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Relativistic Effects in the Chemistry of very Heavy and super heavy Molecules

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Abstract. Relativistic effects are very significant for molecules and clusters containing very heavy and super heavy elements. We demonstrate this further with our recent results of relativistic computations that included complete active space multi-configuration interaction (CAS-MCSCF) followed by multi-reference configuration interaction (MRSDDCI) computations with up to 50 million configurations of transition metal and main group clusters. We shall also be presenting our recent works on substituted fullerenes and actinide complexes of environmental concern. My talk will emphasize these unusual features and trends concerning structure and spectroscopic properties of these very heavy species. We compare the properties of not only the ground electronic states, but also several excited electronic states. We have also carried out extensive computations on very heavy clusters such as gold clusters, ruthenium clusters and assignment of the observed spectra have been suggested. It is shown that the gold clusters exhibit anomalous trends compared to copper or silver clusters. For example, Jahn-Teller distortion is quenched in the case of Au6 by spin-orbit coupling, and for the first time the spin-orbit component of the Au6 ground state has been observed experimentally. We have also carried out relativistic computations for the electronic states of the newly discovered super heavy elements and yet to be discovered elements such as 113 (eka-thallium) 114 (eka-lead) and 114'. Many unusual periodic trends in the energy separations of the electronic states of the elements 114, 113, 114', (113)H, 114H, and Lawrencium and Nobellium compounds. We will be presenting our results on uranium, plutonyl and magmatonyl complexes in aqueous solution using a combined quantum chemical and PCM models for solvation. We have employed coupled cluster levels of theory to obtain the frequencies and equilibrium geometries of these complexes.

Keywords: Relativistic Effects, Very heavy Clusters, super heavy clusters

1. Relativistic Effects

This is the year of centennial celebration of publication of Einstein’s famous 1905 paper on special theory of relativity. Indeed it is an exciting and very fitting that the celebrated work of Einstein penetrated many branches of science and changed our thinking in many ways. In atomic theory and more recently in chemical context, it is now well recognized that Einstein’s special theory of relativity becomes important particularly in the properties of very heavy and superheavy elements and their molecules, as inner electrons in these species travel with speeds comparable to the speed of light. This is a consequence of a large nuclear charge, which is the driving force of the inner electrons, which speed up in order to keep balance with the increased electrostatic attraction. For example, the speed of the 1s electron of gold, which has 79 protons is estimated to be ~66% of the speed of light. Thus to treat the properties of such species one needs to embrace both relativity and quantum mechanics, the latter was viewed with skepticism by Einstein. Nevertheless the combination of two theories provides...
the foundation blocks of modern relativistic quantum mechanics, which is most relevant in dealing with the properties of molecules containing very heavy and superheavy elements.

Relativistic effects are defined as differences in the observable properties of electrons as a consequence of the correct speed of light, as opposed to infinite speed. Many relativistic quantum approaches start with the relativistic analog of the Schrödinger equation well known as the Dirac equation. Then electron correlation effects are introduced in some combination with relativistic techniques since relativistic and electron correlation effects can be coupled in such species with very heavy elements. Although relativistic effects are more important for the core electrons, the valence electrons too experience such relativistic effects as to cause substantial differences in the chemical and spectroscopic properties of atoms and molecules containing heavy atoms such as third row transition metal species, sixth-row main group elements, actinides and superheavy elements.

Relativistic effects can cause substantial changes to the properties of molecules containing very heavy atoms. For example, the contraction of the 6s valence orbital of the gold atom leads to shorter bonds in gold clusters and gold compounds the ionization potentials of the copper, silver and gold atoms. As one goes down a given group in the periodic table, one expects a monotonic decrease in the ionization energy, since the outermost electron is farther from the nucleus. However, gold is an anomaly in that its ionization potential is not only higher than silver but also copper. This anomaly of the gold atom is due to the relativistic stabilization of the outermost 6s electron of the atom, thus, making it strongly bound, leading to higher ionization energy. Yellow color of gold is attributed to relativity.

The inertness of the 6p^2 shell of the lead atom and even more so the 7p^2 shell of element 114 are both due to both mass-velocity and spin-orbit relativistic effects. The relativistic stabilization of the 6s orbital of mercury leads to a larger 6s-6p promotion energy in Hg compared to Cd and Zn. The increase for mercury is a consequence of relativistic stabilization of the 6s^2 shell, which leads to a larger 4s-4p separation for Hg compared to Cd. The 6s^2 shell cannot, thus, form a very strong bond, unless promotion into 6p is achieved. This is the reason for the fact that Hg_2, in its ground state, forms only a van der Waals complex, while in its excited state, it is bound. Mercury is thus a liquid at room temperature due to the formation of weak clusters of mercury atoms, which undergo metal-nonmetal transition by hybridization with 6p as the cluster size increases.

Spin-orbit coupling is another relativistic effect, which can alter the reactivity and spectroscopic properties of very heavy and superheavy species. The spin-orbit coupling can increase or decrease the bond lengths depending on, which states mix. Likewise it can destabilize the chemical bonding as in the case of Bi_2, which forms a less stable bonding than a triple bond. On the other hand, the PtH molecule is considerably more stable compared to PdH. The ground state of the platinum atom is a triplet arising from 5d^96s^1, while it is singlet for Pd arising from the 4d^10 configuration. This is primarily due to the relativistic stabilization of the 6s orbital of Pt, which overcomes the enhanced stability attributed to the closed-shell d^{10} configuration. Consequently, the differences in the chemistry of Pt and Pd containing systems arise from this and the larger spin-orbit splitting in Pt compared to Pd. The entire third row transition metal atoms react more compared to the second row atoms due to relativity. We will demonstrate analogy between mercury and element 114.

In mathematical terms relativity results in a "four-vector" formalism of angular momentum that couples both the spin and spatial angular momenta via spin-orbit coupling and thus a relativistic electron has memory of only total angular momentum symmetry. This results in novel double group symmetry due to the spin-orbit coupling LS operator. Since this operator changes sign upon rotation by 360°, the periodicity of the identity operation is broken and it is thus no longer the identity operation of the group, as exemplified in Figure 1 with a Möbius strip, as one completes a 360° rotation along the Möbius surface there is a sign change since one goes from inside of the surface to the outside. This requires the introduction of a new operation R in the normal point group of a molecule that corresponds to the rotation by 360° which is not equal to E, the identity operation. Hence we have the double group and double-valued representations in relativistic quantum chemistry of molecules with heavy atoms.
Fig 1 A Mobius strip depiction for the double group symmetry of a relativistic hamiltonian. The introduction of spin-orbit coupling into the relativistic Hamiltonian changes the periodicity of the normal point group symmetry into a double group symmetry, as rotation by 360 deg is not the identity operation.

The authors have recently formulated the symmetry double groups of non-rigid molecules recently. The double group character tables of such species have been derived using wreath product groups and their double groups. These character tables grow astronomically in sizes due to large number of operations in the double group. It may also be noted that the double group is not a direct product of the normal single group and the two-valued operational groups. It is this aspect that introduces even-dimensional two-valued representations into the double group. Thus the relativistic spinor representations of molecules containing heavy atoms do not conform to normal spin and spatial symmetries. Two electronic states that have the same symmetry or transform as the same double group representation can mix regardless of their spin multiplicity and spatial symmetries.

We provide here two different sets of species to demonstrate the importance of relativity in the chemistry and bonding of very heavy and superheavy species. The first set of species is from the compounds of late actinides namely, compounds of Nobelium and Lawrencium. The compounds of Nobelium and lawrencium surprisingly exhibit unusual non-actinide properties in that the chemistry of these species is principally determined by the 7s and 7p orbitals rather than the 5f or 6d shells. Since hydrides are the simplest of all species, we have considered high-level relativistic computations for the lawrencium and nobelium dihydrides. The ground and first excited states of lawrencium and nobelium arise from the 7s and 7p shells, and thus the potential energy surfaces of these species are unusual in having 7p characteristics. Both molecules form stable bent ground states reminiscent of a sp$^3$ hybridization with equilibrium bond angles near 120°. The lawrencium compounds exhibit unusual characteristics due to avoided crossings of the potential energy surfaces. As a result of spin-orbit coupling, the $^2$B$^1_2$ state of LrH$_2$ undergoes avoided crossing with the $^4$A$^1_2$ state in the spin double group, which reduces the barrier for insertion of Lr into H$_2$. The Nobelium compounds are considerably less stable compared to the lawrencium compounds due to the relativistic stabilization of the 7s shell of the nobelium atom. The barrier for the insertion of Lr into H$_2$ is lowered by relativity (spin-orbit coupling) while No has to surmount a larger barrier due to the relativistic stabilization of the 7s$^2$ shell.

Lawrencium is the only element in the actinide series with unusually low ionization potential, and NoH$_2$ has an unusually large dipole moment of 59.9 Debye. We have found that the lawrencium and nobelium compounds have periodic similarities to the thallium and radium compounds, respectively.

The ground state of Lr is not 7s$^6$7p$^1$. One could have expected Lr to be similar to Ae or La but in fact the change of this configuration makes it different. The $^3$D$_{5/2}$ state of Lr is however close to the $^3$F$_{5/2}$ state. That is, the $^3$D$_{5/2}$-$^3$P$_{3/2}$ splitting seems quite sensitive to the level of theory. In any case we find that the ground state of Lr is the $^3$F$_{5/2}$ state arising from the 7s7p configuration and the spin-orbit splitting of 7p as measured by the $^3$P$_{3/2}$-$^3$P$_{1/2}$ energy separation is 7790 cm$^{-1}$. The ionization potential of Lr is 4.87 eV, substantially smaller than No or any other actinide. Thus unusually low ionization energy of Lr would result in the ionic character of the Lr compounds. The large drop in the IP from No to Lr is a consequence of relativistic stabilization of the 7s orbital of Lr which leads to very stable Lr$^+$ with 7s$^2$. 


closed-shell configuration, while in the case of $\text{No}$ the ground state of the neutral $\text{No}$ is stabilized due to the $7s^2$ configuration of $\text{No}$ relative to $\text{No}^-$. Thus the IP of $\text{No}$ is substantially larger than $\text{Lr}$. Our computations on the energy levels and atomic states of $\text{Lr}$ and $\text{Lr}^+$ are consistent with the previous relativistic Fock space coupled cluster study of Eliav et al.

Figure 2 shows our computed potential energy surfaces of the electronic states of $\text{LrH}_2$ in the absence of spin-orbit coupling. All three lowest double electronic states considered here correlate into the $\text{Lr}(^3\Pi)+\text{H}_2$ dissociation limit in the absence of spin-orbit coupling. Among these $^2A_1$ state is the lowest, which forms a stable ground state near a bond angle of 120° and this minimum is more stable than the $\text{Lr}(^3\Pi)+\text{H}_2$ dissociation limit. The ground state of $\text{LrH}_2$ is 12 kcal/mole more stable than $\text{Lr}(^3\Pi)+\text{H}_2$ at the CASSCF level and 16 kcal/mole more stable at the second-order CI level. Figure 3 shows the computed potential energy surfaces of $\text{LrH}_2$ including spin-orbit effects. Comparison of these potential energy surfaces reveals dramatic differences. These differences arise from avoided crossings introduced by spin-orbit coupling. As seen from Fig.2 the $^3B_2$ curve crosses the $^3A_1$ curve. Both states correlate into the same $^3\Sigma$ representation in the double group and thus the $^3A_1$ state with open-shell spin can strongly couple with the $^3B_2$ state with spin in the region of curve crossing. The near proximity of the $^3B_2$ state near the dissociation limit could also introduce strong mixing due to spin-orbit coupling. Thus the $^3B_2$ state and $^3A_1$ state undergo avoided crossing, which leads to the lowering of the barrier for insertion of $\text{Lr}$ into $\text{H}_2$.

The potential energy surfaces dissociate quite differently when spin-orbit effects are included, as can be seen from Figure 2. The ground state of $\text{LrH}_2$ including spin-orbit effects dissociates into $\text{Lr}(^3\Pi)+\text{H}_2$. The first excited state arises from the $\text{Lr}(^3\Delta)+\text{H}_2$ dissociation, and the potential energy surface looks very different from the corresponding $^3B_2$ state in the absence of spin-orbit effects due to avoided crossings. The curve has a substantially smaller barrier followed by a shallow minimum. The potential energy curves arising from $\text{Lr}(^3\Delta)$ and $\text{Lr}(^3\Pi)$ exhibit substantially larger barriers, and all of these states form obtuse minima. The substantial differences and the shapes of the potential energy surfaces can be rationalized by consideration of the composition of the electronic states including spin-orbit effects as a function of the $\text{Lr-H}$ bond angle. At $\theta = 20°$, the $^3\Sigma$ state is composed of $61\%$ $^1B_2$, $6.5\%$ $^3B_1$, $9.5\%$ $^3B_2(1a_{1g})$, $2a_{1g}$, $3a_{1g}$, $1b_{2g}$, $2b_{2g}$, $3b_{2g}$, $4b_{2g}$, $5b_{2g}$, and $6b_{2g}$. At $\theta = 60°$ this state is $92\%$ $^2A_1$, $2\%$ $^2B_2$, $0.8\%$ $^2B_3$, and $0.5\%$ $^2B_1$. Thus the $^3A_1$ and $^3B_2$ states undergo avoided crossing near $50°$ regions. Near the minimum bond angle of $115°$, the $^3\Sigma$ state becomes $94\%$ $^2A_1$, $14\%$ $^2B_2$, $0.5\%$ $^2B_1$. The dominant contribution remains the same at longer bond distances but the second important contributor changes to $^2A_1$ near linear geometries. It is also interesting to note that at the linear limit the state attains substantial $\text{Lr}$ ($6d$) character as the $\text{Lr}$ orbital arises from the interaction of the $\text{Lr}(6d_{3/2})$ with the hydrogen $1s$ orbitals all with the same signs. This contrasts with the best geometry for which the $\text{Lr}(7p)$ makes a substantial contribution. The $^1\Sigma$ state is $59\%$ $^1B_1$, $13\%$ $^3\Sigma$ (III), $6\%$ $^1B_2$ (II), $9\%$ $^1A_1$, $7\%$ $^3B_3$, and $3\%$ $^3B_2$. At $\theta = 60°$ this state becomes $77\%$ $^3A_1$, $9\%$ $^3B_3$, and $3\%$ $^3B_2$. At $\theta = 120°$ this state becomes $80\%$ $^3B_2$, $3\%$ $^3B_3$, $1\%$ $^3A_1$. Near the minimum ($\theta = 120°$) this state becomes $34\%$ $^3B_1$, $32\%$ $^3B_2$, $17\%$ $^3A_1$, $6\%$ $^3A_2$, and $1\%$ $^3\Sigma$.
the linear geometry this state becomes $43\% ^2B_1$, $37\% ^2A_1$ (II) so that the state would correlate into a state of 3/2. The analysis of the selected states in the double group reveals the complexity of the electronic states and how the states vary as a function of the bond angle and geometry. The number of avoided crossings exhibited by these electronic states including spin-orbit effects leads to the shapes of the potential energy curves in Figure 2.

Figure 4 shows our computed potential energy surfaces of NoH$_2$ in the absence of spin-orbit coupling while Fig. 5 shows the corresponding curves with spin-orbit effects. Since the No atom has a closed-shell $5f^{14}7s^2$ configuration in contrast to the open-shell configuration of Lr, we expect No to be less reactive with H$_2$. The No$(^3S_0)$ state does not insert into H$_2$ as it has to surpass a large barrier in the absence of spin-orbit coupling. On the other hand, the $^1B_2$ state crosses the $^1A_1$ state before the barrier is reached, and thus spin-orbit effect may have substantial impact in reducing the barrier height. The $^1A_1$ and $^1B_2$ states are considerably higher in energy and they arise from the excited No$(^3P)$ + H$_2$ species. Among these the $^1A_1$ state forms a shallow minimum in the obtuse bond angle. Comparison of Figs 4 and 5 exemplify the differences due to spin-orbit coupling in these electronic states.

![Figure 4](image1.png)  
![Figure 5](image2.png)

Figure 4 The potential energy surfaces of NoH$_2$ in the absence of spin-orbit coupling  
Figure 5 The potential energy surfaces of NoH$_2$ in the absence of spin-orbit coupling

We have been interested in relativistic computations of the properties of molecules containing superheavy elements such as $^{113}$I and $^{14}$I. We have computed the electronic states of ($^{113}$H)$_2$ the eta-thallium hydride and $^{114}$H$_2$ the eta-loaded dithydrine. We have demonstrated that the 6d-electron correlation-spin-orbit effects are so large for ($^{113}$H)$_2$ that they lead to significant shortening of the ($^{113}$H)-H bond and stabilization of the bond. It is shown that the periodic trends of ($^{113}$H)$_2$ are such that ($^{113}$H)$_2$ has a knight's move relation to AuH in exhibiting unusual stability and d correlation-spin-orbit effects. We have also shown that ($^{114}$H)$_2$ exhibits similarity to IhH$_2$ and also considerable spin-orbit coupling that mixes the singlet ($^1A_1$) state of ($^{114}$H)$_2$ with the triplet state ($^3B_2$). The computed potential energy curves of ($^{113}$H)$_2$ are shown below on Fig. 6.

An unusual feature of the ground state of ($^{113}$H)$_2$ is dramatic shortening of the bond length by valence spin-orbit coupling and core-valence spin-orbit coupling. That is, the $r_e$ value of the 0$^+$ ground state is 1.782 Å when no excitations from the 6d shell of $^{113}$I are allowed. The corresponding dissociation energy is 1.45 eV. However when excitations are allowed from the 6d orbitals from a multi-reference set of configurations, there is significant bond contraction and stabilization. The origin of the contraction can be understood through analysis of the composition of the 0$^+$ state. The $^1A_1$ state originating from the excitation of the 6d ($^1D_2$) shell to 7p ($^3P$) orbital is the most important contributor to the contraction of the ($^{113}$H)-H bond. This leads to 4 real configurations, viz., 6d($^1D_2$) 1 $\gamma$, 6d($^3P$) 1 $\gamma$, and 6d($^3P$) 1 $\gamma$, in addition to other reference configurations discussed already. These reference configurations couple with other valence multi-configurations causing the contraction of the ($^{113}$H)-H bond. Consequently this is a core-valence multi-reference spin-orbit and correlation effect. We have also considered the importance of relativistic in bonding and spectroscopic properties of actinide complexes of relevance to the environment.$^{5,10}$ Since these topics have been considered in depth elsewhere, we refer to these works for further details concerning such actinide complexes.
Figure 6 The potential energy surfaces (113)H with of spin-orbit coupling.

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