[46] adopted this strategy (multiple choice of vacuum/reference states) to avoid this problem in their relativistic CC calculations of the Au atom.

In this work, the ground state and ionized or excited state properties are computed using the single particle basis functions generated by solving the Dirac–Fock equations where the one-electron basis functions are constructed from an uncontracted Gaussian basis set.[47] The exponents for the SARC basis of Ag are taken from Ref. 7, and those for the "even-tempered" (ET) basis (Bardo and Ruedenberg[5] type) are generated via the relation $\alpha_i = \alpha_0 \beta^{i-1}$ where parameters α_0 and β are chosen to be 0.008 25 and 2.23, respectively. In order to compare the SARC and ET bases on equal footing, we have employed the same number of basis functions (25s18p13d) in both the cases. The Dirac–Fock energy for the ground state of Ag resulted from the ET and SARC basis is −5 314.627 315 and −5 314.783 713 a.u., respectively. The radial expectation values of the innermost s, p, and d orbitals (in Bohr) determined from the four-component Dirac–Fock calculations with ET and SARC basis sets are also in accordance with those reported by Rolfes *et al.*[7] These 25s18p13d uncontracted Gaussian bases are, however, not good enough for excited/ionized state calculations as there are no polarization functions in these basis sets. To improve the accuracy of the ground and excited/ionized states, 6f, 4g, and 2h functions are added to the existing 25s18p13d basis. Since the correlation contribution from single particle orbitals of energy ϵ greater than ±100 a.u. is negligibly small,[48,49] deep-lying occupied ($\epsilon < -100$ a.u.) and high-lying virtual ($\epsilon > 100$ a.u.) orbitals can be excluded in the post-Dirac–Fock treatment, i.e., in FSMRCC calculations. Here, these energy threshold criteria are applied only for unoccupied orbitals as there are only four occupied orbitals whose single particle energy is less than −100 a.u. (1s, 2s, $2\mathrm{p}_{1/2}$ and $2\mathrm{p}_{3/2}$). FSMRCC calculations, in the present context, are carried out at the single and double excitation (SD) level as full-fledged FSMRCC calculation with single, double, triple, and higher excitation is computationally expensive.

The ionization potential (IP), electron affinity (EA), and excitation energies (EE) of Ag obtained using the relativistic FSMRCC method with SARC and ET basis sets are summarized in Table I along with other correlated calculations[50–52] and with recommended data from the National Institute of Standards and Technology (NIST) database.[53] IP, EE, and EA resulting from the Dyall-v4z (33s25p17d6f4g2h) basis[54] are listed in this table for comparison. The IP of Ag was computed by Neogrady *et al.*[52] using the spin-free DKH orbitals whereas Safronova *et al.*[50] and Nayak *et al.*[51] employed four-component relativistic spinors in their third order many-body perturbation MBPT(3) and FSMRCC calculations. As can be seen in Table I, the CCSD(T) calculations by Neogrady *et al.*[52] reproduce the IP of Ag better than the third order MBPT.[50] These results indicate that the higher order correlation contribution is quite significant in IP calculations for this system. The electron affinity obtained using the SARC basis is quite encouraging. For instance, the electron affinity yielded by relativistic FSMRCC/SARC is 0.067 eV higher than the observed value whereas the same from the ET and Dyall-v4z basis sets is 0.033 and 0.061 eV, respectively, higher than the experimental value of 1.304 eV. SARC and ET based calculations offer results of comparable accuracy where the SARC basis fares marginally better than the ET basis in some cases. While the Dyall-v4z basis provides quite accurate estimates of IP, EE, and low-lying $^2\mathrm{P}_J$ ($J = \frac{1}{2}, \frac{3}{2}$) states, it overestimates EE for high-lying $^2\mathrm{S}_{\frac{1}{2}}$ ($4\mathrm{d}^{10}6\mathrm{s}$), $^2\mathrm{P}_{\frac{1}{2}}$ ($4\mathrm{d}^{10}6\mathrm{p}$), $^2\mathrm{P}_{\frac{3}{2}}$($4\mathrm{d}^{10}6\mathrm{p}$), $^2\mathrm{D}_{\frac{3}{2}}$ ($4\mathrm{d}^{10}5\mathrm{d}$), and $^2\mathrm{D}_{\frac{5}{2}}$ ($4\mathrm{d}^{10}5\mathrm{d}$) states. In fact, $^2\mathrm{D}_{\frac{3}{2}}$ ($4\mathrm{d}^{10}5\mathrm{d}$) and $^2\mathrm{D}_{\frac{5}{2}}$ ($4\mathrm{d}^{10}5\mathrm{d}$) state energies resulted from this basis are found to be above the ionization threshold.

FSMRCC calculations are also performed with an extended basis of size 30s25p20d7f5g2h to improve the accuracy of the computed quantities. This extended basis is constructed by adding few s, p, d, and g functions to the existing 25s18p13d6f4g2h basis. As can be seen in Table I, use of an extended basis improves the accuracy of the estimated quantities. For example, use of the extended basis reduces the difference between the experiment and theoretical estimate of the ionization potential by 0.04–0.05 eV. A similar trend is also observed for $^2\mathrm{S}_{\frac{1}{2}}$–$^2\mathrm{P}_{\frac{1}{2}}$, $^2\mathrm{S}_{\frac{1}{2}}$–$^2\mathrm{P}_{\frac{3}{2}}$, etc., transition energies.

We reiterate that the FSMRCC method for the one-electron detachment process is employed to compute the electron affinity (EA) of the Ag atom. The same strategy is also used to determine its low-lying $^2\mathrm{D}_{\frac{5}{2}}$ ($4\mathrm{d}^9 5\mathrm{s}^2$) and $^2\mathrm{D}_{\frac{3}{2}}$ ($4\mathrm{d}^9 5\mathrm{s}^2$) state energies. It is found that FSMRCC equations for the 4d ionization process encounter serious convergence issues (also called the *intruder state problem*[55]). This convergence problem is avoided by computing the ionization energies via the equation of motion based coupled cluster (EOMCC)[56–63] method, which is formally equivalent to FSMRCC for the one-valence problem.[64] Being an eigenvalue equation, this alternative scheme does not suffer (*normally*) from the convergence problem. EOMCC calculations for the ionization process show that the configuration state function $4\mathrm{d}^9 5\mathrm{s}^2$ contributes 49% and 59% to $^2\mathrm{D}_{\frac{5}{2}}$ and $^2\mathrm{D}_{\frac{3}{2}}$ states wave functions, respectively. Note that this convergence issue in the FSMRCC scheme normally arises for inner-valence ionization and not for outer-valence ionization, and that is why FSMRCC equations for the 5s ionization process were not plagued by the intruder state problem. Despite all, EE values of

TABLE I. Ionization potential (IP), excitation energies (EE), and electron affinity (EA) of Ag (in electron volt) from four-component FSMRCC calculations with even-tempered (25s18p13d6f4g2h) and SARC basis sets. Extended (30s25p20d7f5g2h) basis set results are shown in the parentheses. Selected results from Dyall-v4z (33s25p17d6f4g2h) are also listed here.

State		ET	SARC	Dyall-v4z	Others	NIST
IP	$^2S_{\frac{1}{2}}$ $(4d^{10}5s)$	7.402 (7.458)	7.439 (7.485)	7.520	7.237,[a] 7.542,[b] 7.492[c]	7.577
EE	$^2P_{\frac{1}{2}}$ $(4d^{10}5p)$	3.605 (3.641)	3.605 (3.645)	3.671	3.481,[a] 3.690[b]	3.664
	$^2D_{\frac{5}{2}}$ $(4d^{9}5s^{2})$	4.013 (4.219)	4.044 (4.091)	4.345		3.750
	$^2P_{\frac{3}{2}}$ $(4d^{10}5p)$	3.712 (3.751)	3.716 (3.758)	3.786	3.589,[a] 3.799[b]	3.778
	$^2D_{\frac{3}{2}}$ $(4d^{9}5s^{2})$	4.550 (4.797)	4.605 (4.663)	4.985		4.304
	$^2S_{\frac{1}{2}}$ $(4d^{10}6s)$	5.126 (5.178)	5.159 (5.202)	5.504	5.249[b]	5.277
	$^2P_{\frac{1}{2}}$ $(4d^{10}6p)$	5.845 (5.898)	5.870 (5.913)	6.312		5.988
	$^2P_{\frac{3}{2}}$ $(4d^{10}6p)$	5.871 (5.925)	5.896 (5.943)	6.369		6.014
	$^2D_{\frac{3}{2}}$ $(4d^{10}5d)$	5.879 (5.933)	5.914 (5.960)		5.714,[a] 6.015[b]	6.043
	$^2D_{\frac{5}{2}}$ $(4d^{10}5d)$	5.879 (5.936)	5.916 (5.963)		5.717,[a] 6.018[b]	6.046
EA	$^1S_0$ $(4d^{10}5s^{2})$	1.347 (1.382)	1.371 (1.377)	1.365		1.304

[a] Reference 50.
[b] Reference 51.
[c] Reference 52.

low-lying $^2D_{\frac{5}{2}}$ $(4d^{9}5s^{2})$ and $^2D_{\frac{3}{2}}$ $(4d^{9}5s^{2})$ excited states obtained using FSMRCC for the ionization process are ~0.3 eV higher than the experimental value. More importantly, these calculations predict the $^2D_{\frac{5}{2}}$ $(4d^{9}5s^{2})$ state to be energetically higher than $^2P_{\frac{3}{2}}$ $(4d^{10}5p)$. To address this issue, effect of triples is included in the FSMRCC calculations in an approximate way,[48,49,65] and the results are displayed in Table II. As can be seen in Table II, inclusion of triple excitation (approximate) not only improves the EA value but also provides accurate estimates of the excited states and their relative order (except for the $^2D_{\frac{5}{2}}$ state from extended ET basis FSMRCC calculations). We further note that FSMRCC calculations with the ET and SARC basis estimate the ground $^2S_{\frac{1}{2}}$ $(4d^{10}5s)$ state energy to be −5 314.769 138 and −5 314.759 581 a.u. for electron–electron attachment and detachment processes, respectively. This minuscule

TABLE II. Ionization potential (IP), excitation energies (EE), and electron affinity (EA) of Ag (in electron volt) from four-component FSMRCC(T) calculations with even-tempered (ET) and SARC basis sets. Extended basis set results are shown in the parentheses.

State		ET	SARC	Others	NIST
IP	$^2S_{\frac{1}{2}}$ $(4d^{10}5s)$	7.408 (7.465)	7.442 (7.492)	7.237,[a] 7.542,[b] 7.492,[c]	7.577
EE	$^2P_{\frac{1}{2}}$ $(4d^{10}5p)$	3.615 (3.652)	3.614 (3.657)	3.481,[a] 3.690[b]	3.664
	$^2D_{\frac{5}{2}}$ $(4d^{9}5s^{2})$	3.646 (3.804)	3.678 (3.714)		3.750
	$^2P_{\frac{3}{2}}$ $(4d^{10}5p)$	3.721 (3.761)	3.723 (3.769)	3.589,[a] 3.799[b]	3.778
	$^2D_{\frac{3}{2}}$ $(4d^{9}5s^{2})$	4.157 (4.363)	4.213 (4.262)		4.304
	$^2S_{\frac{1}{2}}$ $(4d^{10}6s)$	5.131 (5.184)	5.162 (5.209)	5.249[b]	5.277
	$^2P_{\frac{1}{2}}$ $(4d^{10}6p)$	5.852 (5.903)	5.875 (5.922)		5.988
	$^2P_{\frac{3}{2}}$ $(4d^{10}6p)$	5.878 (5.933)	5.900 (5.948)		6.014
	$^2D_{\frac{3}{2}}$ $(4d^{10}5d)$	5.884 (5.884)	5.918 (5.968)	5.714,[a] 6.015[b]	6.043
	$^2D_{\frac{5}{2}}$ $(4d^{10}5d)$	5.886 (5.887)	5.920 (5.970)	5.717,[a] 6.018[b]	6.046
EA	$^1S_0$ $(4d^{10}5s^{2})$	1.267 (1.300)	1.286 (1.299)		1.304

[a] Reference 50.
[b] Reference 51.
[c] Reference 52.

TABLE III. Magnetic dipole hyperfine structure constant $\mathcal{A}$ (in MHz), oscillator strengths f, and transition rates A_{fi} (in 10^8 seconds) of the low-lying excited states of Ag from FSMRCC calculations with extended ET and SARC basis sets.

	State					
Property	Initial(i)	Final(f)	ET	SARC	Others	Refs.
$\mathcal{A}$	$4d^{10}5s$		−1726	−1733	−1724,[a] −1760[b]	−1713.00[c]
	$4d^{10}5p_{\frac{1}{2}}$		−167	−171	−180[a]	
	$4d^{10}5p_{\frac{3}{2}}$		−28	−29	−30[a]	
F	$4d^{10}5s$	$4d^{10}5p_{\frac{1}{2}}$	0.2588	0.2577	0.2497[d]	
		$4d^{10}5p_{\frac{3}{2}}$	0.5289	0.5274	0.5134[d]	
	$4d^{10}5p_{\frac{1}{2}}$	$4d^{10}5d_{\frac{3}{2}}$	0.5872	0.5768	0.5773[d]	
	$4d^{10}5p_{\frac{3}{2}}$	$4d^{10}5d_{\frac{3}{2}}$	0.0624	0.0614	0.0613[d]	
		$4d^{10}5d_{\frac{5}{2}}$	0.5584	0.5567	0.5491[d]	
A_{fi}	$4d^{10}5s$	$4d^{10}5p_{\frac{1}{2}}$	1.4886	1.4861		1.3 [e]
		$4d^{10}5p_{\frac{3}{2}}$	1.6147	1.6161		1.4 [e]

[a] Reference 66.
[b] Reference 67.
[c] Reference 68.
[d] Reference 50.
[e] Reference 53.

difference in the estimated ground state energy from two different schemes validates the use of multiple vacuums in the computation of IP, EA, and EE for this system.

The magnetic dipole hyperfine structure constant $\mathcal{A}$ (in MHz) obtained from FSMRCC, multi-configuration Dirac–Fock,[66] and infinite-order regular approximation (IORA) based second order Möller–Plesset (MP2)[67] methods is compared in Table III with the available experimental data.[68] The experimental value of the magnetic dipole hyperfine structure constant, to our knowledge, is available only for the ground ${}^2S_{\frac{1}{2}}$ ($4d^{10}5s$) state, and the present work reproduces this quite well. For example, the deviation in the FSMRCC estimated $\mathcal{A}$ value for the ground ${}^2S_{\frac{1}{2}}$ ($4d^{10}5s$) state from extended SARC and ET basis sets is 20 MHz (1.1%) and 13 MHz (1%), respectively, from the experimental value reported by Wessel and Lew.[68] Among the excited ${}^2P_{\frac{1}{2}}$ ($4d^{10}5p$) and ${}^2P_{\frac{3}{2}}$ ($4d^{10}5p$) states, the agreement between MCDF and FSMRCC is better for $J = \frac{3}{2}$ (differ by 1 MHz, i.e., 3%) than for $J = \frac{1}{2}$ (off by 9 MHz i.e., 5%). Since our computed $\mathcal{A}$ value for the ground state agrees well with the experiment, we trust that $\mathcal{A}$ values predicted for the excited ${}^2P_{\frac{1}{2}}$ ($4d^{10}5p$) and ${}^2P_{\frac{3}{2}}$ ($4d^{10}5p$) states will also be quite accurate. It is pertinent to note that the magnetic hyperfine structure constant for the ground state resulting from the 25s18p13d6f4g2h SARC basis is ~50 MHz less than the experimental value. A similar deviation is also found with the ET basis. This discrepancy may be arising due to the use of an inadequate basis, which fails to provide an appropriate description of the ground ${}^2S_{\frac{1}{2}}$ ($4d^{10}5s$) state wave function near the nucleus. FSMRCC predicted oscillator strengths f and transition rates A_{fi} for ground ${}^2S_{\frac{1}{2}}$ ($4d^{10}5s$), $\longrightarrow$ ${}^2P_{(\frac{1}{2},\frac{3}{2})}$ ($4d^{10}5p$), ${}^2P_{(\frac{1}{2},\frac{3}{2})}$ ($4d^{10}5p$), and $\longrightarrow$ ${}^2D_{(\frac{3}{2},\frac{5}{2})}$ ($4d^{10}5d$) transitions are shown in Table III. Listed also are the MBPT(3) numbers reported by Safranova[50] and NIST values.[53] Similar to the magnetic dipole hyperfine structure constant $\mathcal{A}$, oscillator strengths as well as the transition rates yielded by FSMRCC are also in accordance with the theoretical[50] and NIST[53] values.

III. CONCLUDING REMARKS

The search for an appropriate but relatively small basis functions is of prime importance from an application point of view as the quantum chemical calculations often become highly prohibitive for systems containing heavy elements due to the size of the basis functions. In this connection, segmented all-electron relativistically contracted (SARC) basis, which is primarily designed for quantum chemical calculations at the two-component scalar relativistic level, is, in our opinion, worth venturing. To assess the accuracy that can be achieved with the SARC basis, the ionization potential, electron affinity, and excitation energies of the Ag atom are computed using the relativistic Fock-space multi-reference coupled cluster (FSMRCC) method with the SARC basis and are compared with those obtained using the even-tempered basis with the same number of basis functions. Considering the size and the accuracy of the computed quantities resulting from the SARC basis, it appears that significant computational savings can be achieved by using this basis in combination with the frozen natural orbital scheme.

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AUTHOR DECLARATIONS

Conflict of Interest

The authors have no conflicts to disclose.

Author Contributions

Rajat K Chaudhuri: Conceptualization (equal); Formal analysis (equal); Methodology (equal); Writing – original draft (equal); Writing – review & editing (equal). **Sudip Chattopadhyay**: Conceptualization (equal); Formal analysis (equal); Methodology (equal); Writing – original draft (equal); Writing – review & editing (equal).

DATA AVAILABILITY

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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