Effective Oxidation States Analysis

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Outline

Formal oxidation states

- The concept of oxidation state (OS) is ubiquitous in transition metal (TM) chemistry and in the study of redox and catalytic reactions.

- Many properties such as reactivity, spin-state, spectroscopic and geometrical features of TM complexes are often rationalized on the basis of the oxidation state of the metal center.

- According to IUPAC, in coordination chemistry, the OS is *the charge left on the metal after all ligands have been removed in their normal, closed shell, configuration*.

- Formal OS are obtained by assigning integer number of electrons to the atoms/ligands according to some rules. In complicated bonding situations involving non-innocent ligands or in intermediates or transition states of catalytic reactions the formal OS assignment may be rather ambiguous.

ab initio determination of oxidation states

- A number or empirical approaches to *correlate* atomic distances or populations with transition metal (TM) oxidation states (bond-valence sum scheme).

- Sit et al.[1] used projection techniques to obtain d orbital populations of central metal in transition metal (TM) complexes

- Sit et al.[2] also used the positions of the centers of gravity of maximally-localized Wanier Functions.

- Localized Orbital Bond Analysis (LOBA) [3]: MO localization followed by population analysis (a threshold is introduced)

- ELIBON (electron-localizability-based oxidation number)[4], usually applied to solids.

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1. Inorg. Chem. 2011, 50, 10259   2. Chem. Eur. J. 2011, 17, 12136   3. Phys. Chem. Chem. Phys, 2009, 11, 11297   4. J. Solid State Chem. 2008, 181, 1983.

Our approach

Focus on the *effective* state of the atoms within the molecule

Derive from the WF some set of "atomic orbitals" and occupation numbers that will allow to assign each electron to a given atom.

Desirable properties of the "atomic orbitals"

- Clear-cut separation (in terms of occupation numbers) of core, valence and virtual orbitals
- Applicable on equal footing for any level of theory and basis set (plane waves, core potentials, etc)
- Basis set independent
- Able to treat alpha and beta electrons independently.
- Able to define functional groups/fragments.

Effective atomic orbitals

Let us consider a system with n orthonormalized doubly occupied orbitals $\varphi_i(\vec{r})$, $i = 1, 2 \ldots, n$, and any division of the 3D-space into N_{at} atomic domains Ω_A defined *e.g.*, by a continuous atomic weight function $w_A(\vec{r})$.

For each atom A ($A = 1, 2, \ldots, N_{at}$) one can form the $n \times n$ Hermitian "net atomic overlap matrix in the MO basis.

$$Q_{ij}^A = \int \varphi_i^*(\vec{r}) w_A(\vec{r}) w_A(\vec{r}) \varphi_j(\vec{r}) dv.$$

We diagonalize the Hermitian matrix $\mathbf{Q}^A$ by the unitary matrix $\mathbf{U}^A$:

$$\mathbf{U}^{A\dagger} \mathbf{Q}^A \mathbf{U}^A = \mathbf{\Lambda}^A = diag\{\lambda_i^A\} \quad .$$

It can be shown that every $\lambda_i^A \geq 0$, as is the case for every overlap matrix.

Effective atomic orbitals

For each atom A we can obtain n_A $(n_A \leq n)$ "effective atomic orbitals $\chi_\mu^A(\vec{r})$ as linear combinations of the "intraatomic" parts $\varphi_i^A(\vec{r})$ of the MO-s as

$$\chi_\mu^A(\vec{r}) = \frac{1}{\sqrt{\lambda_\mu^A}} \sum_{i=1}^{n} U_{i\mu}^A \varphi_i^A(\vec{r}) \; ; \qquad \mu = 1, 2, \dots, n_A \; \; ,$$

where n_A is the number of non-zero eigenvalues λ_i^A.

- For each atom one obtains a set of orthogonal atomic hybrids and their respective occupation numbers, adding up to its net atomic population.

1. I. Mayer J. Phys. Chem. 6249 (1996); 2. I. Mayer, P. Salvador J. Chem. Phys. 234106 (2009);
3. I. Mayer Can. J. Chem. 939 (1996) ; 4. P. Salvador, E. Ramos-Cordoba, I. Mayer J. Chem. Phys. 214107 (2013)

eff-AOs have al desired features

- The maximum number of eff-AOs that can be obtained is $N_{at} \times n$, but experience shows that one typically obtains as many eff-AOs with significant occupation numbers as orbitals in the classical minimal basis.

- The eff-AOs of atom A can also be obtained from the diagonalization of the matrix $\mathbf{PS}^A$ in the actual AO basis. This permits the straightforward generalization of the method to correlated WFs and to treat the alpha and beta electrons separately, making explicit use of the $\mathbf{P}^{\alpha}$ and $\mathbf{P}^{\beta}$ matrices.

- They can be obtained even if no atom-centered basis functions where used in the original MO description.

  Mayer et al. Chem. Phys. Lett. 563 97 (2013)
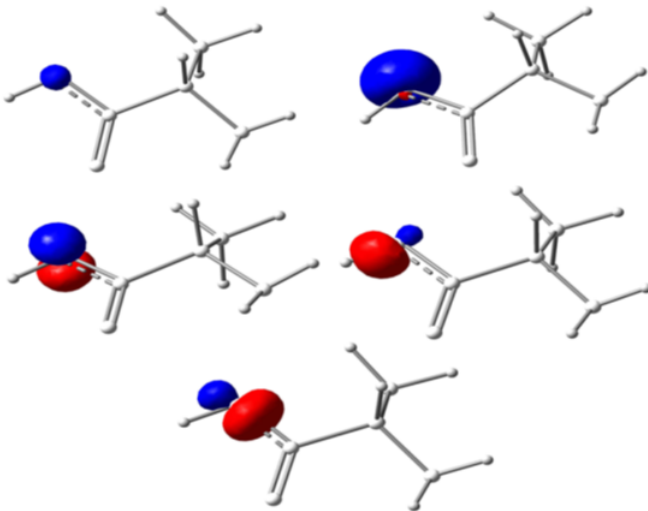
Visualization of the eff-AOs

Figure 1: Occupied oxygen eff-AOs in alanine molecule (TFVC)
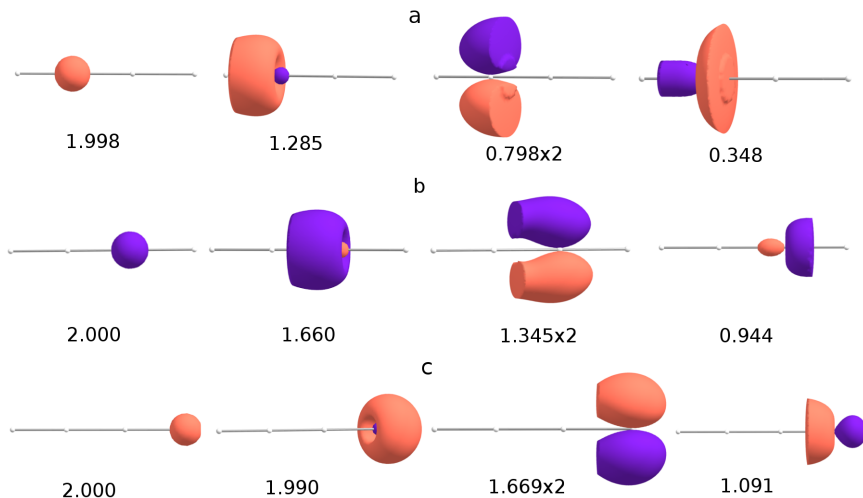
Visualization of the eff-AOs

Figure 2: Highly occupied carbon (a), nitrogen (b), and oxigen (c) orbitals in the HCNO molecule (QTAIM)

ab initio determination of oxidation states

The eff-AOs, and specially their occupation numbers, can be used to retrieve the appropriate oxidation states of the atoms from the wavefunction from first principles.

Strategy

- Obtain $\rho(\vec{r}, \vec{r}')$ from an *ab initio* calculation.
- For each atom, obtain spin-resolved eff-AOs and occupation numbers up to a given theshold (e.g. 0.1)
- Sort all of them according to decreasing occupation number
- Round the occupation numbers to 1 (i.e. assign occupied eff-AOs) starting from the highest occupied eff-AO until the the number of alpha electrons is reached. Do analogously for the beta part.

Ramos-Cordoba et al, J. Chem. Theory Comput., 2015, 11, 1501.

EOS analysis

Alpha effective atomic orbitals for $Fe(CN)_6^{3-}$ at the B3LYP/6-31G(d) level of theory.

Total number of alpha electrons: 54

	Fe				C		N	
eff-AO type	Occup	eff-AO type	Occup	eff-AO type	Occup	eff-AO type	Occup	
1s	1.000	3d	0.876	1s	0.996	1s	1.000	
2s	1.000	3d	0.848	2s	0.694	2s	0.997	
2p	1.000	3d	0.848	2p	0.235	2p	0.728	
2p	1.000	3d	0.344	2p	0.232	2p	0.703	
2p	1.000	3d	0.314	2p	0.153	2p	0.701	
3s	0.991	4s	0.103		0.014		0.020	
3p	0.983		0.050		0.013			
3p	0.983		0.050					
3p	0.982		0.049					

EOS analysis

Beta effective atomic orbitals for $Fe(CN)_6^{3-}$ at the B3LYP/6-31G(d) level of theory.

Total number of beta electrons: 53

	Fe				C		N	
eff-AO type	Occup	eff-AO type	Occup	eff-AO type	Occup	eff-AO type	Occup
1s	1.000	3d	0.827	1s	0.996	1s	1.000
2s	1.000	3d	0.827	2s	0.708	2s	0.997
2p	1.000	3d	0.305	2p	0.246	2p	0.729
2p	1.000	3d	0.263	2p	0.239	2p	0.702
2p	1.000	3d	0.099	2p	0.153	2p	0.665
3s	0.990	4s	0.049		0.150		0.021
3p	0.982		0.048				
3p	0.982		0.048				
3p	0.982		0.032				

A simple scheme for oxidation states

Oxidation states, last occupied eff-AO (LO) and first unoccupied eff-AO (FU) orbitals for $Fe(CN)_6^{3-}$.

Atom/ Fragment	O.S.	λ^{α}_{LOEFF}	λ^{α}_{HUEFF}	λ^{β}_{LOEFF}	λ^{β}_{HUEFF}
Fe	+3	0.850	0.344	0.827	0.305
C	+2	0.694	0.235	0.708	0.246
N	-3	0.701	0.020	0.665	0.021

From the "frontier" occupation numbers one can **derive** a simple index R(%) to **quantify** how close is the electron distribution provided by the actual wavefunction to the formal picture of the oxidation states.

$$R(\%) \equiv 100 \, min(1, max(0, \lambda^{\sigma}_{LO} - \lambda^{\sigma}_{HU} + 1/2), \text{ for } \sigma = \alpha, \beta.$$

OS for simple transition metal complexes

Table 1: Metal OS and R(%) values for a set of 32 octahedral complexes. HS and LS stand for high-spin and low-spin, respectively.

metal/ligands	Cl^- (HS)	H_2O (HS)	H_2O (LS)	CN^- (LS)	CO (LS)
V^{II}	100	100	-	99	100
Mn^{II}	100	100	100	97	100
Mn^{III}	87	100	100	95	93
Fe^{II}	100	100	100	99	97
Fe^{III}	100	100	100	86	91
Ni^{II}	100	-	100	98	100
Zn^{II}	100	-	100	99	100

The analysis also yielded OS of $(H^{(+)})_2O^{(2-)}$, $C^{(2+)}N^{(3-)}$ and $C^{(2+)}O^{(2-)}$ for the different ligands, conforming with chemical expectations.

Oxidation states for simple molecules

Molecule	O.S.	% trust	q_A/q_B
LiF	Li $^{1+}$ F $^{1-}$	100%	0.83/-0.83
CO	C $^{2+}$ O $^{2-}$	100%	1.13/-1.13
CN$^-$	(C $^{2+}$ N $^{3-}$)$^{-1}$	97%	0.62/-1.62
NO$^+$	(N $^{3+}$ O $^{2-}$)$^{+1}$	94%	1.45/-0.45
CO$_2$	C^{4+} (O^{2-})$_2$	100%	2.23/-1.12
SO$_2$	S^{4+} (O^{2-})$_2$	100%	2.76/-1.38
SO$_3$	S^{6+} (O^{2-})$_3$	94%	3.82/-1.27
HCONH$_2$ (formamide)	H^{1-} C^{4+} O^{2-}N^{3-} (H^{1+})$_2$	52%	-0.05/1.67/-1.16 -1.23/0.39
HCNO	H^{1+} C^{2+} N^{1-} O^{2-}	60%	0.15/0.95 -0.69/-0.41

Oxidation states for TM complexes: a hierarchical scheme

- Define atoms/fragments/ligands of the system

$$w_{\Gamma_i}(\vec{r}) \equiv \sum_{A \in \Gamma_i} w_A(\vec{r}) \qquad \mathbf{S}^{\Gamma_i} \neq \sum_{A \in \Gamma_i} \mathbf{S}^A$$

- Obtain spin resolved eff-AOs for all Γ_i fragments
- Distribute the number of electrons among the fragments according to occupations of their eff-AOs
- Get most appropriate atom/ligand Oxidation States and R% index.
- If necessary, the OS for the individual atoms of a given fragment can be subsequently obtained by getting the eff-AOs for every atom and distributing the number of alpha and beta electrons that were assigned to the ligand in the previous step.

Beyond spin density analysis
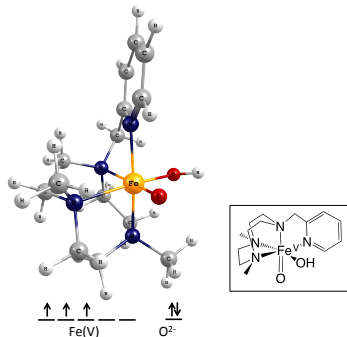
Table 2: d-type eff-AO occupations of the Fe atom in the $[Fe(Pytacn)O(OH)]^{2+}$ species. Occupied eff-AO-s in boldface type.

σ			λ^{σ}		
α	**0.934**	**0.932**	**0.930**	0.495	0.451
β	0.163	0.393	0.462	0.322	0.349
$\alpha - \beta$	0.771	0.539	0.468	0.173	0.102

IUPAC's revision of the concept

- A revision of the concept of OS was requested to a number of experts. Pavel Karen's IUPACs Technical Report summarized their conclusions.

- New definition was provided, along with algorithms to determine the OS in molecular systems and solids.

The OS of a bonded atom equals its charge after **ionic approximation**.

P. Karen et al, Pure Appl. Chem. 2014 86 1017-1081.
P. Karen, Angew. Chem. Int. Ed. 2015, 54, 2-13

Ionic aproximation

- From MO analysis:
  The atom that contributes more to a given MO takes that MOs electrons (usually 2). Bonds between atoms of the same elements are divided equally between the two partners (usually 1 each).

- From electronegativity (EN) comparison:
  An atom of a higher EN is assigned all of the bonds electrons, while bonds between two atoms of the same element are divided equally (exceptions apply, e.g. when the more electronegative atom is bonded as a Lewis acid).

Caveat

There are different EN scales (the authors rely on that of Allen). The EN is regarded as a genuine free atom property, hence same atoms are treated on equal footing irrespective of their chemical environment.

Algorithms for OS assignation

Considering the Lewis structure of the molecule

- Algorithm of moving bonds:
  Bond electrons are moved onto the more negative bond partner identified by ionic approximation.

- Algorithm of summing bond orders:
  An ionic bond order sum (iBOS) is evaluated at each atom and summed with the atoms formal charge (if any) to give the atoms OS .
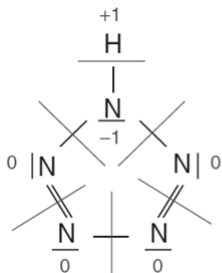
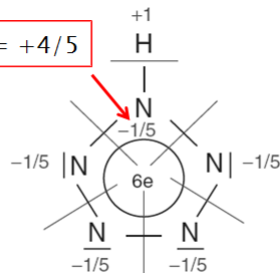$$iBOS = \sum_{i}^{nbonds} sign(i)BO(i)$$
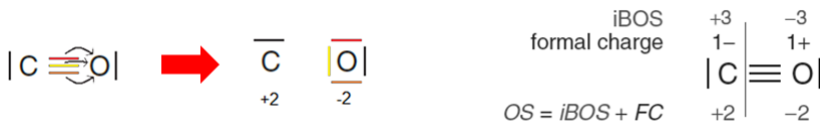
Ambiguities

In the connectivity

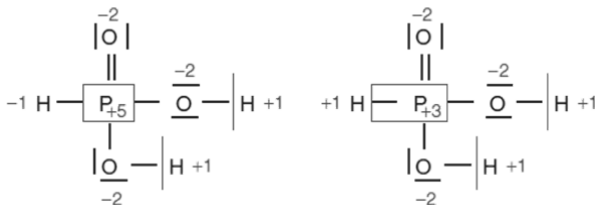Different Lewis structures provide different answers

$$5 - 3 + 6/5 = +4/5$$

Ambiguities

In the application of the ionic approximation

Different EN scales provide different answers

Element	Allen	Mulliken	Pauling
P	2.253	2.46	2.19
H	2.300	2.17	2.20

Computational details

- Electronic structure calculations
  Gaussian 09
  B3LYP/cc-pVTZ (cc-pVTZ-PP for heavy atoms)
- Molecular geometries
  From crystallographic databases:
  Cambridge Crystallographic Data Center (CCDC), Crystallography
  Open Database (COD), Open Chemistry Database (OCD).

  From molecular design:
 Full geometry optimization at B3LYP/cc-pVTZ level

Test set

Simple Molecules		Clusters	
CrO_3	BH_3NH_3	As_4S_4	N_4S_4
CrO_5	$(CH_3)_3NO$	**Hapticity**	
$CuCl_4$	H_3PO_3	$(n6-benzene)_2Cr$	$Fe(C_5H_5)_2$
$CrCO_6$	H_3PO_4	**Non–Innocent ligands**	
BF_4^-	$NBrF_2$	<u>Thiolates</u>	<u>Hydrides</u>
Homonuclear Bonds		$Ni(S_2C_2H_2)_2^0$	$W(CO)_3(n2-H_2)\{P(C_6H_{11})_3\}_2$
H_2S_3	N_5^+	$Ni(S_2C_2H_2)_2^{1-}$	$Ir(CO)Br(H)_2\{P(C_6H_5)_3\}_2$
H_2S_5	N_5H	$Ni(S_2C_2H_2)_2^{2-}$	$RuH_2(\eta2-H_2)_2\{P(C_5H_9)_3\}_2$
I_3^-	N_2O	<u>Nitro ligands</u>	
N_3^-	$S_2O_3^{2-}$	$[Fe(CN)_5(NO)]^{2-}$	$Fe(NO)_4$
Boranes & carboranes		**Lewis Acid–Lewis Base adducts**	
$B_6H_6^{2-}$	$B_{10}C_2H_{12}$	$Au\{B(PC_6H_4)_2(C_6H_5)\}Cl$	$Rh(CO)Cl\{P(C_6H_5)_3\}–SO_2$
B_6H_{10}	$B_{12}H_{12}^{2-}$	$Fe\{B(PC_6H_4)_3(C_6H_5)\}Br$	$RhCl\{P(C_6H_5)_3\}–SO_2$
		$[\kappa4–B(mimBut)_3]Ir(PPh_3)Cl$	$Ru(NO)Cl\{P(C_6H_5)_3\}–SO_2$
		$[\kappa4–B(mimBut)_3]Rh(PPh_3)Cl$	

Test set

Simple Molecules		Clusters	
CrO_3	BH_3NH_3	As_4S_4		N_4S_4
CrO_5	$(CH_3)_3NO$	**Hapticity**	
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$CrCO_6$	H_3PO_4	**Non–Innocent ligands**	
BF_4^-	$NBrF_2$	<u>Thiolates</u>	<u>Hydrides</u>
Homonuclear Bonds		$Ni(S_2C_2H_2)_2^0$	$W(CO)_3(n2-H_2)\{P(C_6H_{11})_3\}_2$
H_2S_3	N_5^+	$Ni(S_2C_2H_2)_2^{1-}$	$Ir(CO)Br(H)_2\{P(C_6H_5)_3\}_2$
H_2S_5	N_5H	$Ni(S_2C_2H_2)_2^{2-}$	$RuH_2(\eta 2-H_2)_2\{P(C_5H_9)_3\}_2$
I_3^-	N_2O	<u>Nitro ligands</u>	
N_3^-	$S_2O_3^{2-}$	$[Fe(CN)_5(NO)]^{2-}$	$Fe(NO)_4$
Boranes & carboranes		**Lewis Acid–Lewis Base adducts**	
$B_6H_6^{2-}$	$B_{10}C_2H_{12}$	$Au\{B(PC_6H_4)_2(C_6H_5)\}Cl$	$Rh(CO)Cl\{P(C_6H_5)_3\}–SO_2$
B_6H_{10}	$B_{12}H_{12}^{2-}$	$Fe\{B(PC_6H_4)_3(C_6H_5)\}Br$	$RhCl\{P(C_6H_5)_3\}–SO_2$
		$[\kappa4–B(mimBut)_3]Ir(PPh_3)Cl$	$Ru(NO)Cl\{P(C_6H_5)_3\}–SO_2$
		$[\kappa4–B(mimBut)_3]Rh(PPh_3)Cl$	

Illustrative examples: CH_3NO (R=55%)
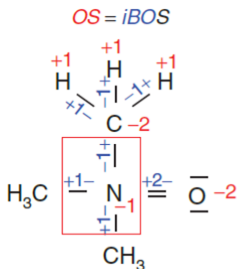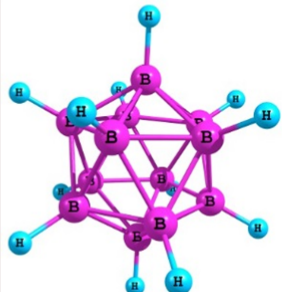
Atom/frag	Empirical OS	EOS
N	-1	-3
O	-2	0
CH_3	+1	+1

Atom/frag	2p eff-AO occupations		
N	0.561	0.561	0.459
O	0.872	0.872	0.404

Illustrative examples: H_3PO_4 (R=99%)
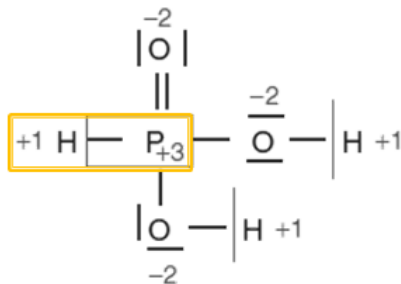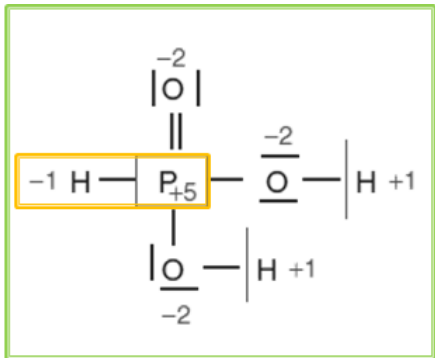
Illustrative examples: $B_{12}H_{12}^{2-}$ (R=70%)

Atom / Fragment	Empirical OS	EOS	Structure
B	+5/6	+5/6	
H	−1	−1	

- The EOS method can provide fractional OS for symmetry-equivalent moieties (degeneracies of the eff-AO occupations)

Illustrative examples: dealing with homonuclear bonds
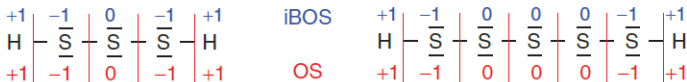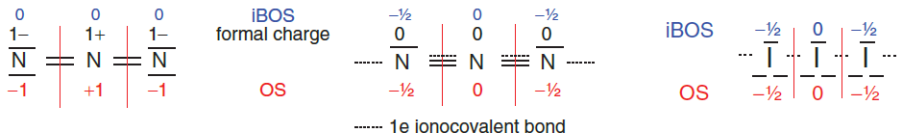
EOS and emprical OS usually differ because i) the molecule is not symmetric or ii) same atoms have different eff-AO occupations (electron assignation is not performed **per bond**).

Summary

- Oxidation states can be extracted from the analysis of the effective atomic/fragment orbitals and their occupancies with a strategy of general application (closed-shell systems, KS or correlated WFs)

- The EOS method is reconciled with the empirical assignation in most cases. However, both are more likely to differ these cases:
    - In the presence of very apolar bonds or atoms with similar electronegativity.
    - When same type of atoms are not strictly symmetry-equivalent in the molecule.

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