

Relativistic and electron correlation effects for molecules of superheavy elements:

All-electron all-virtual spinor space (AVSS) relativistic and nonrelativistic coupled-cluster and atomization energy calculations for the tetravalent superheavy eka-lead tetrahydride $E114 H_4$

Gulzari L Malli ^a

Department of Chemistry, Simon Fraser University,

Burnaby, B.C; Canada V5A 1S6.

^a Email: malli@sfu.ca

Abstract All-electron all-virtual spinor space (AVSS) nonrelativistic (Hartree-Fock) and fully relativistic Dirac-Fock second order Moller-Plesset (RMP2), coupled-cluster singles and doubles (RCCSD), RCCSD (T) (RCCSD plus the triple excitation correction included perturbationally) molecular calculations are reported for E114H₄. Both our DF and NR HF limit SCF calculations predict the ground state of E114H₄ (T_d) to be *bound*, with the predicted atomization energy (A_e) of 4.98 and 8.41 eV, and bond distance of 1.781 and 1.963 Å respectively. There are *antibinding* effects due to relativity of ~ 3.5 eV to the predicted atomization energy (A_e) of E114H₄. Our relativistic coupled-cluster singles and doubles (RCCSD) calculations, which correlate *all* 118 electrons and include all 380 molecular spinors with energies up to ~22714 au in the active space predict the relativistic second order Moller-Plesset (RMP2), RCCSD and RCCSD (T) correlation energies as -2.8007 (-1.1544), -2.7600 (-1.0895) and -2.8185 (-1.1088) au, respectively, whereas the corresponding NR CC energies are given in parenthesis. These are the *first* all-electron AVSS RCCSD and NRCCSD calculation for any superheavy polyatomic molecule and it can be seen from the results that NR MP2,CCSD and CCSD(T) correlation energy is ~ 40 % of the corresponding relativistic correlation energy for tetrahedral (T_d) E114H₄. We predict the DF, RMP2, RCCSD and RCCSD(T) atomization energy for E114H₄ as 4.98,7.56,12.95 and 13.92 eV, respectively and therefore the tetravalent E114H₄, which has very similar atomization energy (A_e) trends to that of its lighter congener PbH₄ [Malli et al. Int.J Quantum Chem, 108, 2299 (2008)] should be stable. This is due to the fact that tetrahedral *sd³ hybridization* can easily occur energetically for E114 (unlike the sp³ hybridization) as can be seen from the s, p and d energy levels of DF E114, given in [Table I](#). No such all-electron AVSS RCCSD calculations have ever been reported before for any superheavy polyatomic molecule like E114H₄. Finally, we invoked *sd³ hybridization* for the first time for the superheavy *tetrahedral* HsO₄ *many years ago* [G.L.Malli, J.Chem.Phys. 117,10441 (2002)].

I. Introduction

The Dirac-Fock (DF) SCF methodology for molecules¹⁻⁹ has been used extensively to investigate the effects of relativity in the chemistry of heaviest elements, for which the effects of relativity are expected to be very pronounced due to the high nuclear charge (Z) on such systems. However, the electron correlation effects are not included in the independent electron model, which underlies the Hartree-Fock as well as relativistic Dirac-Fock (DF) treatment. It is well known that *electron correlation* effects are expected to be very significant for systems of heavy and especially for superheavy elements (SHE), which have numerous electrons. It is also recognized that the relativistic and electron correlation are not independent in general and should be treated simultaneously (on equal footing). Recently we have investigated^{4,7-9} the effects of relativity in the electronic structure and bonding of a number of systems of heavy actinides and a few superheavy elements (SHE) rutherfordium (Rf) through up to ekaplutonium ($Z=126$) using the MOLFDIR code¹⁰ (hereafter referred as code¹⁰). Our goal in this paper is to apply the relativistic coupled-cluster methodology taking as reference our fully relativistic (4-component) all-electron Dirac-Fock (DF) SCF wavefunction¹ in order to calculate relativistic molecular correlation energy and predict atomization energy for the superheavy tetravalent $E114H_4$ (T_d).

II RCC Methodology

The coupled-cluster (CC) method¹¹⁻¹³ which was introduced in nuclear shell theory has emerged to be very powerful for calculating correlation effects in atomic and molecular systems, as it includes electron correlation to high order and is *size extensive*, a property of particular importance for superheavy systems, for which relativistic effects are also very

significant. Relativistic version of coupled-cluster (RCC) methodology has been implemented in the MOLFDIR code¹⁰ by interfacing the relativistic Dirac-Fock SCF theory^{1,2} with the CC method¹¹⁻¹³. Recently we have reported extensive RCC calculations for PbH₄⁹ and preliminary RCC calculations for systems of heavy and superheavy elements:¹⁴⁻¹⁶ using the code¹⁰

The salient features of the RCC method are summarized below. Although the relativistic many-body Hamiltonian for atomic and molecular systems cannot be expressed in closed potential form; nonetheless the nonrelativistic many-body formalism can be extended to the relativistic domain by employing the formalism based on effective potentials and derived with arbitrary accuracy from quantum electrodynamics (QED) as described by Lindgren¹⁷. The transition from the nonrelativistic to the fully relativistic case requires two major modifications: (i.) two-component Pauli-Schrodinger spinorbitals are replaced by *four-component* Dirac *spinors*, (ii) instantaneous electron-electron coulomb interactions are supplanted by the irreducible multiphoton interactions along with the radiative and renormalization counter terms. The starting point for the RCCSD method (with single and double excitations) which includes relativistic and electron correlation effects *simultaneously* to high order for molecules, is the projected Dirac-Coulomb (or Dirac-Coulomb-Breit) Hamiltonian¹⁸

$$H_{+} = H_0 + V, \quad (1),$$

where

$$H_0 = \sum_i \Lambda_i^+ h_D(i) \Lambda_i^+ \quad (2),$$

$$h_D(i) = c\alpha_i \cdot p_i + c^2(\beta_i - 1) + V_{nuc}(i) + U(i) \quad (3),$$

$$V = \sum_{i < j} \Lambda_i^+ \Lambda_j^+ (V_{eff})_{ij} \Lambda_j^+ \Lambda_i^+ - \sum_i \Lambda_i^+ U(i) \Lambda_i^+ \quad (4).$$

The h_D in eq.(13) is the one-electron Dirac Hamiltonian. An arbitrary potential U is included in the unperturbed Hamiltonian H_0 and subtracted from the perturbation V , and this potential is chosen to approximate the effect of electron-electron interaction and it could be the Dirac-Fock self-consistent field potential. The nuclear potential V_{nuc} includes the effect of finite nuclear size. The Λ_+ is a product of projection operators on to the positive energy states of the Dirac Hamiltonian h_D , and because of the projection operators, the Hamiltonian H_+ has normalizable bound state solutions. This approximation is known as the no-pair approximation, since virtual electron-positron pairs are not allowed in intermediate states. products of the spinor operators, $\{r^+s\}$ and $\{r^+s^+ut\}$:The no-pair Dirac-Coulomb(-Breit) Hamiltonian H_+ may be rewritten in second- quantized form in terms of normal-order products of the spinor operators, $\{r^+s\}$ and $\{r^+s^+ut\}$:

$$H = H_+ - \langle 0 | H_+ | 0 \rangle \dots = \sum_{rs} f_{rs} \{r^+s\} + \frac{1}{4} \sum_{rstu} \langle rs || tu \rangle \{r^+s^+ut\}, \quad (5),$$

where f_{rs} and $\langle rs || tu \rangle$ are elements of one-electron Dirac-Fock and antisymmetrized two-electron Coulomb(-Breit) interaction matrices over Dirac four-component spinors, respectively. The effect of the projection operators Λ_+ is now taken over by the normal ordering, denoted by the curly braces in the equation above. The no-pair approximation leads to a natural and straightforward extension of the nonrelativistic coupled-cluster theory to the RCC theory. The implementation of the four-component matrix Dirac-Fock and relativistic CC calculations is carried out by expansion in basis sets of Gaussian 4-component spinors and the kinetic and atomic balance conditions^{10,19} are imposed on the basis to avoid the so-called variational collapse. The four-component method involves

generating the orbitals or spinors by Dirac-Fock calculation, followed by applying the coupled cluster scheme at the singles-and-doubles level. Dirac-Fock wavefunctions and matrix elements are calculated by the code ¹⁰. The coupled-cluster stage is more complicated in the four-component case in comparison with the non-relativistic case due to the appearance of complex orbitals or complex spin-orbit integrals.

We use our universal Gaussian basis set (UGBS) ^{20,21} and the E114 (L: 32s 32p 18d 13f) uncontracted UGBS was used for the large (L) component wavefunction (WF) of E114. The L component basis for E114 was contracted to 12s 15p 11d 6f, using the general contraction scheme along with the atomic balance procedure, as implemented in the code ¹⁰. The UGBS of the small (S) component wavefunction of E114 was obtained from the UGBS of its L component WF, so that the L and S component WF of E114 satisfies the kinetic balance constraint ¹⁹. The S component basis of E114 was contracted to 18s 24p 22d 14f 9g. However, for the nonrelativistic (NR) Hartree-Fock (HF) calculations only the L component(s) of the contracted UGBS was used. The relativistic H.accpvdz and the nonrelativistic HNR.accpvdz basis sets ¹⁰ were used for H in our relativistic DF and HF calculations, respectively. The uncontracted large component of the NR E114 [L:32s 32p 18d 13f] was contracted to NR E114[L:15s 14p 9d 6 f]. Our total DF and HF energy for E114 calculated with our corresponding *contracted* basis set is -49719.6585 and -42688.1067 au, respectively. The Dirac-Fock spinor energies of the 7p₊, 7p₋, 7s, 6d₊ and 6d₋ spinors as calculated with our contracted DF wavefunction for E114 and the corresponding NR orbital energies are given in [Table I](#). It can be easily seen from our data on DF spinor energies that although for DF E114, sp³ hybridization would require about 8-10 eV, the sd³ hybridization (for the relativistic E114 atom) requires less than ~ 2eV. So relativistic E114 can undergo sd³ hybridization without much energy expenditure and form stable four tetravalent tetrahedral bonds in molecules like E114H₄, etc.

III Previous calculations on E114H₄ It is well-known that the stability of the group IV hydrides MH₄ (M=C-E114) decreases with increasing atomic number of M and E114H₄ is expected to be the least stable. However due to the interplay of very pronounced effects of relativity and electron correlation the species E114H₄ may be stabilized enough

to exist. Since all-electron relativistic (Dirac-Fock) all-virtual spinor space relativistic (AVSS) coupled-cluster calculations (which take into account both the effects of relativity and electron correlation *simultaneously*) will be most demanding and time-consuming, only a few *approximate* calculations have been reported for the species E114H₄ so far. Seth et al ^{22,23} have discussed the stability of the oxidation state +4 in Group 14 compounds using the spin-orbit coupled relativistic pseudopotential calculations for E114 H₄. In addition they claim to have performed 4-component Dirac-Fock calculations for E114 H₄ . They used ²² a dual large-component (LC) (26s25p18d12f)/(11s16p14d4f) and a small component (SC) (25s26p25d18f 12g)/(10s14p17d 11f 5g) uncontracted basis at the Dirac-Fock-Coulomb (DFC) level. They neglected all the [SS|SS] integrals and applied the Visscher ²⁴ Coulomb correction . In their DFC correlation treatment , only the 6d7s7p electrons (18 electrons out of 118 electrons) were correlated and virtual orbitals with an energy up to ~ 10 au were included . They reported the destabilization of the oxidation state +4 for element E114 and stated that none of its tetravalent compounds (including E114 H₄) is thermodynamically stable. At MP2 level they calculated a bond distance of 1.75 Å for E114 H₄. In the second calculation ²³ using the same basis set as in their earlier calculation²² , they have reported relativistic and norelativistic bond distances of 1.780 and 1.964 Å , and the corresponding so-called “ dissociation energy” of -151 and +32 kJ mol⁻¹ for E114 H₄, respectively. Finally they have made a strong pronouncement in this paper, viz, “ Hence, the only oxidation state accessible for element 114 will be +2 in agreement with the prediction of Keller et al [.Phys.Chem.74,1127(1970)] more than 30 years ago:”.. However, none of the calculations for E114H₄(T_d) reported so far have included all 118 electrons (Seth et al ^{22,23} included only 18 (6d7s7p) electrons) in their relativistic

DF and NR HF coupled-cluster calculations. Moreover , they have not reported for E114H₄(T_d) and E114 the total energies (NR and DF) , correlation energy at various levels of theory , spinor energies, NR HF and relativistic DF atomization energy of E114H₄ at various levels of theory, the effects of relativity and electron correlation for various quantities of chemical interest,etc. We wish to rectify all these deficiencies of these calculations.

IV Present Relativistic Dirac-Fock and Hartree-Fock calculations for E114H₄ (T_d)

We report here all-electron all-virtual spinor space (AVSS) NR HF and relativistic (DF) MP2, CCSD and CCSD (T) calculations which incorporate *simultaneously* both the *effects of relativity* and *electron correlation* since these two effects are not independent.

The Dirac-Fock (DF) SCF calculations for E114H₄ were performed using the tetrahedral double group (T_d^{*}) which has two *two-dimensional* (designated as e₁ and e₂) and one *four-dimensional* (designated as u) additional or extra irreducible representations (EIR.).

All-electron NR HF as well as fully relativistic Dirac-Fock SCF calculations were performed for E114H₄(T_d), with the code ¹⁰ assuming Gaussian nuclear models for E114 and H at four E114-H bond distances using Our contracted DF UGBS and NR HF UGBS for E114 and H were used in our DF and NR HF calculations. at various E114-H bond distances for E114H₄ (T_d). In order to economize the disk space, we used the following thresholds for the various two-electron integrals involving the large (L) and small (S) component basis sets: [LL|LL] (10⁻¹²), [LL|SS] (10⁻¹⁰) and [SS|SS] (10⁻⁰⁸) and our results for total NR HF and relativistic DF molecular energies as well as spinor energies of the valence molecular spinors along with their dominant atomic spinors are collected in [Table II-III](#). The DF(NR) results were fitted to a polynomial and minimum of DF(NR)

energy was obtained thereby at the corresponding optimized DF(NR) E114-H bond distance for E114H₄ (T_d). The results are presented in footnotes of Table II.

V. Present all-electron all-virtual spinor space (AVSS) coupled-cluster calculations

Before proceeding to the full-fledged RCC and NRCC calculations for the superheavy E114H₄(T_d), I performed all-electron (114 in total) AVSS calculations on the superheavy the relativistic second order Moller-Plesset (MP2), coupled-cluster with single and double substitutions (CCSD) and the CCSD corrected perturbationally for the third order correction (CCSD (T)) calculations for E114. My results for relativistic and NR correlation energy at various levels of theory are collected in Table.IV. All the CC calculations for E114H₄(T_d) were performed using the contracted NR HF and DF UGBS discussed above for E114 and/or H. The relativistic DF, RMP2, RCCSD and RCCSD (T) calculations were performed for E114H₄ at the optimized bond distance E114-H of 1.781 Å including all 118 electrons and all 380 spinors with energy up to 22714 au. The nonrelativistic MP2, CCSD and CCSD (T) calculations were performed similarly for E114H₄ at the optimized bond length of 1.963 Å correlating all 118 electrons and including all 380 orbitals with energies upto ~600 au in the active space.

VI. Results and Discussion

A. Dirac-Fock and Hartree-Fock calculations for E114H₄

The relativistic ground state electron configuration of E114H₄ is written here for the *first* time as: $(1e_1)^2 \dots (11e_1)^2 \dots (1e_2)^2 \dots (12e_2)^2 \dots (1u)^4 \dots (18u)^4$, where we have designated the two *two-dimensional* extra irreducible representations (EIR) as e_1 and e_2 and the one *four-dimensional* EIR of the tetrahedral double group (T_d^{*}) as u . There are 11 e_1 , 12 e_2 and 18 u fully occupied molecular spinors (MS) or relativistic molecular

orbitals (RMO) leading to the closed-shell ground state for the tetrahedral E114H₄ (T_d). There are two major observations, viz.; first, the manifestation of the spin-orbit splitting of the atomic spinors with orbital angular momentum $l > 0$, in the atom E114 and also in all the MS or RMO involving these atomic spinors (AS) or relativistic atomic orbitals (RAO). The spin-orbit interaction, (S-O) which is purely a relativistic effect, splits a non-zero l level into two levels characterized by angular momenta $j = l \pm 1/2$, and the S-O interaction is most pronounced for the 2p, 3p, 3d, 4p, 4d, 4f, etc atomic levels as expected. The RMOs arising from the 2p_{1/2} and 2p_{3/2} RAOs in E114H₄(T_d) are 1e₂ and 1u with orbital energies almost identical to the energies of the 2p_{1/2} and 2p_{3/2} RAOs of E114, except that the energies of *both* the RAOs (2p_{1/2} and 2p_{3/2}) in E114H₄(T_d) are shifted by what is also known as the chemical shift. The S-O splitting of the RMOs in E114H₄ is almost the same as that of the corresponding $l > 0$ RAO of the E114 atom. The various RAOs of the central atom E114 and the 1s RAO's of the four H ligands, give rise to various RMOs (classified according to the various EIRs of the tetrahedral double-group (T_d^{*}) of E114H₄, viz; $s \rightarrow e_1$, $p \rightarrow e_2 + u$, $d \rightarrow e_2 + 2u$, $f \rightarrow 2e_1 + e_2 + u$ and the 1s RAOs of the four H ligands give rise to $e_1 + e_2 + u$ RMOs for E114H₄ (T_d^{*}). The highest energy RAOs involved in the valence RMOs of E114H₄ (T_d^{*}) are the 7p_{1/2} and 7p_{3/2} orbitals with energies of -0.3555 and -0.1843 au, respectively. These combine with the e₂ and u RMOs, respectively arising from the combination of the 1s RAOs of the four H ligands giving rise to the 12e₂ and 18 u RMOs of E114H₄ with spinor energies -0.4964 and -0.3723 au, respectively. The former RMOs consists of 0.50 of E114 (7p_{1/2}) and 0.43 of the e₂ RMO arising from the four H ligands, while the latter consists of 0.23 of E114 (7p_{3/2}) and 0.73 of the u RMO arising from the H ligands. It turns out that 18 u

RMO is the *highest occupied molecular spinor* (HOMS) or *highest occupied relativistic molecular orbital* (HORMO), while $12 e_1$, the *lowest unoccupied molecular spinor* (LUMS) or *the lowest unoccupied relativistic molecular orbital* (LURMO) lies at 0.0106 au and consists of pure H 1s RAO. The HOMS-LUMS or the HORMO-LURMO gap for E114H₄ (T_d) is calculated to be 10.42eV in our DF SCF calculations. The nonrelativistic MO configuration for the closed-shell ground state of E114H₄ (T_d) can similarly be written keeping in mind that the various AOs of the E114 atom give rise to the following MOs in the T_d symmetry: viz; $s \rightarrow a_1$, $p \rightarrow t_2$, $d \rightarrow e + t_2$, $f \rightarrow a_1 + t_1 + t_2$, while the 1s AOs of the four H ligands yield the a_1 and t_2 MOs. The results of our all-electron NR HF and relativistic DF calculations for E114H₄ (T_d) are presented in Tables II-III.

The atomization (dissociation into E114 atom plus 4 H atoms, all in the ground atomic state) energy A_e for E114H₄ (T_d) calculated with our relativistic DF and NR HF SCF wavefunctions is 4.98 and 8.41 eV, respectively, and therefore there are *antibinding effects of relativity* of ~ 3.5 eV to the A_e of E114H₄. Mulliken²⁵ population analysis of our relativistic DF and NR HF wavefunctions for E114H₄ yields charge on E114 of +0.64 and +1.40, respectively; and thus our HF NR wavefunction predicts E114H₄ to be more ionic as compared with that predicted with our relativistic wavefunction. It should be mentioned, however, that population analysis results are highly basis set dependant²⁶ and should be treated with caution. We would like to point out that to the best of our knowledge there has been no discussion about the electronic structure, bonding, HOMO (HOMS), LUMO (LUMS), etc. of E114H₄ so far in the literature. The results of our calculation of atomization energy at the optimized bond lengths are presented in Table

VII. Our calculated valence relativistic DF and NR HF spinor (orbital) energies for E114 atom in its ground state are collected in Table I.

B. Coupled-cluster calculations for E114H₄ The NR HF as well as the relativistic 4-component coupled-cluster (CC) calculations were performed for E114H₄ (T_d) with the code ¹⁰ starting with our NR HF and DF wavefunctions, respectively. In our calculations we employ our contracted NR HF and relativistic DF UGBS for E114 and H discussed above and assume finite Gaussian nuclear model for both the nuclei. The NR HF MP2, CCSD and CCSD (T) calculations were performed at four distances and the results were fitted to a polynomial obtaining thereby minimum of bondlength and the corresponding total energy for E114H₄. We report here as an illustrative example of a RCC calculation for E114H₄ (T_d) in which we neglect all [SS|SS] integrals (we call it the NOSS approximation) and include only 40 electrons and 226 spinors with energies up to ~ 20 au in order to reduce the computational cost of the calculation. A NOSS DF RCC calculation was performed at four H114-H distances of 1.60, 1.80, 1.90 and 2.00 Å using our contracted basis E114 [L:12s 15p11d6f|S:18s24p22d14f9g] which was obtained as discussed above by contracting the uncontracted E114[L:32s32p18d13f|S:32s32p32d18f13g] basis and the H.accpvdz basis was used for H. The results of our NOSS DF MP2, CCSD and CCSD(T) calculations at four E114-H distances are collected in Tables V-VI. No such calculations have been reported so far for any superheavy polyatomic.

The results of our DF (NR HF) CC calculations for E114 and E114H₄ were used to calculate the DF (NR HF) atomization energy for E114H₄ and the results obtained with our DF, RMP2, RCCSD and RCCSD (T) and the corresponding NR HF calculations for

the total and atomization energy at various coupled-cluster levels calculated at the optimized bond distances are collected in Table VII. It can be observed that electron correlation definitely leads to an *increase* in the predicted atomization energy for E114H₄, and remarkably all the CC methods predict the increase to the atomization energy of ~4-9 eV. Therefore, electron correlation effects not only counteract the decrease in Ae due to relativity, but lead to a net increase to the Ae. The CPU for our *single* all-electron all - virtual spinor space (with 380 spinors energies up to 22714 au) RCC calculation at the optimized bond distance of 1.781 Å using our contracted E114 [17s19p15d12f|S:22s28p27d18f15g] and H.accpvdz basis sets was ~ 11 days on our 56-processor (same kind as a Macintosh G5) Robson cluster. The corresponding NR CC *single* all-electron all - virtual spinor space with 360 spinors calculation , however required only ~ 3 days on our cluster. Hence as expected NR CC calculations are much cheaper than the comparable RCC calculations. No such calculations have been reported so far for any super heavy systems. Our results of the various NR and relativistic correlation (for E114) and atomization energies for E114H₄ are collected in Table VII.

Conclusion We have performed the *first* ab initio relativistic coupled-cluster calculations for the ground state of the tetrahedral E114H₄, a molecule of the superheavy element E114. We have used these results in conjunction with the corresponding results for atomic E114 to predict the contribution of electron correlation at various levels to the atomization energy of E114H₄ .

In conclusion, we have performed the *first* all-electron all-active space nonrelativistic and relativistic 4-component coupled-cluster calculations for the ground state of the E114H₄,

the tetravalent molecule of the superheavy element E114. Our major conclusions are that electron correlation effects as calculated using the NR and relativistic coupled-cluster methodologies lead to extra contribution of 4-9 eV to the predicted atomization energy of E114H₄. Moreover, the relativistic effects lead to bond contraction of $\sim 0.18 \text{ \AA}$ for E114H₄. In view of our predicted atomization energy at the DF SCF, RMP2, RCCSD and RCCSD(T) levels of 4.98, 7.56, 12.95 and 13.92 eV, respectively, we certainly believe that tetravalent superheavy E114H₄ should be stable enough to exist like (its lighter congener PbH₄) in complete contrast to the contrary pronouncement of Seth et al.^{22,23}

Acknowledgements: This research used in part resources of the National Energy Research Scientific Computing Center (NERSC), which is supported by the Office of Science of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098. Part of the calculations was carried out on the Beowulf cluster at Simon Fraser University (SFU), Canada funded through a grant from the Canadian Foundation for Innovation (CFI) to HPC@SFU.

References:

1. G.L Malli and J. Oreg, J.Chem.Phys. **63**, 830 (1975).

2. G.L. Malli, (ed), Relativistic and Correlation Effects in Molecules and Solids,
NATO ASI Series, Physics, Series B, vol.318, New York, Plenum 1994).
3. L. Visscher, O. Visser, P.J.C. Aerts, P.J.C.; H. Merenga, and W.C. Nieuwpoort,
Computer Phys. Commun, **81**, 120. (1994)
- 4 Malli, G.L. and J. Styszynski, J.Chem.Phys **101**, 10736 (1994), *ibid*, **104**, 1012, (1996,) *ibid*, **109**, 4448 (1998)
5. K.G. Dyall and H. Partridge, Chem.Phys.Lett **206**, 565 (1993)
6. Saue, T; Jensen, H.J. Aa. J.Chem.Phys., **111**, 6211 (1999)
7. G.L. Malli, Mol.Phys. **101**, 287, (2003).
8. G.L. Malli in *Fundamental World of Quantum Chemistry Vol III*, edited by E.J. Brandas and E.S. Kryachko. (Kluwer Academic Press, Dordrecht, 2004), pp. 323-363.
9. G.L. Malli, M. Siegert and D.P. Turner, Int. J Quantum Chem, 108, 2299 (2008); *ibid* 99, 940 (2004)
- 10 P.J.C Aerts, O. Visser, H. Merenga, W.A. de Jong and W.C. Nieuwpoort
: **MOLFDIR**, University of Groningen, Groningen, 1995
- 11 F. Coester, Nucl.Phys. 1958, 1, 421,
12. F. Coester and H. Kummel, Nucl.Phys., **17**, 477 (1960)
13. Paldus, J, in Relativistic and Electron correlation effects in Molecules and Solids:
NATO ASI Ser Br, vol. **318**, G.L. Malli (ed) Plenum 1994, p 207.
- 14 G.L. Malli, J. Styszynski, U. Kaldor and L. Visscher. " *Relativistic Fock-Space Coupled-Cluster Calculations for Molecules with Heavy Elements: ThF₄ and AuH*" Poster P33 presented at the European Science Foundation Research Conference on Relativistic Effects in Heavy Element Chemistry and Physics: Relativistic Quantum

- Chemistry- Progress and Prospects, Acquafredda di Maratea, Italy, April 10-15, 1999.
15. G.L. Malli in *Fundamental World of Quantum Chemistry* . Erkki J. Brandas and Eugene S. Kryachko (eds), Volume III, Kluwer Academic Publishers, Dordrecht, The Netherlands, pp 323-363, 2004.
16. G.L. Malli, *Theor Chem Acc* , **118**, 473(2007).
17. I. Lindgren, *J. Phys. B*, **7**, 2441 (1974), *ibid*, **24**, 1143.(1991)
18. J. Sucher, *Physical Review A*, **22**, 348: (1980) *ibid*, *Phys. Scr.*, **36**, 271, (1987)
19. R. E. Stanton and S. Havriliak , *J. Chem. Phys.*, **82**, 1910 (1984)
20. G.L. Malli, A.B.F. Da Silva, Y. Ishikawa, *Phys. Rev. A* **47**, 143 (1993). *ibid*, *J. Chem. Phys.*, **101**, 6829 (1994)
21. G.L. Malli and Y. Ishikawa, *J. Chem. Phys.*, **109**, 8759 (1998)
22. M. Seth, Knut Faegri, and P. Schwerdtfeger, *Angew. Chem. Int. Ed.*, **37**, 2493(1998).
23. P. Schwerdtfeger and M. Seth, *J. Nucl. Radiochem. Sci.* **3**, 133 (2002).
24. L. Visscher, *Theor Chem Acc* **98**, 68(1997). It should be pointed out that reference # 20 cited for the Visscher correction given in ref. 23 is incorrect. I have given here the correct citation.
25. R.S. Mulliken, *J. Chem. Phys.* **23**, 1833 (1955)
26. K.R. Roby, *Mol. Phys.* **47**, 81, (1974)

Table I. Calculated Relativistic (DF) and nonrelativistic (NR) energies (in au) for the valence 7p, 7s and 6d orbitals of E114 in the ground state.(G L Malli, unpublished)

spinor/orbital	DF ^a	NR
7p ₊	-0.1837	-0.2268
7p ₋	-0.3549	-0.2268
7s	-0.7211	-0.4127
6d ₊	-0.7906	-1.1289
	-0.9544	

^a It can be easily seen that due to very strong relativistic effects for E114 (with Z=114), its 7s and 7p₋ orbitals (with low angular momentum j=1/2) are *stabilized* (due to direct relativistic effects) while the 7p₊, 6d₊ and 6d₋ (with higher angular momenta j=3/2, 5/2 are *destabilized* (due to indirect relativistic effects). Consequently tetrahedral sd³ hybridization can easily occur for relativistic E114 as it needs less than 2 eV for the hybridization.

Table II. Calculated total nonrelativistic (NR) HF and relativistic

Dirac-Fock (DF) molecular energies (in au) for E114H₄ (T_d),

at various E114-H bond distances (in Å).

E114-H (Å)	E (HF) ^a	E (DF) ^b
1.60		-49721.7990
1.80	-42690.3675	-49721.8381
1.90	--42690.3927	--49721.8265
2.00	--42690.3955	-49721.8040
2.50	-42690.2498	

a The results of NR HF total energy calculated at four E114-H bond distances were fitted to a polynomial obtaining thereby energy of -42690.3968 au at the bond distance of 1.963 Å, and an atomization energy of 8.41 eV for E114H₄ (T_d).

b The results of DF total energy calculated at four E114-H bond distances were fitted to a polynomial obtaining thereby energy of -49721.8385 au at a bond distance of 1.781 Å and relativistic(DF) atomization energy of 4.98 eV for E114H₄ (T_d).

Table III . Spinor energies (in au) of the valence molecular spinors or relativistic molecular orbitals (RMO) of E114H₄ calculated at the optimized E114-H bond distance of 1.781 Å.

R MO	dominant atomic character	this work
16u	E114(6d _{5/2})	0.9671
11e ₁	0.75 E114(7s _{1/2}),0.23H(1s)	0.8247
11e ₂	E114(6d _{5/2})	0.8122
17u	E114(6d _{5/2})	0.79530
12 e ₂	0.50E114(7p _{1/2}),0.43 H(1s)	0.4964
18u ^a	0.73 H(1s),0.23 E114(7p _{1/2})	0.3723
12 e ₁ ^b	H(1s)	0.0106

a. This is the highest occupied molecular spinor (HOMS) or relativistic molecular orbital (HORMO).

b. This is the lowest unoccupied molecular spinor (LUMS) or relativistic molecular orbital (LURMO), and the HORMO-LURMO gap is calculated to be 10.42 eV.

Table IV.Relativistic (DF) and NR MP2, CCSD , T and CCSD(T) correlation energies (Ecorr) (in au) , total DF and NR scf energy (E(scf) (in au) ^a for the ground state of E114.

(Ecorr)	DF ^b	NR ^c
MP2	-2.7058	-1.1120
CCSD	-2.4670	-1.0206
T	-0.0225	-0.0240
CCSD(T)	-2.4895	-1.0446
E(scf)	-49719.6585	-42688.10670

a. All 114 electrons are included in all RCC and NRCC calculations with all spinors with energy up to ~ 22714 and ~ 600 au, respectively.

b. Our calculated DF spinor energies for the $7p_+$, $7p_-$, $7s$, $6d_+$ and $6d_-$ spinors of E114 are given in Table I

c Our calculated (NR) orbital energies for the $7p$, $7s$ and $6d$ orbitals of E114 are given in Table I

Table V.Relativistic (NOSS) MP2, CCSD and CCSD (T)) coupled-cluster total molecular energies (in au) for E114H₄ at various E114-H bond distances (in Å).

E114-H	MP2	CCSD	CCSD(T)
1.60	-49748.1957	-49748.1175	-49748.1397
1.80	-49748.2317	-49748.1609	-49748.1854
1.90	-49748.2214	-49748.1545	-49748.1809
2.00	-49748.20207	-49748.1393	-49748.1684

Table VI. Relativistic (NOSS) MP2, CCSD and T correlation energies (Ecorr) (in au) for E114H₄ at various E114-H bond distances (in Å).

E114-H	MP2 (Ecorr)	CCSD(Ecorr)	T(Ecorr)
1.60	-0.8968	-0.8186	-0.0222
1.80	-0.8942	-0.8234	-0.0245
1.90	-0.8957	-0.8288	-0.0264
2.00	-0.8989	-0.8362	-0.0290

Table VII. Relativistic (DF) and NR MP2, CCSD, T and CCSD(T) molecular correlation energies (Ecorr) (in au), total DF and NR scf energy (E(scf) (in au)^a and predicted relativistic atomization energy (Ae(DF)^b) in eV at RMP2, RCCSD and RCCSD(T) levels for E114H₄ at the optimized E114-H bond distance of 1.781 Å^a.

(Ecorr)	DF	NR	Ae(DF) ^b
MP2	-2.8007	-1.1544	7.56
CCSD	-2.7600	-1.0895	12.95
T	-0.0585	-0.0193	
CCSD(T)	-2.8185	-1.088	13.92
E(scf)	-49721.8386	-42690.4030	

^a All 118 electrons were correlated in all of our RCC and NRCC calculations, including all 380 spinors with energy up to ~ -22714 au and all 360 orbitals with energy up to ~ -600 au in the active space, respectively. The total CPU time required for our *relativistic* and *norelativistic* coupled-cluster calculations was ~ 12 and 3 days, respectively.

^b $A_e = E(\text{E114}) + 4 E(\text{H}) - E(\text{E114H}_4)$

