

# Understanding the eighteen-electron rule

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## Abstract

It is pointed out that the preferred closed-shell electron structures, such as those in typical high-symmetry 18-electron systems, are driven both by the bonding contributions to the centre and by the kinetic-energy (nodal-structure) terms in the ligand subsystem,  $L_n$ . The latter imposes a filling order  $s < p < d$ , even for the  $ML_n$  complex. Then the 18e principle can be right for the right reasons even without any  $np$  contributions at the central atom.

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## 1. Introduction

The 18-electron principle for the stability of certain transition-metal compounds was suggested in 1921 by Langmuir [1], who quoted  $Mo(CO)_6$ ,  $Fe(CO)_5$  and  $Ni(CO)_4$  as examples. Bose [2] included cyanides, chlorides and ammonia as ligands, and Reiff [3] added nitrosyl. A comprehensive summary was given in 1934 by Sidgwick and Bailey [4], who included polynuclear complexes. The important treatise by Sidgwick [5] is less relevant in this particular context. For later discussions, see for instance Craig and Dodgett [6], Mitchell and Parish [7] or Huheey [8]. Some examples on complexes are shown in Table 1 and a list of ligand electron numbers in Table 2.

Mingos and Hawes [9,10] introduced a ‘complementary spherical electron density model’. They used the wave functions for a particle on a spherical shell but did not use the corresponding energy expressions, apart from the order  $s < p < d$ . The nodal structures of these wave functions are also mentioned. Not only the 18e rule but also the stereochemistries were obtained.

In a conventional atomic-orbital picture it could be imagined that the 18e principle corresponds for 3d metals to a krypton-like electronic structure  $(ns)^2(np)^6((n-1)d)^{10}$ ,  $n = 4$ . Indeed, this empirical relation has also been called the ‘rare-gas rule’ [6]. This was the original idea of Sidgwick [4] who talked about ‘effective atomic numbers (EAN)’ like 36 corresponding to krypton. Then, in addition to some  $ns$  and  $(n-1)d$  character at the central atom, some  $np$  character would be expected for the principle to be valid. When very little  $np$  character was found, for certain systems using certain methods of population analysis, Weinhold and Landis [11] suggested that the 18e principle should be overthrown, or replaced by a ‘12e principle’. Parenthetically, their particular population analysis has been criticised by Maseras and Morokuma [12], but in principle the problem remains.

We here make another suggestion: In addition to the bonding contributions to the central atom, the nodal structure (kinetic energy) of the ligands strongly contributes to which orbitals should be occupied. If then the  $s$ -like and  $d$ -like contributions (with zero and two angular nodal surfaces, respectively) are required for good bonding, a  $p$ -like molecular orbital (with one nodal surface) is also required, but it will not necessarily need any  $p$ -like components at the metal  $M$ . This idea is shown in Fig. 1.

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Table 1  
Examples on nominally  $N$ -electron complexes,  $ML_n^q$ , belonging to various symmetry groups, G

$N$	Complex	G	Comments or references
18	W(CO) <sub>6</sub>	O <sub>h</sub>	
18	Ni(CO) <sub>4</sub>	T <sub>d</sub>	
18	Mo(CN) <sub>8</sub> <sup>4-</sup>	D <sub>4d</sub>	In K <sub>4</sub> Mo(CN) <sub>8</sub> · 2H <sub>2</sub> O [32]
18	WAu <sub>12</sub>	I <sub>h</sub>	[16,18]
18	ReH <sub>9</sub> <sup>3-</sup>	D <sub>3h</sub>	In K <sub>2</sub> ReH <sub>9</sub> <sup>a</sup>
18	FeH <sub>9</sub> <sup>4-</sup>	O <sub>h</sub>	In Mg <sub>2</sub> FeH <sub>6</sub> <sup>a</sup>
18	NiH <sub>4</sub> <sup>4-</sup>	T <sub>d</sub>	In Mg <sub>2</sub> NiH <sub>4</sub> <sup>a</sup>
18	CuH <sub>4</sub> <sup>3-</sup>	T <sub>d</sub>	In Ba <sub>7</sub> Cu <sub>3</sub> H <sub>17</sub> <sup>a</sup>
18	Fe(C <sub>5</sub> H <sub>5</sub> ) <sub>2</sub>	D <sub>5h</sub>	D <sub>5d</sub> transition state [25]
18	Cr(C <sub>6</sub> H <sub>6</sub> ) <sub>2</sub>	D <sub>6h</sub>	
20	Th(C <sub>8</sub> H <sub>8</sub> ) <sub>2</sub>	D <sub>8h</sub>	[28,29]

<sup>a</sup> For further MH<sub>*n*</sub><sup>*q*</sup> species, see King [33].

Table 2  
Examples on electron-counts for various ligands

Group	Electron count
–H	1
–X, halogen	1
–alkyl, –aryl, acyl	1
–NR <sub>2</sub> , amide	1
–SiR <sub>3</sub> , silyl	1
–AuPR <sub>3</sub>	1
–PR <sub>2</sub> , phosphide	1
–CO	2
–PR <sub>3</sub>	2
–NR <sub>3</sub>	2
–NN	2
η <sup>2</sup> -H <sub>2</sub>	2
η <sup>2</sup> -alkene	2
η <sup>2</sup> -alkyne	2
–CNR, isocyanide	2
–N=O, bent nitrosyl	1
–N≡O, linear nitrosyl	3
(μ <sup>3</sup> )-Bi	3
(μ <sup>3</sup> )-S	4
N (interstitial)	5
η <sup>5</sup> -(C <sub>5</sub> H <sub>5</sub> )	5
η <sup>6</sup> -(C <sub>6</sub> H <sub>6</sub> )	6
η <sup>8</sup> -(C <sub>8</sub> H <sub>8</sub> )	8

The ‘neutral atom’ convention [8] is used. With acknowledgments to Table 15.1. of Huheey et al. [8] and Table 1 of Owen [34].

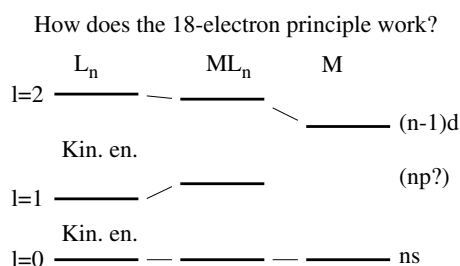


Fig. 1. The energy-level schemes for the ligand and metal subsystems and for their complex.

## 2. Calculations

### 2.1. Simple model: a spherical ligand

As a prelude, consider a spherical ligand. In other words, suppose that the bonding electrons between the ligand and the metal are moving on the surface of a sphere at a distance  $R$  from the metal nucleus. For an angular-momentum  $l$ , the energy levels (in atomic units) become

$$E_l = \frac{l(l+1)}{2R^2}. \quad (1)$$

The resulting splittings and their order are comparable with those found for real-world ligand systems for  $R$  values at or below the M–L bond length; a reasonable estimate could be half the bond length.

We then proceed to some illustrative calculations at DFT level. As discussed [13–15], the Kohn–Sham orbital energies and coefficients *can* be used for qualitative interpretation of chemical bonding.

### 2.2. WAu<sub>12</sub>

This icosahedral molecule was predicted by Pyykkö and Runeberg [16] and experimentally produced in the group of Lai-Sheng Wang [17]. For further theoretical work, see Ref. [18,19]. Four other predicted valence isoelectronic species have also been produced [17,20]. For other systems with the same 18e count, notably by Teo, see the review [21], p. 4435. Note that some of the systems have very low symmetries. In the 18e count, the peripheral gold atoms contribute one electron each while a central transition-metal atom also contributes its d-electrons, which strongly participate in the bonding.

In the icosahedral case I<sub>h</sub>, the angular momenta  $l = 0, 1$  and  $2$  for the spherical ligand, or the central-atom  $s, p$  and  $d$  orbitals, span the irreducible representations (irreps)  $a_{1g}, t_{1u}$  and  $h_g$ , respectively. The calculated energy levels for Eq. (1) and the orbital energies for the bare ligand shell and the molecule are shown in Fig. 2. The first two columns fully confirm the present idea that the ligand nodal structure suffices to produce the shell structure needed for the 18e principle. Even if the 6p-type basis functions at W in the full molecule are totally omitted, a very similar level scheme is obtained.

The calculations at BP86 level used a 14-VE (valence-electron) SDD pseudopotential for W with the default basis. To avoid complications from gold 5d–6s hybridization, the Au atoms were first treated using a 1-VE pseudopotential [22] (Fig. 2, middle). The MP2 W–Au bond length of 268.0 pm [16] was assumed. Finally, a ‘large’ DFT calculation was performed using a 19-VE Stuttgart pseudopotential for Au. A large VQZPP5p (8s7p6d3f)/[7s5p4d3f] basis was used for both elements, together with a TPSS functional. (If it was replaced by a BP86 functional, almost no change occurred in the eigenvalue spectrum.) The results are shown in the right-hand column of Fig. 2.

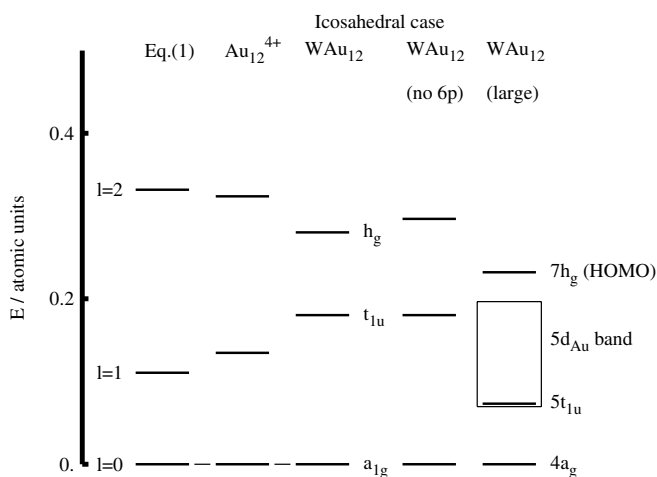


Fig. 2. The relative energy-level schemes for a sphere ( $R = 3.0067$  a.u. or  $159.1$  pm), the  $\text{Au}_{12}^{4+}$  ligand shell and the neutral  $\text{WAu}_{12}$  molecule. For details, see the text.

Now a 120-electron 5d band from the twelve gold atoms overlaps the relevant orbitals but the basic picture remains the same. The MOs are shown for the ‘large’ calculation in Fig. 3. Summarizing, the ‘18 electrons’ now occupy the  $(4a_{1g})^2(5t_{1u})^6$  at the bottom and the  $(7h_g)^{10}$  HOMO at the top of the occupied valence band. The lower-lying  $4h_g$  inside the  $5d_{\text{Au}}$  band also has some W–Au bonding character.

### 2.3. Hexacarbonyls

This case has lower symmetry,  $O_h$  instead of  $I_h$ , and is hence slightly less straightforward to relate to Eq. (1): while the  $l = 0$  and 1, or central-atom  $s$  and  $p$  orbitals still span the irreps  $a_{1g}$  and  $t_{1u}$ , respectively, the  $l = 2$  or  $d$  orbitals are now split to the non-degenerate  $e_g$  and  $t_{2g}$ .

For the real-world CO ligands, three orbitals are relevant for the complex bonding. One is the carbon  $\sigma$  lone pair, which spans the  $1a_{1g}$ ,  $1t_{1u}$  and  $1e_g$  orbitals at the bottom of the valence band. The other dominant ligand orbital is the  $\pi^*$  that contributes to the  $2t_{2g}$  HOMO of  $\text{W}(\text{CO})_6$ . These four MOs now hold the ‘18 electrons’.

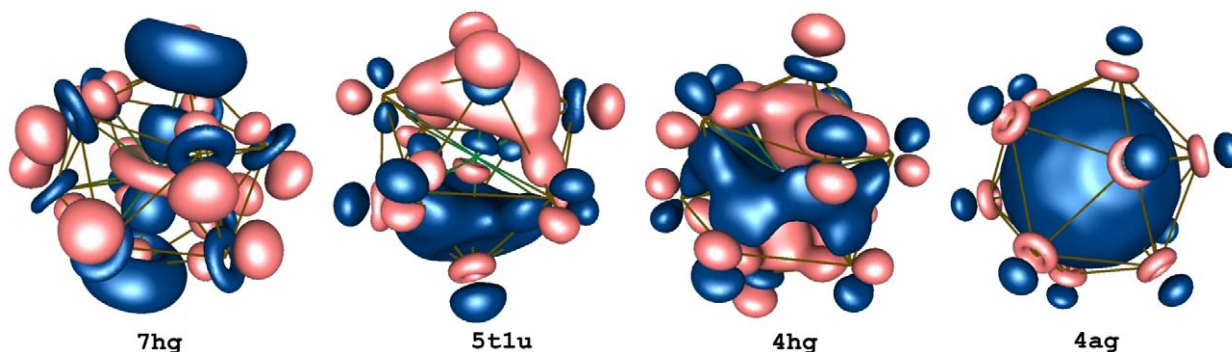


Fig. 3. The bonding MOs of  $\text{WAu}_{12}$ . Produced using ‘gOpenMol’ [30,31].

In addition, in the middle of the valence band there is another set  $2a_{1g}$ ,  $2e_g$ ,  $3t_{1u}$  mainly spanned by the intra-CO  $\sigma$  bonds. Overlapping with it, there is a set  $1t_{2g}$ ,  $2t_{1u}$ ,  $1t_{2u}$ ,  $1t_{1g}$  with mainly CO  $\pi$  parentage. The latter one is given in Fig. 4 as a box.

This qualitative MO structure of metal hexacarbonyls has been known for some time [23,24] and no essential deviations from the traditional order are proposed by the present calculations.

Density-functional calculations are again reported using the BP86 functional. The Stuttgart ‘SDD’ pseudopotential for the central atom and a 6-31g\* basis for the light elements were used.

Fig. 4 shows the  $\sigma$ -like energy levels of  $\text{W}(\text{CO})_6$  and compares them with the ligand network (without a central atom, at the same geometry). It is seen that the orbital order from Eq. (1) survives in the ligand system  $(\text{CO})_6^{4+}$  while in the full molecule  $\text{W}(\text{CO})_6$  the  $e_g$  and  $t_{1u}$  cross.

Summarizing, in the archetypal Group-6 hexacarbonyl [1,4] 18e systems, these ‘18 electrons’ mainly reside in the orbitals  $1a_{1g}$ ,  $1t_{1u}$ ,  $1e_g$  and  $2t_{2g}$  of a sturdy closed-shell

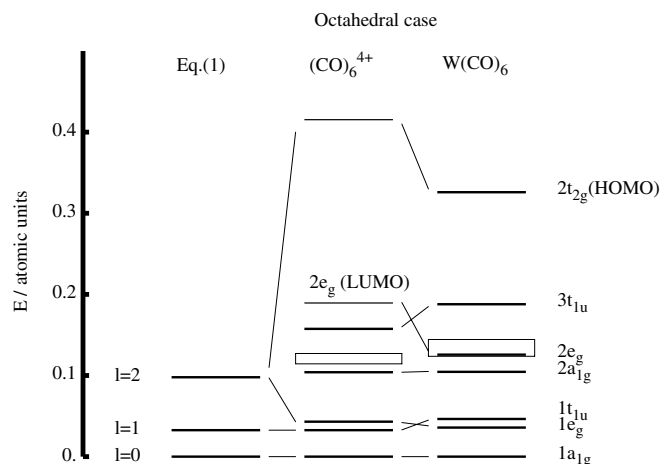


Fig. 4. The relative energy-level schemes for  $\text{W}(\text{CO})_6$  and its ligand subsystem. For the first column,  $R = 5.5385$  a.u. or  $293.0$  pm, now fitted to the  $t_{1u}$  level, only. The boxes stand for the four  $t$  orbitals spanned by the CO  $\pi$  orbitals, see text.

system. The splitting of the  $1t_{1u}$  from its neighbours is still comparable with the kinetic-energy argument, Eq. (1), and does not necessarily require any 6p character at W. Indeed, if the 6p basis functions at W were removed, almost no change occurred in the calculated eigenvalue spectrum of  $W(CO)_6$ .

#### 2.4. Metallocenes

Two of the earliest metallocenes are ferrocene,  $Fe(C_5H_5)_2$ , and dibenzenechromium,  $Cr(C_6H_6)_2$ . We next show a simple way to qualitatively describe their bonding. The amount of  $np$  occupation is not addressed here. A concise way to describe the bonding in these systems is the cartoon in Fig. 5. We have used similar diagrams earlier for linear systems, as described in the next chapter. In this schematic local-orbital presentation, the nine spd orbitals of the transition metal atom yield a left-hand  $\sigma$ , a right-hand  $\sigma$  and a 'doughnut  $\sigma$ ', two degenerate left-hand  $\pi$ , two degenerate right-hand  $\pi$  orbitals and a doubly degenerate ' $\delta$  ring' in the middle, all symmetries referring to the molecular symmetry axis. Each of these orbitals can bond to localised ligand orbitals of the same symmetry. The  $\pi$  system (about the molecular plane) of each neighbouring aromatic ring, originally with a  $6\pi$  occupation, then offers, using here axial symmetry labels, one occupied  $\sigma$  and two  $\pi$  orbitals on each side as potential donors, and two empty  $\delta$  orbitals as a potential acceptor.

Concerning  $Fe(C_5H_5)_2$ , and dibenzenechromium,  $Cr(C_6H_6)_2$ , their bonding was just analysed by Rayón and Frenking [25], who concluded that their bonding is dominated by the  $\pi$ -type and  $\delta$ -type metal–ligand interactions for the two molecules, respectively.

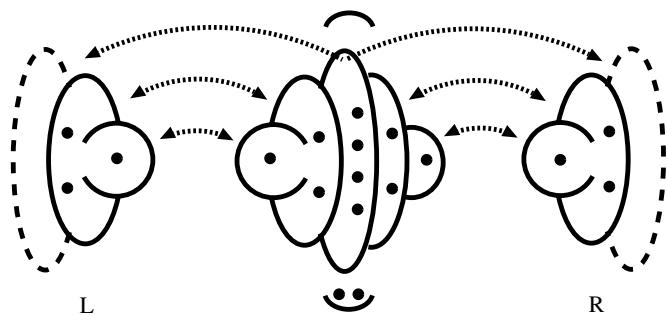


Fig. 5. A compact way of describing the 18-e bonds in ferrocene or dibenzenechromium. Only the  $\pi$  orbitals of the aromatic left- (L) and right-hand (R) ligands are shown. The metal atom stands in the centre and its spd-orbitals are hybridized to a  $\sigma_L\pi_L\delta\pi_R\sigma_R$  combination, plus a 'doughnut  $\sigma$ ' that actually can be identified with the  $a_{1g}^+$  HOMO of ferrocene. The  $\delta$  orbitals of the metal donate to the  $\delta$  orbitals of the ligands. Both left- and right-hand  $\sigma$  and  $\pi$  orbitals are enjoying a covalent interaction. In a shared, Lewis sense the central atom is surrounded by 18 electrons and the figure shows where they schematically are. The labels  $\sigma$ ,  $\pi$  and  $\delta$  refer to rotations about the molecular axis.

### 3. Further aspects

#### 3.1. Below 18

Consider again an atom in a linear geometry. As well known, the sp orbitals for a main-group atom then yield the directed hybrids  $\sigma_{\text{left}}\pi_{\text{ring}}\sigma_{\text{right}}$ . If all are filled, like for carbon in acetylene, a Lewis octet is obtained for it.

For transition metals the localised combinations of the spd orbitals become  $\sigma_{\text{left}}\pi_{\text{left}}\delta_{\text{ring}}\sigma_{\text{doughnut}}\pi_{\text{right}}\sigma_{\text{right}}$ , as explained above. For pictures and examples, see Ref. [26,27]. The non-trivial question is, which ones of these are occupied and which ones empty, for a given case with less than 18 electrons? For instance in the diatomic, triple-bonded PtC, with C on the 'right' of Pt, the  $\sigma_{\text{left}}\pi_{\text{left}}$  at Pt are left empty while the  $\delta_{\text{ring}}\sigma_{\text{doughnut}}\pi_{\text{right}}\sigma_{\text{right}}$  are occupied, either in the full sense or the shared Lewis sense. Thus the Pt metal atom here has a 12e electron count. That is reduced to 10e, 8e, 6e and 6e in diatomic RuC, TaN, TiC and ScB, respectively (see Ref. [27], Fig. 3). It should be added that very similar results are obtained whether molecular orbitals or local orbitals are used for these inspections.

#### 3.2. Beyond 18

Thorocene,  $Th(COT)_2$  ( $COT = C_8H_8$ ) is a clear example on a 20e closed-shell electronic structure whose central-atom character is, for symmetry orbitals about the molecular axis, in this energetic order,  $(\sigma_g)^2(\sigma_u)^2(\pi_g)^4(\pi_u)^4(\delta_g)^4 - (\delta_u(\text{HOMO}))^4$ , see Ref. [28,29]. After a gap, a set of more-or-less 5f-like, compact  $\phi$ ,  $\sigma$ ,  $\pi$  and  $\delta$  levels will follow. Thus the possibility for a '32e principle' for actinide compounds, or other cases with a single atomic centre, does not look promising. Going far beyond 20 is not likely.

### 4. Conclusion

Summarizing, we cautiously advance the Gordian proposal that the 18-electron principle is entirely correct, but 'driven', not only by the orbitals partially occupied at the metal atom, but also by a succession of combinations of ligand orbitals with increasing kinetic energy. The two together can explain and legalise the 18e principle, even in the absence of any central-atom p-contributions. In such cases the p-like shell is a 'free passenger', that must be filled due to its energetic position  $s < p < d$ , valid also in the complex, even when the p-shell does little or no bonding to the central metal atom.

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