Teaching Chemistry with Electron Density Models. 2. Can Atomic Charges Adequately Explain Electrostatic Potential Maps?

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Abstract: Electrostatic potential maps generated from quantum mechanical calculations are widely used to teach students about molecular polarity and assign atomic charges (Shusterman, G. P.; Shusterman, A. J. *J. Chem. Educ.* **1997,** *74,* 771–776; Hehre, W. J.; Shusterman, A. J.; Nelson, J. E. *The Molecular Modeling Workbook for Organic Chemistry;* Wavefunction: Irvine, CA, 1998). The assumption that potential equals charge is only valid, however, when comparing atoms of similar size. The proper use of potential maps requires consideration of atomic charge, atomic radius, and the electron configuration (orbital occupancy) of the atom in question. These points are illustrated through the analysis of the potential maps of various halogen-containing molecules.

Introduction[§]

Chemists use the notion of atomic charge to account for a diverse set of phenomena. For example, atomic charges are routinely used to explain trends in dipole moment, solubility, NMR chemical shift, chemical stability, and chemical reactivity.

Students are also expected to have a good grasp of atomic charge. They are expected to draw Lewis structures with correct formal charges, to assign oxidation states, to use electronegativity differences to identify polar covalent bonds and compare bond polarity, and to predict the effect of resonance on charge distributions.

It is interesting to note, then, that such a central concept as atomic charge lacks a clear definition. Atomic charges are not physically observable quantities, and so all definitions of atomic charge (and many definitions have been given) are necessarily arbitrary. This may help explain why the various quantum mechanical methods for calculating atomic charges have found little use in chemical education. The methods cannot help but give arbitrary results. Another contributing factor is likely to be the numerical nature of calculated charges. Lists of numbers are hard to use.

Some of these difficulties have been overcome by the development of new computer programs for performing quantum mechanical calculations. Programs like *PC Spartan Pro* [1] can perform a quantum mechanical calculation and then convert the results into a graphical model that shows how electron density is distributed. These so-called electron density models are easy to make and easy to use, and they have proven to be useful tools for teaching students about electronic structure [2].

One type of electron density model, the electrostatic potential map (referred to hereafter as potential map), has already found widespread usage in chemistry textbooks because it can give information about atomic charges at a glance [3]. Take the case of hydrogen fluoride, HF. The standard potential map generated by *PC Spartan Pro* (Figure 1) shows the electrostatic potentials found around the perimeter of the molecule's electron cloud [4]. The red region near fluorine corresponds to the most negative potential found on the cloud's perimeter (-27 kcal mol^{-1}) and the blue region corresponds to the most positive potential ($+78$ kcal mol^{-1}) (note: intervening potentials are color-coded using the standard red < orange < yellow < green < blue color spectrum). With this in mind, we can see immediately that HF is a polar molecule, and that the atomic charge distribution most consistent with this map is $H^{\delta+}$–$F^{\delta-}$.

Unfortunately, equating electrostatic potentials with atomic charges is not always a valid procedure, even for simple molecules. This paper illustrates this problem using the potential maps of several simple halogen-containing molecules. Even when potentials are correlated with charges, other factors, such as atom size and orbital occupancy, must also be considered. Fortunately, atom size and orbital occupancy are familiar concepts, so a satisfactory interpretation of potential maps is still within easy reach.

### Hydrogen Halides: Potential Equals Charge?

PC Spartan Pro-generated potential maps of HF, HCl, HBr, and HI are shown in Figure 2. The maps all use the same color-coding scheme to represent electrostatic potential: red ≤ -20, orange ≈ -11, yellow ≈ 2, green ≈ 25, blue ≥ 70 kcal mol^{-1}. Thus, we can see that positive potentials (green or blue) are always found near hydrogen (left side of map), and negative potentials (orange or red) are always found near the halogen (right side of map). A positive potential at any location means that a (point-like) positively charged ion at this spot would be repelled by the molecule. Thus, the potential maps in Figure 2 suggest that all of the hydrogen atoms carry partial positive charges. Similarly, a negative potential at any location means that a positively charged ion at this spot would
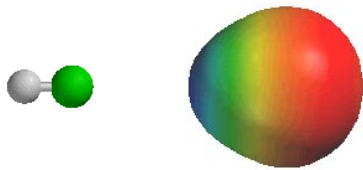
Figure 1. Ball-and-spoke model (left) and potential map (right) of hydrogen fluoride (hydrogen is the white atom, fluorine is the green atom). Molecular size and orientation are the same in both images. Potential range equals –27 to +78 kcal mol^{-1}.
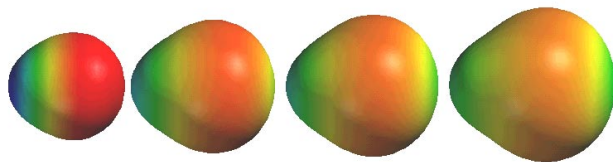
Figure 2. Potential maps of hydrogen halides: HF (left), HCl, HBr, HI (right). The molecules are arranged in the same orientation as HF in Figure 1 with hydrogen on the left side. The potential range is –20 to +70 kcal mol^{-1}.
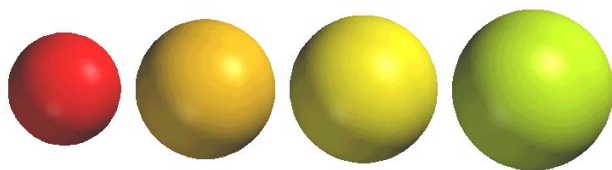
Figure 3. Potential maps of halide ions: F$^-$ (left), Cl$^-$, Br$^-$, I$^-$ (right). The potential range is –200 to 0 kcal mol^{-1}.

be attracted by the molecule. Thus, the maps appear to tell us that the halogens all carry partial negative charges.

The potential maps in Figure 2 not only paint a vivid picture of hydrogen halides as polar molecules, they also seem to describe a trend in molecular polarity. The *magnitude* of the positive potential decreases: H in HF (dark blue) > H in HCl > H in HBr > H in HI (green), and the *magnitude* of the negative potential decreases: F (dark red) > Cl > Br > I (orange). Thus, the potential maps suggest that molecular polarity (charge separation) decreases: HF > HCl > HBr > HI, a clear indication that halogen electronegativity falls F > Cl > Br > I.

Unfortunately, as we shall demonstrate, this potential-equals-charge analysis is overly simplistic. There are many situations where it can be used, but many more where it cannot. The following sections show how the analysis can break down and what additional factors might need to be considered for a successful analysis.

Halide Ions: Map Size Is Important

The potential maps of the halide anions, F$^-$, Cl$^-$, Br$^-$, and I$^-$ (Figure 3), provide a glaring failure of the potential-equals-charge analysis. The four halide ions have identical charges of –1, but the potential varies widely from fluoride (red, –204 kcal mol^{-1}) to iodide (yellow or green, –139 kcal mol^{-1}).

Clearly, trends in potential do not necessarily give trends in atomic charge.

The potential maps of the halides look different because the ions are different *sizes*. To see why ion size is important, we must review the basic definition of electrostatic potential. The potential at a selected coordinate (x, y, z) is the *change* in electrostatic energy that occurs when a point-like +1 ion (the "probe" ion) is moved from infinity (zero potential) to the selected coordinate. In the case of the halide ion potential maps, the selected coordinate is a point on the halide ion's potential map. All of the halide ions attract the probe ion, but the final distance between the halide ion and the probe ion depends on the radius of the potential map, or on ion size. Fluoride ion has the smallest radius, so the most negative potential is found on this map. Iodide ion has the largest radius and the least negative potential. (A more elaborate analysis of the halide anion potential maps can be found in the appendix.)

Electrostatic potential is *not* a reliable indicator of charge, but it can still be a reliable indicator of charge density (charge/ionic radius), a quantity with many useful applications. For example, it is well-known that the aqueous solvation enthalpy of halide ions becomes less exothermic as one goes from fluoride to iodide. The explanation for this trend is that solvation enthalpy depends on ion size or, equivalently, charge density. The charge in a larger anion is spread over a larger volume and is more diffuse (small charge density). This stabilizes the ion in the gas phase because the charge is more delocalized, but destabilizes the ion in water because the ion forms weaker hydrogen bonds. Potential maps show how ion charge density (ion size) and the strength of ion–dipole interactions (hydrogen bonds) are related. The smallest, least diffuse, halide (F$^-$) has the most negative potential (largest charge density) and forms the strongest hydrogen bonds. The largest, most diffuse, halide (I$^-$) has the least negative potential (smallest charge density) and forms the weakest hydrogen bonds.

Hydrogen Halides: Potential Is Not Equal to Charge

Our previous potential-equals-charge analysis of the hydrogen halides (Figure 2) did not consider atom size as a contributing factor. If we re-examine these molecules and focus on the portion of each map that is closest to the halogen atom, we see that atom size increases: F (in HF) < Cl (in HCl) < Br (in HBr) < I (in HI). This is the same trend seen for the isolated halide ions (Figure 3) and it leads to the same conclusion. Namely, the trend in potential near the halogen does not indicate the trend in halogen charge, but the trend in charge density instead. F (in HF) clearly has the most negative potential and the largest charge density, but it is uncertain whether this is due to the partial charge on F (most negative), the size of F (smallest halogen), or a combination of these factors.

Fortunately, there is a simple way to interpret these maps without having to worry about map size or charge density. All of the molecules contain hydrogen, and the size of this atom does not change much from one molecule to the next [5]. Consequently, the potential near hydrogen is a useful index of hydrogen charge and, also, hydrogen charge density. The potential near hydrogen falls in the order H in HF (most positive) > H in HCl > H in HBr > H in HI (least positive), and it is reasonable to conclude that the partial positive charge on
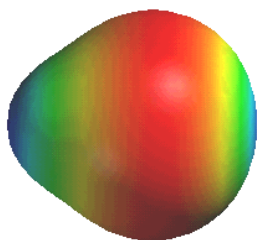
Figure 4. Potential map of hydrogen iodide. The map is oriented the same way as the one shown in Figure 2. The potential range is –9.7 to +35.6 kcal mol^{-1}.
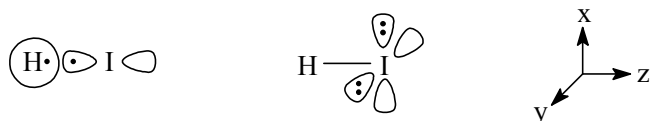
Figure 5. Orbital pictures of the H–I bond (left), I lone pairs (right).

hydrogen decreases in the same way. This result, along with the fact that the molecules are neutral, then gives us the trend in halogen charges: F in HF (most negative) < Cl in HCl < Br in HBr < I in HI (least negative).

At this point, it would seem that we have reached a conclusion, potential is not equal to charge, that directly contradicts statements made by one of us (AJS) elsewhere (see, for example, "Electrostatic Potential Maps and Molecular Charge Distributions" [6]). In fact, the contradiction is more apparent than real, as can be seen from the following example. Suppose we wanted to use the potential maps of acetate ion, $CH_3CO_2^-$, and thioacetate ion, CH_3COS^-, to establish their charge distributions. Clearly, the three oxygen atoms in these ions have similar sizes, so the potentials near these atoms should give reasonably accurate charges. Atom size does not vary much for atoms that lie close together (and on the same row) in the periodic table. This means that rough comparisons can also be made between carbon and oxygen atoms. The comparison that *cannot* be made is between sulfur and any of the other atoms. Sulfur is much larger than either oxygen or carbon, and the potential near sulfur is a useful indicator of charge density only.

Hydrogen Iodide: Orbital Occupancy Is Important

Even when one has assigned reasonable charges to atoms, the interpretation of potential maps can be problematic. For example, the potential map of hydrogen iodide shown in Figure 4 contains two features that simply cannot be explained by treating the atoms as point-like charges. (Note: the map in Figure 4 is identical to the one in Figure 2 except that the colors are assigned differently. The red and blue regions in Figure 4 correspond to the most negative (–9.7 kcal mol^{-1}) and most positive (+35.6 kcal mol^{-1}) potentials on this map, respectively.)

The first problematic feature is the fact that both positive and negative potentials are found near iodine. A significantly positive potential (+32.2 kcal mol^{-1}) occurs on the HI bond axis near iodine, and the most negative potential (–9.7 kcal mol^{-1}) occurs in a circular band around iodine. If potentials could be predicted accurately by treating each atom as a

partially charged particle, that is, by thinking of this molecule as $H^{\delta+}$–$I^{\delta-}$, only negative potentials would be found near iodine. The fact that large positive potentials are found near iodine, and far away from hydrogen, shows one of the basic shortcomings of the atomic charge picture [7].

A second problematic feature is the shape of the potential map. Chemists like to think of atoms as spheres (a space-filling model of HI would look like two overlapping spheres), but the potential map is clearly nonspherical in the region around iodine. The distance from the iodine nucleus to the map surface is greatest along the line perpendicular to the HI bond axis and is smallest along the bond axis itself. In other words, the map is compressed towards iodine along the bond axis. Because the map surface is an electron density isosurface, the map's shape tells us that electron density falls off relatively slowly perpendicular to the bond axis and, more rapidly, along the bond axis.

Both of these puzzling features, the variation in electrostatic potential and the compression of the map surface, can be explained by using an orbital picture to describe the hydrogen iodide covalent bond. According to this picture, the bond is due to the overlap of two singly occupied orbitals, a 1s orbital on hydrogen and a $5p_z$ orbital on iodine (assume the bond axis to be the z axis). The other valence orbitals on iodine, 5s, $5p_x$, and $5p_y$, are doubly occupied (Figure 5).

If the valence orbitals of iodine were all occupied by the same number of electrons (as in iodide anion), the valence-electron density would be distributed spherically around iodine giving this part of the potential map a roughly spherical shape. The $5p_z$ orbital, however, has a lower occupancy than the other orbitals (this is true even if the bonding electrons are partially polarized towards iodine). As a result, there is less electron density along the HI bond axis, compressing the map towards iodine along this axis, and driving the electrostatic potential positive in this region. To put it another way, the variation in electrostatic potential and the shape of the potential map are both indicators of variations in 5p occupancy.

Other Halogen-Containing Compounds

Orbital occupancy affects the potential maps of most halogen-containing compounds, but the effects vary with the halogen and with the compound. For example, the potential maps of all of the hydrogen halides show variations in potential similar to hydrogen iodide, that is, the potential near the halogen is more positive on the bond axis and less positive away from the axis. If we define the difference in electrostatic potential, ΔEP, as:

$$\Delta EP = |(\text{potential on bond axis near } X) - (\text{most negative potential near } X)|$$

we find that ΔEP increases: HF (2.7 kcal mol^{-1}) < HCl (25 kcal mol^{-1}) < HBr (36 kcal mol^{-1}) < HI (42 kcal mol^{-1}). There is a systematic trend in ΔEP, and ΔEP is very small for HF. All of these results are consistent with the HX bonding electrons being most polarized towards the halogen (and creating the highest p_z occupancy) when the halogen is most electronegative, that is, when X = F. Replacing fluorine with a less electronegative halogen makes the bond less polarized and reduces the p_z electron population [8].
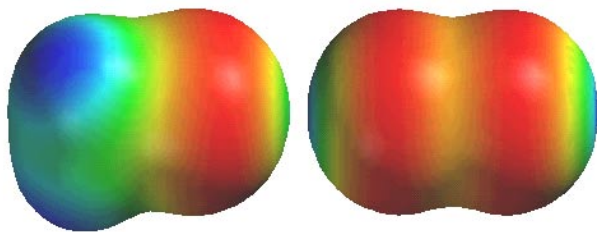
Figure 6. Potential maps of H$_3$CCl (left) and Cl$_2$ (right). The potential range is –21 to +20 (H$_3$C–Cl), and –6 to +33 kcal mol^{-1} (Cl$_2$). The most positive potentials in H$_3$CCl are found around the hydrogen atoms, but the potential also becomes more positive on the C–Cl bond axis (near Cl). The most positive potentials in Cl$_2$ are found on the bond axis.

As a final example, we consider potential maps of CH$_3$Cl and Cl$_2$ (Figure 6). Each map shows the predicted variation in potential around chlorine. The most negative potentials are found away from the bond axis, and the potential become more positive as one moves towards the bond axis. The map of Cl$_2$ is especially distorted because the Cl–Cl bond is not polarized towards either atom and the p$_z$ orbital is essentially singly occupied.

Summary

Electrostatic potential maps provide a compelling picture of hydrogen halides as polar molecules, and they are useful tools for teaching students about electron density distributions. One must be cautious, however, in how one relates trends in potential to trends in atomic charge. The trend in potential near the hydrogen atoms can be used to describe trends in partial charge because these "identical atoms" have similar sizes. The trend in potential near the halogen atoms cannot be used in this way because the potential is affected more by atom size than by atomic charge. Some features of electrostatic potential maps also require one to think about how electrons are distributed spatially around each atom (orbital occupancy).

Appendix

The electrostatic potential, $EP(\mathbf{R})$, created by an atom at a point $\mathbf{R}$ is the sum of two terms. The first term describes the electrostatic energy between a point-like +1 "probe" charge and the atomic nucleus. The second term describes the electrostatic energy between the probe charge and the atom's electron density distribution. Combining these energies gives $EP(\mathbf{R})$:

$$EP(\mathbf{R}) = Z/|\mathbf{R}| - \int \big[\rho(\mathbf{r})/|\mathbf{R}-\mathbf{r}|\big] dV$$

The electrostatic energy created by the probe–nucleus interaction is given by $Z/|\mathbf{R}|$ where Z is the atomic number, $|\mathbf{R}|$ is the distance between the probe charge and the atom's nucleus, and distance and energy are expressed in atomic units.

The electrostatic energy created by the probe-electron density interaction is given by the integral of $-\rho(\mathbf{r})dV/|\mathbf{R}-\mathbf{r}|$ over all space. $\rho(\mathbf{r})dV$ is the electron density located in a small volume dV centered at point $\mathbf{r}$, and $|\mathbf{R}-\mathbf{r}|$ is the distance between this electron density and the probe charge.

The integral describing the probe-electron density interaction can be replaced by a simpler formula whenever an atom or ion has a spherical electron density distribution (this is the type of distribution found in the halide anions). In this situation, the integral is equal to $-Q(\mathbf{R})/|\mathbf{R}|$, where $Q(\mathbf{R})$ is the total electron density found within a distance $|\mathbf{R}|$ of the nucleus. This is equivalent to concentrating at the nucleus all of the electron density that lies closer to the nucleus than the probe charge does and allowing this accumulated electron density to interact with the probe charge. The electron density that lies farther away from the nucleus than the probe charge does not contribute to the electrostatic potential.

Using this new expression for the probe-electron density interaction gives the following expression for the electrostatic potential:

$$EP(\mathbf{R}) = \big[Z - Q(\mathbf{R})\big]/|\mathbf{R}| \approx -1/|\mathbf{R}|$$

Since the standard potential map encloses nearly all of an ion's electron density, the numerator, $Z - Q(\mathbf{R})$, roughly equals the overall charge on the ion, or –1 for the halide anions. Consequently, the potentials that are observed in Figure 3 are inversely related to map radius (or ion radius), $|\mathbf{R}|$. Larger anions have less negative potentials, while smaller anions have potentials that are more negative.

References and Notes

1. *PC Spartan Pro,* ver. 1.0.3, Wavefunction, Inc., 18401 Von Karman, Suite 370, Irvine, CA, 92612 (www.wavefun.com).

2. Shusterman, G. P.; Shusterman, A. J. *J. Chem. Educ.* **1997,** *74,* 771–776.

3. Umland, J. B.; Bellama, J. M. *General Chemistry,* 3rd ed.; Brooks/Cole: Pacific Grove, CA, 1999; Jones, L.; Atkins, P. *Chemistry: Molecules, Matter and Change,* 4th ed.; W.H. Freeman: New York, NY, 1999; Ebbing, D. D.; Gammon, S. D. *General Chemistry,* 6th ed.; Houghton Mifflin: New York, NY, 1998; McMurry, J. *Organic Chemistry,* 5th ed.; Brooks/Cole: Pacific Grove, CA, 2000; Carey, F. A. *Organic Chemistry,* 4th ed.; McGraw-Hill: Boston, MA, 2000; Solomons, T. W. G.; Fryhle, C. B. *Organic Chemistry,* 7th ed.; Wiley: New York, NY, 2000; Bruice, P. Y. *Organic Chemistry,* 3rd ed.; Prentice-Hall: Upper Saddle River, NJ, 2001.

4. All of the potential maps in this paper were generated using standard algorithms found in *PC Spartan Pro,* ver. 1.0.3 [1]. Molecular geometries were optimized, and electron Density distributions and electrostatic potentials were calculated using BP/DN** (Becke–Perdew exchange-correlation functionals + DN** basis set). All of the potential maps use the default electron density isosurface (electron density = 0.002 a.u.). This isosurface is comparable in size and shape to a space-filling model of the molecule, and it encloses nearly all of the molecule's electron density.

5. The size of hydrogen, or equivalently, the size of the potential map near hydrogen, increases slightly from H in HF (smallest) < H in HCl < H in HBr < H in HI (largest). The variation in hydrogen size is much smaller, however, than the corresponding variation in halogen size. In addition, the variation in hydrogen size is consistent with the variation in potential. Transfer of electron density from hydrogen to halogen is greatest in HF, making this hydrogen the smallest, and making the potential near this hydrogen the most positive.

6. Hehre, W. J.; Shusterman, A. J.; Nelson, J. E. *The Molecular Modeling Workbook for Organic Chemistry;* Wavefunction: Irvine, CA, 1998.

7. The variation in electrostatic potential seen in hydrogen iodide is not unique to this molecule. All of the hydrogen halides display a similar variation in potential with more negative potentials found away from the bond axis and a more positive potential on the bond axis. The variation in potential, however, is greatest in hydrogen iodide.

8. This argument contains at least two flaws that should be pointed out. First, the argument does not take into account the atomic charge on hydrogen and its effect on ΔEP. Second, the argument assumes that the halogen's valence s orbital is doubly occupied. This is not the case. Each halogen uses a unique mixture of valence s and p_z orbitals for bonding. When the s orbital is used for bonding, the p_z orbital acts more like a nonbonding orbital and takes on a larger occupancy.