Teaching Chemistry with Electron Density Models[1]

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Linus Pauling once said that a topic must satisfy two criteria before it can be taught to students. First, students must be able to assimilate the topic within a reasonable amount of time. Second, the topic must be relevant to the educational needs and interests of the students. Unfortunately, the standard general chemistry textbook presentation of "electronic structure theory", set as it is in the language of molecular orbitals, has a difficult time satisfying either criterion. Many of the quantum mechanical aspects of molecular orbitals are too difficult for most beginning students to appreciate, much less master, and the few applications that are presented in the typical textbook are too limited in scope to excite much student interest.

This article describes a powerful new method for teaching students about electronic structure and its relevance to chemical phenomena. This method, which we have developed and used for several years in general chemistry (G.P.S.) and organic chemistry (A.J.S.) courses, relies on computer-generated three-dimensional models of *electron density* distributions, and largely satisfies Pauling's two criteria. Students find electron density models easy to understand and use, and because these models are easily applied to a broad range of topics, they successfully convey to students the importance of electronic structure. In addition, when students finally learn about orbital concepts they are better prepared because they already have a well-developed three-dimensional picture of electronic structure to fall back on. We note in this regard that the types of models we use have found widespread, rigorous application in chemical research (*1, 2*), so students who understand and use electron density models do not need to "unlearn" anything before progressing to more advanced theories.

The following sections describe the electron density method. We discuss first the rather limited quantum mechanical background students need in order to understand electron density models. Then, we show a few ways in which we use electron density models of electronic *ground states* to teach electronic structure, bonding concepts, and molecular properties. (The published versions of these models are more difficult to use than the original full-size, computer-generated graphics. Teachers who would like to know how to reproduce these models using SPARTAN or would like to access our model database should contact us directly.) Finally, the computational methods used to generate electron density models are briefly described.

Quantum Mechanical Foundation

Very little knowledge of quantum mechanics, and no knowledge of quantum mechanical *methodology*, is required in order to use electron density models. The only two things a student needs to start with are an appreciation of the quantum postulate that electron positions cannot be defined precisely and an understanding of what is meant by the phrase "electron density".

The first point can be made in any number of ways. One can simply start with the Heisenberg uncertainty principle as a fundamental postulate of what can be measured, and conclude from this that electron positions can never be known. Another approach, one that we find more satisfying, is to describe the behavior of electrons in simple diffraction experiments (*3*). These experiments neatly demonstrate the strange wavelike properties of electrons and the need for a special language for talking about electron position.

The definition of "electron density" can also be approached in several ways. One is to use the notion of *probability.* Quantum mechanics provides a recipe for calculating the probability of finding an electron at a particular point in space, and this quantity is called the "probability density" (or "electron density"). Therefore, a map that shows how the probability density varies from point to point in a molecule is a model of the molecule's electronic structure. An equivalent approach is to think about an electron's electrical *charge.* Since we cannot say exactly where the electron is, we might say that the electron's charge is not concentrated at a single point (a localized charge would allow the electron's position to be defined), but is instead spread out *nonuniformly* over a region of space. Each point in space has some fractional or partial charge, called the "charge density" or "electron density", which is identical to the probability density. A map of total electron density—that is, the cumulative charge distributions of all of the molecule's electrons, thus provides a model of the molecule's electronic structure.

Once this very minimal foundation has been established, students are ready to use computer-generated electron density models. From this point onward they can examine and describe the electronic structure of atoms, molecules, reactive intermediates, and even reaction transition states in a simple, uniform way, and a vast new range of chemical information and reasoning is opened up to them.

The Electronic Structure of Atoms

The simplest electron density models are models of atoms. We can construct a model of a lithium (or any other) atom by taking a plane that slices through the atom and mapping the variation in electron density in this plane. This kind of model is called an "electron density slice"; it provides a two-dimensional contour map of the electron density. The electron density slice that passes through the lithium nucleus is shown in Figure 1a. The electron density varies considerably in this plane, and a color code based on the visual spectrum is used to show this variation: red (lowest density) < orange < yellow < green < blue (highest density). The variation in electron density in this particular map turns out to be sufficiently great that the full variation cannot be coded with only five principal colors. Therefore, the *blue* circle corresponds to any spot where the elec-

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tron density is greater than or equal to 0.01 electron/bohr^3, and the *red* region corresponds to any spot where the electron density is less than or equal to 0.0001. (Note: all electron densities are given in units of electron/bohr^3, where 1 bohr = 0.529 Å; these units will be omitted for convenience.) The "slice" model displays several interesting and typical atomic features, including (i) the electron density is distributed isotropically around the nucleus, (ii) the variation in electron density is in qualitative agreement with simple electrostatic principles—the highest density is found near the positively charged nucleus, and the density steadily decreases as the distance from the nucleus increases; and (iii) the electron cloud does not have a sharp, well-defined boundary.

Another way to construct an electron density model of lithium is to choose a particular value of the electron density and show all points in space where the density has the chosen value. This kind of model is called an "isodensity" model or surface; it provides a three-dimensional picture of the electron distribution. Two isodensity models of lithium are superimposed in Figure 1b: the "solid" model corresponds to a density of 0.02 and the "mesh" model corresponds to a density of 0.002 (a "mesh" was chosen for the outermost model because it is "transparent" and allows us to see the inner model). As expected, both models are spherical, implying that the electron density is distributed isotropically in *three* dimensions. Another typical feature of these isodensity surfaces is that the lower isodensity surface lies outside the higher isodensity surface. This means that points of low electron density are located farther away from the nucleus than points of high electron density (electron density decreases as we move away from the nucleus).

We will see in the following sections that different types of isodensity models have specific applications. The 0.002 isodensity model, for example, can be used to define the size and shape of the electron cloud, since nearly all of the electron density (typically ≥ 98%) lies inside this surface (*4*). It is also a useful surface for mapping properties that affect intermolecular interactions. Isodensity models corresponding to higher levels of electron density, on the other hand, are useful for investigating bonding interactions inside a molecule.

Size and Shape

The shape and size of an atom or molecule are defined by the size and shape of its electron cloud. Therefore, electron density models are useful tools for investigating atomic and molecular structure, and they complement the information provided by chemical formulas. Consider, for example, Li and Li$^+$. Their chemical symbols tell us that these species differ by one electron, but the symbols do not give us structural information. On the other hand, 0.002 isodensity models immediately reveal that while both Li and Li$^+$ are spherical, the cation is smaller than the neutral atom—that is, the electron cloud contracts in size when one electron is removed (Figs. 1b and 1c). However, not all parts of the electron cloud contract to the same degree. The 0.02 surfaces of Li and Li$^+$ are virtually the same size (Figs. 1b and 1c), suggesting that the "core" of the electron cloud, the region of high electron density, is only slightly affected by ionization. Most of the change occurs in the outer region where the electron density is very low.

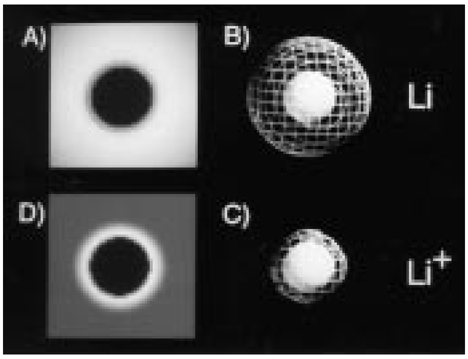


Figure 1. Electron density models of Li and Li$^+$: (A) Li slice (red ≤ 0.0001, blue ≥ 0.01); (B) Li isodensity (mesh = 0.002, solid = 0.02); (C) Li$^+$ isodensity (mesh = 0.002, solid = 0.02); (D) Li$^+$ slice (red ≤ 0.0001, blue ≥ 0.01).

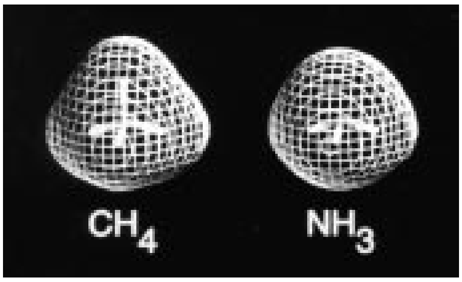
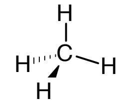
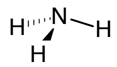


Figure 2. The 0.002 isodensity models of CH_4 and NH_3.

The differences between Li and Li$^+$ can also be investigated using electron density slices (Figs. 1a and 1d). Removing an electron does not appear to affect the high electron density "core" (blue region), but the outer region is another matter. The large region of low or diffuse electron density in Li (yellow-orange region in Fig. 1a) almost disappears in Li$^+$ (Fig. 1d), and the latter has a more rapid transition from high (blue) to low (yellow-red) electron density. This is essentially the same conclusion we reached above using isodensity models. (These models are also excellent tools for describing the spatial differences between 2*s* and 1*s* atomic orbitals.)

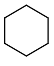
A comparison of methane, CH_4, and ammonia, NH_3, provides an example of how electron density models can be used to define molecular shape. Chemical formulas suggest that ammonia, with one fewer hydrogens, should have a flattened shape compared to methane:



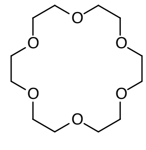


The 0.002 isodensity models, however, tell a different story. The electron cloud around nitrogen bulges out away from the rest of the molecule, making its shape more similar to that of methane (Fig. 2).

The important relationship between electron density and molecular shape/volume is even more striking in the case of a cyclic molecule. The chemical formulas of cyclohexane and 18-crown-6 seem to imply a cavity exists in each molecule:



cyclohexane



18-crown-6

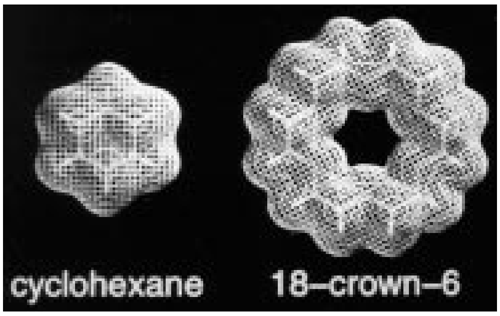


Figure 3. The 0.002 isodensity models of cyclohexane and 18-crown-6.

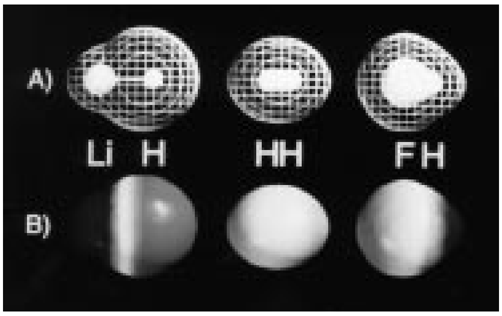


Figure 4. Electron density models of LiH, H_2, and HF: (A) isodensity (mesh = 0.002, solid = 0.08); (B) elpot (red ≤ −30 kcal/mol, blue ≥ 50 kcal/mol).

However, 0.002 isodensity models show that there is no cavity in cyclohexane, and the cavity in 18-crown-6 is much smaller than we may have anticipated (Fig. 3). Interestingly, 18-crown-6 binds metal cations (*5*), and binding strength is related to the size of the cation (the best binding occurs when the cation's 0.002 isodensity surface is slightly *larger* than the size of the cavity in 18-crown-6), so beginning chemistry students can use isodensity models to explore an important type of chemical selectivity.

Bonding in Molecules

Most textbooks present chemical bonding in terms of orbital overlap and other orbital-based concepts. Unfortunately, this linking of bonds and orbitals makes bonding an unnecessarily difficult subject for many students. A better and much simpler alternative is to describe bonds in qualitative terms using electron density models. G.P.S. has used electron density models for several years in her general chemistry course as a tool for describing various types of bonds, and this presentation paves the way for a subsequent orbital-based description. The following discussion illustrates how electron density models can be used to distinguish ionic, covalent, and polar covalent bonding, identify covalent bonds of different bond orders, and distinguish localized and delocalized bonds and charges.

Ionic, Covalent, and Polar Covalent Bonds

A dramatic way to illustrate the variable nature of chemical bonds is to compare a series of molecules that are superficially the same. For example, the "covalent" Lewis structures of LiH, H_2, and HF suggest that the hydrogen atom environment is identical in each molecule, and that each molecule is held together by a covalent bond:

$$\mathrm{H{-}Li}\qquad \mathrm{H{-}H}\qquad \mathrm{H{-}\ddot{\underset{..}{F}}{:}}$$

However, 0.002 isodensity models reveal major differences between the hydrogen atoms (Fig. 4a). The radius of the 0.002 surface in the immediate vicinity of each hydrogen atom (i.e., the axial distance from the hydrogen nucleus to the surface) varies considerably, decreasing in the order $LiH > H_2 > HF$. If we assume that the radius and the amount of electron density on hydrogen are correlated, then the amount of "hydrogen" electron density falls in the same order, $LiH > H_2 > HF$.[2] If we also make the reasonable assumption that the atoms of H_2 are uncharged, we can conclude that H carries a partial negative charge in LiH and a partial positive charge in HF. The existence of partial charges can be explained, of course, by invoking the idea of electronegativity; but the electron density models eliminate most of the hand waving that usually accompanies this concept. The models make obvious (i) the transfer of electron density between bonded atoms, (ii) the meaning of electronegativity as the ability of an atom to attract electron density, and (iii) the increase in electronegativity, Li < H < F. Moreover, students who examine these models quickly realize that chemical formulas and Lewis structures may be too simplistic to provide an accurate picture of electronic structure, and that an atom's electronic properties can vary drastically depending on its neighbors.

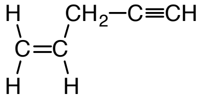
Another feature of the covalent Lewis structures shown above is the suggestion that the atoms in each molecule "share" a pair of electrons. Although we cannot easily "count" electrons using electron density models, we can examine the degree of electron sharing by looking at 0.08 isodensity models of each molecule (Fig. 4a). H_2 and HF have similar 0.08 surfaces; a single surface encloses the two atomic nuclei and also the region lying between the nuclei. The observation that "high" electron density lies in the internuclear region can be taken as a visible sign of electron "sharing", and we can call the bonds in these molecules covalent (purely covalent in H_2 and polar covalent in HF). The 0.08 isodensity model of LiH, on the other hand, shows two separate surfaces, one enclosing each nucleus. The absence of "high" electron density in the internuclear region rules out electron "sharing", and this bond must be ionic.

Another kind of model that is very useful for describing electron density distributions is the electrostatic potential map, or "elpot" map. A molecule's electrostatic potential is defined as the potential energy that a point-like, positively charged "probe" particle would experience in the presence of the molecule. This potential is an idealized quantity in the sense that we assume the probe does not perturb any part of the molecule's charge distribution, either the shape of the electron density cloud or the positions of the atomic nuclei. Since all of the charged particles in the molecule contribute to the electrostatic potential, an elpot model can provide more information about the total electron density than any single isodensity surface.

Figure 4b shows elpot maps of LiH, H_2, and HF. These were created by calculating the electrostatic potential at various points on each molecule's 0.002 isodensity surface, and using color to display the variation in potential. The potential in these maps increases in the order red (potential ≤ −30 kcal/mol) < orange < yellow < green < blue (potential ≥ 50 kcal/mol). Since the potential is usually dominated by the *local* charge distribution we can use these maps to evaluate the atomic charges in these molecules. The regions of lowest potential—that is, the red regions—attract the positive probe the most, and we infer that these regions are the most electron-rich. Likewise, the regions of highest potential, the blue regions, repel the positive probe the most and we infer that these regions are the most electron-poor. Thus, H in LiH and F in HF are both electron-rich (red), while Li in LiH and H in HF are both electron-poor (blue). The atoms in H_2 are neither electron-poor nor electron-rich in comparison, and this is just what we expect for a homonuclear diatomic molecule.

Bond Order and the Structure of Multiple Bonds

Electron density models are also useful tools for introducing the concept of multiple bonding or covalent bond order. Figure 5 shows several models of pent-4-en-1-yne, a hydrocarbon molecule that contains CC single, double, and triple bonds:



pent-4-en-1-yne

A single 0.08 isodensity surface encloses all the nuclei and all of the internuclear regions, consistent with the completely covalent nature of this molecule (Fig. 5a, mesh). However, examination of the 0.2 isodensity model (Fig. 5a, solid) reveals that *the highest levels of electron density are found only in the immediate vicinity of the atomic nuclei and in the two internuclear regions corresponding to CC multiple bonds.* The 0.2 surface associated with the triple bond is somewhat larger than the surface associated with the double bond, so there even appears to be a correlation between the internuclear electron density and the bond order. If we think of the analogy frequently made between bonding pairs of electrons and glue, we see that a similar analogy might be made between electron *density* and glue. Multiple bonds have more "glue" in their internuclear regions, and are stronger and shorter than single bonds.

An elpot model of pent-4-en-1-yne reveals several additional features of the electron density distribution (Fig. 5b). As usual, the red regions identify the most negative potentials and the most electron-rich regions. In this molecule, these regions turn out to be CC multiple bonds; the triple bond is surrounded by an electron-rich cylinder, while the double bond has electron-rich regions above and below the plane containing the $CH{=}CH_2$ nuclei. (Many students find this picture of multiple bonding less confusing than the standard pi model, which fails to convey the cylindrical symmetry of the triple bond.)

Another interesting feature of the elpot model is the blue regions—the regions of highest potential, which identify electron-poor atoms. In this molecule, as in the vast majority of neutral hydrocarbons, the hydrogens are more electron-poor than the carbons. However, not all the hydrogens are alike. The –C≡CH hydrogen is dark blue and very electron-poor, while the others are pale blue—almost green. The variation in potential implies a variation in partial charge (all the hydrogens carry small partial positive charges), with charge increasing in the order alkane H < alkene H << alkyne H. The logical inference is that this is due to variations in carbon electronegativity, with electronegativity increasing in the order alkane C < alkene C << alkyne C.

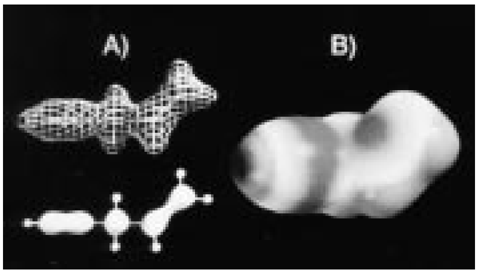


Figure 5. Electron density models of pent-4-en-1-yne: (A) isodensity (mesh = 0.08, solid = 0.2); (B) elpot (red ≤ -20 kcal/mol, blue ≥ 40 kcal/mol).

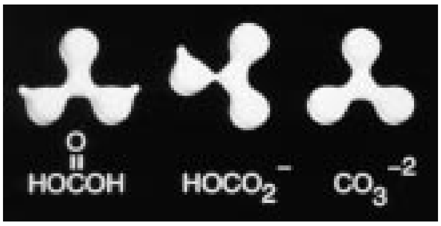


Figure 6. The 0.2 isodensity models of carbonic acid, bicarbonate anion, and carbonate dianion.

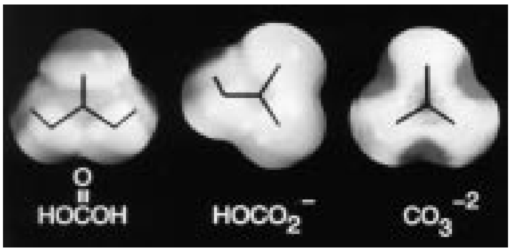
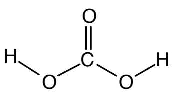


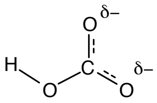
Figure 7. Elpot models of carbonic acid (red ≤ -30 kcal/mol, blue ≥ 70 kcal/mol), bicarbonate anion (red ≤ -160 kcal/mol, blue ≥ 60 kcal/mol), carbonate dianion (red ≤ -270 kcal/mol, blue ≥ 240 kcal/mol). Black lines show molecular orientation.

Delocalized Molecules

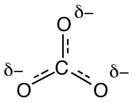
The electronic structure of a delocalized molecule such as benzene or carbonate ion presents a unique problem for chemistry students because it cannot be described using a single Lewis structure. Electron density models, on the other hand, treat all molecules, localized and delocalized, in a uniform fashion and help demystify this subject. Moreover, they offer students a visual model of what a delocalized molecule really "looks like". There is no need to mentally assemble and weight various resonance contributors to get a picture of a molecule. One can simply look at the model and decide what resonance contributors might best describe it.

The utility of electron density models is illustrated by the series carbonic acid (H_2CO_3), bicarbonate ion (HCO_3^-), and carbonate dianion (CO_3^{2-}). The bonds in carbonic acid are normally viewed as localized CO single and double bonds. Bicarbonate and carbonate, on the other hand, are normally viewed as resonance hybrids with delocalized charges and bonds. Bicarbonate contains two equivalent delocalized CO bonds, and carbonate contains three equivalent bonds (the delocalized bonds cannot be described as either single or double).


carbonic acid



bicarbonate ion



carbonate ion

The 0.2 isodensity surfaces provide information about the bonding pattern in each molecule without the need for multiple Lewis structures (Fig. 6). Thus, carbonate clearly has threefold symmetry, while carbonic acid and bicarbonate seem to have two identical CO bonds and one unique CO bond. The differences between these bonds can be understood by appealing to the correlation between internuclear electron density and bond order described above. The amount of electron density can be derived, in turn, from the size of the "high" (≤ 0.2) electron density region in each internuclear region. Thus, the unique CO bond in carbonic acid has a higher bond order than the other two equivalent bonds, whereas the situation is reversed in bicarbonate.

The degree of charge delocalization in each of these molecules is easily assessed using elpot models. Since the electrostatic potential becomes considerably more negative each time we remove a proton from the molecule (i.e., as we move from neutral carbonic acid to negatively charged bicarbonate to doubly charged carbonate), we will use a different color scale to map the potential in each molecule (Fig. 7). Remembering that red is used to identify the most negative potentials (and thus the location of partial negative charges), we see that (i) the carbonyl oxygen in carbonic acid is more electron-rich than the hydroxyl oxygens, (ii) the negative charge in bicarbonate is spread over two oxygens, and (iii) the double negative charge in carbonate is fully delocalized over all three oxygens.

One strange feature of the carbonate elpot model is that it seems to imply that the "charges" lie in the molecular plane and *in between* the oxygen atoms. This interpretation is misleading because the regions of highest electron density, although lying in the molecular plane, actually lie close to the oxygen nuclei. The strange appearance of the elpot model derives from the additive nature of the electrostatic potential: the red regions have more negative potentials than their surroundings simply because they lie close to *two* oxygens. Interestingly, the elpot model does successfully predict the coordination chemistry of these ions—they bind metal cations in a bidentate manner, the metal lying between two oxygens and in the molecular plane.

Intermolecular Interactions and Chemical Reactivity

Elpot models are also useful for studying intermolecular interactions that are primarily electrostatic, such as ion–ion, ion–dipole, and dipole–dipole interactions. The models allow students to quickly identify reactive sites and propose structural models for intermolecular complexes. They also provide a strong visual framework for discussing such fundamental properties as solubility, hydrogen bonding, and complexation.

Table 1. Basis Sets Used for Electron Density Models

Basis Set	Molecule
STO-3G	18-crown-6
3-21G	cytosine, guanine, cyclohexane, pent-4-en-1-yne
6-31G*	Li, Li^+, H_2, HF, CH_4, NH_3, H_2CO_3, CH_3CO_2H, H_2SO_4
6-31+G*	LiH, HCO_3^-, CO_3^{2-}

Acid–base behavior provides the simplest example of a chemical reactivity pattern that can be predicted using elpot models. For example, the increased acidity of sulfuric acid, H_2SO_4, relative to acetic acid, CH_3CO_2H, can be predicted by comparing elpot models of the two acids (Fig. 8). Using the same color scale for both models so that their potentials can be compared directly, we see that the hydrogens of sulfuric acid are much more electron-poor than the carboxyl hydrogen of acetic acid (blue identifies the most positive potential). Hence, the OH bond in sulfuric acid is more polar and this should be the stronger acid. Similar reasoning can be applied to the unsaturated hydrocarbon in Figure 5c: the alkyne hydrogen is much more electron-poor and should be more acidic than the other hydrogens. (Note that this type of reasoning works best when the atom bonded to H is the same in both acids, since the differences in acidity are more likely to be dominated by bond polarity.)

Intermolecular interactions between biological molecules such as DNA are often controlled by hydrogen bonding, and this too can be visualized using elpot models. Elpot models of guanine and cytosine, for example, show that the faces of these rings are relatively nonpolar (green), while the perimeter of each ring contains several partially charged sites (Fig. 9). Aligning the two molecules according to the Watson–Crick base-pairing model matches three sites of opposite polarity in each molecule; that is, the molecules are held together by three hydrogen bonds.

Building Electron Density Models

All electron density models described in this article (slices, isodensity surfaces, and elpot models) were constructed using standard algorithms contained in versions 3 and 4 of SPARTAN running on a Silicon Graphics Indigo workstation.[3] Molecular models were constructed by optimizing each model's geometry using an ab initio restricted Hartree–Fock (RHF) wave function (basis sets are listed in Table 1), and then using this wave function to construct the desired electron density models. Models of neutral Li were constructed using an unrestricted Hartree–Fock, or UHF, wave function (*6*). Photographs of the models were obtained by photographing each image as it appeared on the computer screen with a 35 mm camera (automatic shutter setting) in a darkened room.

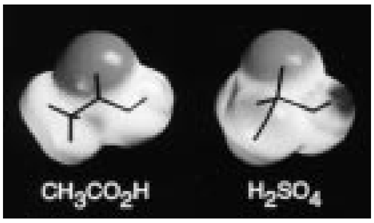


Figure 8. Elpot models of acetic acid and sulfuric acid (red $\le$ –20 kcal/mol, blue $\ge$ 90 kcal/mol). Black lines show molecular orientation.

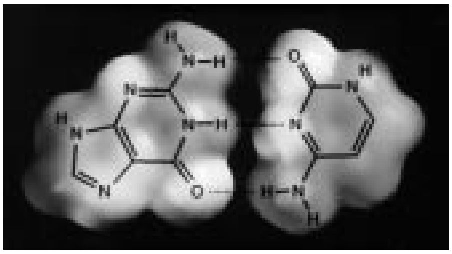


Figure 9. Elpot models of guanine and cytosine (red $\le$ –70 kcal/mol, blue $\ge$ 65 kcal/mol).

Summary

Electronic structure plays an important role throughout chemistry, affecting molecular size, shape, bonding, stability, reactivity, and many other characteristics. Unfortunately, relatively few of these subjects have been included in traditional general chemistry curricula because the tools normally used to describe electronic properties, namely, "orbital" theories, are so difficult to use. We believe that computer-generated electron density models provide a student-friendly option for describing electronic structure and for studying the role of electronic structure in a wide variety of chemical phenomena. These models have a sound theoretical basis, yet are easy to generate, manipulate, and interpret. Also, the rapid pace of computer hardware and software development is bringing these tools to the personal computer, making them accessible to individual students.

Acknowledgments

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Notes

1. Presented as part of the symposium on "Integrating Computational Chemistry into the Curriculum", 12th Biennial Conference on Chemical Education, August 1992, University of California-Davis, Davis, CA. Color versions of the figures are shown on the cover of this issue. The complete text of this article with color figures is also available on JCE Online (*http://jchemed.chem.wisc.edu/*)

2. This conclusion is based on the assumption that the size of the 0.002 isodensity surface is related to the *amount* of electron density around a hydrogen atom, and not just the spatial distribution of the electron density. This assumption is only valid when atoms with identical nuclei are being compared. Thus, we cannot use the size of the 0.002 surface near H and Li to deduce the total electron density on each atom; Li has a much larger nuclear charge and this will attract a larger amount of electron density into its "core" region.

3. SPARTAN is a product of Wavefunction, Inc., 18401 Von Karman Ave., Suite 370, Irvine, CA 91711 (email: *sales@wavefun.com*).

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