COMMUNICATION

CrossMark
← click for updates

U@C$_{28}$: the electronic structure induced by the 32-electron principle†

Xing Dai,[ab] Yang Gao,[ab] Wanrun Jiang,[ab] Yanyu Lei[ab] and Zhigang Wang*[ab]

First principles calculations show that the 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 fills all the s-, p-, d-, and f-type valence shells of the uranium atom. The remaining two valence electrons cannot break the electronic configuration and thus are located 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 the initial fullerene formation. The metal selectivity of M@C$_{28}$ should be attributed to the unique electronic structure of the 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 metals, such as Ti, Zr, and Hf, into the C$_{28}$ cage could form a stable closed-shell M^{4+}@C$_{28}$$^{4-}$ system.[2] However, for U@C$_{28}$, the U–cage interaction may be more complex because uranium has six valence electrons and the special 5f electrons possess both ionic and covalent properties. 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 the important rules of electronic configuration and is especially suitable for "core-shell" molecules containing a 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 closed-shell electronic structure using the bonding s-, p-, d-, and f-type orbitals of the metal. The valence shells of the central 5f-metal were thus fully 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$_{28}$ obviously does 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 broken 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 currently 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, the density functional theory (DFT) method has become a relatively reliable and widely accepted method for calculating the 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 2012[12,13] programs were employed to perform the relevant calculations, as each of them has its own advantages. In Gaussian 09 program, in order to consider scalar relativistic effects, DFT with the relativistic effective core pseudopotential (RECP) method was applied for all geometric optimizations and electronic state 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 ESI†), and the PBE[14,15] results are presented 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

^{a} *Institute of Atomic and Molecular Physics, Jilin University, Changchun, 130012, People's Republic of China. E-mail: wangzg@jlu.edu.cn*

^{b} *Jilin Provincial Key Laboratory of Applied Atomic and Molecular Spectroscopy (Jilin University), Changchun, 130012, People's Republic of China*

used for the uranium and carbon atoms, respectively. Vibrational frequencies were calculated after the geometric optimizations were performed to confirm that the structures we obtained were true minima on the potential energy surface. For verification, 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 the uranium atom.

To ensure the reliability of calculations in this work, we first 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 the ESI†). 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 Part 2 of the ESI†). [U@C_{28}]$^{2+}$ has a closed-shell ground state with T_d symmetry. The 7s, 7p, 6d, and 5f orbitals of the central U atom 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.

Furthermore, geometric optimizations at a series of symmetries and multiplicities at DFT/RECP levels show that the neutral U@C_{28} (T_d, triplet) has the lowest total energy (see Part 3.1 of the ESI†). The molecular orbital (MO) configuration of U@C_{28} (T_d, triplet) is presented in Fig. 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 orbital. 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 (*i.e.* 10a_1, 17t_2, 7t_1, 16t_2, 15t_2, 7e and 9a_1 in Fig. 1) indicate that all the valence shells of U should be fully closed upon hybridization with the cage, similar to the [U@C_{28}]$^{2+}$ report,[6] and form a stable quasi-closed-shell 32-electron system. Meanwhile, such strong hybridizations 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 that of [U@C_{28}]$^{2+}$.[6] And these results also indicate that the role of covalent bonding (about 74%) dominates the total interactions between U and C_{28}. From the 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 the C_{28} cage. Therefore, the electronic structure of the neutral U@C_{28} can be characterized as (cage).[2]

In essence, the electronic structure of the 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 the ESI†), 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 slightly higher total energies (0.04 eV, 0.06 eV, 0.02 eV, according to PBE results, see Table S6, ESI†) than (T_d, triplet), corresponding to three low-lying excited states. This implies that the geometry and electronic state of U@C_{28} may be easily transformed. In spite of this, through careful examination of the MOs we could confirm 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 holds in these three electronic states. Hence, each of the low-lying states of neutral U@C_{28} has a (cage)^2 electronic state.

As verification, scalar relativistic ZORA also predicted a (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 Fig. S6, ESI†). The T_d geometric symmetry and the strong hybridizations of the s-, p-, d-, and f-type
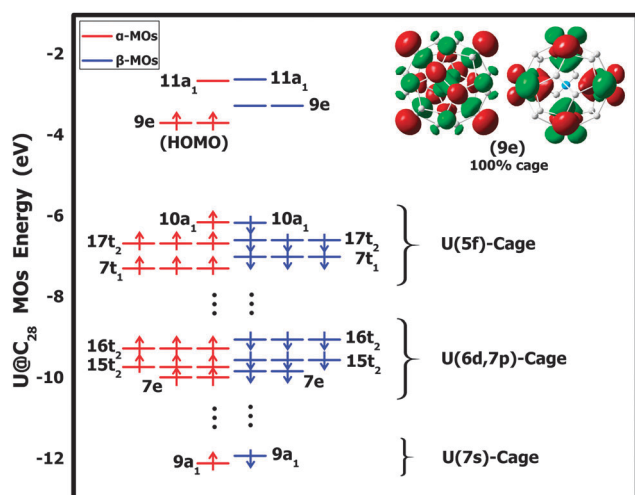

Fig. 1 The MO energy diagram (left) and the double-degenerated 9e orbital (right, isosurface = 0.035) of neutral U@C_{28} (T_d, triplet) calculated at the PBE/RECP level. The 9e orbitals are completely contributed from the cage. The ZORA-PBE results are well in agreement with those of PBE/RECP (see Fig.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

This journal is © the Owner Societies 2015

Phys. Chem. Chem. Phys., 2015, **17**, 23308–23311 | **23309**

orbitals of U with the cage orbitals can also be found in the 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 the 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 that U@C$_{28}$ has a double-degenerated HOMO completely contributed from the cage orbital, which is in agreement with the DFT/RECP and scalar relativistic ZORA results (see Fig. S6, ESI†), 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 the scalar and spin–orbit relativistic ZORA methods are 2.51 eV and 2.54 eV, respectively, which further support the stability of the electronic structure arising from the 32-electron rule.

The present (cage)^2 conclusion using DFT calculations is different from the previous (5f)^1(cage)^1 report using CI calculations, which can be mainly attributed to the different numbers 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 (the corresponding 32 electrons) were considered in our calculations.

Interestingly, the existence of two unpaired electrons on the cage has not been found in other known EMFs. The spin states of the 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 atom would not contribute to the spin state of neutral U@C$_{28}$, because all the valence shells 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 be performed to confirm the ground state of neutral U@C$_{28}$ in the future. Previously, an ESR study has confirmed that Gd@C$_{82}$ has a septet ground state and a low-lying nonet excited state which is only 1.79 meV higher than the septet.[25] Meanwhile, we have recently reported that the super small septet–nonet energy gap can be well reproduced by using DFT methods.[10] Therefore, we also expect that the interesting electronic structure of neutral U@C$_{28}$ can be confirmed in the future.

Additionally, the stability of the 32-electron principle was also found for the [U@C$_{28}$]$^+$ cation. The last valence electron should be located on the cage orbital and thus the [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 the [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 the [U@C$_{28}$]$^+$ cation can be compared with the previous study,[26] in which the 18-electron principle also induced the geometric degeneration in the [W@Au$_{12}$]$^-$ ion.

Conclusion

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 closed-shell singlet ground state with T_d symmetry, in agreement with the previous report of the 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-, and f-type orbitals of 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 is completely contributed from the cage to form a (cage)^2 triplet ground state. The precedence of the 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 the neutral U@C$_{28}$. Meanwhile, this representative EMF examines the performance of the long developed and most widely used DFT methods. We expect that the conclusion and the methodological considerations could provide support for future EMF studies.

Acknowledgements

Notes and references

1 T. Guo, M. D. Diener, Y. Chai, M. J. Alford, R. E. Haufler, S. M. McClure, T. Ohno, J. H. Weaver, G. E. Scuseria and R. E. Smalley, *Science*, 1992, **257**, 1661–1664.

2 P. W. Dunk, N. K. Kaiser, M. Mulet-Gas, A. Rodríguez-Fortea, J. M. Poblet, H. Shinohara, C. L. Hendrickson, A. G. Marshall and H. W. Kroto, *J. Am. Chem. Soc.*, 2012, **134**, 9380–9389.

3 J. M. L. Martin, *Chem. Phys. Lett.*, 1996, **255**, 1–6.

4 K. Zhao and R. M. Pitzer, *J. Phys. Chem.*, 1996, **100**, 4798–4802.

23310 | *Phys. Chem. Chem. Phys.*, 2015, **17**, 23308–23311

This journal is © the Owner Societies 2015

5 J.-P. Dognon, C. Clavaguéra and P. Pyykkö, *Angew. Chem., Int. Ed.*, 2007, **46**, 1427–1430.

6 J.-P. Dognon, C. Clavaguéra and P. Pyykkö, *J. Am. Chem. Soc.*, 2008, **131**, 238–243.

7 J.-P. Dognon, C. Clavaguéra and P. Pyykkö, *Chem. Sci.*, 2012, **3**, 2843–2848.

8 K. Jackson, E. Kaxiras and M. R. Pederson, *J. Phys. Chem.*, 1994, **98**, 7805–7810.

9 X. Dai, C. Cheng, W. Zhang, M. Xin, P. Huai, R.-Q. Zhang and Z. G. Wang, *Sci. Rep.*, 2013, **3**, 1341.

10 X. Dai, Y. Gao, M. S. Xin, Z. G. Wang and R. H. Zhou, *J. Chem. Phys.*, 2014, **141**, 244306.

11 M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski and D. J. Fox, *Gaussian 09, Revision D.01*, 2013.

12 E. J. Baerends, T. Ziegler, J. Autschbach, D. Bashford, A. Bérces, F. M. Bickelhaupt, C. Bo, P. M. Boerrigter, L. Cavallo, D. P. Chong, L. Deng, R. M. Dickson, D. E. Ellis, M. v. Faassen, L. Fan, T. H. Fischer, C. F. Guerra, A. Ghysels, A. Giammona, S. J. A. v. Gisbergen, A. W. Götz, J. A. Groeneveld, O. V. Gritsenko, M. Grüning, S. Gusarov, F. E. Harris, P. v. d. Hoek, C. R. Jacob, H. Jacobsen, L. Jensen, J. W. Kaminski, G. v. Kessel, F. Kootstra, A. Kovalenko, M. V. Krykunov, E. v. Lenthe, D. A. McCormack, A. Michalak, M. Mitoraj, J. Neugebauer, V. P. Nicu, L. Noodleman, V. P. Osinga, S. Patchkovskii, P. H. T. Philipsen, D. Post, C. C. Pye, W. Ravenek, J. I. Rodríguez, P. Ros, P. R. T. Schipper, G. Schreckenbach, J. S. Seldenthuis, M. Seth, J. G. Snijders, M. Solà, M. Swart, D. Swerhone, G. t. Velde, P. Vernooijs, L. Versluis, L. Visscher, O. Visser, F. Wang, T. A. Wesolowski, E. M. v. Wezenbeek, G. Wiesenekker, S. K. Wolff, T. K. Woo and A. L. Yakovlev, *ADF 2012.01, SCM, Theoretical Chemistry*, Vrije Universiteit, Amsterdam, 2012, http://www.scm.com.

13 G. t. Velde, F. M. Bickelhaupt, S. J. A. v. Gisbergen, C. Fonseca, E. J. Baerends, J. G. Snijders and T. Ziegler, *J. Comput. Chem.*, 2001, **22**, 931–967.

14 J. P. Perdew, K. Burke and M. Ernzerhof, *Phys. Rev. Lett.*, 1996, **77**, 3865–3868.

15 J. P. Perdew, K. Burke and M. Ernzerhof, *Phys. Rev. Lett.*, 1997, **78**, 1396.

16 X. Cao and M. Dolg, *THEOCHEM*, 2004, **673**, 203–209.

17 W. J. Hehre, R. Ditchfield and J. A. Pople, *J. Chem. Phys.*, 1972, **56**, 2257–2261.

18 P. C. Hariharan and J. A. Pople, *Theor. Chem. Acc.*, 1973, **28**, 213–222.

19 K. Morokuma, *J. Chem. Phys.*, 1971, **55**, 1236–1244.

20 K. Morokuma, *Acc. Chem. Res.*, 1977, **10**, 294–300.

21 T. Ziegler and A. Rauk, *Theor. Chim. Acta*, 1977, **46**, 1–10.

22 J. Han, X. Dai, Y. Gao, Y. Meng and Z. G. Wang, *Phys. Chem. Chem. Phys.*, 2014, **16**, 22784–22790.

23 X. Wu and X. Lu, *J. Am. Chem. Soc.*, 2007, **129**, 2171–2177.

24 X. Liu, L. Li, B. Liu, D. Wang, Y. Zhao and X. Gao, *J. Phys. Chem. A*, 2012, **116**, 11651–11655.

25 K. Furukawa, S. Okubo, H. Kato, H. Shinohara and T. Kato, *J. Phys. Chem. A*, 2003, **107**, 10933–10937.

26 X. Li, B. Kiran, J. Li, H.-J. Zhai and L.-S. Wang, *Angew. Chem., Int. Ed.*, 2002, **41**, 4786–4789.