

Comment on “Are polynuclear superhalogens without halogen atoms probable? A high-level *ab initio* case study on triple-bridged binuclear anions with cyanide ligands” [J. Chem. Phys. 140, 094301 (2014)]

Cite as: J. Chem. Phys. 145, 147101 (2016); <https://doi.org/10.1063/1.4964502>

Submitted: 07 August 2016 . Accepted: 27 September 2016 . Published Online: 11 October 2016

Manuel Díaz-Tinoco , and J. V. Ortiz 



View Online



Export Citation



CrossMark

ARTICLES YOU MAY BE INTERESTED IN

[Composite electron propagator methods for calculating ionization energies](#)

The Journal of Chemical Physics 144, 224110 (2016); <https://doi.org/10.1063/1.4953666>

[Are polynuclear superhalogens without halogen atoms probable? A high-level *ab initio* case study on triple-bridged binuclear anions with cyanide ligands](#)

The Journal of Chemical Physics 140, 094301 (2014); <https://doi.org/10.1063/1.4867009>

[Vertical and adiabatic ionization energies of \$\text{NH}_4^-\$ isomers via electron propagator theory and many body perturbation theory calculations with large basis sets](#)

The Journal of Chemical Physics 87, 3557 (1987); <https://doi.org/10.1063/1.453000>

Lock-in Amplifiers

Find out more today



Zurich
Instruments



Comment on “Are polynuclear superhalogens without halogen atoms probable? A high-level *ab initio* case study on triple-bridged binuclear anions with cyanide ligands” [J. Chem. Phys. 140, 094301 (2014)]

 Manuel Díaz-Tinoco^{a)} and J. V. Ortiz^{b)}

Department of Chemistry and Biochemistry, Auburn University, Auburn, Alabama 36849-5312, USA

(Received 7 August 2016; accepted 27 September 2016; published online 11 October 2016)

[\[http://dx.doi.org/10.1063/1.4964502\]](http://dx.doi.org/10.1063/1.4964502)

Yin *et al.* have asserted¹ that calculations on the vertical electron detachment energies (VDEs) of triply-bridged $\text{Mg}_2(\text{CN})_5^-$ superhalides performed with the Outer Valence Green Function^{2–5} (OVGF) fail, with discrepancies over 1 eV, for isomers D, E, and F (see Fig. 1) when compared with results obtained with the coupled-cluster singles and doubles plus approximate triples (CCSD(T)) method.⁶ They also report a difference of 0.16 eV between the OVGF VDEs of isomers A and B, whereas their CCSD(T) difference equals -0.04 eV. In their attempts to perform CCSD(T) calculations on ground-state doublets, these authors have chosen the wrong irreducible representation for isomers B, D, E, and F, have employed excited self-consistent-field (SCF) solutions for isomers G and H, and for isomer A have employed a SCF solution whose canonical orbitals do not transform according to the irreducible representations of the C_{3v} point group. When OVGF and CCSD(T) calculations on the structures obtained by Yin *et al.* are performed with Gaussian 09⁷ on the same states with their TZ3 basis set (see Table I), excellent agreement, summarized in Fig. 2 and Table II, is evident. OVGF’s average signed error, mean unsigned error, standard deviation, and maximum error with respect to CCSD(T) are 0.09, 0.09, 0.05, and 0.19 eV,

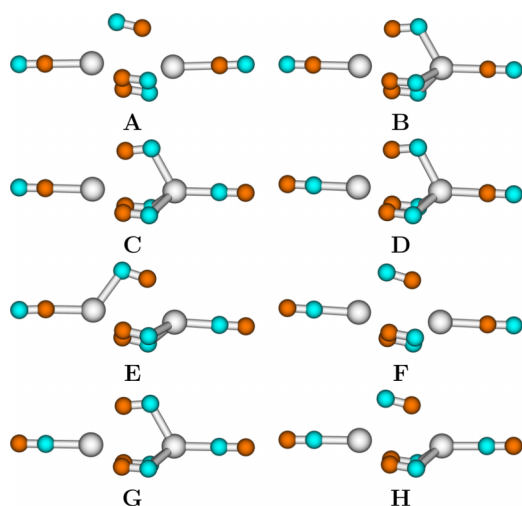


FIG. 1. MP2/TZ1 structures of $\text{Mg}_2(\text{CN})_5^-$ triply-bridged superhalides. Mg: white, C: red, and N: blue.

^{a)}Electronic address: mad0031@auburn.edu

^{b)}Electronic address: ortiz@auburn.edu

TABLE I. Basis-set abbreviations.

Basis	C and N	Mg
TZ1	6-311+G* ^{14,15}	TZVP ^{16,17}
TZ2	6-311+G(3df) ¹⁸	TZVP
TZ3	TZVP+ ^a	Def2-TZVP ¹⁹

^aDiffuse basis from 6-311+G.

respectively. Only for isomer C, Yin *et al.* have compared OVGF and CCSD(T) results for the same state. For isomers D, E, and F, they have assumed that the OVGF prediction for the highest occupied molecular orbital (HOMO) corresponds to the lowest VDE. (Results in bold type correspond to states that were ignored by Yin *et al.*; those in regular type agree closely with their OVGF/TZ2 and CCSD(T)/TZ3 results.) OVGF, with its fifth-power arithmetic scaling factor, has been a reliable predictor of defects in the Koopmans ordering of final states for decades. Fig. 3 shows the close spatial correspondence between unrestricted Hartree–Fock (UHF) spin densities for doublets and amplitudes of canonical Hartree–Fock (HF) orbitals of the anions. OVGF Dyson orbitals (i.e., canonical HF orbitals multiplied by square roots of pole strengths) provide reliable guides for initiating UHF calculations and subsequent CCSD(T) estimates of correlation energies. Fig. 2 and Table II indicate that isomer A, not B as predicted by Yin *et al.*, has the highest first VDE by 0.1 eV.

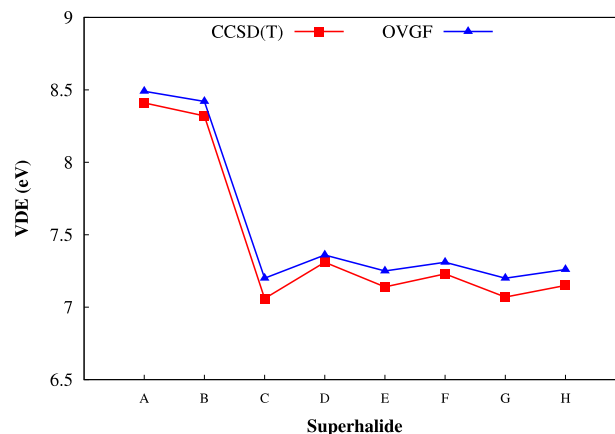
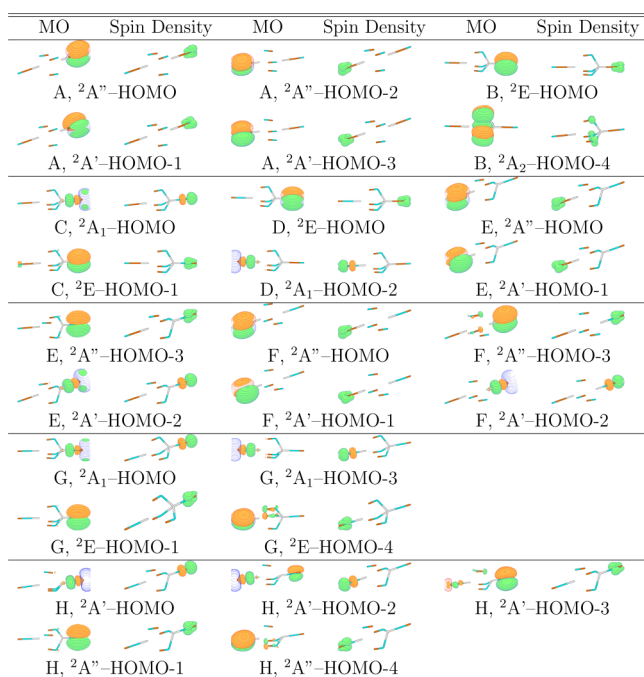


FIG. 2. Comparison between first VDEs predicted with OVGF and CCSD(T).

TABLE II. Vertical electron detachment energies of $\text{Mg}_2(\text{CN})_5^-$ isomers (eV).^a

Isomer	State ^b	Orbital ^c	OVGF ^d	CCSD(T)	Isomer	State ^b	Orbital ^c	OVGF ^d	CCSD(T)
A	$^2A''$	HOMO	8.49	8.41	F	$^2A''$	HOMO	8.50	8.42
A	$^2A'$	HOMO-1	8.49	8.41	F	$^2A'$	HOMO-1	8.49	8.42
A	$^2A''$	HOMO-2	8.57	8.49	F ^e	$^2A'$	HOMO-2	7.31	7.23
A	$^2A'$	HOMO-3	8.57	8.50	F	$^2A''$	HOMO-3	8.72	8.65
B	2E	HOMO	8.42	8.32	G ^e	2A_1	HOMO	7.20	7.07
B	2A_2	HOMO-4	9.08	9.13	G	2E	HOMO-1	8.69	8.50
C ^e	2A_1	HOMO	7.20	7.06	G ^e	2A_1	HOMO-3	7.37	7.32
C	2E	HOMO-1	8.67	8.49	G	2E	HOMO-4	8.77	8.74
D	2E	HOMO	8.42	8.33	H ^e	$^2A'$	HOMO	7.26	7.15
D ^e	2A_1	HOMO-2	7.36	7.31	H	$^2A''$	HOMO-1	8.71	8.59
E	$^2A''$	HOMO	8.57	8.51	H ^e	$^2A'$	HOMO-2	7.41	7.24
E	$^2A'$	HOMO-1	8.58	8.51	H	$^2A'$	HOMO-3	8.61	8.59
E ^e	$^2A'$	HOMO-2	7.25	7.14	H	$^2A''$	HOMO-4	8.74	8.71
E	$^2A''$	HOMO-3	8.70	8.58					

^aBold type: doublets ignored in Ref. 1.^bElectronic state of $\text{Mg}_2(\text{CN})_5^-$.^cCanonical Hartree-Fock orbital of $\text{Mg}_2(\text{CN})_5^-$.^dAll pole strengths exceed 0.85.^eStates with $\langle S^2 \rangle_{UHF} = 1.24-1.25$ and T_1 diagnostic¹³ = 0.037-0.038.FIG. 3. UHF spin densities for $\text{Mg}_2(\text{CN})_5^-$ and canonical molecular orbitals (isovalue = 0.02 a.u.) for $\text{Mg}_2(\text{CN})_5^-$.

Yin *et al.* have published similar criticisms of OVGF for other superhalogens with Mg atoms^{8,9} that have been refuted on the basis of symmetry criteria^{10,11} and have repeated them recently in this journal.¹² Despite these critiques, OVGF remains an efficient, accurate predictor of VDEs and Koopmans defects and, through the interpretation of Dyson orbitals, a reliable guide to the performance of more computationally demanding

total-energy calculations on ground and excited states of doublet superhalogens.

The National Science Foundation supported this work through Grant No. CHE-1565760 to Auburn University. The Alabama Supercomputer Center is acknowledged for a generous allocation of computer time.

¹B. Yin, T. Li, J.-F. Li, Y. Yu, J.-L. Li, Z.-Y. Wen, and Z.-Y. Jiang, *J. Chem. Phys.* **140**, 094301 (2014).²L. S. Cederbaum, *J. Phys. B.* **8**, 290 (1975).³W. von Niessen, J. Schirmer, and L. Cederbaum, *Comput. Phys. Rep.* **1**, 57 (1984).⁴V. G. Zakrzewski, J. V. Ortiz, J. A. Nichols, D. Heryadi, D. L. Yeager, and J. T. Golab, *Int. J. Quantum Chem.* **60**, 29 (1996).⁵J. V. Ortiz, in *Computational Chemistry*, edited by J. Leszczynski (World Scientific, Singapore, 1997), Vol. 2, pp. 1-61.⁶K. Raghavachari, G. W. Trucks, J. A. Pople, and M. Head-Gordon, *Chem. Phys. Lett.* **157**, 479 (1989).⁷M. 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 *et al.*, GAUSSIAN 09, Revision D.01, Gaussian, Inc., Wallingford, CT, 2009.⁸M.-M. Li, J.-F. Li, H. Bai, Y.-Y. Sun, J.-L. Li, and B. Yin, *Phys. Chem. Chem. Phys.* **17**, 20338 (2015).⁹J.-F. Li, M.-M. Li, H. Bai, Y.-Y. Sun, J.-L. Li, and B. Yin, *ChemPhysChem* **16**, 3652 (2015).¹⁰M. Diaz-Tinoco and J. V. Ortiz, *Phys. Chem. Chem. Phys.* **18**, 15456 (2016).¹¹M. Diaz-Tinoco and J. V. Ortiz, *ChemPhysChem* **17**, 2945 (2016).¹²Y.-Y. Sun, J.-F. Li, M.-M. Li, F.-Q. Zhou, J.-L. Li, and B. Yin, *J. Chem. Phys.* **144**, 054303 (2016).¹³T. J. Lee and P. R. Taylor, *Int. J. Quantum Chem.* **36**, 199 (1989).¹⁴K. Raghavachari, J. S. Binkley, R. Seeger, and J. A. Pople, *J. Chem. Phys.* **72**, 650 (1980).¹⁵T. Clark, J. Chandrasekhar, G. W. Spitznagel, and P. V. R. Schleyer, *J. Comput. Chem.* **4**, 294 (1983).¹⁶A. Schaefer, H. Horn, and R. Ahlrichs, *J. Chem. Phys.* **97**, 2571 (1992).¹⁷A. Schaefer, C. Huber, and R. Ahlrichs, *J. Chem. Phys.* **100**, 5829 (1994).¹⁸M. J. Frisch, J. A. Pople, and J. S. Binkley, *J. Chem. Phys.* **80**, 3265 (1984).¹⁹F. Weigend and R. Ahlrichs, *Phys. Chem. Chem. Phys.* **7**, 3297 (2005).