

Self-Consistent Relativistic Molecular Calculations of Superheavy Molecules: $(_{110}X)F_6$

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Using new relativistic molecular calculations within the Dirac-Slater scheme it is now feasible to study theoretically molecules containing superheavy elements. This opens a new era for the prediction of the physics and chemistry of superheavy elements. As an example we present the results for $(_{110}X)F_6$, where it is shown that relativistic effects are nearly of the same order of magnitude as the crystal-field splitting.

In recent years a number of atomic calculations have been carried out in the region of superheavy elements. With sophisticated interpretations of these results one was able to perform relatively realistic extrapolations and thus got a first idea

of the physical and chemical properties of the still-unknown superheavy elements. These results have been reviewed by Hermann¹ and Fricke.² Many authors¹⁻³ also have emphasized that further development in this field is dependent

on realistic (which in this case means relativistic) calculations for molecules containing superheavy elements. A better knowledge of their chemical and physical properties is the condition for the successful extraction and identification of possibly artificially generated superheavy atoms.

We emphasize that the development of relativistic molecular methods⁴ makes it now possible to perform realistic calculations for molecules containing superheavy atoms. As an example, we present the results of a calculation for $({}_{110}X)F_6$ although any other element or molecule could have been chosen. Such calculations provide a new tool which will be useful in predicting the physical and chemical properties of superheavy atoms. Up to now, only one nonrelativistic calculation (within the muffin-tin approximation) for $({}_{110}X)F_6$ exists⁵ as well as some relativistic one-center calculations for hydrides.⁶ These one-center calculations may be useful for hydrides but surely not for the more complex molecules which will be of interest in the study of the superheavy elements.

The calculations can briefly be described as follows: The relativistic one-electron Hamiltonian is given by

$$h = c\vec{\alpha} \cdot \vec{p} + \beta mc^2 + V(\vec{r}), \quad (1)$$

where $c\vec{\alpha} \cdot \vec{p} + \beta mc^2$ are the kinetic- and rest-energy operators and where $V(\vec{r})$ is the potential-energy operator, which can be divided, as usual, in the Coulomb and exchange terms. In the Dirac-Slater method the free-electron exchange potential with an exchange parameter $\alpha = 0.7$ has been used. A variational method has been applied to find the molecular wave functions which are approximated by a linear combination of symmetry orbitals according to

$$\psi_n = \sum_m \chi_m(\vec{r}, s) C_{mn}. \quad (2)$$

The symmetry orbitals χ_m are given as linear combinations of relativistic four-component numerical basis functions generated with an atomic Dirac-Slater program. The Hamiltonian and overlap matrix elements in the secular equation are evaluated with a discrete variational method⁷ with use of a numerical integration procedure. After each iteration, the molecular eigenfunctions are analyzed according to the Mulliken population scheme in terms of the input atomic basis functions to determine orbital charges (occupation numbers for the atomic basis functions) as in recent nonrelativistic calculations.⁸ These orbital charges are then used to construct the new

molecular potential and the calculations are continued until self-consistency is obtained.

In Fig. 1 we present the results of our calculations for $({}_{110}X)F_6$. (This molecule is being discussed as one possible compound to be used in extracting superheavy elements from a target which has been bombarded by a heavy-ion beam.²) At the left we present the atomic orbital eigenvalues for the elements ${}_{110}X$ and F from nonrelativistic calculations, and at the right those from relativistic calculations. Already, the strong influence of relativistic effects becomes obvious. The outermost s electrons are bound relatively strongly by direct relativistic effects. The outer d levels show a significant spin-orbit splitting and are also less tightly bound (compared with the nonrelativistic levels) because of the increased shielding of the nucleus by the other electrons. One of the unsolved problems of interpretation which arose from the earlier relativistic atomic

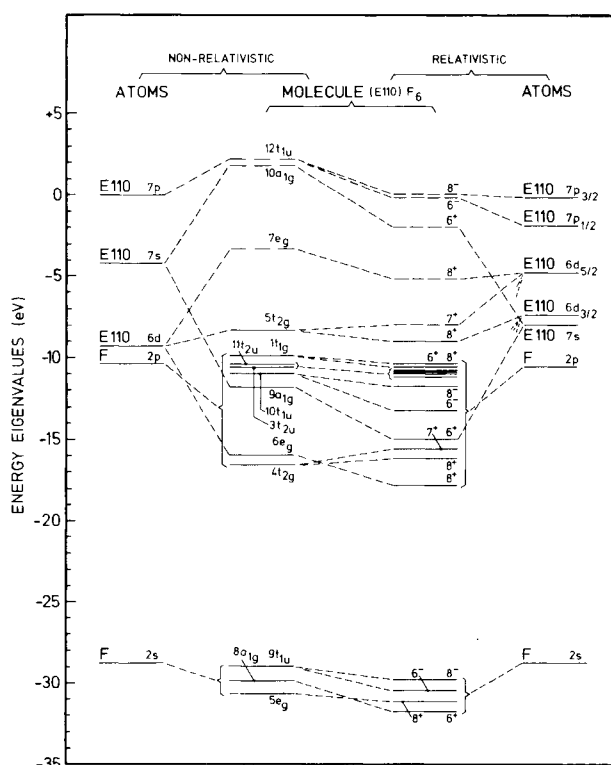


FIG. 1. Comparison of nonrelativistic and relativistic self-consistent-charge eigenvalues for ${}_{110}X$, F, and $({}_{110}X)F_6$ (where E110 denotes ${}_{110}X$). The notation 6^+ , 8^+ , etc., for the relativistic molecular levels refer to 6^+ , 8^+ , etc., symmetry. The $5t_{2g}$ or 8^+ level contains 4 electrons. Vacant levels are indicated by dashed lines. The connection lines between the levels refer to the main contributions.

calculations was the question of importance of the reversal of the s and d levels, as compared to the nonrelativistic calculations as well, to the lighter homologs and how that would influence the level scheme for the superheavy molecules. This is now solved by these calculations.

In the middle of Fig. 1 we see on the left the results of the nonrelativistic and on the right the relativistic calculations. In order to get a better survey we have linked the appropriate levels of the atomic levels and the two full-scale calculations using group theory. One sees that, in general, the levels of the relativistic calculations are more bound than in the nonrelativistic ones. Crystal-field splittings and spin-orbit splittings are nearly of the same order of magnitude and thus lead to a more complicated level scheme than that for the $5d$ -metal hexafluorides.^{9,10} Note that the "crystal-field" splitting between the relativistic analog of the t_{2g} and e_g levels is somewhat smaller in the relativistic calculation than in the nonrelativistic one. By chance the highest occupied level is at the same energy in both calculations and probably will have the same ionization energy. Using transition-state calculations¹¹ we get an ionization energy for the last electron of ≈ 13 eV for the relativistic case. This value is very close to the theoretical ionization energy of the homolog compound PtF_6 . This correspondence of ${}_{110}X$ is not connected with the chosen value for the bond distance of 1.82 \AA (the values for the homologs are nearly constant), because the change of the relevant outer levels is smaller than 1 eV for the ionization energy, even for a change of the bond distance of 10%. Furthermore, the changes of the lowest transition energies are still smaller within the uncertain region of the bond distance. This is a strong evidence that the chemical behavior will be very similar to Pt.

For the detection of the superheavy elements, it is very important to know their spectral behavior. Our calculation shows that the first two excited states are just 1 and 4 eV above the ground state whereas the nonrelativistic calculations yield one level at about 5 eV above the ground state. Similar values were also obtained for the homolog PtF_6 .⁹ The experimental spectrum of PtF_6 was analyzed by using an intermediate-coupling scheme between the LS and jj -coupled states obtained from the $(t_{2g})^4$ configuration.¹⁰ A direct comparison of the experimental absorption transitions between the intermediate states and our one-electron eigenvalue transitions is therefore not so simple. Experimentally the

most energetic absorption band has the energy $32\,000 \text{ cm}^{-1} \approx 4 \text{ eV}$, which is in good agreement with the theoretical value for the transition $t_{2g} - e_g$. This agreement for PtF_6 shows that the above predictions for $({}_{110}X)\text{F}_6$ are probably rather reliable. We do not want to overinterpret the values calculated here, because we know that their error bars will be relatively large. The argument is that the calculated values and trends within the homologs can be connected with the experimental values and trends which, as an overall behavior, show strong parallelism between ${}_{110}X$ and Pt.

An important difference between the present calculation and that for PtF_6 is the 20% larger "spin-orbit" splitting between the 8^+ and 7^+ state in $({}_{110}X)\text{F}_6$. Moreover, taking into account the stronger jj coupling in the case of $({}_{110}X)\text{F}_6$ as compared with PtF_6 , the general trend will be a slight energetical increase of the lowest three absorption bands and a nonchanging fourth band.¹⁰ This superheavy-element compound might be detected with the use of lasers in resonance ionization spectroscopy¹² or resonance fluorescence.¹³ Just recently it has been shown that one-atom detection is possible using this method.¹² A normal Pt extraction procedure has to proceed of course.

In summary this Letter demonstrates that realistic calculations of molecules containing superheavy elements are now possible; this will allow further and more-detailed extrapolations of the chemical behavior of superheavy elements as well as physical quantities which will be needed for their detection. Instead of our particular example of $({}_{110}X)\text{F}_6$, any other molecule or element could have been chosen for study.

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