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Electronic structure of actinocenes and actinofullerenes

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Abstract

Spin-orbit configuration-interaction calculations have been carried out on actinide complexes using relativistic core potentials and contracted Gaussian atomic orbitals. At present, this type of calculation gives moderate-accuracy results on ground states and excited states and on a number of molecular properties. Our previous work on uranocene has been continued with protactinocene, neptunocene, and plutonocene, giving the patterns of low-lying f→f states and higher-lying f→d and π→d states. Accurate magnetic moment values are obtained from these wavefunctions. The U@C_{60} and U@C_{28} complexes show extensive mixing of π orbitals with both 6d and 5f orbitals. The lower states of U@C_{28} are of π*f and f^2 character with the ground state appearing to be a π*f state with mainly singlet character.

1. Introduction

Actinocene complexes were first reported [1] in 1968 and uranocene in particular has been studied extensively [2]. Actinofullerenes were first reported [3] in 1990 and more extensively very recently [4]. Questions of principal interest include magnetic properties, nature of metal–ligand bonding, electron coupling in the ground state, and visible, Raman, and photoelectron spectra. Electronic structure theory methods capable of addressing all of these questions have only been developed and become practical in the late 1980s [5, 6].

This paper reviews work described in detail in a series of publications [2, 7–10] and assesses the results and areas for future improvement.

2. Theoretical methods

In making the relativistic treatment necessary when heavy atoms are present, the relativistic core approximation has two principal advantages [5]. (1) the core region, where the electrons move the fastest, is described by a core potential derived from a relativistic atomic calculation; and (2) a large number of electrons are removed from explicit treatment. We chose to use the core potentials of Christiansen and coauthors [11, 12], and we also used their valence spin-orbit operators.

The atomic basis sets used are generally contracted Gaussian functions. Their size was kept moderate because they needed to describe little more than the valence region. Our choices were essentially at the double zeta level and are given in detail in the individual papers [2, 7–10]. Since the cyclooctatetraene ligands are negative, we examined the effect of enlarging the carbon p basis to triple zeta, but found little change in the results [8].

In order to obtain suitable molecular orbitals (MOs) for use in the spin-orbit configuration-interaction (CI) calculations, self-consistent-field (SCF) calculations were done for an average of all the $5f^n$ states for the complex. Since an SCF wavefunction is not defined for individual states in intermediate-coupling conditions, the SCF results are not particularly useful except to provide MOs. Unoccupied MOs were chosen by the improved virtual orbital method [13]. The number of MOs (active MOs) kept for the CI calculations was restricted to the minimal set needed to describe valence excitations.

Spin-orbit CI calculations were then carried out in terms of double-group-adapted functions [6], usually with expansion lengths of 5000 to 10 000 and occasionally up to 70 000.

The computer programs used are from the COLUMBUS suite of programs and are described in detail in the first paper in this series [2].

In general terms, quantum chemical calculations at this level can be expected to describe the MOs reasonably well, having useful flexibility about each atom in a radial sense, but they lack the polarization functions

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needed to provide a good description of angular changes in the MOs about each atom. The coulomb and exchange (including ligand-field) interactions and the spin-orbit interactions should be described reasonably well. The detailed coupling of open-shell electrons should be described well. Some correlation energy is included, but neither the basis set nor the CI expansion length are adequate for a thorough treatment of electron correlation.

3. Actinocene results

For the actinocenes, 110 electrons were replaced by the metal and carbon core potentials and 84 electrons were kept frozen in the CI calculation in that no excitations were allowed from these MOs. The number of active MOs in the CI were the 21 5f, 6d, 7s, highest π (e_{2u}, e_{2g}) and lowest π^* (e_{3u}, e_{3g}) MOs. The number of active electrons varied from 9 for protactinocene to 12 for plutonocene. The CI calculations usually involved all single excitations from the 5f reference configurations except for protactinocene where double excitations were included extensively. All actinocene calculations used the uranocene crystal-structure geometry [14].

3.1. Protactinocene [10]

The lower states are $5f^1$ states and they, along with the lowest $6d^1$ state are shown (with double-group notation) in Fig. 1. Note that the $5f_{\pm 2}$ (e_{2u}) states are raised in energy compared to the other 5f states [2] because of the interaction of the $5f_{\pm 2}$ orbitals with the highest occupied ligand π MOs (also e_{2u}). The $5f_{\pm 3}$ (e_{3u}) states are lowered to a small extent by interaction with the unoccupied ligand π^* e_{3u} MOs. The 6d states are split apart much more due to their considerably stronger interactions [2] with ligand π orbitals, leaving only the $6d_0$ (a_{1g}) state at low energy.

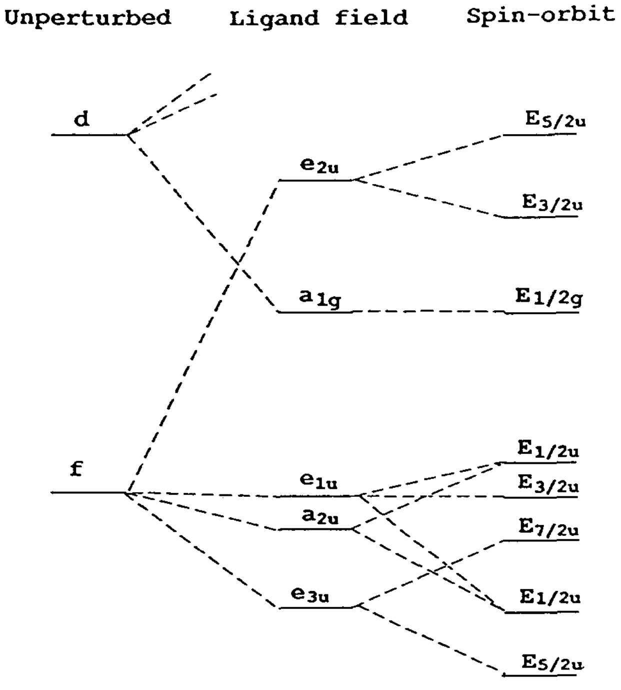

Fig. 1. $Pa(C_8H_8)_2$ energy level diagram.

The ground state is thus $E_{5/2u}$ and transitions from it to the other $5f^1$ states and the low-lying $6d^1$ state are not allowed (Table 1), although a transition from the first excited state ($E_{1/2u}$) to the low 6d state ($E_{1/2g}$) would be allowed if the $E_{1/2u}$ state were sufficiently populated. The lowest charge-transfer excited states are π (e_{2u}) to 6d (a_{1g}) in character, but are all forbidden from the ground state because they also involve a change in the 5f orbital in the principal terms in the wavefunction. The lowest allowed state is computed at 3.67 eV. The experimental solution absorption is estimated [15] from tetramethylcyclooctatetraene spectra to be at 3.40 eV. The low-lying 6d level corresponds to relativistic Hartree–Fock Slater one-electron energy results [16].

3.2. Uranocene

Many properties of this molecule have been studied experimentally and references are given in [2]. The agreement in areas of overlap of experimental and theoretical information has been quite reassuring [2] and suggests confidence in the experimentally unverified theoretical results. A summary of results [2] is that:

(1) the ground state is weak field $5f^2$ $^3H_4$ E_{3g} because the wavefunction for this state contains the minimum population of the high-energy $5f_{\pm 2}$ orbitals;

(2) as shown from photoelectron spectra, the bonding is principally due to 6d-to-π interactions;

(3) the electron coupling is intermediate but closer to LS than jj;

(4) the visible spectrum is due to transitions to excited states which are principally of 5f→6d nature.

The states of most interest are listed in Table 2. Computed excitation energies are approximately 50% higher than the experimental ones; this would have made the comparison of results rather difficult if ex-

TABLE 1. $Pa(C_8H_8)_2$ energies

State	Type	Energy (eV)	Transition
$E_{3/2g}$	$\pi \rightarrow d$	3.67	Allowed (x, y)
$E_{3/2g}$	$\pi \rightarrow d$	3.49	Forbidden
$E_{1/2g}$	d^1	0.93	Forbidden
$E_{1/2u}$	f^1	0.17	Forbidden
$E_{5/2u}$	f^1	0.00	–

TABLE 2. $U(C_8H_8)_2$ energies

State	Type	Energy (eV)	Transition
E_{3u}	f→d	2.905	Allowed (z)
A_{2u}	f→d	2.893	Forbidden
E_{2u}	f→d	2.837	Allowed (x, y)
E_{1u}	f→d	2.385	Forbidden
A_{1u}	f→d	2.280	Forbidden
B_{1g}	f^2	0.364	Forbidden
B_{2g}	f^2	0.360	Forbidden
E_{2g}	f^2	0.109	Forbidden
E_{3g}	f^2	0.0	

TABLE 3. $Np(C_8H_8)_2$ energies

State	Type	Energy (eV)	Transition
$E_{1/2g}$	π→d	2.82	Forbidden
$E_{3/2g}$	f→d	2.71	Allowed (x, y)
$E_{5/2g}$	f→d	2.63	Allowed (z)
$E_{7/2u}$	f^3	0.18	Forbidden
$E_{3/2u}$	f^3	0.14	Forbidden
$E_{5/2u}$	f^3	0.00	–

perimental polarization and temperature dependence results were not available [2]. The experimental excitation energies [17, 18] in eV are 0.058 (E_{2g}) [17], 0.290 (B_{2g}, B_{1g}) [18], 1.939 (E_{2u}) [17], and 2.017 (E_{3u}) [17]. The assignments of the uranocene electronic states in terms of double-group (or crystal-field) notation are mostly among the choices discussed previously. The assignment of the visible spectrum transitions to 5f→6d transitions had not been suggested previously.

3.3. Neptunocene

The computed [8] electronic states and excitation energies are given in Table 3. The ground state was found to be $5f^3\,{}^4I_{9/2}$ $E_{5/2u}$, and the first excited state to be $E_{3/2u}$. The lowest g excited states are two allowed 5f→6d states starting at 2.63 eV. Above these are a series of π→6d charge-transfer states. The experimental solution spectrum [19] shows a series of transitions starting at 2.1 eV, which we are reluctant to make detailed comparison with until more accurate theoretical values and more detailed experimental information are available.

3.4. Plutonocene

The computed [8] electronic states and excitation energies are given in Table 4. The ground state was found to be $5f^4\,{}^5I_4$ A_{1g}, and first excited state to be E_{1g}. The lowest u excited states are two forbidden 5f→6d states starting at 2.77 eV. Above these are a series of π→6d charge-transfer states with the first allowed state at 2.92 eV. The experimental spectrum [19] shows a series of bands starting at 2.4 eV, which we are reluctant to make detailed comparison with until more accurate theoretical values and more detailed experimental information are available.

TABLE 4. $Pu(C_8H_8)_2$ energies

State	Type	Energy (eV)	Transition
E_{1u}	π→d	2.92	Allowed (x, y)
E_{2u}	π→d	2.91	Forbidden
E_{3u}	f→d	2.84	Forbidden
E_{2u}	f→d	2.77	Forbidden
B_{2g}	f^4	0.29	Forbidden
B_{1g}	f^4	0.29	Forbidden
E_{1g}	f^4	0.14	Forbidden
A_{1g}	f^4	0.00	–

TABLE 5. Actinocene magnetic moments (Bohr magnetons)

	Calc.	Exp.[a]
$Pa(C_8H_8)_2$	1.96	–
$U(C_8H_8)_2$	2.30	2.36
$Np(C_8H_8)_2$	1.73	1.73
$Pu(C_8H_8)_2$	0	0

[a] Ref. 19.

3.5. Magnetic moments

Ground-state actinocene magnetic moments were calculated [8, 10, 20] by computing all matrix elements of the magnetic moment operator among the (degenerate) ground-state wavefunctions, and then diagonalizing the resulting matrix. Where experimental comparisons are available [19], it is seen that our overall moderate-quality wavefunctions give good values. This is probably due to the fact that magnetic moments are primarily sensitive to having correct angular momentum properties in the principal terms in the wavefunction, which we expect of our wavefunctions. In retrospect it is clear that the correct ground-state crystal-field (M_J) angular momentum may be found simply by dividing the observed magnetic moments by the weak-field Landé g factor.

4. Actinofullerene results

The number of core electrons replaced by core potentials is 78 for uranium and 2 for each carbon atom. Since the number of carbon atoms in the actinofullerenes are considerably larger than the 16 in the actinocenes, we found our computer software and disk space to be more limiting. The geometries used were computed structural values [4, 21].

4.1. U@C_{60}

This complex is sufficiently large that we did not attempt to do CI calculations. Since no information was available about the electronic structure, we investigated [7] the very basic question of how many electrons would migrate from the uranium atom to the C_{60} cage. This was done with SCF calculations in which we assumed six unpaired electrons with parallel spin and various orbital occupancies of the U 5f, 6d, and 7s shells and the C_{60} t_{1u} initially unoccupied shell. As found with many other metals [7], the outer s shell is destabilized by the C_{60} cage. Thus we found [7] the lowest energy arrangement to be $5f^3\ 6d^2\ t_{1u}{}^1$, but quite close in energy were $5f^3\ 6d^1\ 7s^1\ t_{1u}{}^1$ at 0.07 eV and $5f^3\ 6d^1\ 6_{1u}{}^2$ at 0.19 eV. Thus we feel that the true ground state will have one or two electrons transferred from the metal to the cage and the uranium will not be in a high oxidation state. This is consistent with our other results in that for isolated molecules the C_{60} cage acts as a mildly electronegative ligand. The Mulliken population analysis gives a uranium charge of -0.07 as the result of strong mixing of the 6d uranium orbitals into ligand orbitals with lesser contributions from 5f. The ionization potential should be [7] close to 4.4 eV and correspond to removing an electron from the t_{1u} shell.

4.2. U@C_{28}

We were delighted to learn [4] of the existence of the U@C_{28} complex because it is sufficiently smaller than U@C_{60} that we felt we could do CI calculations on it. Guo *et al.* [4] found that uranium seemed to catalyze the formation of fullerenes and that there is an unusually high yield of uranium metallofullerenes.

The computed geometry [4] of C_{28} is a T_d structure with carbons at the four vertices of a regular tetrahedron and six-carbon rings displaced out from each of the four faces. The electronic structure is computed [4] to be $a_1{}^1\ t_2{}^3\ {}^5A_2$, having four unpaired electrons in π-like orbitals on the vertex atoms. The distance from the center of the tetrahedron to the centers of the six-carbon rings is very close to that in uranocene, suggesting strong uranium-to-aromatic-ring bonding. We used this C_{28} geometry [4] to study U@C_{28}.

Our initial expectations were that:

(1) four uranium electrons would move to the half-occupied a_1 and t_2 ligand shells, filling them up;

(2) there would be very strong mixing of 6d orbitals into ligand orbitals and lesser mixing of 5f; and

(3) the two remaining uranium electrons would be in the 5f shell to give a ground state of $5f^2$ type, perhaps paramagnetic.

Our calculations agreed with the first two expectations but not the third one.

The computational method used [9] was the same as used with the actinocenes. Relativistic effective core potentials replaced 134 electrons, leaving 126 valence electrons, of which 110 were frozen in the spin-orbit CI calculations and 16 were active, expected to be 14 in the highest π shells and 2 on uranium. There were 24 active MOs consisting of $\pi(t_1, a_1, t_2)$, $\pi^*(e, t_1)$, $5f(a_1, t_2, t_1)$, and $6d(e, t_2)$. The Mulliken population analysis showed a U charge of -1.49, again showing very heavy 6d and 5f character in the ligand π MOs, suggesting strong binding.

The CI results are shown in Fig. 2. The lowest cluster of states has a $5f(a_1)^1\ \pi^*(e)^1$ electron configuration and a (diamagnetic) mostly singlet E ground state closely followed by T_1 and T_2 excited states which are mostly triplet and both have magnetic moments of 0.55 Bohr magnetons. Higher up is a cluster of $5f(t_2)^1\ \pi^*(e)^1$ states and then, between 0.5 and 0.6 eV, the lowest $5f^2$ states.

The somewhat surprising ground state shows the low-lying nature of the C_{28} $\pi^*(e)$ unoccupied orbital and the substantial electron affinity of C_{28} computed [9] to be 2.02 eV.

We feel that our present computer programs are quite extended in a calculation of this size and we have less confidence in the U@C_{28} results than in the actinocene results. We investigated using MOs from an e^2 SCF calculation rather than the f^2 ones described.

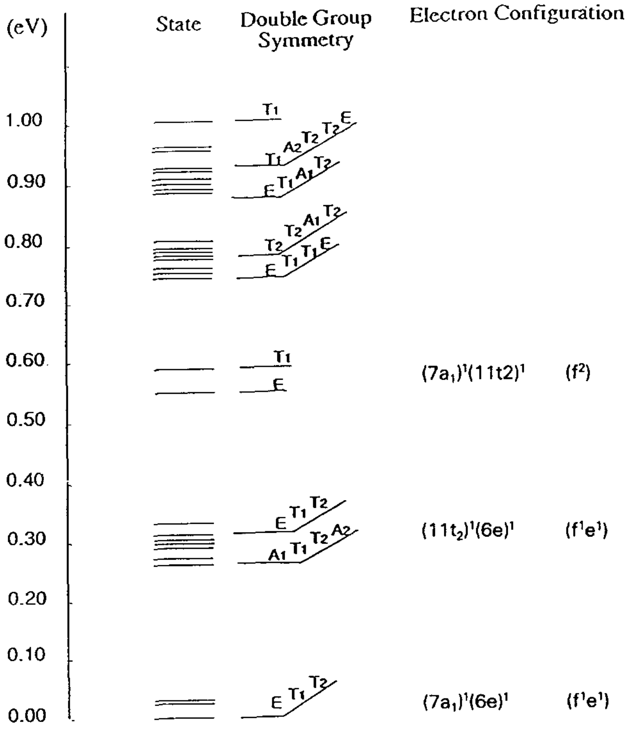

Fig. 2. U@C_{28} spin-orbit CI energy levels.

The total energies of the low-lying states were somewhat higher, suggesting poorer MOs, but the lowest electron configuration was the same although the individual states were in a different order. We expect that a substantially improved electron correlation treatment would lower the f^2 states compared to the f^1 e^1 states because the electrons are closer together in the former than in the latter. Although correlation energy estimates have been made for fulleride ions [22], the additional complications of extensive mixing with metal orbitals and correlation effects directly involving electrons in metal orbitals make us reluctant to do so for metallofullerenes. Since neither the f^1 e^1 wavefunctions nor the lower f^2 wavefunctions contain significant terms with doubly occupied orbitals, it is not clear whether a differential lowering of 0.5 eV or more would be obtained or not.

The chemical properties of the complex differ in that an f^2 state has the unpaired electrons at the center and should be less reactive than an f^1 e^1 complex where one unpaired electron is on the outside of the molecule. The fact that enough sample was collected [4] to obtain a photoemission spectrum and that this spectrum is consistent with a U^{+4} oxidation state [4] is suggestive of an f^2 ground state.

5. Conclusions

The relativistic effective core potential and spin-orbit CI method as implemented in the COLUMBUS programs is able to provide extensive information on actinocenes and actinofullerenes, much of which is as yet unavailable experimentally. On uranocene, where much comparison can be made, the experimental and theoretical results agree substantially. Weaknesses in the theoretical method show up in insufficient accuracy in actinocene excitation energies and possibly incorrect order of low-lying states for actinofullerenes. Substantial software and methodological improvements are clearly needed.

Important new results are obtained in choosing among previous assignments in uranocene and the nature of the transitions in its visible spectrum, energy-level and magnetic-moment values for protactinocene, energy-level information for neptunocene and plutonocene, and all electronic structure information for $U@C_{60}$ and $U@C_{28}$.

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