

## Exploring the Actinide–Actinide Bond: Theoretical Studies of the Chemical Bond in $\text{Ac}_2$ , $\text{Th}_2$ , $\text{Pa}_2$ , and $\text{U}_2$

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**Abstract:** Multiconfigurational quantum chemical methods (CASSCF/CASPT2) have been used to study the chemical bond in the actinide diatoms  $\text{Ac}_2$ ,  $\text{Th}_2$ ,  $\text{Pa}_2$ , and  $\text{U}_2$ . Scalar relativistic effects and spin–orbit coupling have been included in the calculations. In the  $\text{Ac}_2$  and  $\text{Th}_2$  diatoms the atomic  $6d$ ,  $7s$ , and  $7p$  orbitals are the significant contributors to the bond, while for the two heavier diatoms, the  $5f$  orbitals become increasingly important.  $\text{Ac}_2$  is characterized by a double bond with a  $^3\Sigma_g^-(0_g^+)$  ground state, a bond distance of 3.64 Å, and a bond energy of 1.19 eV.  $\text{Th}_2$  has quadruple bond character with a  $^3D_g(1_g)$  ground state. The bond distance is 2.76 Å and the bond energy ( $D_0$ ) 3.28 eV.  $\text{Pa}_2$  is characterized by a quintuple bond with a  $^3\Sigma_g^-(0_g^+)$  ground state. The bond distance is 2.37 Å and the bond energy 4.00 eV. The uranium diatom has also a quintuple bond with a  $^7O_g(8_g)$  ground state, a bond distance of 2.43 Å, and a bond energy of 1.15 eV. It is concluded that the strongest bound actinide diatom is  $\text{Pa}_2$ , characterized by a well-developed quintuple bond.

### 1 Introduction

We have recently demonstrated that multiconfigurational quantum chemistry can be used to explore the chemical bond that is formed between two uranium atoms,<sup>1</sup> and also for the corresponding dipositive ion,  $\text{U}_2^{2+}$ .<sup>2</sup> Other earlier studies of possible multiple bonds between two uranium ions include molecules such as  $\text{PuUPh}^3$  and a number of chlorides and formates.<sup>4</sup> Here we give a more detailed account of the  $\text{U}_2$  study and also add results from similar calculations of the diatoms of the three earlier actinides, Ac, Th, and Pa.

Not much is known experimentally about the chemical bond between actinide atoms. The uranium molecule has been detected in gas phase, but it has never been isolated.<sup>5</sup> The dissociation energy was estimated to be 52(5) kcal/mol, a value which must be considered as highly uncertain.  $\text{U}_2$  and  $\text{U}_2^+$  have also been seen using laser vaporization of a solid uranium target.<sup>6</sup> Of the other diactinides  $\text{Th}_2$  has been detected both in gas phase<sup>6</sup> and in a rare gas matrix,<sup>7</sup> but no properties are yet known of either of these two molecules.

The study of the uranium diatom showed a very complex electronic structure. A quintuple bond connects the two atoms.

It is built from three electron pair bonds formed by  $7s$  and  $6d\pi$  orbitals. Four singly occupied orbitals form the additional bonding. In addition, there are two localized  $5f$  electrons; thus, in total there are six unpaired electrons with parallel spins and maximum angular momentum, resulting in a septet state with a  $\Lambda$  value of 11. Therefore, both  $7s$ ,  $6d$ , and  $5f$  atomic orbitals participate in the bonding in the uranium diatom. For the earlier actinides we may expect less contribution from  $5f$  orbitals, and the bonding will instead be dominated by  $6d$  and  $7s$ . Actually, for  $\text{Ac}_2$  the  $7p$  orbitals will also play a prominent role in the bond formation.

### 2 The Theoretical Approach

The results presented below have been obtained using multiconfigurational quantum chemical methods. The complete active space (CAS) SCF method<sup>8</sup> is used to generate wave functions for a predetermined set of electronic states. Dynamic correlation energy is added using second-order perturbation theory, CASPT2.<sup>9,10</sup> Relativistic effects are included based on the Douglas-Kroll–Hess (DKH) Hamiltonian.<sup>11,12</sup> The scalar part of this Hamiltonian is used in the generation of the CASSCF/CASPT2 wave functions. Spin–orbit (SO) effects are included using an effective one-electron spin–orbit Hamiltonian based on an atomic mean field approximation of the two-electron part.<sup>13</sup> All CASSCF wave functions of the appropriate symmetries are used as

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basis functions to set up an SO Hamiltonian, where CASPT2 energies are used in the diagonal elements. This approach has been shown to work very well in a number of earlier applications (see ref 14 for a more detailed account of the approach).

The choice of an adequate active space is crucial in the CASSCF/CASPT2 approach. Here, this choice is especially complicated because of the large number of atomic orbitals that may potentially participate to form the chemical bond. It turns out that the bonding pattern is quite different in the four molecules, and the choice of the active space will therefore be discussed separately for each case.

The AO basis set used is of the atomic natural orbital type and has been especially designed to include the effects of the scalar relativistic terms of the DKH Hamiltonian. A primitive set *27s24p18d14f6g3h* was contracted to *9s8p6d5f2g1h*.<sup>15</sup> All calculations were performed with the computer software MOLCAS-6.<sup>16</sup> The program VIBROT in MOLCAS was used to compute spectroscopic constants through numerical integration of the rovibrational Schrödinger equation.

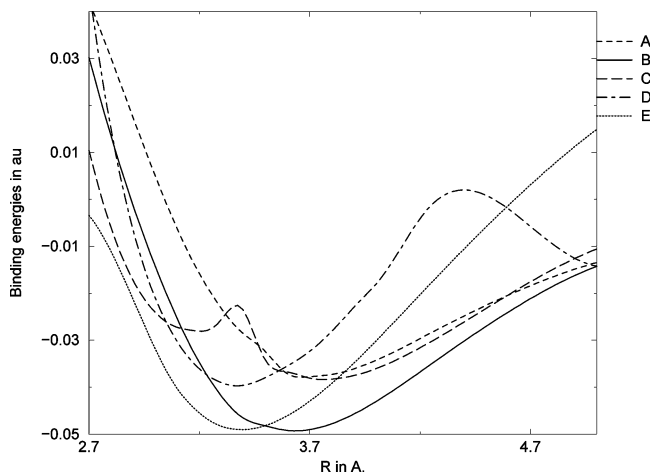
One quantity that will be used in the discussion is the *effective bond order*, EBO. It is defined as follows: Each bonding orbital *i* has a natural orbital occupation number *b<sub>i</sub>*. The corresponding antibonding orbital has the occupation number *ab<sub>i</sub>*. The EBO is then defined as:

$$\text{EBO} = \sum_i \frac{(b_i - ab_i)}{2}$$

This definition allows for fractional bond orders. If *b<sub>i</sub>* is close to two and *ab<sub>i</sub>* close to zero the contribution to EBO is one corresponding to the creation of a complete bond. If, on the other hand both *b<sub>i</sub>* and *ab<sub>i</sub>* are close to one, no bond is formed. The two electrons are then localized one on each atom. This happens, for example, in the U diatom. Intermediate cases also exist in weakly bonded molecules as we shall see below. It is thus not certain that what would formally be called a quintuple bond really has five fully developed bonds. Some of them may be quite weak, and the EBO may be appreciably smaller than five. The natural orbital occupation numbers that are used to define the EBO are very stable quantities with respect to variations in the basis set and the quality of the wave function once the most important active orbitals are included. It is therefore a good and stable measure of bond order.

### 3 Results

**3.1. The Actinium Diatom.** The actinium atom has the electronic ground state  $(6d)^1(7s)^2, ^2D_{3/2}$ . One would not expect this state to be able to form a chemical bond, due to the repulsion between the closed *7s* shells, which hinders the *6d* orbital to get close enough to interact. However, as we shall see below, this becomes possible through *7s7p* hybridization, a unique feature of the Ac–Ac bond. A triple bond can in principle be formed from the valence excited states  $(6d)^2(7s)^1, ^4F_{3/2}$ , which are located 1.14 eV above the ground level, but the bond energy would have to be larger than 2.28 eV to overcome the necessary valence excitation energy. Another possibility is a mixed dissociation limit with one atom in the ground state and the other in the valence excited state, which requires a promotion energy of 1.14 eV and can in principle give a bond of the order 2.5. Only explicit calculations can determine which choice is energetically most favorable. The natural choice of active orbitals for such a study are the *6d* and *7s* orbitals of both atoms,



**Figure 1.** CASPT2 potentials for the lowest electronic states of Ac<sub>2</sub>. All states with a binding energy larger than 1 eV are shown. Labels: A = B =  $^3\Sigma_g^-$ , C =  $^3\Pi_u$ , D =  $^3\Sigma_u^+$ , E =  $^5\Sigma_u^-$ .

**Table 1.** Calculated Spectroscopic Constants for the Ground State of Ac<sub>2</sub>

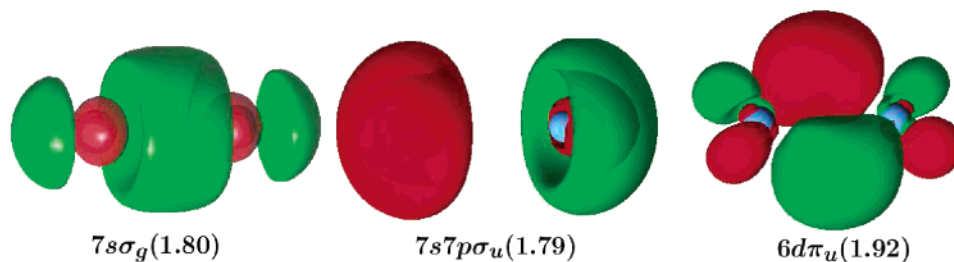
	<i>R<sub>e</sub></i> (Å)	<i>D<sub>0</sub></i> (eV)	$\Delta G_{1/2}$ (cm <sup>-1</sup> )	<i>T<sub>e</sub></i> (cm <sup>-1</sup> )
Results without Spin–Orbit Coupling				
$^3\Sigma_g^-$	3.635	1.336	89	–
$^5\Sigma_u^-$	3.391	1.328	102	56
$^3\Sigma_u^+$	3.373	1.081	128	2243
Results with Spin–Orbit Coupling				
$^3\Sigma_g^-(0_g^+)$	3.631	1.185	92	–
$^3\Sigma_g^-(1_g)$	3.633	1.184	88	135
$^5\Sigma_u^-(2_g)$	3.392	1.166	95	151
$^5\Sigma_u^-(1_g)$	3.393	1.165	98	165
$^5\Sigma_u^-(0_u^-)$	3.393	1.165	99	170
$^3\Sigma_u^+(0_g^-)$	3.751	0.923	84	2112
$^3\Sigma_u^+(1_g)$	3.371	0.908	126	2234

in total 12 orbitals with 6 active electrons. Such calculations were performed but were not successful. The potential curves were not continuous. At certain distances the nature of the active orbitals changed, resulting in abrupt changes of the energy. Inspection showed that the *7p* orbitals played an important role, and it was decided to include them in the active space, which then increased to 18 orbitals. The resulting potential curves were now perfectly smooth. They are shown in Figure 1 for a number of the lowest electronic states (so far without the inclusion of spin–orbit coupling).

In all, 12 singlet, 11 triplet, and 11 quintet potential curves were computed. The density of states is high, but two states,  $^3\Sigma_g^-$  and  $^5\Sigma_u^-$ , are well separated and are both candidates for the ground state of Ac<sub>2</sub>. The  $^3\Sigma_g^-$  state has a bond length of 3.64 Å and a bond energy (*D<sub>0</sub>*) of 1.34 eV. This state dissociates to two ground state atoms. The  $^5\Sigma_u^-$  state has a bond length of 3.39 Å and a bond energy of 1.33 eV. This state dissociates to the mixed limit. The computed energy separation at infinite distance is 1.13 eV, 0.05 eV less than the experimental value. The two states are thus degenerate at this level of theory. More details are given in Table 1.

Inclusion of spin–orbit coupling reduces the bond energy for the  $^3\Sigma_g^-$  state to 1.18 eV but has very small effects on other spectroscopic parameters. The reason is that the spin–orbit coupling is small around equilibrium. Spin–orbit effects will stabilize the Ac atom by 0.166 eV (assuming the Landé interval

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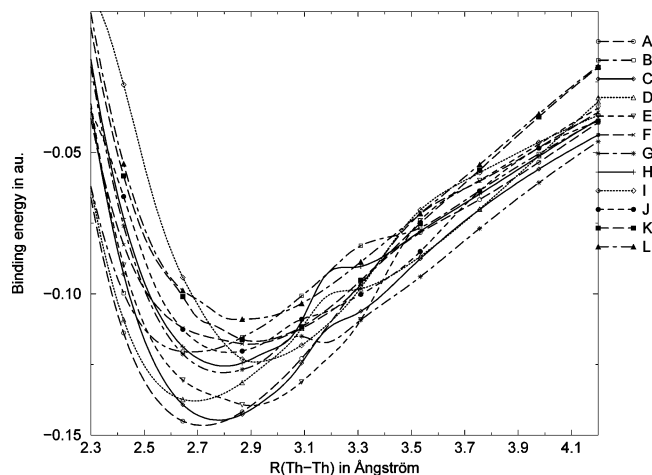
**Figure 2.** Four strongly occupied molecular orbitals in  $\text{Ac}_2$ . Labels and occupation numbers are given in the figure.

rule to be valid).<sup>17</sup> A recent study of the atom using the present theoretical approach gave the same result.<sup>15</sup> However, here it has not been possible to include all electronic states that would be needed for a complete treatment of the spin–orbit coupling, and the SO stabilization at infinite distance is only 0.170 eV, half of the experimental value for two Ac atoms. It is likely that the error is much smaller at equilibrium, and we therefore estimate the true binding energy of  $\text{Ac}_2$  to be about 1.0 eV.

This value is too small to allow a triple bond to be formed. Thus, we expect a single bond only. However, the appearance of the  $7p$  orbitals gives another possibility. The dominant electronic configuration of the ground state is:  $(7s\sigma_g)^2(7s7p\sigma_u)^2(6d\pi_u)^2$  with the following Mulliken populations:  $7s^{1.52}7p^{0.46}6d^{0.95}5f^{0.04}$ . The bonding orbitals  $7s\sigma_g$  and  $6d\pi_u$  give rise to a double bond with  $\text{EBO} = 1.72$ . The  $7s7p\sigma_u$  orbital is an  $sp$  hybrid, which yields a lone pair orbital with only little antibonding character. Thus, the chemical bond in  $\text{Ac}_2$  is effectively a double bond. We show the orbitals in Figure 2.

The lowest excited state,  ${}^5\Sigma_u^-$  and also the next state,  ${}^3\Sigma_u^-$ , both have the leading configuration  $(7s\sigma_g)^2(7s7p\sigma_u)^1(6d\pi_u)^2(6d\sigma_g)^1$  but with different spin coupling in the  $6d\pi_u$  shell. The energy difference between the minima of the potential curves,  $T_e$ , are 56 and 2243  $\text{cm}^{-1}$ , respectively. One more binding orbital results in a shorter bond distance of 3.37–3.39 Å and an EBO of 2.5. The results with spin–orbit coupling show five levels within an energy range of less than 200  $\text{cm}^{-1}$ . It is clear that the accuracy of the calculations does not allow an unambiguous determination of the lowest level.

**3.2. The Thorium Diatom.** The thorium atom has the electronic ground level  $(6d)^2(7s)^2, {}^3F_2$ , but the  $(6d)^3(7s)^1, {}^5F_1$ , level is located only 0.69 eV above the ground state. It is thus not unlikely that a quadruple bond can be formed between the two atoms. Such a bond would have the  $7s\sigma_g$  and  $6d\pi_u$  orbitals doubly occupied and the remaining two electrons occupying orbitals (mainly  $6d$  in character) of other symmetries. On the basis of this reasoning, an active space of 12 orbitals was chosen, characterized as  $6d$  and  $7s$  on both atoms. This specifies mainly the symmetries of the active orbitals. The MCSCF procedure will determine the exact mixture of atomic shells ( $6d$ ,  $7s$ ,  $7p$ , and  $5f$ ). It is, however, unlikely that the  $5f$  orbitals will contribute. They are not occupied in the ground state atoms, and they form much weaker bonds than the  $6d$  and  $7s$  orbitals. What about the  $7p$  orbitals that were so important for the actinium diatom? They are much less important here with a total population of only about 0.1 electrons in the two lowest electronic states. There is thus no need to include them in the active space.



**Figure 3.** CASPT2 potentials for the lowest electronic states of  $\text{Th}_2$ . Labels: A =  ${}^3\Delta_g$ , B =  ${}^3\Sigma_g^-$ , C =  ${}^1\Sigma_g^+$ , D =  ${}^1\Delta_g$ , E =  ${}^3\Sigma_u^+$ , F =  ${}^3\Delta_u$ , G =  ${}^3\Phi_u$ , H =  ${}^3\Pi_u$ , I =  ${}^1\Phi_g$ , J =  ${}^3\Pi_g$ , K =  ${}^3\Phi_g$ .

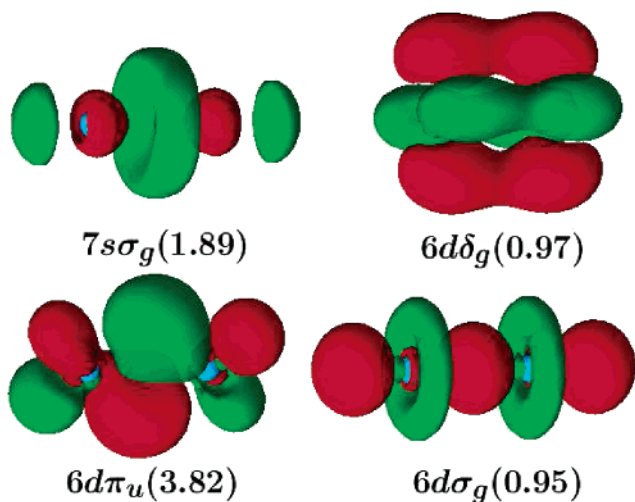
**Table 2.** Electronic Configurations and Spectroscopic Constants for  $\text{Th}_2$  at the CASPT2 Level of Theory

state	configuration	$R_e$ (Å)	$D_0$ (eV)	$\Delta G_{1/2}$ ( $\text{cm}^{-1}$ )
${}^3\Delta_g$	$(7s\sigma_g)^2(6d\delta_g)(6d\sigma_g)(6d\pi_u)^4$	2.72	3.98	183
${}^1\Sigma_g^+$	$(7s\sigma_g)^2(6d\sigma_g)^2(6d\pi_u)^4$	2.78	3.93	186
${}^3\Sigma_u^+$	$(7s\sigma_g)^2(6d\sigma_g)(6d\pi_u)^4(7s\sigma_u)$	2.90	3.79	185
${}^1\Delta_g$	$(7s\sigma_g)^2(6d\delta_g)(6d\sigma_g)(6d\pi_u)^4$	2.68	3.74	182
${}^3\Phi_u$	$(7s\sigma_g)^2(6d\delta_g)(6d\sigma_g)^2(6d\pi_u)^3$	2.80	3.48	173
${}^3\Pi_u$	$(7s\sigma_g)^2(6d\delta_g)(6d\sigma_g)^2(6d\pi_u)^3$	2.80	3.42	180
${}^1\Phi_g$	$(7s\sigma_g)^2(6d\sigma_g)^2(6d\pi_u)^3(7s\sigma_u)$	2.92	3.37	205
${}^1\Phi_u$	$(7s\sigma_g)^2(6d\delta_g)(6d\sigma_g)^2(6d\pi_u)^3$	2.82	3.28	167
${}^3\Sigma_g^-$	$(7s\sigma_g)^2(6d\delta_g)^2(6d\sigma_g)^2(6d\pi_u)^2$	2.68	3.27	139
${}^3\Delta_u$	$(7s\sigma_g)^2(6d\delta_g)(6d\pi_u)^4(7s\sigma_u)$	2.89	3.20	149
${}^3\Pi_g$	$(7s\sigma_g)^2(6d\sigma_g)^2(6d\pi_u)^3(7s\sigma_u)$	2.92	3.17	172
${}^1\Delta_u$	$(7s\sigma_g)^2(6d\delta_g)(6d\pi_u)^4(7s\sigma_u)$	2.72	3.01	168
${}^3\Phi_g$	$(7s\sigma_g)^2(6d\sigma_g)^2(6d\pi_u)^3(7s\sigma_u)$	2.84	2.96	117

CASPT2 potentials were generated for 22 singlet and 23 triplet states. As the lower electronic states were found to have gerade symmetry, we performed spin–orbit calculations only for this symmetry. Twenty-three electronic states of gerade symmetry were used as the basis for the spin–orbit Hamiltonian.

The resulting CASPT2 potentials are shown in Figure 3. The figure shows a very congested set of energy levels with 12 electronic states within an energy range of less than 1 eV. The calculations give  ${}^3\Delta_g$  as the ground state but  $T_e$  to the  ${}^1\Sigma_g^+$  state is only 400  $\text{cm}^{-1}$ . It is thus impossible from these calculations to give a definite answer concerning the ground state of  $\text{Th}_2$ . The spectroscopic constants for the lower electronic states are presented in Table 2. Both candidates for the ground state gives the same bonding pattern. A quadruple bond is formed with six of the eight electrons in the strongly bonding orbitals  $7s\sigma_g$  and  $6d\pi_u$ . The two remaining electrons are distributed in  $6d$ -based bonding molecular orbitals: the  ${}^1\Sigma_g^+$

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**Figure 4.** Molecular orbitals forming the quadruple bond in  $Th_2$ . Labels and occupation numbers are given in the figure.

**Table 3.** Lowest Energy Levels for  $Th_2$  with Spin–Orbit Coupling

state	$\Omega$	$R_e$ (Å)	$D_0$ (eV)	state	$\Omega$	$R_e$ (Å)	$D_0$ (eV)
$^3\Delta_g$	1	2.76	3.28	$^1\Delta_g$	2	2.72	2.82
$^1\Sigma_g^+$	0	2.78	3.08	$^3\Sigma_g^-$	0	2.73	2.64
$^3\Delta_g$	2	2.74	3.22	$^3\Sigma_g^-$	1	2.73	2.42
$^3\Delta_g$	3	2.75	3.00				

state has  $6d\sigma_g$  doubly occupied, while one electron is moved to  $6d\delta_g$  in the  $^3\Delta_g$  state. In both cases a quadruple bond is formed. EBO is 3.67 in the  $^3\Delta_g$  state.

The natural orbital occupation numbers for the strongly occupied orbitals for the  $^3\Delta_g$  state are  $(7s\sigma_g)^{1.89}(6d\pi_u)^{3.82}(6d\delta_g)^{0.97}(6d\sigma_g)^{0.95}$ . The quadruple bond is thus fully developed with only a small population of the antibonding orbitals. The situation is similar for the  $^1\Sigma_g^+$  state. The bonding orbitals are shown in Figure 4. The strength of the quadruple bond manifests itself in a surprisingly large bond energy, which is close to 4 eV at the CASPT2 level of theory for the lowest two electronic states (cf. Table 2).  $Th_2$  is thus a much more stable molecule than  $Ac_2$ .

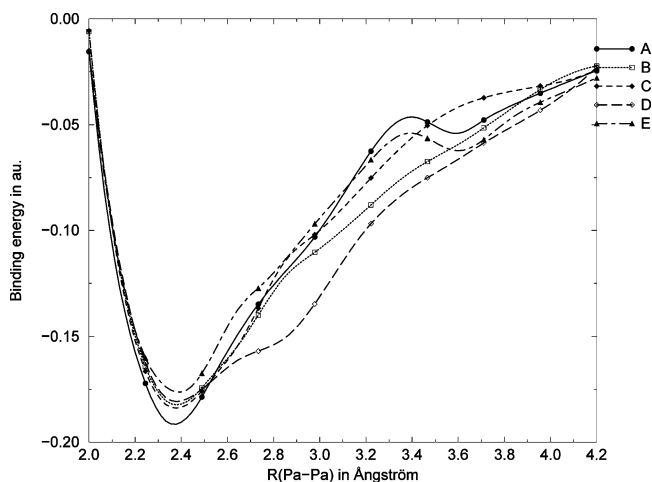
Adding spin–orbit coupling to these results stabilizes the  $^3\Delta_g$  state by 0.14 eV at equilibrium, while the  $^1\Sigma_g^+$  state is hardly affected at all. Calculation on the separate atoms gives an SO stabilization of 0.84 eV at the dissociation limit. The dissociation energy is thus reduced by 0.70 eV for the triplet state and by 0.84 eV for the singlet state. We conclude that  $^3\Delta_g$  ( $1_g$ ) is the ground state of  $Th_2$  with a bond distance of 2.76 Å and a bond energy of 3.28 eV. More details are given in Table 3.

**3.3. The Protactinium Diatom.** The protactinium atom has the ground level  $(5f)^2(6d)(7s)^2$ ,  $4K_{1/2}$ . The  $J$ -averaged energy is 0.77 eV higher. The first known level with  $7s$  singly occupied is  $(5f)^2(6d)^2(7s)$ ,  $^6L_{1/2}$ , located 0.87 eV above the ground level. Thus, the valence excitation needed to form a quintuple bond between two Pa atoms is 1.74 eV, slightly higher than the energy needed for the quadruple bond in  $Th_2$ .

We can expect, based on the results obtained for  $Th_2$ , that a strong triple bond is formed from the orbitals  $7s\sigma_g$  and  $6d\pi_u$ . The remaining bonds are most likely one-electron bonds involving  $6d\sigma$  and  $6d\delta$  orbitals with involvement of  $5f$ . We have based the selection of active orbitals on this assumption and allowed the distribution of the ten valence electrons among the 16 orbitals of  $\sigma$ ,  $\pi$ , and  $\delta$  character.

**Table 4.** Electronic Configurations and Spectroscopic Constants for the Lowest Gerade Levels of  $Pa_2$  at the CASPT2 Level of Theory

state	configuration	$R_e$ (Å)	$D_0$ (eV)	$\Delta G_{1/2}$ ( $cm^{-1}$ )
$^3\Sigma_g^-$	$(7s\sigma_g)^2(6d\pi_u)^4(6d\delta_g)^2(6d\sigma_g)^2$	2.37	5.19	383
$^1\Gamma_g$	$(7s\sigma_g)^2(6d\pi_u)^4(6d\delta_g)^2(6d\sigma_g)^2$	2.38	4.99	326
$^5\Sigma_g^+$	$(7s\sigma_g)^2(6d\pi_u)^4(6d\delta_g)^2(6d\sigma_g)^1(5f\sigma_g)^1$	2.38	4.90	295
$^5\Sigma_u^+$	$(7s\sigma_g)^2(6d\pi_u)^4(6d\delta_g)^2(5f\sigma_g)^1(7s\sigma_u)^1$	2.39	4.78	330
$^3\Delta_g$	$(7s\sigma_g)^2(6d\pi_u)^4(6d\delta_g)^3(6d\sigma_g)^1$	2.44	4.65	159

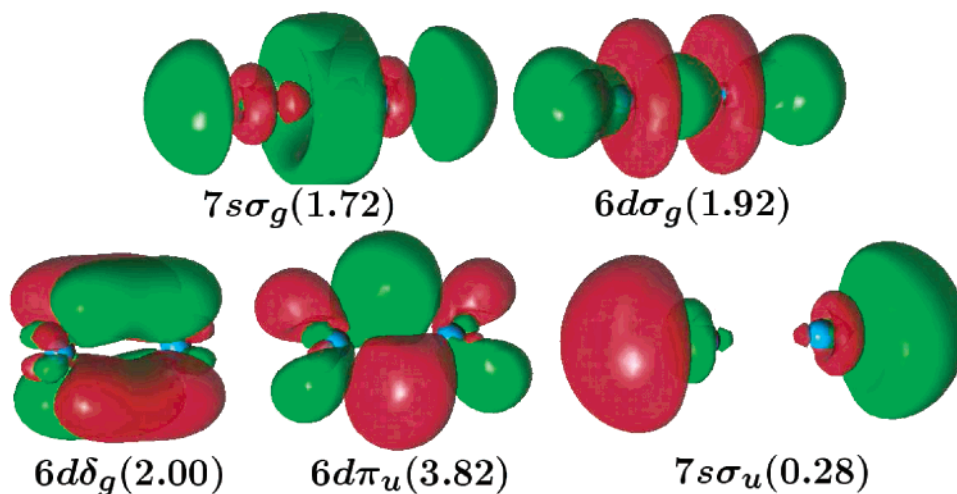


**Figure 5.** CASPT2 potentials for the lowest electronic states of  $Pa_2$ . Labels: A =  $^3\Sigma_g^-$ , B =  $^1\Sigma_g^+$ , C =  $^3\Gamma_g$ , D =  $^5\Sigma_g^+$ , E =  $^5\Sigma_u^+$ .

The results for the CASPT2 calculations are shown in Table 4. These results show that the choice of active space was adequate. A strong quintuple bond is formed. Three two-electron bonds ( $(7s\sigma_g)^2(6d\pi_u)^4$ ) and in addition two one-electron bonds are formed from the  $6d\delta_g$  orbitals, and one more two-electron bond is formed that involves a hybrid between  $6d\sigma_g$  and  $5f\sigma_g$ . The double occupancy of the  $6d\delta_g$  shell gives rise to three electronic states,  $^3\Sigma_g^-$ ,  $^1\Gamma_g$ , and  $^1\Sigma_g^+$ . The lowest state is  $^3\Sigma_g^-$  with a binding energy of 5.2 eV and a bond distance of 2.37 Å. The two other states are 0.20–0.25 eV higher. The CASPT2 potentials for the lower electronic states are shown in Figure 5, and the most strongly occupied molecular orbitals are shown in Figure 6.

The occupancy of the binding MOs are very similar in the three lower states:  $(7s\sigma_g)^{1.72}(6d\pi_u)^{3.82}(6d\sigma_g)^{1.92}(6d\delta_g)^{2.00}$ . Remaining electrons occupy antibonding orbitals. This yields an EBO of 4.51 for all three lowest electronic states. The protactinium diatom thus exhibits a well-developed and strong quintuple bond. This is the highest bond order and bond energy computed for the diatoms studied here. The bond energy will be reduced by the inclusion of spin–orbit coupling but will still be larger than those for  $Th_2$  and  $U_2$ .

Adding spin–orbit coupling will split the  $^3\Sigma_g^-$  state into  $0_g^+$  and  $1_g$  components with the latter lowest in energy. The energies for the five lowest levels are presented in Table 5. We notice that the bond distance for the  $^3\Sigma_g^-$ -derived levels has not changed, while the bond energy is reduced by 1.2 eV. The SO stabilization of the  $0_g^+$  level is only 0.22 eV, while it is 1.41 eV for the free atoms, which should be compared to the experimental value 1.54 eV. Again, there is a problem with the balance between the atomic and molecular values of this quantity. Both are most certainly underestimated in the calcula-



**Figure 6.** Molecular orbitals forming the quintuple bond in  $\text{Pa}_2$ . Labels and occupation numbers are given in the figure.

**Table 5.** Lowest Energy Levels for  $\text{Pa}_2$  with Spin–Orbit Coupling

state	$\Omega$	$R_e$ (Å)	$D_0$ (eV)	state	$\Omega$	$R_e$ (Å)	$D_0$ (eV)
$^3\Sigma_g^-$	0	2.37	4.00	$^5\Sigma_g^-$	2	2.40	3.51
$^3\Sigma_g^-$	1	2.37	3.79	$^3\Delta_g$	3	2.45	3.41
$^1\Gamma_g$	4	2.38	3.55				

tions, and the relative error could well be 0.1–0.2 eV. Therefore, our estimate of the dissociation energy is not very accurate. We can, however, conclude that  $\text{Pa}_2$  is the most strongly bound among the molecules studied here. In the next section we shall show that the uranium diatom has a much lower bond energy and a less developed quintuple bond. Extrapolation to the heavier diatoms becomes possible, and we can conclude that  $\text{Pa}_2$  is the most stable diactinide. Even so, it is most unlikely that it will ever be made because of its high toxicity.

**3.4. The Uranium Diatom.** Our original study of the  $\text{U}_2^1$  showed that the ground state of  $\text{U}_2$  has a very complex electronic structure. We have here extended the study of  $\text{U}_2$  by considering several electronic states of different spin multiplicities, namely 38 septet states lying up to 0.36 eV ( $2930\text{ cm}^{-1}$ ) and 32 quintet states lying up to 0.78 eV ( $6290\text{ cm}^{-1}$ ) above the ground state. These states have been allowed to interact via the spin–orbit coupling Hamiltonian, resulting in 386 spin–orbit states. For all these states we have computed some points around the equilibrium bond distance.

The uranium atom has the ground-state electronic configuration  $(5f)^2(6d)^1(7s)^2, ^5L_6$ . In the  $\text{U}_2$  molecule each uranium atom has in principle six electrons available for forming chemical bonds. Trial studies including different sets of valence orbitals in the active space showed that a strong triple bond was formed involving the  $7s\sigma_g$  and  $6d\pi_u$  orbitals. The occupation numbers of these three orbitals were close to two with small occupation of the corresponding antibonding orbitals. It was therefore decided to leave these orbitals outside the active space and also to remove the antibonding orbitals  $7s\sigma_u$  and  $6d\pi_g$ . This approximation should work well around equilibrium but of course prevents the calculation of full potential curves. The remaining six electrons occupy the remaining  $5f$  and  $6d$  orbitals, resulting in a final active space of six electrons in twenty orbitals (6/20). The most stable electronic state is a septet state (where the six electrons have parallel spins) and has a total orbital angular momentum ( $\Lambda$ ) value of 11. A quintuple bond connects

the two atoms. It is built from three electron pair bonds formed by  $7s$  and  $6d\pi$  orbitals, and four singly occupied orbitals form the additional bonding. The total EBO is 4.2 because the bonding involving  $5f$  atomic orbitals is weak with large occupations of the antibonding orbitals. In addition there are two localized  $5f$  electrons. The spin–orbit calculations showed that the spin and orbital angular momenta combine to form a  $\Omega = 8$  state. The final label of the ground state is thus  $^7O_8$ . The computed bond energy for this state is, however, only 1.15 eV, and a second state with  $\Omega = 8$  ( $\Lambda = 12$ ) lies only 0.01 eV higher in energy and has a bond distance of 2.46 Å. It is thus impossible from this study to uniquely determine the ground state of  $\text{U}_2$ . It should also be emphasized that the determination of the bond energy is uncertain due to the difficulty of achieving a balanced description of the spin–orbit stabilization of the energy. The bond energy was computed using the total energy of two uranium atoms obtained with an active space comprising the necessary  $7s$ ,  $6d$ , and  $5f$  orbitals, which is not completely balanced compared to the active space used for the molecule.

The main terms of the multiconfigurational wave function are:

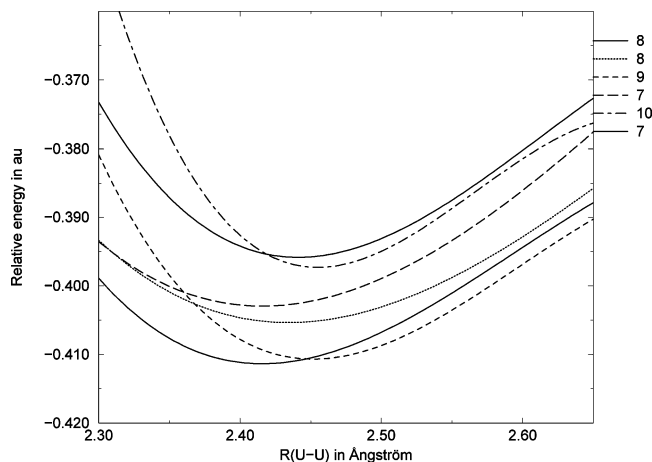
$$\psi (S = 3, \Lambda = 11) = 0.782(7s\sigma_g)^2(6d\pi_u)^4(6d\sigma_g)(6d\delta_g) \\ (5f\pi_u)(5f\phi_u)(5f\phi_g) + 0.596(7s\sigma_g)^2(6d\pi_u)^4(6d\sigma_g)(6d\delta_g) \\ (5f\delta_u)(5f\pi_g)(5f\phi_u)(5f\phi_g)$$

The energy levels around equilibrium are incredibly dense. With the inclusion of spin–orbit coupling 64 states lie within 1 eV above the ground state. Limited portions of the potential energy curves with the inclusion of spin–orbit coupling, for the lowest states are reported in Figure 7. The equilibrium bond distances and the spin-free composition of these states are reported in Table 6.

## 4 Summary and Discussion

Above we have presented the results of the quantum chemical calculations for each of the diatoms separately. Here we shall summarize these results and compare them to see the trends and possibly make some extrapolations to consider the possibility of forming diatoms of the heavier actinides.

Let us first find the common elements in the electronic structure. We present the main electronic configurations in Table



**Figure 7.** CASPT2-SO potential energy curves for the lowest electronic states of U<sub>2</sub>.

**Table 6.** Lowest Gerade Energy Levels for U<sub>2</sub> with the Inclusion of Spin–Orbit Coupling

Λ	Ω	R <sub>e</sub>	D <sub>0</sub>	ω <sub>e</sub>	Λ	Ω	R <sub>e</sub>	D <sub>0</sub>	ω <sub>e</sub>
		(Å)	(eV)	(cm <sup>-1</sup> )			(Å)	(eV)	(cm <sup>-1</sup> )
11	8	2.43	1.15	331	11	8	2.44	1.00	293
12	9	2.46	1.14	389	10	7	2.43	0.93	292

**Table 7.** Electronic Structure of the Early Diactinides

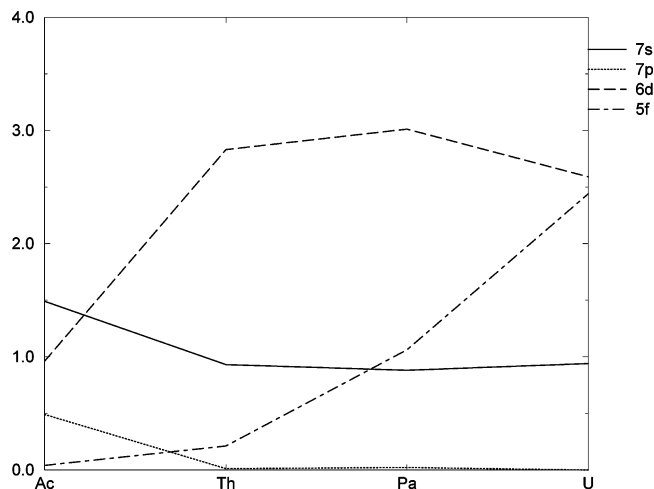
Ac <sub>2</sub>	(7sσ <sub>g</sub> ) <sup>2</sup> (7s7pσ <sub>u</sub> ) <sup>2</sup> (6dπ <sub>u</sub> ) <sup>2</sup>	<sup>3</sup> Σ <sub>g</sub> <sup>-</sup>
Th <sub>2</sub>	(7sσ <sub>g</sub> ) <sup>2</sup> (6dπ <sub>u</sub> ) <sup>4</sup> (6dδ <sub>g</sub> ) <sup>1</sup> (6dσ <sub>g</sub> ) <sup>1</sup>	<sup>3</sup> Δ <sub>g</sub>
Pa <sub>2</sub>	(7sσ <sub>g</sub> ) <sup>2</sup> (6dπ <sub>u</sub> ) <sup>4</sup> (6dδ <sub>g</sub> ) <sup>2</sup> (5f6dσ <sub>g</sub> ) <sup>2</sup>	<sup>3</sup> Σ <sub>g</sub> <sup>-</sup>
U <sub>2</sub>	(7sσ <sub>g</sub> ) <sup>2</sup> (6dπ <sub>u</sub> ) <sup>4</sup> (6dσ <sub>g</sub> ) <sup>1</sup> (6dδ <sub>g</sub> ) <sup>1</sup> (5fδ <sub>g</sub> ) <sup>1</sup> (5fπ <sub>u</sub> ) <sup>1</sup> (5fφ <sub>u</sub> ) <sup>1</sup> (5fφ <sub>g</sub> ) <sup>1</sup>	<sup>7</sup> O <sub>g</sub>

**Table 8.** Mulliken Populations (per atom), Bond Distances (R<sub>e</sub>), and Bond Energies (D<sub>0</sub>) for the Early Diactinides

	7s	7p	6d	5f	R <sub>e</sub> (Å)	D <sub>0</sub> (eV)
Ac <sub>2</sub>	1.49	0.49	0.96	0.04	3.63	1.2
Th <sub>2</sub>	0.93	0.01	2.83	0.21	2.76	3.3
Pa <sub>2</sub>	0.88	0.02	3.01	1.06	2.37	4.0
U <sub>2</sub>	0.94	0.00	2.59	2.44	2.43	1.2

7. The main bonding motif in all of these elements is represented by the orbitals 7sσ<sub>g</sub> and 6dπ<sub>u</sub>. They are the strongest bonding orbitals and are completely filled in all diatoms except Ac<sub>2</sub> where the atomic promotion energy is too large to allow a complete decoupling of the 7s orbitals. Instead a lone-pair orbital is formed through 7s,7p hybridization. The remaining electrons reside in 6d,5f hybrid orbitals, which form weaker one-electron bonds (except in Pa<sub>2</sub> where a second σ<sub>g</sub> orbital is doubly occupied).

Table 8 and Figure 8 give the Mulliken populations on each atom. Some trends emerge from these numbers: the 7s orbital is singly occupied, except in Ac<sub>2</sub> as noted above. Only in this diatom is there any appreciable contribution from the 7p orbital. The 6d population increases up to Pa<sub>2</sub> and then starts to decrease, while the population of 5f continuously increases, as expected. It is small for Ac and Th, which are more similar to the corresponding transition metal series. Up to Pa<sub>2</sub> the more strongly bonding 6d orbitals can contribute to the bonding orbitals, even if there is some hybridization with 5f. For U<sub>2</sub> this is no longer possible. The atomic promotion energy is too large. As a result, the electronic structure retains some of its atomic character with one nonbonding electron on each atom and two only weakly bonding 5f-generated MOs.



**Figure 8.** Populations of the different atomic shells (7s,6p,6d,5f) in the atoms of the actinide diatoms.

The bond in U<sub>2</sub> is consequently weaker than that of Pa<sub>2</sub>. Table 8 also presents the bond distances and the bond energies. The latter have rather large uncertainties (due to the difficulty of achieving a balanced treatment of spin–orbit coupling), but the trends are clear. The bonds get shorter and stronger up to Pa<sub>2</sub>, and then the trends reverse for U<sub>2</sub> where the 5f to 6d promotion becomes less effective. Only Th<sub>2</sub> and Pa<sub>2</sub> are able to use all electrons effectively to create a quadruple and quintuple bond, respectively.

What about the heavier actinides? The next is neptunium, which has a (5f)<sup>4</sup>(6d)<sup>1</sup>(7s)<sup>2</sup> ground state. The first level with more unpaired electrons is (5f)<sup>4</sup>(6d)<sup>2</sup>(7s)<sup>1</sup>, 0.88 eV above the ground level. A triple bond would thus have to overcome an atomic promotion energy of 1.76 eV, which might be possible with some help of the weakly bonding 5f electrons, but the bond will certainly be weak. Plutonium has the ground-state configuration (5f)<sup>6</sup>(7s)<sup>2</sup> with no 6d orbitals occupied. A (5f)<sup>5</sup>(6d)<sup>1</sup>(7s)<sup>2</sup> level is located 0.78 eV above the ground level, but 2.58 eV is needed to unpair the 7s orbital. Only a weak bond can possibly be formed in this case. The promotion energies then increase further for the heavier elements. At the same time the 5f orbitals become more and more corelike and unlikely to participate in the bonding. We thus do not expect any of the heavier actinides to form diatoms with bond energies as large as those obtained here.

We are then in the position to summarize the properties of the actinide diatoms. The strongest bond is found for Pa<sub>2</sub> with the bond for Th<sub>2</sub> slightly weaker. It is possible that the Np diatom is also stable, but this is probably the end of the story. The crucial features in the bond formation are the access to a singly occupied 7s orbital on each atom and low promotion energies from 5f to 6d.

It is interesting to extend the view to the rest of the periodic table. Quintuply bonded molecules also exist among the transition metals and their ions. The molecule ArCrCrAr was recently synthesized.<sup>18</sup> The Cr(I)–Cr(I) unit has a short bond distance (1.8 Å), and subsequent quantum chemical calculations showed that a weak quintuple bond is formed with a bond

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energy of about 3 eV.<sup>19</sup> More strongly quintuply bound diatoms of transition metals may exist. A strong candidate is Nb<sub>2</sub> because Nb has a  $4d^4s^1$  ground state in contrast to V and Ta. Earlier theoretical studies seem to confirm that this is the case.<sup>20</sup>

The highest bond order found in the periodic table is the hexuply bound W<sub>2</sub> molecule with a bond energy of about 5 eV.<sup>21</sup> It has an EBO of 5.2. No other diatom has a higher bond

order. It is interesting to note that one of the diatoms that comes closest to this value is the Pa<sub>2</sub> molecule with EBO = 4.5.

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