Valence Electron Rules for Three- and Four-membered Atomic Rings: High-row Representative Elements

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Valence electron rules are proposed for the stability and instability of three- and four-membered atomic rings of high-row representative elements in the singlet states. Regular polygons with $4N+2$ and $8N+6$ valence electrons are the ground states of three- and four-membered rings, respectively. The rules are not necessarily applicable out of the range of the number of valence electrons (N_{ve}): $4m \le N_{ve} \le 6m$ for the groups 14–16 and $3m+[1-(-1)^m]/2 \le N_{ve} \le 6m$ for the group 13 where m is the number of the ring members.

There are some rules related to the number of electrons in chemistry.[1] Here we theoretically proposed simple rules for the atomic rings where each atom of rings is not bonded to any exocyclic entities but only to the neighboring atoms on both sides.

The basis set atomic p orbitals are classified into radial (p_ρ), tangential (p_τ), and perpendicular (p_π) orbitals (Figure 1). The array of the p_τ orbitals in the three-membered ring is of the Möbius conjugation, while the others are of the Hückel conjugation.[2] The patterns of the energy levels in the Hückel and Möbius conjugations are well known (Figure 2). The qualitative energy level diagrams (Figure 3) show the number of valence electrons necessary to give closed-shell electronic structures. Suppose that each orbital in the s-orbital set is occupied by a pair of electrons since the s-orbital energies are low and separate from the p-orbital ones especially for heavy atoms: $n(s) = 6$ for the three-membered rings and $n(s) = 8$ for the four-membered rings. The Hückel and Möbius conjugations require $4n+2$ and $4n$ electrons for the closed-shell structures, respectively: $n(p_\rho) = 4r+2$ and $n(p_\pi) = 4p+2$ for the three- and four-membered rings; $n(p_\tau) = 4t$ and $n(p_\tau) = 4t+2$ for the three- and four-membered rings, respectively. The total numbers of the valence electrons, $N_{ve} = n(s) + n(p_\rho) + n(p_\tau) + n(p_\pi)$, for the closed-shell structures are $4(r+t+p+2)+2$ and $4(r+t+p+3)+2$ for the three- and four-membered rings, respectively. The ground states of atomic rings with $4N+2$ valence electrons are of regular polygons, whereas those with $4N$ valence electrons are not.

A correction is necessary for the $4N+2$ rule for the four-membered rings, where both p_ρ and p_τ orbitals are of the Hückel conjugations. The orbitals in one set have almost the same energies as the corresponding orbitals in the other set. The orbitals occupied by 9–12th and 16–22th electrons are almost degenerate. Regular polygons are not of closed-shell structures even if the number of valence electrons is 10 or 18. As a result, $8N+6$ valence electrons allow regular polygons to be the ground states whereas $8N+2$ valence electrons do not.

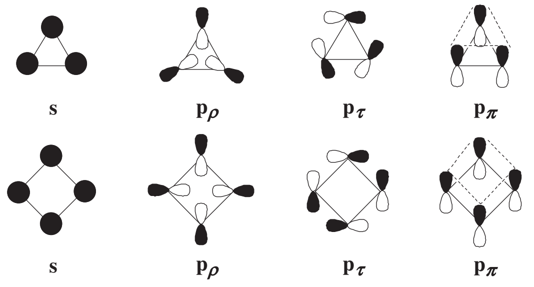
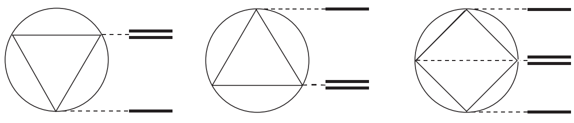
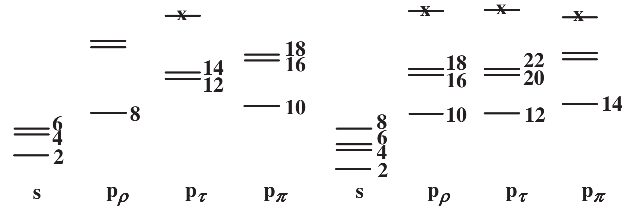


Figure 1. Basis set orbitals: s orbitals, radial (p_ρ), tangential (p_τ), and perpendicular (p_π) p orbitals.



(a) Hückel conjugation (b) Möbius conjugation (c) Hückel conjugation

Figure 2. Orbital energy level of the three- and four-membered rings.



(Hückel)(Hückel)(Möbius)(Hückel) (Hückel)(Hückel)(Hückel)(Hückel)
(a) Three-membered ring (b) Four-membered ring

Figure 3. Qualitative energy level diagram.

There is an inapplicable range of $4N+2$ and $8N+6$ valence electron rules. For the minimum number of electrons to satisfy the octet rule, as many valence electrons as possible are shared by bonded atoms. An atom shares four electrons with each of adjacent atoms (maximum unsaturation in Figure 4a). The lower limit is $4m$ for the m-membered rings. For the maximum number of electrons, a pair of electrons are shared by the bonded atoms while the remaining are lone pairs (full saturation in Figure 4b). The upper limit is $6m$. For the group 13, a smaller number of valence electrons may be allowed for the lower limit. Monomeric BH_3 suggests the "sextet" rule might be applicable.

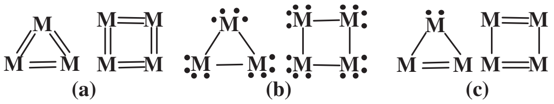


Figure 4. Lower and upper limits of valence electron number for the ring structures.

Table 1. The ground state geometries of the three-membered rings[a]

Number of Valence Electrons						
$4N+2$			$4N$			
10	14	18	8	12	16	20
Al_3^- (D_{3h})[b,c]	Si_3^{2-} (D_{3h})	S_3 (C_{2v})[e]	Al_3^+ ($D_{\infty h}$)	Si_3 (C_{2v})	P_3^- ($D_{\infty h}$)	S_3^{2-} (C_{2v})
Ga_3^- (D_{3h})[c]	Ge_3^{2-} (D_{3h})	Se_3 (D_{3h})[e,f]	Ga_3^+ ($D_{\infty h}$)	Ge_3 (C_{2v})	As_3^- ($D_{\infty h}$)	Se_3^{2-} (C_{2v})
Si_3^{2+} ($D_{\infty h}$)	P_3^+ (D_{3h})[d]				S_3^{2+} (C_{2v})	
Ge_3^{2+} ($D_{\infty h}$)	As_3^+ (D_{3h})				Se_3^{2+} (C_{2v})	

[a] Calcualted at the UB3LYP/6-31+G(d) level. [b] Slight distortion from the D_{3h} symmetry of the RB3LYP/6-31+G(d) structure is considered as an artifact. [c] A. E. Kuznetsov and A. I. Boldyrev, *Struct Chem.*, **13**, 141 (2002). [d] W. W. Schoeller and U. Tubbesing, *Theochem*, **343**, 49 (1995). [e] J. D. Goddard, X. Chen, and G. Orlova, *J. Phys. Chem. A.*, **103**, 4078 (1999); R. I. Billmers and A. L. Smith, *J. Phys. Chem.*, **95**, 4242 (1991). [f] S. Kohara, A. Goldbach, N. Koura, M.-L. Saboungi, and L. A. Curtiss, *Chem. Phys. Lett.*, **287**, 282 (1998).

Table 2. The ground state geometries of the four-membered rings[a]

Number of valence electrons								
$4N+2$					$4N$			
$8N+2$			$8N+6$					
10	18	26	14	22	12	16	20	24
Al_4^{2+} ($D_{\infty h}$)[b]	Si_4^{2-} (D_{2d})[c]	S_4^{2-} (C_2)	Si_4^{2+} (D_{4h})	P_4^{2-} (D_{4h})[g]	Al_4 (C_{2h})	Si_4 (D_{2h})	P_4 (T_d)	S_4 (D_{2d})
Ga_4^{2+} ($D_{\infty h}$)	Ge_4^{2-} (D_{2d})	Se_4^{2-} (C_2)	Ge_4^{2+} (D_{4h})	As_4^{2-} (D_{4h})[g,h]	Ga_4 (C_{2h})	Ge_4 (D_{2h})	As_4 (T_d)	Se_4 (D_{2d})
	P_4^{2+} (D_{2d})		Al_4^{2-} (D_{4h})[d,e]	S_4^{2+} (D_{4h})[i,j]				
	As_4^{2+} (D_{2d})		Ga_4^{2-} (D_{4h})[d,f]	Se_4^{2+} (D_{4h})[k,l]				

[a] Calcualted at the UB3LYP/6-31+G(d) level. [b] A. Martinez and A. Vela, *Phys. Rev. B: Con. Matt. & Mat. Phys.*, **49**, 17464 (1994). [c] A. F. Cuthbertson and C. Glidewell, *Inorg. Chim. Acta*, **49**, 91 (1981). [d] C-G. Zhan, F. Zheng, and D. A. Dixon, *J. Am. Chem. Soc.*, **124**, 14795 (2002).; A. I. Boldyrev and A. E. Kuznetsov, *Inorg. Chem.*, **41**, 532 (2002). [e] X. Li, A. E. Kuznetsov, H. F. Zhang, A. I. Boldyrev, and L. S. Wang, *Science*, **291**, 859 (2001). [f] Ref. 3. [g] A. E. Kuznetsov, H.-J. Zhai, L.-S. Wang, and A. I. Boldyrev, *Inorg. Chem.*, **41**, 6062 (2002); F. Kraus, J. C. Aschenbrenner, and N. Korber, *Angew. Chem. Ed. Eng.*, **42**, 4030 (2003). [h] J. Roziere, A. Seigneurin, C. Belin, and A. Michalowicz, *Inorg. Chem.*, **24**, 3710 (1985). [i] R. A. J. Janssen, *J. Phys. Chem.*, **97**, 6384 (1993). [j] M. P. Murchie, J. P. Johnson, J. Passmore, G. W. Sutherland, M. Tajik, T. K. Whidden, P. S. White, and F. Grein, *Inorg. Chem*, **31**, 273 (1992). [k] I. Krossing and J. Passmore, *Inorg. Chem.*, **38**, 5203 (1999). [l] R. J. H. Clark, T. J. Dines, and L. T. H. Ferris, *J. Chem. Soc., Dalton Trans.*, **11**, 2237 (1982).

Maximum unsaturation is illustrated in Figure 4c. So the lower limits are 10 and 12 for the three- and four-membered rings, receptively ($3m + [1-(-1)^m]/2$ in a general formula). As a result, the octet (sextet) rule suggests that the $4N+2$ and $8N+6$ valence electron rules can not be necessarily applicable out of the range: $4m \leq N_{\mathrm{ve}} \leq 6m$ for the groups 14–16 and $3m + [1-(-1)^m]/2 \leq N_{\mathrm{ve}} \leq 6m$ for the group 13.

The valence electron rules were supported by ab initio calculations (Tables 1 and 2). There are no exceptions in the $4N$ valence electron rule, and only three exceptional three-membered rings (Si_3^{2+}, Ge_3^{2+}, and S_3) in the $4N+2$ valence electron rule. Si_3^{2+} and Ge_3^{2+} (10e) are out of the applicable range. For S_3 (18e), the lone pairs repulsion may destabilize the ring. In the Se_3 ring, the lone pair repulsion is weaker because of the smaller overlap.

The $8N+2$ and $8N+6$ rules were perfectly substantiated by the calculated four-memebered species (Table 2). The present valence electron rules are also expected to be applicable to the species containing even higher-row elements (In_4^{2-}, Te_4^{2+}).[3,4]

In summary, we proposed and demonstrated rules for the stability of three- and four-membered atomic rings of high-row representative elements in the singlet states. (1) $4N$ valence electrons do not allow regular polygons as the ground states for both three- and four-membered rings; (2) regular polygons with $4N+2$ valence electrons in the singlet states are the ground states for the three-membered rings; (3) $8N+2$ valence electrons do not allow regular polygons as singlet ground states for four-membered rings; (4) regular polygons with $8N+6$ valence electrons are the ground states for four-memebred rings; (5) the $4N+2$ and $8N+6$ valence electron rules are not necessarily applicable out of the range: $4m \leq N_{\mathrm{ve}} \leq 6m$ for the groups 14–16 and $3m + [1-(-1)^m]/2 \leq N_{\mathrm{ve}} \leq 6m$ for the group 13.

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