textbook forum

Common Textbook and Teaching Misrepresentations of Lewis Structures

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Current freshman chemistry textbooks commonly advise the drawing of Lewis structures with much emphasis on the reduction of formal charge and little on the preservation of the octet rule. This currently accepted method produces structures different from the original Lewis structures, which rarely had expanded valence shells on central atoms (1). Valence-shell expansion, particularly of third period or higher elements, is advised in the modern method if needed to lower atomic formal charges because elements such as sulfur and phosphorus can promote electrons from s or p into d orbitals to provide more unpaired electrons to form bonds (2). In addition to lowering the formal charges (supposedly to make the molecule more stable), this produces results more consistent with experimental bond lengths (3); measured bond lengths are often too short to be accurately represented by the single bonds that the original Lewis structure would imply.

This modern way of drawing Lewis structures is often confusing for beginning chemistry students, who cannot always determine in which cases the octet rule would apply, and in which cases reduction of formal charge would override the octet rule. To quote a respected introductory chemistry textbook (2),

> ... you may be wondering if the structures that you learned previously [which followed the octet rule] are wrong. They are not wrong, but they are not the best structures that can be given for these molecules. The structures that you may have learned previously ... are the structures that Lewis wrote for these molecules and ions and they are therefore correct Lewis structures ... but these structures have subsequently been modified so that they are in better agreement with experimental data, such as bond lengths, and because it has been recognized that elements such as sulfur do not need to obey the octet rule in all their compounds.

The authors go on to mention the concept of resonance, which provides a more accurate way of describing molecules that cannot be accurately represented by any single Lewis structure due, for example, to delocalization of some bonding electron pairs over more than two atoms. The "best" Lewis structure corresponds to the resonance structure of highest weighting, whereas "inferior" Lewis structures are presumed to have lower percentage weighting in the composite resonance hybrid.

The leading resonance structures to depict a molecule could, in principle, be determined if accurate solutions of Schrödinger's equation were available. Until fairly recently, this was nearly impossible for all but the simplest molecules. However, the development of powerful ab initio quantum-chemistry programs such as *Gaussian 92* (4) has made it possible to evaluate wavefunctions for complex molecules at a useful level of chemical accuracy (5). In addition, the more recent natural bond orbital (NBO) (6) and natural resonance theory (NRT) (7) methods have made it

possible to describe these wavefunctions in terms of a localized bonding picture corresponding closely to the chemist's Lewis structure concept. Thus, the issue of the best Lewis structural representation can now be addressed by alternative, purely theoretical means.

Surprisingly, the results of NRT analysis for many "textbook examples" of Lewis structures are in better accordance with Lewis' original proposals than with the modern structures. As will be described below, the leading structures of the NRT expansion of the wavefunction are commonly found to be quite consistent with the octet rule, with no significant valence-shell expansion to reduce formal charge. The details of these wavefunctions also suggest how the observed bond lengths can be reasonably rationalized in terms of atomic charge distributions, bond orders, and valencies that are essentially consistent with the original Lewis picture.

Criteria for Optimal Lewis Structures
Natural Bond Orbitals

Given an N-electron wavefunction $\psi(1, 2, ..., N)$ associated with electron density $\rho = \rho(\mathbf{r})$,

$$\rho = N\int |\psi^2| \, d\tau_2 ... d\tau_N$$

a standard program option of *Gaussian 92* (4) allows one to calculate the natural bond orbitals (NBO's) for an optimal "natural Lewis structure" of the system. The NBO's are an orthonormal set of localized 1- and 2-center functions that allow the electron density to be partitioned into Lewis-type ($\rho^{(L)}$) and non-Lewis-type ($\rho^{(NL)}$) components,

$$\rho = \rho^{(L)} + \rho^{(NL)}$$

The $\rho^{(L)}$ components correspond to the formal bonds and lone pairs of the Lewis structure, each filled with an electron pair, whereas the $\rho^{(NL)}$ components correspond to antibonding and extra-valence-shell Rydberg orbitals that are formally "empty" in the idealized Lewis picture. Roughly speaking, the NBO's are chosen to maximize the contribution of $\rho^{(L)}$ or to minimize the "error" $\rho^{(NL)}$ (6).

The NBO program usually searches for all possible ways of drawing the Lewis structure and returns the unique structure of optimal $\rho^{(L)}$. However, given two competing Lewis structure formulas (α, β), one can use the program $CHOOSE option to find NBO's for each alternative Lewis structure,

$$\rho = \rho_\alpha^{(L)} + \rho_\alpha^{(NL)}$$

$$= \rho_\beta^{(L)} + \rho_\beta^{(NL)}$$

The structure with smaller error ($\rho_\alpha^{(NL)}$ or $\rho_\beta^{(NL)}$) would therefore better describe the electron density ρ. This constitutes a general NBO criterion for comparing the proposed Lewis structures.

Natural Resonance Theory

A second criterion can be based on the more recent natural resonance theory (NRT) (7), which provides a method for directly calculating the relative weights of distinct resonance structures. Roughly speaking, the NRT variational procedure determines an optimal resonance-averaged description of electron density

$$\rho = \sum_\alpha w_\alpha \rho_\alpha^{(L)}$$

with positive weights (w_α's) summing to unity. The relative NRT weightings w_α and w_β, therefore directly measure the relative importance of structures α and β, and one expects that w_α is greater than w_β when $\rho_\alpha^{(NL)} < \rho_\beta^{(NL)}$, that is, when α is a "better" Lewis structure. The default NRT procedure automatically generates a candidate list of resonance structures, but the $NRTSTR program option can be used to include Lewis structures that possibly contribute to the resonance weightings but were ignored in the default procedure.

Still other NBO/NRT bond indices can be used to assess the validity of a proposed Lewis structure. For example, the resonance-weighted NRT bond order (b_{AB}) and atomic valency (V_A)

$$V_A = \sum_{B(\neq A)} b_{AB}$$

can be compared with bond connectivities of a candidate Lewis diagram. The program also calculates atomic charge (q_A) (8) and bond polarity (percentage ionic character) parameters to describe more subtle aspects of the electron distribution.

Ab Initio Theory

In this paper we use NBO/NRT criteria at two levels of ab initio theory (5)

- RHF/6-31G* from Hartree–Fock molecular orbital theory
- MP2/6-31G* from second-order Møller–Plesset theory

(both evaluated with "double zeta plus polarization" variational basis). The criteria determined from Hartree–Fock molecular orbital theory correspond to the uncorrelated single-configuration picture commonly used in freshman chemistry courses, whereas the criteria from second-order Møller–Plesset theory include corrections due to electron correlation. The qualitative determination of the best Lewis structure is rather insensitive to the level of theory, so the RHF/6-31G* and MP2/6-31G* results may be taken as representative of higher-level ab initio treatments, equivalent to the best solutions of Schrödinger's equation that are currently attainable.
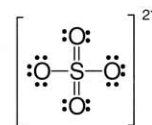
Some Textbook Examples

An Accurate Representation of Sulfate Ion

One of the most frequently cited examples of the modern way of drawing Lewis structures is the sulfate ion, SO_4^{2-}. Almost all textbooks draw the leading structure for this

ion with six bonds around the sulfur as in **1a** (one of twelve equivalent resonance structures, denoted "12 r.s."), eliminating sulfur formal charge in the molecule (2, 9, 10),

1a (12 r.s.)

This structure suggests a bond order ($b_{SO} = 1.5$) for each SO bond and a sulfur valency ($V_S = 6$). Some textbooks will mention the original, solely single-bonded Lewis structure,
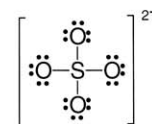
1b

but most agree that the formal charges of +2 on the sulfur and −1 on each oxygen render this structure improbable (9), particularly in light of the experimental bond length of 1.49 Å, which is rather short for a normal SO single bond.

However, in the NRT expansion for the sulfate ion, resonance structure **1a** is given no weight at all. Instead, the original Lewis structure **1b** is given a 66.2% weighting, whereas most of the remaining weighting (23.1%, from 12 equivalent structures each weighted 1.9%) is associated with more highly ionic structures (**1c**) with one oxygen atom double-bonded to sulfur but another oxygen completely detached.
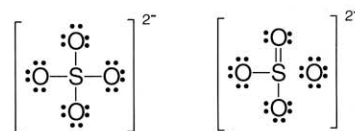
1b, 66.2%   **1c** (12 r.s.), 1.9% ea.

If the $\rho^{(NL)}$ test is carried out for **1a** using the $CHOOSE option, the resulting $\rho_{1a}^{(NL)} = 1.0549$ is larger (but only slightly) than that of **1b**, $\rho_{1b}^{(NL)} = 0.9045$. But this near-equality of $\rho^{(NL)}$ values is deceiving. Closer examination of the $CHOOSE structure for **1a** shows that the second S–O "π_{SO} bond" is polarized about 95.8% toward the oxygen atom and is thus essentially a pure oxygen lone pair (practically identical to **1b**).

Other NBO/NRT parameters indicate similarly that the actual electron distribution is far closer to that suggested by **1b** than **1a.** The calculated charge on sulfur ($q_S = +2.916$) is even higher than the formal +2 charge of **1b**, which is quite remote from the "electroneutrality" suggested by **1a.** The calculated NRT sulfur valency is $V_S = 4.0$ (not 6), and the SO bond orders are $b_{SO} = 1.0$ (not 1.5), consistent with Lewis's original **1b** and quite inconsistent with **1a.**

The suggestion that sulfur achieves the high valency of **1a** by significant d-orbital participation is refuted by the calculated d-orbital occupancies, which are quite small (less than $0.19e$ in the entire d shell) and inconsistent with any significant valence-shell expansion. The strong polarity of SO bonds is further indicated by the high calculated percentage ionic character (45.3%). Thus, the sulfate ion is much more accurately represented[1] by **1b** (with small corrections of form **1c**).

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[1]If we repeat the calculation with additional diffuse functions (6-31+G* basis) to better model the anionic charge distribution, we obtain $q_S = +2.882$, $q_O = -1.221$, $V_S = 4.000$, $b_{SO} = 1.000$ (43.3% ionic), $R_{SO} = 1.4898$ Å, and $\rho_{mod}^{(NL)} = 1.050$, $\rho_{orig}^{(NL)} = 0.868$, $w_{orig} = 67.1\%$, which are in reasonably close agreement with the 6-31G* values of Tables 1 and 2.

Perchlorate Ion

Similar results are found for ClO_4^- and PO_4^{3-} anions. The perchlorate ion, which most books write with three double bonds (see, for example, ref 2),
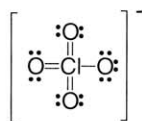
2a (4 r.s.)

is granted no weight in the NRT expansion (even when forced with the $NRTSTR option).

Instead, 60.9% weighting is given to a single-bonded structure **2b** (analogous to SO_4^{2-} **1b**), and most of the remainder (totaling 31.4%) to more highly ionic structures **2c** (analogous to SO_4^{2-} **1c**).
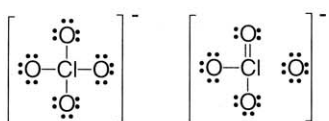

2b, 71.0%   **2c** (12 r.s.), 1.8% ea.

The $\rho^{(NL)}$ error of **2a** is also significantly larger ($\rho_{2a}^{(NL)}$ = 1.359 vs. $\rho_{2b}^{(NL)}$ = 1.040), and the calculated NBO/NRT indices

- q_{Cl} = +2.87 (not "electroneutral")
- V_{Cl} = 4.0 (not 7)
- b_{ClO} = 1.00 (not 1.75)

are in significantly poorer agreement with **2a** than with **2b**. The low occupancy of d orbitals on Cl (0.26e) is essentially consistent with the octet rule, and quite inconsistent with "expansion of the valence shell to 14 electrons" as suggested by **2a**.
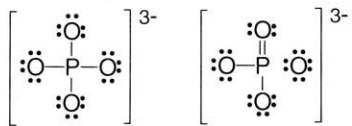
Phosphate Ion

For the phosphate ion, which is usually written in textbooks as
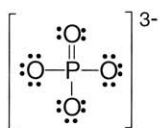
3a (4 r.s.)

The NRT expansion grants 71.0% weighting to Lewis's original single-bonded structure **3b** with smaller weightings (totaling about 20.3%) for more highly ionic structures **3c** (and none for **3a**).


3b, 71.0%   **3c** (12 r.s.), 1.7% ea.

The superiority of **3b** to **3a** is also evident in the values of $\rho^{(NL)}$, that is, $\rho_{3a}^{(NL)}$ = 0.810 vs. $\rho_{3b}^{(NL)}$ = 0.769, with only 3.48% of "π_{PO} bond" on P,

- q_P = +2.75 (not "electroneutral")
- V_P = 3.989 (not 5)
- b_{PO} = 1.00 (not 1.25)

Table 1 presents a systematic comparison of NBO/NRT bond indices and calculated and experimental bond lengths for the three XO_4^{n+} oxyacid anions, X = P, S, CL (as well as other examples treated below), showing the expected smooth variations with electronegativity in this series. Table 2 summarizes the basic $\rho^{(NL)}$ values and NRT weightings for all examples considered in this work.

Both tables also include corresponding values calculated at the MP2/6-31G* level of theory. The MP2 results tend to give slightly longer (~0.03 Å) bond lengths and somewhat higher (~0.5–0.8e) delocalization (leading, for example, in the case of ClO_4^- to four "alt" structures **2c** (15.2% each) with composite weight exceeding that of **2b**), but the overall patterns are otherwise similar to the RHF/6-31G* results described above. (If anything, the average MP2/6-31G* bond orders and valencies are marginally lower, and thus even farther removed from "mod" structures.) Qualitatively similar conclusions would therefore be drawn from the higher level of theoretical treatment.

Other revealing confirmations of the octet rule are found for SO_3 and SO_2, two other common textbook examples that are alleged to violate the octet rule in order to reduce their formal charge (2, 3, 11). The modern Lewis structures for these species
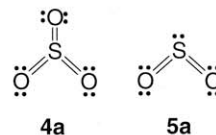
4a   **5a**

are found to be quite inferior to octet-conforming structures of the form

Table 1. NBO/NRT Bond Indices of XO_n^{q-} Species (X = P, S, Cl)

Calculated Atomic Charges (q_X, q_O), Atomic Valency (V_X), Bond Order (b_{XO}), Percentage Ionic Character, and X–O Bond Length (R_{XO}) at RHF/6-31G*, MP2/6-31G* Levels of Theory

species	atomic charge		NRT bond indices			R_{XO} (Å)	
	q_X	q_O	V_X	b_{XO}	% ionic	calcd	exptl
RHF/6-31G*							
PO_4^{3-}	+2.747	−1.437	3.989	0.997	62.4	1.5673	1.54[a]
SO_4^{2-}	+2.916	−1.229	4.000	1.000	45.3	1.4867	1.49[b]
ClO_4^-	+2.874	−0.969	4.000	1.000	22.9	1.4503	1.44[a]
SO_3	+2.776	−0.925	3.993	1.331	45.5	1.4046	1.43[b]
SO_2	+1.856	−0.928	3.000	1.500	49.6	1.4141[c]	1.43[b]
MP2/6-31G*							
PO_4^{3-}	+2.398	−1.350	3.941	0.985	62.8	1.5989	
SO_4^{2-}	+2.582	−1.145	3.944	0.986	46.6	1.5206	
ClO_4^-	+2.561	−0.890	3.950	0.988	27.3	1.4829	
SO_3	+2.455	−0.818	3.915	1.305	43.7	1.4594	
SO_2	+1.476	−0.738	2.977	1.489	46.2	1.4781[d]	

[a]*International Tables for Crystallography;* Wilson, A. J. C., Ed.; Kluwer: Boston, 1992; Vol. C, p 684.
[b]*Inorganic Sulphur Chemistry;* Nickless, B., Ed.; Elsevier: Amsterdam, 1968.
[c]angle OSO = 118.82° (exptl: 119.54°)
[d]angle OSO = 119.82°

4b (3 r.s.)   **5b** (2 r.s.)
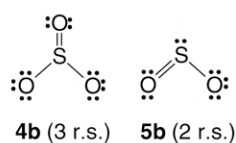
For example, $\rho_{5b}^{(NL)} = 0.657$ is significantly superior to $\rho_{5a}^{(N\,D)} = 1.041$ for SO_2, and the NRT expansion gives more than 95% weighting to the two resonance forms **5b** (and none to **5a**).

Discussion

The *Gaussian 92* program can optimize the geometry of the molecule before completing NBO/NRT analysis. For the sulfate ion, the bond length is calculated to be 1.4867 Å (RHF/6-31G[1] level; compare with Table 1), in close agreement with the experimental value. Results in qualitative agreement with experimental data are also found for the other examples considered in this work. So one can conclude that the program finds no problem with these short bond lengths being represented as single bonds.

The key to understanding this apparent disparity between data and conclusions is the high ionic character of the bonds, which is associated with the large electronegativity differences between the atoms. Increased electronegativity difference (higher ionic character) tends to be associated with shorter, stronger bonds (*12*). This can be rationalized in terms of the expected variation of atomic radius with effective nuclear charge, particularly the contraction of the highly stripped central atom. Because electronegativity is known to significantly decrease from second- to third-period atoms of the same family, one should further anticipate that the ionic character of X–O bonds is greater for X = S than for X = O (and for X = P than for X = N), or equivalently, that higher formal charge differences should appear in Lewis structures for third-period atoms. Although the X–O bond lengths are shorter than normal, the abnormality should be associated with larger formal charges (higher ionic character), not with "increased double-bond character". Our results are also in line with the modern theoretical view (*13*) that d-orbital participation is too often invoked and plays a small role in hypervalency of species such as SF_6.

Conclusion

Computational results from *Gaussian 92* have shown us that the leading resonance structures cited in freshman chemistry textbooks are often not the most accurate to represent the molecules and are, at best, minor resonance structures, whose presentation is not worth the confusion that it causes for many first-year students. Instead, the Lewis structures that most accurately represent these molecules are the original Lewis structures, which generally abide by the octet rule. If the octet rule is more strongly stressed in the teaching of Lewis structures—thus avoiding the many complications and sources of confusion related to valence-shell expansion and reduction of formal charge—freshman chemistry students will be able to rest a little easier at night.

Acknowledgments

Table 2. Comparison of Non-Lewis Density Errors ($\rho_{mod}^{(NL)}$, $\rho_{orig}^{(NL)}$) and NRT Resonance Weights (w_{mod}, w_{orig})

Modern (Octet-Violating) vs. Original (Octet-Conforming) and Alternative (Ionic Octet-Conforming, Analogous to **1c**) Lewis Structures of Common Textbook Examples, Showing the General Superiority of Lewis's Original Formulation for Describing Modern Wavefunctions (RHF/6-31G*, MP2/6-31G*)

species	"Error"		NRT Weightings		
	$\rho_{mod}^{(NL)}$ (e)	$\rho_{orig}^{(NL)}$ (e)	w_{mod} (%)	w_{orig} (%)	w_{alt} (%)
RHF/6-31G*					
PO_4^{3-}	0.810	0.769	0.0	71.0	20.3
SO_4^{2-}	1.055	0.905	0.0	66.2	23.1
ClO_4^-	1.359	1.040	0.0	60.9	31.4
SO_3	1.193	1.072	0.0	87.9	5.9
SO_2	1.041	0.657	0.0	95.2	4.8
MP2/6-31G*					
PO_4^{3-}	1.471	1.444	0.0	53.1	28.4
SO_4^{2-}	1.728	1.582	0.0	46.9	49.8
ClO_4^-	2.189	1.845	0.0	36.8	60.7
SO_3	1.826	1.700	0.0	77.3	9.2
SO_2	1.376	1.144	0.0	90.2	8.6

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