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Taming the Electronic Structure of Lead and Eka-lead (Flerovium) by the Relativistic Coupled Cluster Method

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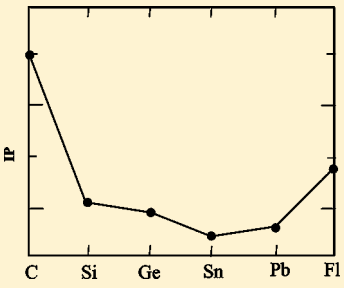
ABSTRACT: Theoretical investigations of the superheavy elements (SHEs) are extremely challenging and are often the sole source of useful chemical information. Relativistic Fock-space multireference coupled cluster (RFS-MRCC) computations have been carried out for evaluating the ionization potential (IP), excitation energies (EE), nuclear magnetic hyperfine constant (A), lifetime (τ), and Landé g factor of singly ionized eka-lead (Fl II). To judge the accuracy of Fl II results, similar calculations are performed for Pb II, which shows a nice and consistent agreement with known experimental values. Thus, we believe that our predictions for Fl are reliable and useful for the simulation of experimental behavior. To the best of our knowledge, no prior theoretical and/or experimental information is available for A, τ, and g-factor of this SHE. The higher IPs and EEs of Fl II, with respect to Pb II, indicate the former to be more inert and less metallic than Pb. This is contingent on the effects of the relativistic stabilization of the 7s and $7p_{1/2}$ orbitals. The present analysis demonstrates the influence of higher-body cluster operators on atomic properties. The close agreement with the experiment (having an estimated error within 1−2%) indicates that the FS-MRCC method is a reliable predictive tool in cases where the experimental results are not readily available, such as the SHEs. The remaining source of error possibly stems out from the omission of the full-blown triple virtual excitations and the absence of Breit interaction.



I. INTRODUCTION

The study of the superheavy elements (SHE) having atomic numbers greater than 100 has gained tremendous impetus during the last few decades owing to the motivation obtained from the search for the "island of stability",[1] culminating in the extension of the modern form of the periodic table.[2,3] Significant progress has been made in recent years in creating new SHEs.[4−25] After the synthesis of elements 110−112 in 1994−96,[26−28] elements 114 and 116 were reported in 1999[29,30] and 2000.[31] The latter atoms are a subject of great interest, as they fall within the "island of stability" predicted by nuclear physics. The exact location of this island is not certain. The SHEs are bestowed with the presence of heavy nuclei, and the relativistic effects that stem out of this makes the study of these elements an interesting field of research, in addition to the typical nuclear properties associated with them. The SHEs also exhibit certain exotic chemical properties[22−24] that are not prevalent in their lighter analogues, and on many occasions one misses the expected kinship of the electronic environment of the SHEs with their lighter analogues. For instance, Lawrencium, which has a 7p valence shell instead of the 6d, is hypothesized from its resemblance of it with the electronic configuration of Lu; eka-gold (E111) has been attributed with a ground state electronic configuration of d^9s^2[32,33] contrary to the $d^{10}s^1$ configurations of the lighter coinage metals; while the bipositive cations of Zn, Cd, and Hg have a d^{10} configuration, the divalent eka-mercury (E112) cation has a d^8s^2 ground state.[34] It was also predicted[35] that eka-thallium (E113) would have different chemical properties compared to its lighter analogue Tl, say in its tendency to be anionic, eka-radon (E118) is found to be possessing positive electron affinity, though it is a rare gas.[36] In a nutshell, the studies on the SHEs pave the path for a systematic understanding of the chemical facets of the new elements in light of their lighter analogues and as a consequence ascertain justifiable positions for the new elements in the periodic table.

Quantum mechanical calculations play a pivotal role in the development of key ideas associated with the SHEs because of

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the difficulties linked with the experimental chemical investigations of the SHEs.[22−24,37] It is now well-accepted that relativity and electron correlation are dual complicated problems for the computational investigation of heavy and SHEs.[38] Although a variety of many-body methods are available for incorporating relativistic and dynamical electron correlation contributions into descriptions of many-electron systems, the relativistic coupled cluster (RCC) method has emerged as one of the most powerful and effective tool for a high precision description of electron correlations and relativistic effects. The CC is an all-order nonperturbative method and yields upon iteration an order-by-order many-body perturbation theory. However, at present, it is difficult to achieve the same precision as nonrelativistic CC calculations through RCC for small molecules containing light elements. The limiting factors are the number of electrons which need to be correlated, the size of the required one-particle basis sets, the more complicated electronic structure of many heavy elements, and the less-developed technology for relativistic CC calculations. In view of this, in recent years, the RCC methodologies have emerged as one of the major research activities in the realm of relativistic electronic structure theory.

In the present paper, our interest is focused on flerovium, Fl (E114, eka-Pb).[39] The present research on Pb and Fl by various groups attests to the chemical significance of this species as well as its intricate electronic structure. A remarkable property of the one electron picture for Fl is the huge spin−orbit splitting of the valence 7p level which yield it a closed-shell configuration: $[...]6d^{10}7s^{2}7p_{1/2}^{2}$.[40] This was indeed found to be true via the highly accurate ab initio calculations.[41] Theoretical estimates for a series of SHEs (including Fl) have been reported at the Dirac−Fock[42] and Dirac−Fock−Slater[32] level of theories. Dzuba et al.[43] reported second-order perturbation (with certain types of diagrams summed to all orders) calculations without Breit corrections. Incorporating Breit interaction, all electron calculations using single reference CC (SRCC) have also been done by Seth et al.[44] Johnson et al.[45] and Shukla et al.[46] demonstrated that the incorporation of Breit interaction is useful to explore electronic structure of SHEs. Electronic states of Fl were also calculated using the relativistic complete active space multiconfigurational self-consistent field (CASMCSCF)/configuration interaction (CI)/spin−orbit relativistic CI (RCI) techniques.[47] Generalized relativistic effective core potential (RECP) parameters accounting for Breit effects were also developed for elements 112−114.[48] Eliav and his group demonstrated that the RCC method is very effective to study the SHEs such as E111,[33] E112,[34] E113,[35] E118,[36] and E114.[41]

In view of its structural flexibility, recently, the valence universal (VU) or Fock space (FS) multireference coupled cluster (MRCC) method with four-component relativistic spinors has emerged as a method of choice for interpretation of the spectral properties of various relativistic systems.[34,35,49−63] Good agreement between experimental (whenever available) and theoretical estimates has been obtained. It is now widely recognized that the FS-MRCC[64−70] methodology (supporting size-extensivity and size-consistency) is one of the most powerful CC techniques for studying the electronic structure of atoms and molecules of spectroscopic interest. The FS-MRCC method permits an efficient description of the dynamical correlation effects through the cluster expansion and simultaneously accounts for the nondynamical correlation effectively. It is also capable of providing description of a hierarchy of systems with a different number of electrons, for example, with an increasing number of valence electrons. The FS-MRCC approach is based on exponential parametrization of the wave operator within the framework of Bloch equation, which leads to coupled nonlinear equations. By construction, the FS MRCC method has been tailored to treat differential correlation effects and orbital relaxation accompanying ionization, electron attachment, or excitation. Both effects play a crucial role in shaping diverse structural and spectroscopic properties. Therefore, the FSMRCC method provides a convenient scheme not only for excitation energy (EE) calculations but also for determination of ionization potentials (IP) and electron affinities (EA), that is, quantities which require consideration of systems with different number of electrons. The FS-MRCC approach has been augmented and improved by various workers.[71−74]

The coupled cluster linear response theory (CCLRT)[75] and closely related equation of motion (EOM-CC)[76] method are another choice for computing accurate energy differences of spectroscopic interest. As that of the FS-MRCC method, both of the aforesaid approaches directly compute the spectroscopic energies in the sense that they give a spectrum of electronic states in a single calculation. Owing to the fact that they preserve the CI-like structure of the working equations, the well-known merit of the EOM-CC (and also CCLRT) method over the conventional FS-MRCC are free from the intruders. The FS-MRCC approach offers an important advantage over the EOM-CC/CCLRT scheme by providing the rigorous size-extensive results and a correct description of the charge transfer excitations which are of universal importance.[77] However, this undesirable feature of EOM-CC is not as debilitating as it is in a truncated CI description of the ground state. Of course, EOM-CC or CCLRT does not offer a general solution to pronounce multireference situation. One can also notice that CCLRT or EOM-CC and IHFSCC (intermediate-Hamiltonian FS-MRCC method)[41] or eigenvalue independent partitioning based FS-MRCC (an alternative—to the intermediate Hamiltonian—way to reduce inefficient iterative solutions of the FS equations to a robust matrix diagonalization)[71,72] are similar in the sense that they both rely on diagonalization of a matrix representation of some operator. The symmetry adapted cluster configuration interaction (SAC-CI) approach of Nakatsuji and co-workers[78] is also closely related, although some additional approximations are invoked compared to EOM-CC and CCLRT.

In this paper, we study the electronic structural properties of spectroscopic interest of Fl II (eka-Pb) by calculating its ionization potential (IP), excitation energies (EE), nuclear magnetic hyperfine constant (A), lifetime, and Landé g factor by employing the FS-MRCC method (at singles−doubles and singles−doubles−(partial) triples excitation levels) in conjunction with very large basis sets. To our knowledge, this is the first time any MR variant of CC theory has been applied to determine the atomic properties such as the nuclear magnetic hyperfine constant, lifetime, and Landé g factor, which are expected to be useful to experimentalists in this area and in the search for any new physics beyond the standard model. In passing, we want to mention that a CC study of the atomic ground, excited, and ionized states of Pb and Fl as well as an exhaustive bibliography of earlier calculations is presented by Landau et al.[41] In ref 41, the IHFSCC[79] method with inclusion of the Breit term has been applied to neutral and ionized Pb and Fl. The IHFSCC method allows many more valence orbitals than that of FS-MRCC one and, consequently, many more states. Results of Landau et al.[41] can be used to calibrate

our present results. At this juncture, we point out that, to judge the relative performance of our method, we have included benchmark results obtained using other standard methods[40] in a variety of basis sets and approximations. However, we emphasize that this sort of a comparison is not truly appropriate from a quantitative standpoint owing to the varied nature of basis sets in conjunction with approximation(s) used, and one should opt for a comparison within the same basis set under the same truncation stratagem. Nevertheless, such a comparison in this context represents the effectiveness of the method in a truly qualitative sense and is not intended for carrying any quantitative prediction whatsoever. Using such a comparison one can judge whether our results are headed toward the correct direction or not. We are confident that many new and long-standing chemical problems of heavy and superheavy elements will be solved by FS-MRCC methods in the coming years.

This paper is organized as follows. Section II starts with an overview of relativistic four-component methodology. We then proceed to describe the FS-MRCC approach, followed by the discussion of the magnetic dipole hyperfine structure, lifetime, and Landé-g factor equations. Computational details are discussed in the subsequent subsection. Section III contains the results of our calculation with an in-depth discussion. Finally, in Section IV we conclude and highlight the findings of our present work.

II. THEORETICAL AND COMPUTATIONAL ASPECTS

In this section we have provided a brief account of theoretical and computation aspects relevant to our applications.

A. Dirac−Coulomb Hamiltonian. The relativistic many-electron Hamiltonian cannot be written in closed form. The simplest form is the Dirac−Fock−Coulomb (DFC) Hamiltonian, where the nonrelativistic one-electron terms in the Schrödinger equation are replaced by the one-electron Dirac operator (include relativistic effects) and the two-electron repulsion (Coulomb term) remains in the nonrelativistic form:

$$H = \sum_{i=1}^{N} [c\vec{\alpha}_i.\ \vec{p}_i + (\beta_i - 1)mc^2 + V_{\mathrm{nuc}}(r_i)] + \frac{1}{2}\sum_{i\neq j}\frac{e^2}{|\vec{r}_i - \vec{r}_j|} \quad (1)$$

in which the Dirac operators $\vec{\alpha}$ and β are expressed by the matrices

$$\vec{\alpha} = \begin{pmatrix} 0 & \vec{\sigma} \\ \vec{\sigma} & 0 \end{pmatrix} \qquad \beta = \begin{pmatrix} I & 0 \\ 0 & -I \end{pmatrix} \quad (2)$$

where $\overline{\sigma}$ stands for the Pauli matrices and I is the (2×2) unit matrix. V_{nuc} is the nuclear attraction operator, with the nucleus modeled as a point or finite-size charge. The other symbols have their own significance. All equations are in atomic units. Approximate one-electron solutions may be obtained by self-consistent field procedure. Here, Hartree−Fock orbitals are replaced by four component spins. To capture the effect arising from finite-size-nuclear correction, we have used a charge distribution inside the Fermi nucleus of the form

$$\rho^{\mathrm{nuc}}_{\mathrm{Fermi}}(r) = \rho_0[1 + \exp((r - b)/a)]^{-1} \quad (3)$$

where b is the cutoff radius at which $\rho^{\mathrm{nuc}}_{\mathrm{Fermi}}(b) = \rho_0/2$. The parameter a is related to skin thickness (t) by

$$t = 4 \ln 3a \quad (4)$$

In the present calculation, skin thickness (t) is set to 2.30 fm.

Correlation is no less important in the relativistic regime than it is for lighter elements and may be included in a similar manner. The four-component method, complemented by high-level treatment of correlation, provides the very effective and useful approach (say FS-MRCC) to heavy and superheavy atoms. In our work the DFC equations are solved first,[80] and correlation is included by the FS-MRCC method.

B. Fock-Space Multireference Coupled Cluster Method. The FS-MRCC method[64−70] is well-documented, and here we briefly outline the method (relevant to our applications) for the sake of completeness. In this approach, we begin with the N-electron closed-shell Dirac−Fock reference state $|\Phi\rangle$ and seek the solution of the Schrödinger equation $H\Psi_K = E_K\Psi_K$ for the K^{th} state of the system. The basic assumption in the FS-MRCC method is that of a common vacuum. The vacuum is chosen to be the closed shell Hartree−Fock (Dirac−Fock in relativistic regime) solution of the N-electron state. The wave function Ψ_K is constructed by operating with the valence universal wave operator $\Omega = \Omega_c\Omega_v = \exp(T)\{\exp(S)\}$ on the model function, where $\{\}$ denotes the normal-ordered form. Calling $\exp(-T)\ H\ \exp(T)$ as $\bar{H}$, the CC equations determining the T amplitudes can be compactly written as [solution of cluster equations for the (0,0) valence sector]

$$\langle\Phi_l^*|\bar{H}|\Phi\rangle = 0;\ \forall\ l \quad (5)$$

and $\langle\Phi_l^*|\Phi\rangle = 0$. So the underlying exponential ansatze simultaneously describe the ground and the excited states. As the exponential of a connected operator, all of the extensive properties of CC theory are properly included in all states. This means there are no unlinked diagrams like there are in CI. The FS Bloch equation for k-hole and l-particle valence sector can be written as ($\mathcal{P} = \sum_{\mathrm{I}}^{\mathrm{M}} |\Phi_{\mathrm{I}}\rangle\langle\Phi_{\mathrm{I}}|$ and $\mathcal{Q}$ are the model and virtual space projector, respectively)[64−70]

$$\begin{aligned} \mathcal{Q}^{(k,l)}\overline{\bar{H}\Omega_v}\mathcal{P}^{(k,l)} &= \mathcal{Q}^{(k,l)}\overline{\Omega_v\bar{H}}_{\mathrm{eff}}\mathcal{P}^{(k,l)} \\ \mathcal{P}^{(k,l)}\overline{\bar{H}\Omega_v}\mathcal{P}^{(k,l)} &= \mathcal{P}^{(k,l)}\overline{\Omega_v\bar{H}}_{\mathrm{eff}}\mathcal{P}^{(k,l)} \end{aligned} \quad (6)$$

where the dressed Hamiltonian (or similarity transformed Hamiltonian), defined as $\bar{H} = \exp(-T)\ H\ \exp(T)$ is a connected (extensive) operator and H_{eff} is the effective Hamiltonian (also extensive operator) and is given by $\mathcal{P}^{(k,l)}\bar{H}\Omega_v\mathcal{P}^{(k,l)}$, which upon diagonalization, gives the state-to-state energies we seek. In our applications, the FS-MRCC approach starts from a reference state, correlates it, then adds and/or removes electrons one at a time, recorrelating the whole system at each stage. The general feature of the FS-MRCC approach is that in order to solve the equations for the (k,l) sector, solutions for all lower sectors (i,j); with $i = 0$, k and $j = 0$, l must be known. This has sometimes been called the subsystem embedding condition.[68,70] The sector (k,l) of the Fock space includes all states obtained from the reference determinant by removing k electrons from designated occupied orbitals (termed as valence holes), and adding l electrons in designated virtual orbitals (termed as valence particles). The energy difference with respect to the reference state can be obtained directly by removing the term $H^{(0,0)}_{\mathrm{eff}} = E_{\mathrm{ref}}$ from eq 6. After convergence is achieved in a particular sector, H_{eff} is diagonalized to yield all energies of $\mathcal{P}^{(k,l)}$ states in that sector relative to the correlated energy of the reference determinant.

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Another advantage of the method is that full spatial and spin symmetry is built in by including all relevant determinants (or configurations) in P. With $|\Phi\rangle$ taken as the vacuum, the operators T, S, and H are all spin scalars and hence all are represented in terms of unitary generators. The level of truncation of cluster operator reflects the quality of the approximation, that is, the extent to which the complementary Q space is taken into account in the evaluation of the H_{eff}. The scheme used here involves the fully self-consistent, iterative calculation of all one-, two-, and partly three-body virtual excitations amplitudes, and sums all diagrams with these excitations to infinite order. As negative energy states are excluded from the Q space, the diagrammatic summations in the CC equations are carried out only within the subspace of the positive energy branch of the DFC spectrum.

Since the ground state of Pb II and Fl II (i.e, Pb^+ and Fl^+) ions contains only one electron in its outermost occupied p orbital, the ground and excited state energies (also the properties) of these systems can be conveniently computed through the FS-MRCC method and its variants. In the actual computation, the Dirac−Fock−Coulomb (DFC) equations are first solved for the M^{2+} (M = Pb and/or Fl), which defines the (0h,0p) valence sector (closed-shell reference state). Note that (mh, np) valence sector corresponds to the set of all excited (N−m+n) electron determinants with m hole and n particle occupancies in the active hole, particle orbitals. The ion is then correlated by CCSD, and one electron is then added, following the Fock-space scheme[68−70]

$$M^{2+}(0,\,0) + e \rightarrow M^{+}(0,\,1) \tag{7}$$

When the valence electron is attached to the first unoccupied p orbital of the ion M^{2+} we get the ground state of M^+. Similarly, the valence electron can be attached to any arbitrary virtual orbital to obtain the excited states of M^+.

It is worth mentioning that the CCLRT[75]/EOM-CC[76] methods in this particular one electron attachment process (i.e., one-valence sector of the FS) are formally equivalent to FS-MRCC one and give identical eigenvalues per se.[81] It has long been known that the principal IP's and EA's obtained by EOM-CC/CCLRT and FS-MRCC are precisely the same,[77,82] but the respective eigenvectors differ, although they are connected through a simple transformation. The detailed connections of FS-MRCC approach with the EOM-CC/CCLRT has been discerned.[72,77]

The one-electron properties, like transition matrix elements between any two states, can be computed using the following expression:

$$\langle O\rangle_{fi} = \frac{\langle \Psi_f^{(1,0)}|O|\Psi_i^{(1,0)}\rangle}{\sqrt{\langle \Psi_f^{(1,0)}|\Psi_f^{(1,0)}\rangle\langle \Psi_i^{(1,0)}|\Psi_i^{(1,0)}\rangle}} \tag{8}$$

which can be further simplified to

$$\begin{aligned}\langle O\rangle_{fi} = {} & \langle \Phi_f^{(1,0)}|\overline{\{1+S^\dagger\}\bar{O}\{1+S\}}|\Phi_i^{(1,0)}\rangle \\ & /[\langle \Phi_f^{(1,0)}|\overline{\{1+S^\dagger\}\Lambda\{1+S\}}|\Phi_f^{(1,0)}\rangle\langle \Phi_i^{(1,0)}| \\ & \overline{\{1+S^\dagger\}\Lambda\{1+S\}}|\Phi_i^{(1,0)}\rangle]^{1/2}\end{aligned} \tag{9}$$

where $\bar{O} = \overline{\exp T^\dagger\, O \exp T}$, $\Lambda = \overline{\exp T^\dagger \exp T}$, and $|\Phi^{(1,0)}\rangle$ is the model space function for the (1,0) valence sector. As both the numerator and denominator of eq 9 are nonterminating in nature, the properties estimated through this procedure will be always plagued by the truncation error. Nevertheless, reasonably accurate estimate can be obtained by truncating the series at $\overline{T^\dagger O T}$ and $\overline{T^\dagger T}$ provided the higher order terms are negligible. The error related to the truncation of cluster operators can be attenuated efficiently by invoking analytic gradient based FS-MRCC[83] and/or biorthogonal formulation of EOM-CC (also CCLRT) method,[75,74] and work in this direction is in progress in our group. We conclude this section by noting that we have implemented the biorthogonal based formulation for (h−p) excited states of helium-like ions embedded in plasma environment using relativistic CCLRT in the frame of the Debye screening model.[84]

C. Magnetic Dipole Hyperfine Structure and Lifetime Calculations. The magnetic dipole hyperfine constant A is defined as[85]

$$A = \mu_N\left[\frac{\mu_I}{I}\right]\frac{\langle J||T^{(1)}||J\rangle}{\sqrt{J(J+1)(2J+1)}} \tag{10}$$

where μ_I and μ_N are the nuclear dipole moment and nuclear magneton, respectively, and $T^{(1)} = \sum t_i^{(1)}$. The single-particle reduced matrix element of the electronic part $t_i^{(1)}$ is given by

$$\begin{aligned}\langle \kappa m|t_i^{(1)}|\kappa' m'\rangle = {} & -\langle -\kappa m|C_i^{(1)}|\kappa' m'\rangle(\kappa+\kappa') \\ & \times \int r^{-2}[P_\kappa(r)Q_{\kappa'}(r) + Q_\kappa(r)P_{\kappa'}(r)]\mathrm{d}r\end{aligned} \tag{11}$$

where

$$\begin{aligned}\langle \kappa||C^{(k)}||\kappa'\rangle = {} & (-1)^{j+1/2}\sqrt{(2j+1)(2j'+1)} \\ & \times \begin{pmatrix} j & k & j' \\ 1/2 & 0 & -1/2\end{pmatrix}\pi(l,\,k,\,l')\end{aligned} \tag{12}$$

with

$$\pi(l,\,k,\,l') = \begin{cases} 1 & \text{if } l+k+l' \text{ even} \\ 0 & \text{otherwise}\end{cases} \tag{13}$$

The magnetic dipole transition probability $A_{f\rightarrow i}^{M1}$ (in sec^{-1}) from upper state (f) to a lower state (i) is determined by using the formula:

$$A_{f\rightarrow i}^{M1} = \frac{1}{\tau} = \frac{2.6973\times 10^{13}}{\lambda^3(2J_f+1)}S_{f\rightarrow i}^{M1} \tag{14}$$

where $S_{f\rightarrow i}^{M1}$ (usually expressed in terms of magnetic dipole matrix element) is the transition line strength for magnetic dipole transition (M1) in a.u., λ is the transition wavelength in Å, and $(2J_f+1)$ is the degeneracy of the upper level (f). The single-particle reduced matrix elements for the $M1$ transition are given by

$$\begin{aligned}\langle \kappa_f||m1||\kappa_i\rangle = {} & \left(\frac{6}{\alpha\kappa}\right)\langle j_f||C_q^{(1)}||j_i\rangle \times \left(\frac{\kappa_f+\kappa_i}{2}\right) \\ & \times \int \mathcal{J}_1(kr)(\mathcal{P}_f\mathcal{Q}_i + \mathcal{Q}_f\mathcal{P}_i)\mathrm{d}r\end{aligned} \tag{15}$$

Here the j's and κ_i [$= \pm(j_i + 1/2)$]'s are the total orbital angular momentum and the relativistic angular momentum quantum numbers, respectively. k is defined as $\omega\alpha$, where ω is the single particle difference energy and α is the fine-structure constant. We use atomic units ($\hbar = m_e = |e| = 1$) in this paper. The single-particle orbitals are expressed in terms of the Dirac spinors with

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$\mathcal{P}_i$ and $\mathcal{Q}_i$ as the large and small components for the i-th spinor, respectively. The angular coefficients are the reduced matrix elements of the spherical tensor of rank m and are expressed as

$$\langle \kappa_f \| C_q^{(m)} \| \kappa_i \rangle = (-1)^{j_f+1/2} \times \sqrt{(2j_f+1)(2j_i+1)} \times \begin{pmatrix} j_f & m & j_i \\ 1/2 & 0 & -1/2 \end{pmatrix} \pi(l_f, k, l_i) \tag{16}$$

When κr is sufficiently small, the spherical Bessel function $\mathcal{J}_1(\kappa r)$ is approximated as

$$\mathcal{J}_1(\kappa r) \approx \frac{(\kappa r)^n}{(2n+1)!!} \tag{17}$$

D. Landé *g* Factor. The Landé g factor g_J is defined by the magnetic moment μ of the atom in state $|JM_J\rangle$ as[85]

$$\mu = -g_J \mu_B J \tag{18}$$

with $\mu_B = eh/4\pi mc$ being the Bohr magneton. Since the interaction energy $W = \langle H' \rangle = \langle -\mu \cdot B \rangle = g_J \mu_B \langle J \cdot B \rangle$, one can make use of the projection theorem to show that

$$g_J = \frac{1}{2\mu_B} \frac{\langle J \| N^{(1)} \| J \rangle}{\sqrt{J(J+1)(2J+1)}} \tag{19}$$

where

$$N_q^{(1)} = \sum \mu_q^{(1)} = -\sum ie\sqrt{8\pi/3}\, e\alpha \cdot Y_{1q}^{(0)}(\hat{r}) \tag{20}$$

and

$$\langle \kappa m | \mu_q^{(1)} | \kappa' m' \rangle = \langle -\kappa m | C_q^{(1)} | \kappa' m' \rangle (\kappa + \kappa') \times \int r(P_\kappa Q_{\kappa'} + Q_\kappa P_{\kappa'}) \mathrm{d}r \tag{21}$$

where

$$\langle \kappa m | C_q^{(1)} | \kappa' m' \rangle = (-1)^{j-m} \begin{pmatrix} j & k & j' \\ -m & q & m' \end{pmatrix} \langle \kappa \| C_q^{(1)} \| \kappa' \rangle \tag{22}$$

in which

$$\langle \kappa \| C_q^{(1)} \| \kappa' \rangle = (-1)^{j+1/2} \sqrt{(2j+1)(2j'+1)} \times \begin{pmatrix} j & k & j' \\ -\frac{1}{2} & 0 & \frac{1}{2} \end{pmatrix} \pi(l, k, l') \tag{23}$$

E. Corrections to the Landé *g* Factor. According to quantum electrodynamics, the electron g factor g_s is not exactly 2 but is

$$g_s = 2\left[1 + \frac{\alpha}{2\pi} - 0.328\frac{\alpha^2}{\pi^2} + \cdots\right] \approx 2 \times (1.001160) \tag{24}$$

which leads to a correction to the interaction Hamiltonian[86]

$$\Delta H' = 0.001160 \mu_B \beta \Sigma \cdot B \tag{25}$$

where the β and Σ have their usual meaning. The correction to the Landè-g factor is expressed as

$$\Delta g_J = 0.001160 \frac{\langle J | \Delta N^{(1)} | J \rangle}{\sqrt{J(J+1)(2J+1)}} \tag{26}$$

where

$$\Delta N_q^{(1)} = \Sigma \Delta \mu_q^{(1)} \tag{27}$$

and

$$\langle \kappa' m' | \Delta \mu_q^{(1)} | \kappa m \rangle = \langle -\kappa' m' | C_q^{(1)} | \kappa m \rangle (\kappa + \kappa' - 1) \times \int (P_{\kappa'} P_\kappa + Q_{\kappa'} Q_\kappa) \mathrm{d}r \tag{28}$$

F. Computational Details. Both the DFC and relativistic CC programs utilize the angular momentum decomposition of the wave functions and CC equations. Using the Jucys−Levinson−Vanagas theorem,[87] the Goldstone diagrams are expressed as products of angular momentum diagrams and reduced matrix element. This procedure simplifies the computational complexity of the DFC and relativistic CC equations. As the Dirac Hamiltonian is not bound from below, failure to observe correct boundary conditions leads to variational collapse[88] where the admixture of negative energy solutions may generate energies much below the experimental. Appropriate constraints[89] are also imposed to avoid "variational collapse" and "continuum dissolution"[88] (see ref 90 for further details). In the our computation, the DFC ground state and ionized or excited state properties are computed using the finite basis set expansion method (FBSE)[91] with Gaussian functions of the form[92]

$$F_{i,k}(r) = r^k \cdot \mathrm{e}^{-\alpha_i r^2} \tag{29}$$

where $k = 0, 1, \ldots$ for $s, p, \ldots$ type functions, respectively. For the exponents, the even tempering condition

$$\alpha_i = \alpha_0 \beta^{i-1} \tag{30}$$

is applied. In the present work, α_0 and β are chosen to be 0.00925 and 2.73, respectively. The self-consistent DFC orbitals are stored on a grid.

III. RESULTS AND DISCUSSION

As already stated, in this work we intend to present our investigation of the relativistic FS-MRCC (RFS-MRCC) method with SD and SDT truncation schemes for Pb and Fl which cannot properly be described with a single-reference approach. To assess the accuracy of our basis sets and electron correlation procedures applied in the Fl calculations, we also conduct an analogous treatment of Pb as experimental results for it are available in the literature.[93] Moreover, this also allows a meaningful comparison between the two elements. We present here theoretical estimates of IPs, EEs, nuclear magnetic hyperfine constant (A), lifetime, and Landé g factor using very large basis sets: 38s34p28d15f10g8h (Basis I) and 38s34p28d15f10g8h4i (Basis II) even-tempered Gaussian basis functions. [He] and [Ne] core electrons were frozen for Pb and Fl, respectively. The atomic properties reported here are also very useful to predict or simulate the adsorption behavior of the elements on inert or transition metal surfaces. Presently, experiments are underway to study the adsorption behavior of Fl relative to that of Pb. Information about the interaction of Fl with inert surfaces is very important for designing its transfer from the accelerator to the detectors.[94]

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Table 1. Ionization Potentials (IPs) and Excitation Energies (EEs) of Pb II Determined at the Dirac−Fock (DF) and RFS-MRCC Levels of Calculations with 38s34p28d15f10g8h (Basis I) and 38s34p28d15f10g8h4i (Basis II) Even-Tempered Gaussian Basis Functions[a]

		present work					
		Basis I		Basis II			
	transition	RFS-MRCCSD	RFS-MRCCSD(T)	RFS-MRCCSD	RFS-MRCCSD(T)	other experiments[93]	
IP (cm^{-1})	$6s^2$ ($^1S_0$)	120431 (114058)	121273	120438	121279	121077[41]	121245
						120077[96]	
						121898[97]	
						122382[95]	
EE (cm^{-1})	$6s^26p(^2P_{3/2})$	13817 (13600)	14118	13818	14117	13885[41]	14081
						13700[96]	
						13857[97]	
						14029[95]	
	$6s^27s(^2S_{1/2})$	58587 (55276)	59483	58592	59488	59253[41]	59449
	$6s^27p(^2P_{1/2})$	73863 (69331)	74463	73868	74468		74459
	$6s^27p(^2P_{3/2})$	76648 (71868)	77262	76654	77268		77273
	$6s^28s(^2S_{1/2})$	88387 (83222)	89429	88393	89437		89180

[a][He] core orbitals were kept frozen for Pb. The reference state configuration of Pb II is $[Xe]4f^{14}6s^26p$ ($^2P_{1/2}$). The Dirac−Fock estimates of IPs and EEs from 38s34p28d15f10g8h basis are shown in the parentheses.

Table 2. Ionization Potential (IP) and Excitation Energies (EE) of Fl II [$[Ra]5f^{14}7s^27p_{1/2}(^2P_{1/2})$] from RFS-MRCC Calculations with 38s34p28d15f10g8h4i Even-Tempered Gaussian Basis Functions[a]

		present work			
	transition	Dirac−Fock	RFS-MRCCSD	RFS-MRCCSD(T)	CCSD[41]
IP (cm^{-1})	$7s^2(^1S_0)$	130693	136220	137482	136074
EE (cm^{-1})	$7s^27p(^2P_{3/2})$	41496	39881	40991	39355
	$7s^28s(^2S_{1/2})$	69441	71533	72953	71993
	$7s^28p(^2P_{1/2})$	83879	87430	88461	
	$7s^28p(^2P_{3/2})$	90944	94899	95075	
	$7s^29s(^2S_{1/2})$	99049	103495	104756	

[a][Ne] core orbitals were kept frozen for Fl. The reference state configuration of Fl II is $[Rn]5f^{14}7s^27p(^2P_{1/2})$.

The core electrons, which experience the largest effects of relativity, have a negligible effect on the electronic response properties of the atom. The deep lying 1s, 2s, and 2p orbitals of Fl and 1s orbital of Pb are not included in the coupled calculations as these low lying occupied orbitals have been found to contribute very little to the transition energies and associated properties. Likewise, high lying virtual orbitals with orbital energies 1000.0 (for s), 800.0 (for p), 100.0 (for d and f), 50.0 (for g), 10.0 (for h), and 2.0 (for i) are eliminated in the post-Dirac−Fock calculations, constituting in effect a post-SCF contraction. It has been observed that high energy virtual orbitals have insignificant effect on the transition energies and other properties we calculate, as these orbitals have nodes in the inner regions of the atom and correlate mostly the inner-shell electrons, which we do not correlate anyway. The atomic weight of Pb was taken as 207.2, and for Fl we used 289 (see ref 30). The speed of light is 137.0599 au.

By comparison with the known chemistry of the Group 14 elements, the most likely oxidation states of Fl are 2+ and 4+. We compute the ionization potential and excitation energies of Pb II and Fl II via FS-MRCC for electron attachment process. In the present calculation, we start with Pb III/Fl III (i.e, Pb^{2+}/Fl^{2+}) and add an electron. Thus, the reference state used in these calculations for Pb II and Fl II are $[Xe]6s^2\ 6p_{1/2}$ (neutral Pb i.e, Pb I is $[Xe]6s^26p^2$) and $[Rn]7s^27p_{1/2}$ (neutral Fl i.e, Fl I is $[Rn]7s^27p^2$).

Our calculated ionization energies (IPs and EEs) of Fl and Pb in several ionization states using FS-MRCC with different truncation schemes and basis sets are given in Tables 1 and 2. For Pb, we also reported experimental results in Table 1 to calibrate our present estimates. The IPs and EEs estimated at the Dirac−Fock level are also listed here to demonstrate the effect of electron correlation on these properties. The salient feature of the calculated transition energies is that their behavior with the amount of correlation is accounted for. In the case of Pb, we notice a good performance of FS-MRCCSD with both the basis sets, yielding results that are very close to the corresponding previously published values indicating effectiveness of our code. We note that the FS-MRCCSD(T) calculations show improvements over the FS-MRCCSD in describing the IPs and EEs. Our FS-MRCCSD(T) results with both basis sets considered here are better than that of the previously reported values.[41,95−97] For Pb, the average deviations of the FS-MRCCSD and FS-MRCCSD(T) IPs from experiment are respectively 810 cm^{-1} and 31 cm^{-1}. It is noteworthy that the deviation due to IHFSCCSD calculations[41] with very large primary model spaces is 168 cm^{-1}. If we now turn our attention on EEs of the Pb system, we find that our results are very close in proximity to the corresponding values of the IHFSCCSD method[41] (whenever available). The FS-MRCCSD and FS-MRCCSD(T) methods yield EEs very close to those of the experimental data. The maximum deviation deviation from experiment (in cm^{-1}) for the FS-MRCCSD and

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FS-MRCCSD(T) EE calculations of $6s^26p(^2P_{3/2})$ are 264 and 37 respectively. The maximum error (in cm^{-1}) of EEs for $6s^27s(^2S_{1/2})$ due to these two methods are 862 and 44, respectively. The error for IHFSCCSD values these two states are 196 cm^{-1}. The average maximum deviations of the FS-MRCCSD(T) (and FS-MRCCSD) results from experiments for $6s^27p(^2P_{1/2})$ and $6s^27p(^2P_{3/2})$ states are 8 cm^{-1} (and 610 cm^{-1}). Thus, the FS-MRCCDT calculations offer a more accurate description of the EEs for the $6s^26p(^2P_{3/2})$, $6s^27s(^2S_{1/2})$, $6s^27p(^2P_{1/2})$, and $6s^27p(^2P_{3/2})$ states of Pb. However, it should be emphasized that for $6s^28s(^2S_{1/2})$ state, the error of FS-MRCCSD(T) EE (FS-MRCCSD) is 249 cm^{-1} (792 cm^{-1}). This high deviation for such a high lying state might be due to the infiltration of the intruder states or multiple/unphysical multiple solutions problem.[98,99] The intermediate Hamiltonian FS-MRCC method[41] avoids or at least attenuates this difficulty while at the same time allowing the use of large model spaces, improving significantly the accuracy of the calculation. The IH-based approach (proposed by Malrieu et al.[100] in the framework of degenerate perturbation theory) increases the scope of applicability of FS-MRCC approach in terms of states amenable to calculation. Another way out of this problem is to use incomplete model spaces[101] or eigenvalue independent partitioning scheme.[71,72]

Comparison of the IPs and EEs show that our FS-MRCC method is consistently closer to the experimental values than those reported previously.[95−97] It is evident from Table 1 that the extent of deviation of the estimated IPs and EEs for Pb from the corresponding experimental data for a given basis set decreases as the level of truncation scheme is increased. For a given truncation of the cluster operators, we also note that the decreases of the deviation from experimental values is not negligibly small with the increase in the size of basis sets. The close proximity of FS-MRCC results of Pb with the corresponding experimental results indicates that the FS-MRCC method with singles−doubles−(partial)triples in conjunction with very large basis sets provides good predictions for the electronic spectrum of this SHE, Fl. It is worth mentioning that the FS-MRCC predicted transition energies of Fl show IPs higher than those reported by Landau et al.[41] and Seth et al.[44]

From the results displayed in Tables 1 and 2, it can be seen that the first ionization potentials for Fl and the lowest excitation energy (which is usually interpreted by chemists as "promotion energy") for Fl are significantly larger than the corresponding quantities for it lighter homologue, Pb. At this point, we reiterate the fact that the usual trend of IPs decreasing for heavier atoms holds from C to Sn; reversal of this trend begins in Pb and increases greatly for Fl, with IPs surpassing those of Si (see Figure 1 for a schematic illustration).[102] In Fl, the strong spin−orbit splitting of the valence 7p level leads to the $7p_{3/2} \rightarrow 7p_{1/2}$ gap being larger than its $6p_{3/2} \rightarrow 6p_{1/2}$ counterpart for Pb, and the doubly degenerate $7p_{1/2}$ level is significantly lower than the $6p_{1/2}$ level in Pb. On the basis of this fact, one might ascribe that the closed-shell configuration of $Fl([\cdots]6d^{10}7s^27p_{1/2}^2)$ is extremely stable with respect to Pb. Many years ago these findings lead to the hypothesis of the rare-gas-like behavior of Fl,[13] which became popular after a series of thermochromatographic experiments.[21] Previous relativistic electronic structure calculations[41,97] for the Fl system also support the hypothesis of the rare-gas-like nature of Fl. Results of an earlier work[103] (based on atomic calculations) on the stability of some Fl^{2+} and Fl^{4+} compounds

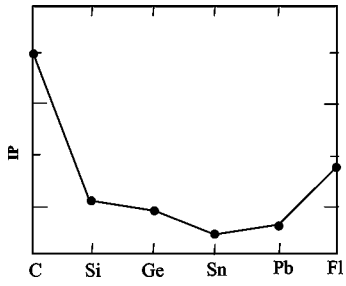

Figure 1. Schematic representation of the first ionization potentials of group 14 elements. After Si, enhancement of IPs is due to relativistic stabilization of the valence s and $p_{1/2}$ orbitals, which becomes pronounced in SHEs, say Fl.

also lead to the conclusion of a lower reactivity of Fl. In this context we want to mention that recent theoretical calculations agree on the fact that Fl-dimer is stronger bound than a typical van der Waals system but weaker than Pb_2.[37] Fl with its quasiclosed $7p_{1/2}^2$ shell is also expected to be highly volatile. Due to the relativistic stabilization of the $7p_{1/2}$ electrons of Fl, the 2+ state should predominate over the 4+ state to a greater extent than in the case of Pb. Relatively long half-lives of various isotopes of Fl allow us to perform experimental investigations of its chemistry. The results have been interpreted as indicative of the particular chemical inertness of this element, similar to those of heavy rare gases.[21,94] In support of this observation, we should mention that the ion exchange behavior of Pb in hydrohalic acids was proposed as a homologue for the corresponding behavior of Fl.[104] A study on mixed metal−metal species demonstrated that Fl would form weaker bonds than Pb[105] and would exhibit lower adsorption on surfaces.[106] Due to the same reason, the estimated van der Waals radius of Fl is smaller than that of Pb. High level density functional theoretical calculations including relativistic effects show that Fl would be more electronegative than Pb.[107] Four-component density functional theory and ECP-CCSD(T) investigation due to Liu et al.[37] also demonstrated that the bonds in Fl compounds are considerably weaker than those of Pb. It is noteworthy that the polarizability of Fl is the smallest in group 14, due to the relativistic stabilization and contraction of the outer $7p_{1/2}$ orbital.[106] Our present findings are also augmented by the previous observations due to the state-of-the-art experiments[29,30,93] and calculations[41,97] whenever available.

We now focus our attention to the computation of nuclear magnetic hyperfine constant (A), lifetime (τ), and Landé g factor. This information is more scarce for the SHEs. The estimations of these quantities using reliable high-precision relativistic ab initio methods for these systems are, therefore, highly desirable. To our knowledge, the A, τ, and Landé g factor calculations described here constitute the first FS-MRCC calculations. The FS-MRCC results are summarized in Table 3. Also included are other computations and experimental data[108,109] for comparison. For Fl, the lifetimes reach the 1s-range; this heavier element seems unnameable to traditional chemical investigation. Table 3 indicates that our predicted A, τ and g factors for Pb II are in general agreement with experiments. In case of IP and EE values, a close observation of the numerical results of the FS-MRCCSD(T) [summed to all orders of the one-, two-, and (partial) three-electron excitations] method, which are assembled in Table 3, exhibits that the overall performance of our code is better and more consistent over the previous works[96,97] reported in the table.

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Table 3. Magnetic Hyperfine Matrix Elements (A), Lifetime (τ), Landé g Factor g_J, and Δg_J of Pb II and Fl II from FS-MRCC Calculations with 38s34p28d15f10g8h4i Even-Tempered Gaussian Basis Set[a]

		present work				
	state	Dirac−Fock	RFS-MRCCSD	RFS-MRCCSD(T)	others	experiment
			A (in MHz)			
Pb II						
	$6s^26p(^2P_{1/2})$	11297	12651	12645	12903[96] 12872[95]	13000[108]
	$6s^26p(^2P_{3/2})$	902	619	618	623[96] 513[95]	583[108]
Fl II						
	$7s^27p\ (^2P_{1/2})$	70204	72476	72466		
	$7s^27p\ (^2P_{3/2})$	1176	−1523	−1522		
			τ (in sec)			
Pb II	$6s^26p(^2P_{3/2})$	0.0456	0.0445	0.0417	0.0440[96] 0.0409[95]	0.0412 ± 0.0007[109]
Fl II	$7s^27p(^2P_{3/2})$	0.0020	0.0022	0.0021		
			g_J			
Pb II	$6s^26p(^2P_{1/2})$	0.8164	0.6545	0.6545		
	$6s^26p(^2P_{3/2})$		1.3340	1.3339		1.33[93]
	$6s^27s(^2S_{1/2})$	2.4493	1.9998	1.9998		2.01[93]
Fl II	$6s^27p(^2P_{1/2})$	0.8163	0.6547	0.6548		
	$6s^27p(^2P_{3/2})$		1.3323	1.3323		
	$6s^28s(^2S_{1/2})$	2.4492	2.0007	2.0007		
			Δg_J			
Pb II	$6s^26p(^2P_{1/2})$		0.0025	0.0025		
	$6s^26p(^2P_{3/2})$		−0.0019	−0.0020		
	$6s^28s(^2S_{1/2})$		−0.0036	−0.0036		
Fl II	$6s^27p(^2P_{1/2})$		0.0025	0.0025		
	$6s^27p(^2P_{3/2})$		−0.0020	−0.0020		
	$6s^28s(^2S_{1/2})$		−0.0080	−0.0080		

[a]Magnetic moment used in these calculations for Pb is 0.58219. In all calculations, [He] and [Ne] core orbitals were kept frozen for Pb and Fl, respectively. Magnetic moment for Fl is chosen to be 1 as it is not available.

The performance of FS-MRCCSD(T) is better than its SD variant that strongly suggests that the inclusion of higher order correlation corrections is necessary for an accurate determination of A, τ, and Landé g. As that of the transition energies, the A, τ, and g factor reported here for Fl are expected to be as reliable as those our Pb. At this juncture, we emphasize that a precise determination of the $^2P_{1/2} \rightarrow {}^2P_{3/2}$ transition energy is necessary for an accurate prediction of the lifetime of the $^2P_{3/2}$ state. In addition, we also report the correction to the Landé g factor for the S and P states of Pb II and Fl II. At this point, it is difficult to assess the accuracy of our predicted Δg_J values since no prior theoretical results are available for this quantity. As our estimated transition energies, lifetime and magnetic hyperfine structure constants for Pb II are in good agreement with the available theoretical and experimental data (whenever available), we believe that our computed Δg_J is expected to be reliable. In passing, we note that the Dirac−Fock estimates of these properties are substantially off from the experiment as well from the correlated calculations, which reestablish the fact that the electron correlation must be taken into account for reliable and accurate predictions of these properties.

In a nut-shell, the transition energies and other properties of Fl reported here ought to be roughly as accurate as those of Pb and provide therefore good predictions for future experimental values as well as also increase our knowledge about the electronic structure properties of Fl. Information emerged from the present investigation using state-of-the-art theoretical calculations might be contribute to a better understanding of the theory of nuclear shell structure of SHEs, which underlies predictions of an "Island of Stability". Present in combination with previous[2,3] studies indicated that the heaviest elements are basically homologues of their lighter congeners in the chemical groups, though their properties may be rather different due to very large relativistic effects. This is also a reason why trends in atomic (and molecular) properties may change in going over to the heaviest elements.

From the foregoing analysis (augmented by state-of-the-art experimental findings), one can say that the properties of SHEs may differ from those of lighter elements in the same group of the periodic table due to relativistic effects. Therefore, straightforward extrapolations of the properties in same groups of the periodic table may lead to incorrect predictions. Relativistic ab initio calculations proved to be the most reliable tool. The relativistic CC implementation we are pursuing here opens the possibility of high precision calculation of electronic atomic properties of SHEs due to the arbitrary cluster excitation level and multireference expansions. This gives confidence that the RFS-MRCC method may give reliable predictions of the fine structure splitting of similar systems for which experimental data are not available. This paper is not to advocate replacement of the other previous investigated approaches; rather, it is to throw light on the role of the scheme of partial inclusion of triples in the treatment of the SHEs. We believe that the deviation from experimental data in our computation mainly arises due to the absence of the Breit interaction in our calculations, and efforts are underway to enable including these

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effects. We conclude this section by stating that relativistic effects stabilize s orbitals more as compared to the d orbitals, and correlation has an exactly opposite effect. When both effects are important and the results are not obvious a priori, one should confide on the methods like RFS-MRCC, which are inherently attuned to treat the effects stemming out of relativity and correlation simultaneously to high degree of accuracy

IV. CONCLUSION

The superheavy elements (SHEs) are most challenging and intriguing from a theoretical standpoint due to the intricate interplay of relativistic (owing to the large spin−orbit coupling) and correlation effects. Due to the presence of large relativistic effects, a simple picture of electronic states of proper spatial and spin symmetries no longer holds for these systems. Moreover, the properties of the SHEs say, flerovium, Fl [eka-Pb or E114] are not expected to follow simple periodic trends due to this effect. From a purely fundamental standpoint, the Fl presents a very challenging and interesting case for relativistic and electron correlation study that needs to comprehend the electronic states and spectroscopic properties of the elements and its compounds. Relativistic Fock space multireference coupled cluster (FS-MRCC) approach treats both relativistic and electron correlation effects simultaneously to high order in a balanced and consistent manner. The FS-MRCC emphasizes computation of differential correlation energy attendant on excitation or ionization/electron attachment relative to a ground state of predominantly single-reference in character. Moreover, the multistate nature of FS-MRCC greatly simplifies calculations of properties relevant to spectroscopic study. The accuracy and usefulness of FS-MRCC within a given truncation scheme can be systematically improved (up to the exact FCI results) by incorporating higher-body excitations explicitly or perturbatively.

In the present paper, the transition energies (such as ionization potential and excitation energy), magnetic (A) hyperfine matrix elements, lifetime, and Landé g factor of the Fl are reported by means of the relativistic FS-MRCC method with different basis sets and truncation schemes of the cluster operators. Simultaneous inclusion of relativistic terms in the Hamiltonian (via Dirac−Fock operator) and correlation effects [all products and powers of single, double, and (partial) triple virtual excitations] has been achieved. Fl has received considerable attention in present times due to the strong stabilization of the assumed outer shell configuration $7s^27p_{1/2}^2$. The mixing of different electronic states such as $^3P_2$, $^1D_2$, or $^3P_0$ ground states with $^1S_0$ excited state is particularly interesting for the case of 114 as all of these states arise from the same $7s^27p^2$ valence configuration. The FS-MRCC method is tailored to describe dynamic and nondynamic correlation effects simultaneously (which is crucial for correct interpretation of the complicated spectrum of Fl emerging from the mixing of different electronic states) at relatively low computational cost. In our calculations, spin−orbit coupling effects have been fully incorporated by exploiting the four-component Dirac-Coulomb Hamiltonian from the outset. We have also reported the estimates for Pb (by applying the same treatment to Pb as that of Fl) as reference values so that one can judge whether our results are directed toward the right direction or not. We observe a close behavior between the FS-MRCC methods and IHFSCC results for Pb. It should be emphasized here that the IHFSCC calculations include contributions from the Breit interactions that are omitted in our calculations. The errors in our best estimated IPs and EEs values are lower than the overall error of the IHFSCCSD calculations due to Kaldor and coworkers. The closeness of the performance of the FS-MRCCSD to the experimental estimates increases after inclusion of even partial triple excitations, indicating the necessity of using higher-order cluster operator to interpret the spectrum of Pb (the same holds for Fl). The close agreement of FS-MRCC estimates for Pb with experimental values indicates that the FS-MRCC values of Fl provide good predictions for the electronic spectrum of this SHE. According to the transition energies diagnostic, we found that the IP and EE of Fl are significantly higher than the analogous Pb values, making it less reactive than lead. This is due to the relativistic stabilization of the 7s and $7p_{1/2}$ orbitals. In view of this fact, Fl is expected to be less metallic and inert than lighter homologue, Pb. It should be noted that the errors of our calculated values are within 1−2% of experiment. Properties of Fl which are not known experimentally can be predicted. To our knowledge, no prior theoretical data provided by state-of-the-art calculations are available for the magnetic hyperfine constant, lifetime and g-factor of Fl. However, it should be emphasized that it remains to be determined whether the inclusion of Breit interaction as well as full-blown triple virtual excitations in our calculations improves accuracy of these computed quantities. We want to examine this issue in a future study. The FS-MRCC method may be extended to other sectors of the Fock space of Pb and Fl; applications are under way and will be reported in the future. As a final note, we do not claim that the relativistic FS-MRCC is a superior method for general use to study the electronic structure of relatively long-lived SHE isotopes; rather, we hope the present work might be helpful to unveil the complex puzzle that nature has posed in the context of "island of stability" for the SHEs.

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Notes

The authors declare no competing financial interest.

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