

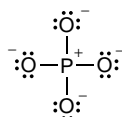
Lewis Structures in General Chemistry: Agreement between Electron Density Calculations and Lewis Structures†

Gordon H. Purser

Department of Chemistry, The University of Tulsa, Tulsa, OK 74104; gordon-purser@utulsa.edu

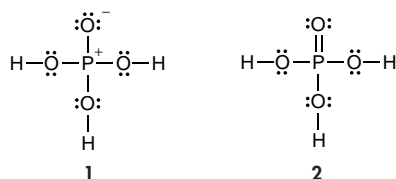
Instruction on how to draw Lewis structures is included in every general chemistry textbook available. The skill is important because accurate Lewis structures can be used to predict such properties as molecular geometry, bond order, relative bond enthalpies, relative bond strengths, and dipole moments. In spite of their importance, there is significant debate about how to best represent molecules and ions in which nonmetal atoms beyond the second period are bonded to a terminal atom. The debate, often carried on within the pages of this *Journal* (1–3), has led to a great inconsistency in how textbook authors present the topic. For example, contrast the way the bonding in phosphoric acid and phosphate ion is described in two well-established textbooks (4, 5). From ref 4 (p 279):

Recent theoretical calculations, based on quantum mechanics, suggest that the structure (below) is the best single Lewis structure for the phosphate ion. In general, when choosing between alternative Lewis structures, you should choose the one that satisfies the octet rule if it is possible to do so.



From ref 5 (p 370):

For H_3PO_4 , two possible Lewis structures are



Structure 2 has lower formal charges, so it is a more important resonance form.

Recently the Schustermans published an excellent paper on the advantages of and methods for using electron density models to teach chemistry (6). In their work, quantum calculations were performed on organic molecules and ions containing bonds of varying bond orders, and isodensity surfaces based on the calculations were drawn and displayed graphically. Their work demonstrated a relationship between the bond order indicated by the Lewis structure and the calculated electron density in the molecule.

† Presented at the 219th National Meeting of the American Chemical Society, March 2000, San Francisco, and again as part of the symposium "Simulations and Modeling in the Learning of Chemistry" at the 16th Biennial Conference on Chemical Education, August 2000, Ann Arbor, MI.

Given the current uncertainty about how to draw Lewis structures for molecules and ions in which nonmetal atoms beyond the second period are bonded to a terminal oxygen atom, and the observed relationship between calculated electron density and bond orders predicted by Lewis structures for second-period elements, it is reasonable that electron density models might resolve the debate concerning how to best draw Lewis structures for molecules and ions like phosphoric acid and phosphate ion. This paper explores the relationship between electron density models and those Lewis structures in question and attempts to resolve the debate that has led to the disparities found among current textbooks.

Methods

All calculations were made using PC Spartan Pro, version 1.1, licensed from Wavefunction, Inc., Irvine, California. Either non-local density functional calculations using numerical polarization basis sets (pBP/DN*) or Hartree–Fock molecular orbital calculations using the 6-31G** basis set were used to calculate the equilibrium geometry of each species.

After the equilibrium geometry of a species is calculated, successively increasing electron isodensity surfaces are drawn. The value at which the electron density in the bond disappears is taken to be the maximum electron density in the bond. The units of all electron density values reported in this work are electrons bohr^{-3} (1 bohr = 52.9 pm).

Table 1. Internuclear Electron Densities Determined from Density Functional and Hartree–Fock Calculations

Bond	Maximum Electron Density		Species
	Density Functional	Hartree–Fock	
C–C	0.18	0.25	$\text{H}_3\text{C–CH}_3$
C=C	0.25	0.36	$\text{H}_2\text{C=CH}_2$
C≡C	0.29	0.40	$\text{HC}\equiv\text{CH}$
C–N	0.20	0.26	$\text{H}_3\text{C–NH}_2$
C=N	0.28	0.38	$\text{H}_2\text{C=NH}$
C≡N	0.39	0.51	$\text{HC}\equiv\text{N}$
C–O	0.20	0.26	$\text{H}_3\text{C–OH}$
C=O	0.34	0.46	$\text{H}_2\text{C=O}$
C≡O	0.43	0.51	$\text{C}\equiv\text{O}$
N–N	0.25	0.31	$\text{H}_2\text{N–NH}_2$
N=N	0.37(cis); 0.38(trans)	0.47(cis); 0.48(trans)	HN=NH
N≡N	0.52	0.63	$\text{N}\equiv\text{N}$
N–O	0.24	0.31	$\text{H}_2\text{N–OH}$
N=O	0.41	0.52	HN=O
N≡O	0.59	0.67	$\text{N}\equiv\text{O}^+$
O–O	0.21	0.30	HO–OH
O=O	0.39	0.53	O=O
O≡O	0.62	0.69	$\text{O}\equiv\text{O}^{2+}$

Results

The internuclear electron densities for a series of 19 species containing only second-period elements were calculated using both density functional and Hartree–Fock methods. The results are shown in Table 1. Three important observations can be made from these data: the absolute values of electron density vary significantly between different calculations for the same molecule; the trends within each method of calculation always increase with increasing bond order as predicted by the Lewis structure; and the observed electron density values are dependent on the bonded atom pairs. That is, the electron density value of a C–O bond may be compared to that of another C–O bond, but should never be compared to that of a bond involving any other pair of atoms, such as N–O.

The relationship between the bond order predicted by the Lewis structure and the calculated electron density is easily recognized when pictures of the electron density models are shown side by side as in Figure 1. In this figure, the isodensity surfaces for hydrazine, diazene, and nitrogen are shown at four different isodensity values. All three molecules have an electron density of at least 0.20 between the nitrogen atoms, but whereas diazene and nitrogen have an electron density of greater than 0.30, hydrazine does not.

The results of the analogous treatment of a series of phosphorus, sulfur, and chlorine species containing oxygen atoms are shown in Table 2. The internuclear electron densities were calculated using the density functional method. Without exception, the calculated electron densities agree with predicted bond orders only when formal charge is minimized, even if it requires an expanded octet. (Minimizing formal charge refers to achieving zero formal charge on all atoms in a neutral molecule and having only as many atoms with +1 or –1 charge as the total charge on an ion.)

Figure 2 shows the 0.20-isodensity surface for sulfuric acid, sulfur monoxide, and sulfur dioxide. It shows that the electron density in the S–OH bond is much less than that in the terminal S–O bonds. This graphical presentation makes it clear that terminal S–O bonds in sulfuric acid and S–O bonds in sulfur dioxide have about the same electron density as the S–O bond in sulfur monoxide, a species that does not require an expanded octet to form a double bond. At the beginning of this paper, the Lewis structures of phosphoric acid and phosphate ion were used to contrast the way Lewis structures are presented in textbooks. Figure 3 shows the 0.18-isodensity surface for phosphoric acid and phosphate ion obtained from Hartree–Fock calculations. These isodensity surfaces confirm that the best structure for phosphoric acid is one in which the P–O terminal bond (shown in the 12 o'clock position) has a greater electron density and therefore higher bond order than the P–OH bond (shown in the 7 o'clock position). Also, the electron density in the P–O bonds in the phosphate ion, while less than that of the P–O terminal bond, is greater slightly than that for the P–OH bond in phosphoric acid. This result is consistent with resonance Lewis structures containing one P=O (double) bond and three P–O (single) bonds. Finally, Table 3 shows the average and standard deviation of the calculated electron density for the single and double bonds predicted by Lewis structures of molecules that do not exhibit resonance and that minimize formal charge.

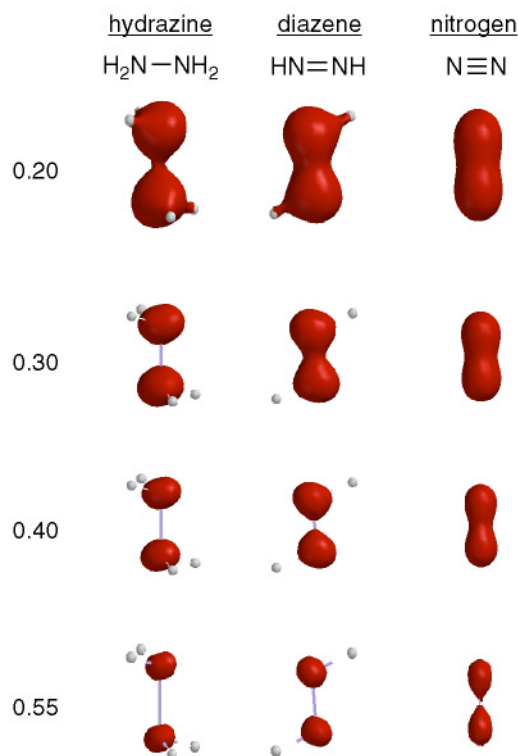


Figure 1. Isodensity surfaces for hydrazine, diazene and nitrogen shown at 0.20, 0.30, 0.40 and 0.55 electrons bohr⁻³ from density functional calculations using pBP/DN*.

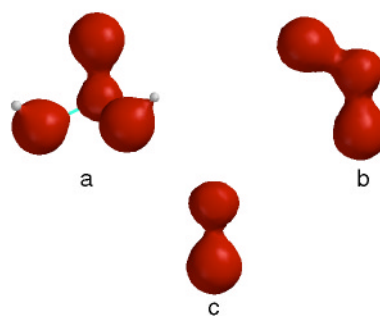


Figure 2. The 0.20-isodensity surface for (a) sulfuric acid, (b) sulfur dioxide, and (c) sulfur monoxide produced from density functional calculations (pBP/DN*).

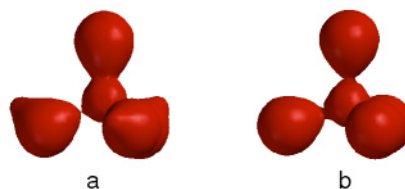


Figure 3. The 0.18-isodensity surface for (a) phosphoric acid and (b) phosphate ion produced from Hartree–Fock calculations using the 6-31G** basis set.

Table 2. Calculated Electron Densities for Some Phosphorus, Sulfur, and Chlorine Species Containing Oxygen Atoms

Compound	Electron Density/(electrons bohr ⁻³)	
	X-O(bridging)	X-O(terminal)
F ₃ PO	—	0.22
(CH ₃) ₃ PO	—	0.19
H ₃ PO ₄	0.15	0.19
P ₄ O ₁₀	0.14	0.21
(CH ₃ O) ₃ PO	0.16	0.20
F ₂ POPF ₂	0.14	—
SO	—	0.21
(CH ₃) ₂ SO	—	0.23
SO ₂	—	0.25
SO ₃	—	0.24
F ₂ SO	—	0.27
F ₂ SO ₂	—	0.25
(CH ₃) ₃ SO ⁺	—	0.25
H ₂ SO ₄	0.17	0.24
(CH ₃ O) ₂ SO ₂	0.18	0.24
(CH ₃ O) ₂ S	0.17	—
ClO ⁺	—	0.28
FCIO ₂	—	0.30
FCIO ₃	—	0.30
F ₃ ClO	—	0.30
HClO ₄	0.17	0.30
Cl ₂ O ₇	0.14	0.29
HOCl	0.15	—
Cl ₂ O	0.16	—
CH ₃ OCl	0.16	—

NOTE: Electron densities determined using density functional calculations (pBP/DN*).

The very small standard deviations indicate that there is a meaningful relationship between the appropriate Lewis structure and the calculated internuclear electron density.

Conclusions

This work shows that calculated internuclear electron density values agree well with Lewis structures for ions and molecules containing only second-period elements. While either density functional calculations or Hartree–Fock calculations can be used, it is important that only electron densities from a single method be compared.

A fundamental piece of information provided by an accurate Lewis structure is the bond order. If bond order is to have any classical meaning, it must reflect the internuclear electron density in the bond. Only Lewis structures that mini-

Table 3. Average Calculated Internuclear Electron Densities as Function of Predicted Bond Order

Central Atom X	X–OR (bridging)	X=O (terminal)
P	0.15 ± 0.01	0.20 ± 0.01
S	0.17 ± 0.01	0.24 ± 0.02
Cl	0.16 ± 0.01	0.30 ± 0.01

mize formal charge and expand octets coincide exactly with the results of quantum mechanical modeling. Thus it is clear that the best representations for oxygen-containing species of nonmetals beyond the second period are those that minimize formal charge even at the expense of expanding the octet.

The results of this work reinforce the concept that greater electron density is associated with the shorter bond lengths observed between a central atom and a terminal oxygen atom, compared to the bond length observed between the central atom and a bridging oxygen atom. Furthermore, this observation supports the conclusions of Straub (2) that the M⁺–O[–] formulation for terminal oxygen is inadequate to explain the observed bond lengths.

Finally, the consistency of the calculated electron densities for single and double bonds predicted by Lewis structures suggest that when formal charges cannot be minimized, and two equally good Lewis structures can be drawn, calculated electron densities might be used to identify the best Lewis structure. Such might be the case for determining the S–S bond order in thiosulfate ion.

Minimizing formal charge is critical to obtaining Lewis structures that agree with quantum electron density calculations. If instructors and textbook authors emphasize this point, the current variance in the way Lewis structures are presented to beginning students and the corresponding confusion will disappear.

Literature Cited

1. Suidan, L.; Badenhop, J. K.; Glendening, E. D.; Weinhold, F. *J. Chem. Educ.* **1995**, *72*, 583–586.
2. Straub, D. K. *J. Chem. Educ.* **1995**, *72*, 889–891.
3. Purser, G. H. *J. Chem. Educ.* **1999**, *76*, 1013–1018.
4. Brown, T. L.; LeMay, H. E.; Bursten, B. E. *Chemistry: The Central Science*, 7th ed.; Prentice Hall: Upper Saddle River, NJ, 1997.
5. Silberberg, M. S. *Chemistry: The Molecular Nature of Matter and Change*, 2nd ed.; McGraw-Hill: Boston, 2000.
6. Shusterman, G. P.; Shusterman, A. J. *J. Chem. Educ.* **1997**, *74*, 771–776.