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U@C_{28}: The Electronic Structure Induced by 32-Electron Principle

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First principle calculations show that neutral U@C_{28} has a (cage)^2 ground state with T_d symmetry instead of the long believed (5f)^1(cage)^1 ground state with D_2 symmetry. Its 34 valence electrons preferentially obey the 32-electron principle which fulfills all the s-, p-, d-, f-type valence layers of the uranium. The remaining two valence electrons cannot break the electronic configuration and thus occupy on the cage.

Experimental studies have shown that the smallest endohedral metallofullerene (EMF), M@C_{28}, could only wrap Ti, Zr, Hf and U as the encapsulated species.[1, 2] Among them, uranium appears to be very efficient in catalyzing initial fullerene formation. The metal selectivity of M@C_{28} should be attributed to the unique electronic structure of C_{28} fullerene. Theoretically, the most stable C_{28} fullerene has an open-shell $(a_1)^1(t_2)^3$ ground state with T_d symmetry. The four single-occupied electrons correspond to four dangling bonds distributed on the cage.[3] Consequently, encapsulating appropriate tetravalent metal, such as Ti, Zr, and Hf, into C_{28} cage could form a stable close-shell M^{4+}@C_{28}^{4-} system.[2] However, for U@C_{28}, the U-cage interaction maybe more complex because uranium has six valence electrons and the special 5f electrons possess both ionic and covalent abilities. So far, only one theoretical study of early configuration interaction (CI) in 1996 indicated that U@C_{28} has a (5f)^1(cage)^1 ground state with D_2 symmetry.[4]

The 32-electron principle is one of important electronic configuration rule and especially suitable for "core-shell" molecule containing 5f-element as the central metal, such as small sized EMFs. This principle can be described as that the core atom and the surrounding shell atoms share 32 electrons to form a stable close-shell electronic structure using the bonding s-, p-, d-, f-type orbitals of the metal. The valence layers of the central 5f-metal were thus full closed. Theoretical studies showed that the electronic structures of An@Pb_{12} (An = Pu, Am^+), An@C_{28} (An = Th, Pa^+, U^{2+}, Pu^{4+}) and $[U@Si_{20}]^{6-}$ satisfy the 32-electron principle.[5-7] Meanwhile, an earlier C_{28} study implied that all the 7s, 7p, 6d and 5f valence orbitals of U have the ability to hybridize with the molecular orbitals of C_{28}.[8] However, the (5f)^1(cage)^1 explanation of U@C_{28} is obvious not agree with the 32-electron principle, because it implies that not all f-type orbitals of U are bonded with the cage. Thus, a new question is that whether the 32-electron principle can be broke when adding two electrons for $[U@C_{28}]^{2+}$, namely for the neutral U@C_{28} case? This confusion prompts us to reconsider the geometric symmetry and electronic structure of neutral U@C_{28} at the current acknowledged theoretical level.

For actinide systems, solving electronic structure by performing high-precision *ab initio* calculations is quite difficult due to the large amount of electrons. In recent years, density functional theory (DFT) method becomes the relative reliable and widely accepted method in calculating electronic structures of actinide systems, particularly in actinide EMFs.[6, 9, 10] Within DFT methods, the electron correlation, relativistic and spin-orbit effects are also effectively considered. These are crucial for reasonably describing the electronic structures of actinide systems.

In this work, both Gaussian 09[11] and ADF[12, 13] programs were employed to perform the relevant calculations, as each of them has their own advantages. In Gaussian 09 program, in order to consider scalar relativistic effects, DFT with relativistic effective core pseudopotential (RECP) method was applied for all geometric optimizations and electronic states calculations of the neutral U@C_{28}, as well as its monovalent and bivalent cations. Eight exchange-correlation functionals were used (see part 3.1 of the supporting information (SI)) and the PBE[14, 15] results are present in the main text. The small core RECP (including 60 core electrons) with its corresponding (14s13p10d8f6g)/ [10s9p5d4f3g] valence basis set[16] and 6-31G*[17, 18] basis set were used for the uranium and carbon atoms, respectivily. Vibrational frequencies were calculated after the geometric optimizations to confirm the structures we obtained are true minima on the potential energy surface. As verifications, geometries and electronic state of neutral U@C_{28} were also calculated using both scalar and spin-orbital relativistic zero-order regular approximation (ZORA) in ADF program. The PBE[14] functional and the TZP Slater basis set (relativistic valence triplet-ζ with polarization function) were selected. The frozen-core approximation was applied for the 1s-4d electrons of uranium atom.

To ensure the reliability of calculations in this work, we firstly calculated the electronic structure of the empty C_{28} fullerene and $[U@C_{28}]^{2+}$. The $(a_1)^1(t_2)^3$ electronic ground state[3] of C_{28} has been reproduced in our calculations (see Part 1 of SI). Then, according to the previous ZORA-PBE study[6], the ground electronic state of $[U@C_{28}]^{2+}$ was also perfectly reproduced by our DFT/RECP calculations (see Parts 2 of SI). $[U@C_{28}]^{2+}$ has a close-shell ground state with T_d symmetry. The 7s, 7p, 6d, and 5f orbitals of the central U should hybridize with the C_{28} cage orbitals, and that 4 electrons from the metal and 28 electrons from the cage should combine to form the 32-electron system.

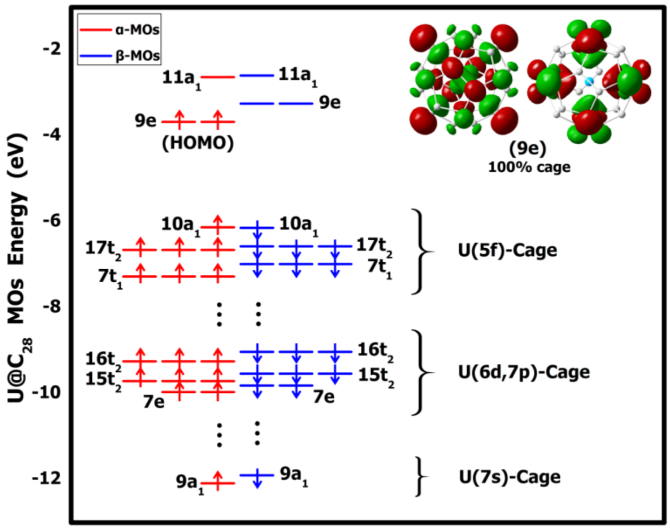

Fig. 1 The MOs energy diagram (left) and the double-degenerated 9e orbital (right, isosurface = 0.035) of neutral U@C_{28} (T_d, Triplet) calculated at PBE/RECP level. The 9e orbitals are completely contributed from the cage. The ZORA-PBE result is well in agreement with PBE/RECP (see Figure S6). The neglected MOs are from pure C_{28} cage contribution. More detailed MOs are showed in Figure S5.

Furthermore, geometric optimizations at a series of symmetries and multiplicities at DFT/RECP levels show that neutral U@C_{28} (T_d, Triplet) has the lowest total energy (see Part 3.1 of SI). The molecular orbitals (MOs) configuration of U@C_{28} (T_d, Triplet) is presented in Figure 1. In fact, here the 32-electron principle can clearly be observed in this electronic structure. The $10a_1$, $17t_2$ and $7t_1$ MOs reflect the hybridizations of U-5f orbitals and the cage orbitals. The U-5f contributions of these three MOs are about 23.69%, 24.07% and 19.65%, respectively. Such large compositions indicate that all the U-5f orbitals could mix with the cage. The $16t_2$ and $15t_2$ MOs are contributed from the mixture of U-6d, 7p orbitals and the cage orbitals. The 7e and $9a_1$ MOs correspond to the hybridizations of 6d-cage and 7s-cage, respectively. These 32 single-occupied MOs in (i.e. $10a_1$, $17t_2$, $7t_1$, $16t_2$, $15t_2$, 7e and $9a_1$ in Figure 1) indicate that all the valence lays of U should be fully closed by hybridizing with the cage, similar to the $[U@C_{28}]^{2+}$ report[6], and form a stable quasi close-shell 32-electron system. Meanwhile, such strong hybradizations are also reflected by Morokuma-type bond energy decomposition analysis (EDA).[19-21] This method has also been used in our previous work to explore the interactions between U and the graphene surface.[22] Here, the calculated orbital and electrostatic interaction energies are -141.29 and -50.13 eV, respectively, which are comparable with the $[U@C_{28}]^{2+}$.[6] And the results also indicate that the role of covalent (about 74%) dominates the total interactions between U and C_{28}. From above analysis, we can approximately consider that the electronic structure of $[U@C_{28}]^{2+}$ is contained in that of neutral U@C_{28}. Thus, the 32-electron principle reappears in the neutral U@C_{28}. The lowest unoccupied molecular orbital (LUMO), $11a_1$ orbital, has the 5f-cage anti-bonding character. The highest occupied molecular orbital (HOMO), 9e orbital, is double-degenerated and completely contributed from the orbitals of C_{28} cage. Therefore, the electronic structure of the neutral U@C_{28} can be characterized as $(\text{cage})^2$.

In essence, the electronic structure of neutral U@C_{28} is guided by the 32-electron rule. Our calculations show that the HOMO-LUMO gap of $[U@C_{28}]^{2+}$ is about 2.79 eV (see part 2 of SI), in agreement with the previous report.[6] For the neutral U@C_{28}, the 9e-$10a_1$ gap (for α-orbitals) calculated at PBE is about 2.45 eV, which is very close to the HOMO-LUMO gap of $[U@C_{28}]^{2+}$. This implies that the 32 of 34 valence electrons of U and C_{28} (6 from U plus 28 from C_{28}) should preferentially adopt the 32-electron principle to form a stable electronic structure to maximally lower the MOs energy, just like $[U@C_{28}]^{2+}$. The remaining two electrons could not break the strong U-cage interactions and thus are filled in the double-degenerated HOMO (9e orbital) in a spin-parallel manner.

On the other hand, we should also note that the (D_2, Singlet), (D_{2d}, Singlet) and (D_{2d}, Triplet) electronic states of U@C_{28} have slight higher total energies (0.04 eV, 0.06 eV, 0.02 eV, according to PBE results, see Table S6) than (T_d, Triplet), corresponding three low-lying exited states. This implies that the geometry and electronic state of U@C_{28} may be easily transformed. In spite of this, through carefully examine the MOs we confirmed that all these electronic states show two electrons occupied on the frontier MOs (HOMO, or HOMO and HOMO-1) which are completely contributed from the cage and the 32-electron principle still exists in these three electronic states. Hence, each of the low-lying states of neutral U@C_{28} has a $(\text{cage})^2$ electronic state.

As verifications, scalar relativistic ZORA also predicted a $(\text{cage})^2$ triplet ground state of U@C_{28} with T_d symmetry, and the geometric and electronic structures are consistent with the DFT/RECP results (see Figure S6). The T_d geometric symmetry and the strong hybridizations of the s-, p-, d-, f-type orbitals of

U with the cage orbitals can also be found in spin-orbital relativistic ZORA prediction. Thus, the spin-orbit effect does not invalidate the 32-electron principle in U@C_{28}. This conclusion was also suggested in the previous $[U@C_{28}]^{2+}$ study and was explained as that spin-orbit effects are “diluted” by the presence of the fullerene cage, causing no large effects on the ground-state molecular properties.[6] More importantly, spin-orbit relativistic ZORA calculations also pointed out the U@C_{28} has a double-degenerated HOMO completely contributed from the cage orbital which is in agreement with DFT/RECP and scalar relativistic ZORA results (see Figure S6), implying that the last two valence electrons should locate on the cage. Thus, the $(cage)^2$ ground state of neutral U@C_{28} has been confirmed by both scalar and spin-orbit relativistic DFT calculations. Moreover, the calculated (HOMO)-(HOMO-1) gaps from scalar and spin-orbital relativistic ZORA methods are 2.51 eV and 2.54 eV, respectively, which further support the stability of electronic structure arising from the 32-electron rule.

The present $(cage)^2$ conclusion from DFT calculations is different from the previous $(5f)^1(cage)^1$ report from CI calculations, which can be mainly attributed to the different amount of effective electrons considered in the two studies. In the previous CI work, only 5f electrons of U were considered in the active MOs, whereas all the 5s to 7s electrons of U (corresponding 32 electrons) were contained in our calculations.

Interestingly, the existence of two unpaired electrons on the cage has not been found in other known EMFs. The spin state of EMFs are generally contributed from the net spins of the inner metal[23] (no unpaired electron on the cage), or from the spin coupling between the net spins on the metal and the cage[24] (no more than one unpaired electron on the cage). However, the uranium would not contribute to the spin state of neutral U@C_{28}, because all the valence layers of U are fully closed by sharing electrons with the cage. And the remaining two electrons are exactly single-occupied on the double-degenerate HOMO in a spin-parallel manner forming a triplet ground state. Therefore, the spin state of neutral U@C_{28} should completely originate from the carbon cage.

Experimental studies with high precision, such as the electron spin resonance (ESR) studies, are expected to perform to confirm the ground state of neutral U@C_{28} in the future. Previously, an ESR study has confirmed Gd@C_{82} has a septet ground and a low-lying nonet exited state which is only 1.79 meV higher than septet.[25] Meanwhile, we have recently reported that the supper small septet-nonet energy gap can be well reproduced by DFT methods.[10] Therefore, we also expect the interesting electronic structure of neutral U@C_{28} can be confirmed in the future.

Additionally, the stability of 32-electrons principle was also found in $[U@C_{28}]^+$ cation. The last valence electron should occupy on the cage orbital and thus $[U@C_{28}]^+$ cation has a $(cage)^1$ doublet ground state. Nevertheless, as we mentioned above that the HOMO of T_d U@C_{28} is double degenerated, the T_d $[U@C_{28}]^+$ ion would not be stable because of the Jahn-Teller effect. Geometric optimizations show that the symmetry of $[U@C_{28}]^+$ cation should degenerate to D_2 in order to possess a non-degenerated HOMO. The 32-electron principle induced degeneration of geometric symmetry in $[U@C_{28}]^+$ cation can be compared with the previous study[26], in which the 18-electron principle also induced the geometric degeneration in $[W@Au_{12}]^-$ ion.

Conclusions

In summary, we studied the ground state electronic structure of the neutral U@C_{28} and its monovalent and bivalent cations using scalar and spin-orbit relativistic DFT methods. Our results confirmed that $[U@C_{28}]^{2+}$ has a close-shell singlet ground state with T_d symmetry, in agreement with the previous report of 32-electron principle. The neutral U@C_{28} has T_d geometric symmetry and the valence electrons of the metal and the cage should preferentially adopt the 32-electron principle using the bonding s-, p-, d-, f-type orbitals of the uranium. The remaining two valence electrons cannot break the strong U-cage interactions caused by the 32-electron principle and thus are spin-parallel filled in the double-degenerated HOMO which completely contribute from the cage to form a $(cage)^2$ triplet ground state. The precedence of 32-electron principle was also found in $[U@C_{28}]^+$, with the geometric symmetry degenerating to D_2 to possess a non-degenerated HOMO.

Based on comprehensive DFT calculations, this work confirms the feasibility of the 32-electron principle in neutral U@C_{28}. Meanwhile, this representative EMF examines the performance of the long developed and most widely used DFT methods. We expect the conclusion and the methodological considerations could provide supports for the future EMF studies.

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Notes and references

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