Electrostatic Potential maps

Electrostatic Potential maps, also known as electrostatic potential energy maps, or molecular electrical potential surfaces, illustrate the charge distributions of molecules three dimensionally. These maps allow us to visualize variably charged regions of a molecule. Knowledge of the charge distributions can be used to determine how molecules interact with one another.

Introduction

Electrostatic potential maps are very useful three dimensional diagrams of molecules. They enable us to visualize the charge distributions of molecules and charge related properties of molecules. They also allow us to visualize the size and shape of molecules. In organic chemistry, electrostatic potential maps are invaluable in predicting the behavior of complex molecules.

The first step involved in creating an electrostatic potential map is collecting a very specific type of data: electrostatic potential energy. An advanced computer program calculates the electrostatic potential energy at a set distance from the nuclei of the molecule. Electrostatic potential energy is fundamentally a measure of the strength of the nearby charges, nuclei and electrons, at a particular position.

To accurately analyze the charge distribution of a molecule, a very large quantity of electrostatic potential energy values must be calculated. The best way to convey this data is to visually represent it, as in an electrostatic potential map. A computer program then imposes the calculated data onto an electron density model of the molecule derived from the Schrödinger equation. To make the electrostatic potential energy data easy to interpret, a color spectrum, with red as
the lowest electrostatic potential energy value and blue as the highest, is employed to convey the varying intensities of the electrostatic potential energy values.

**Analogous System**

Electrostatic potential maps involve a number of basic concepts. The actual process of mapping the electrostatic potentials of a molecule, however, involves factors that complicate these fundamental concepts. An analogous system will be employed to introduce these basic concepts.

Imagine that there is a special type of mine. This mine is simply an explosive with some charged components on top of it. The circles with positive and negative charges in them are the charged components. If the electric field of the electric components are significantly disturbed, the mine triggers and explodes. The disarming device is positively charged. To disarm the mine, the disarming device must take the path of least electric resistance and touch the first charged mine component on this path. Deviating from this minimal energy path will cause a significant disturbance and the mine will explode. The specific charged components within the mine are known.

Q. How do you disarm the following mine?

![Mine Diagram](Image)

A. Touch the bottom most portion of negatively charged component, red, with the disarming device.

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**Introduction to Coulomb's Law and Electrostatic Energy**

Coulomb's Law Formula

\[ F = k \frac{q_a q_b}{r^2} \]

with

- \( F \) is the force
- \( q_a \) is the charge of particle \( a \)
- \( q_b \) is the charge of particle \( b \)
The electrostatic Energy Formula

\[ \text{Electrostatic Energy} = \text{Force} \times \text{Change in Distance} \]

This answer to the previous question is derived from physics. The charged components in this mine create an electric field. A charged particle, the disarming device, \( q_2 \), experiences a force when in an electric field. To touch the charged component, the disarming device must be moved. This involves electrostatic energy. Electrostatic energy is the energy required to move a charged particle through an electric field. Coulomb’s Law predicts the force, but the distance is arbitrary. Provided that the disarming device starts from the same distance from the two charges, both \( q_1 \) independently, the energy involved in moving the positively charged disarming device toward the negatively charged component is significantly lower than the energy associated with the alternative pathway. It is important to note that both components affect the particle and that the total energy involved in moving the particle is the sum of the energy required to move the particle along the pathway with respect to each charged component. Consequently the absolute minimum energy pathway is attained when the particle begins and ends as far from the positive component as possible.

\[ \text{Total Energy} = \sum \text{Electrostatic Energy} \]

But what if the mine looks like this?

Note: the size of the component is directly related to the magnitude of the charge.

There is no equation that would simply provide an answer. A sequence of electrostatic energy equations must be carried out. To solve this problem, measure the energy required to touch the every single point on the surfaces of these component. Then find the minimum value calculated to find your answer. But note the variability in distance. Each starting point would result in a different energy value. Scientists found a way to factor out this variability by using Potential Energy.
**Potential Energy**

Potential energy is a measure of the work it takes to move a charged particle from an infinite distance to a particular distance in an electric field, where zero is the origin of the electric field. A particle at an infinite distance experiences zero force from the electric field.

\[
\text{Electrostatic Energy} = \text{Force} \cdot \Delta \text{Distance} = \Delta (F_iD_i - F_fD_f)
\]

\[\text{When } F_i = 0 \]

\[
\text{Electrostatic Energy} = F_fD_f - 0 \cdot D_i = F_fD_f
\]

Thus the potential energy is solely the force acting on the particle at the final distance times the distance the particle is from the source of the field. Thus the equation for electrostatic potential energy is Coulomb's law times the radius which, simplified, is the equation shown below. This is equivalent to the definite integral of Coulomb’s Law integrated from infinity to the final position.

\[
\text{Electrostatic Potential Energy} = K \frac{q_1q_2}{r}
\]

\[\int_{\text{infy}}^{D_f} \text{Coulomb's Law} = \text{Electrostatic Potential Energy} \]

Note that one of the charges in the electrostatic potential energy equation is the charged component in the mine, and the other charge must be the positively charged disarming device. The disarming device is a test charge in this scenario. Additionally, note that the prior total energy is now the total electrostatic potential energy.

\[
\text{Total Electrostatic Potential Energy} = \sum \text{Electrostatic Potential Energy}
\]

**Why Use Electrostatic Potential Maps?**

The total energy of a pathway is the sum of the energies of the particle interacting with every electric field producing component along the pathway. It requires the sum of nine separate electric potential equations to find the electric potential at one point. Each position on the surface of the components experiences a different total potential energy. To get an accurate indication of the absolute minimum energy, presume it would take ten readings per component. There are nine components, ten readings per component, and ten calculations per reading. To find the total range of potential energies would take 900 calculations.

How do you go about using 900 sets of data? You could graph it, the electrostatic potentials are clear pieces of data, but creating coordinates that correspond to specific locations on specific charged components is a complicated process that convolutes the interpretation of the data.

The best way to represent this data is to map it, imposing the data onto a model that is analogous to the real object to preserve the spatial coordinates of the data. It would then be possible to place the electrostatic potential values with their corresponding positions. But it would be inconvenient to analyze the trends of 900 numerical electrostatic potentials on a map. To resolve this issue, a color spectrum could be incorporated.
Spectral extremes would be associated with extremes in electrostatic potential energy, and the color coded map would be easy to interpret and understand. Color the calculated points on the replica model with the corresponding electrostatic energy potentials color, extrapolate the blank regions from surrounding points, and you have created an electrostatic potential map.

Here is what a very hypothetical electrostatic potential map of the complicated mine would look like:

![Electrostatic Potential Map](image)

Touch the mine component that corresponds to the reddest portion of the electrostatic potential map to disarm it.

**Mapping Molecular Electrostatic Potentials**

Although the map above is an electrostatic potential map, in the field of chemistry such maps highlight the electrostatic potential energies of varying positions on the isosurface of a molecule. There are fundamental parallels between the electrostatic mapping of mines and molecules but, predictably, the mapping of molecules is a more complex process. The isosurface is one of these complicating variables.

**Isosurfaces**

In the hypothetical scenario, the surface of the mine was a definite point. Molecules do not have such a definite surface. Scientists resolved this issue by picking a radial value that they believed would best approximate the size and shape of the molecule as it interacts with other molecules. This radial value is actually a particular electron density, \(0.002 \text{ e}/(a_0)^3\), where \(a_0\) is the Bohr radius. Given that the radial value of the isosurface is dependent on the electron density, larger molecules with more
electrons will have larger isosurface values than smaller molecules with fewer electrons. The radial value of the isosurface is the radius value that will be used in the electrostatic potential energy equations.

Note that as larger molecules have larger isosurfaces they have have larger electrostatic potential maps as well.

**Coulomb's Law and Molecules**

One of the major similarities is that, like with mines, the charged components of molecules are known. The nuclei are known, the number and charges of the electrons are known, and quantum mechanics provides a statistically satisfactory indication of where these charged components are located. Consequently, the electrostatic potential energy integration of Coulomb's law can be used to calculate the electrostatic potential energy of various regions along the isosurface of the molecule. However, the nature of electron clouds and electron sharing between atoms in a molecule convolutes calculations. Trying to calculate how each electron and each nucleus interacts with one another is complicated. But computational calculations, like Mulliken Population Analysis, can be used to find the net charge on each atom and simplify calculations. That is not to say that it is impossible to calculate the interactions between every nucleus and every electron with the test charge. It is possible, but it would take a great deal of quantum mechanical calculations. Note that the more rigorous the computations the better the model.

Another important similarity is that both mines and molecules use a positive test charge to calculate electrostatic potential energies. The appropriate data can then be input into the integration of Coulomb's law to find the electrostatic values of various points along the isosurface of the molecule.

**Reactive Sites and Molecules**

The purpose of assessing the electrostatic potential of a mine from the previous section was to find the disarming site. Similarly, in chemistry, one of the purposes of finding the electrostatic potential is to find the reactive site of a molecule. The reactive site is a particularly charged region of a molecule that has an affinity for interacting with charged particles.

If the mine were a molecule, the mine would have been attracting a positive charge, the disarming device, to its reactive site, the region of least electrostatic potential energy resistance. Similarly, a molecule that has a region of very low potential energy would have a very strong influence on positively charged particles or regions of particles nearby. Knowledge of the molecular reactive site enables scientists to predict how simple molecules interact with other molecules. But, as with our hypothetical mines, electrostatic potential maps also illustrate the reactive sites of complex molecules whose polarity is not easy to intuitively deduce.

**Three-Dimensional Electrostatic Potential Models**

One of the more conspicuous differences is that while the hypothetical mine was two dimensional, molecules are three-dimensional. This has consequences for the electrostatic potential maps of molecules, as well as the calculations. Calculations regarding electrostatic potentials require only scalar distances and are coordinate less. The addition of a third coordinate would only necessitate the use of a three-dimensional distance formula. However, to accurately represent the actual molecule the model must be three-dimensional. The number of calculations must then be increased significantly to measure the electrostatic potentials of the entire three dimensional isosurface of the molecule. A useful electrostatic map must be accurate to be useful.
Consequently, the electrostatic potential values are laid onto quantum mechanical models that three dimensionally predict the approximate size and shape of the molecule.

**Electrostatic Potential Maps and Charge Distributions**

Molecular electrostatic potential maps also illustrate information about the charge distribution of a molecule. Electrostatic potential maps convey information about the charge distribution of a molecule because of the properties of the nucleus and nature of electrostatic potential energy. For simplicity, consider moving a positively charged test charge along the spherical isosurface of an atom. The positively charged nucleus emits a radially constant electric field. A region of higher than average electrostatic potential energy indicates the presence of a stronger positive charge or a weaker negative charge. Given the consistency of the nucleus's positive charge, the higher potential energy value indicates the absence of negative charges, which would mean that there are fewer electrons in this region. The converse is also true. Thus a high electrostatic potential indicates the relative absence of electrons and a low electrostatic potential indicates an abundance of electrons. This property of electrostatic potentials can be extrapolated to molecules as well.

Here is a simplified visual representation of the relationship between charge distribution and electrostatic potential. Keep in mind the equation used to find the electrostatic potential.

\[
\text{Total Electrostatic Potential Energy} = \sum \text{Electrostatic Potential Energy}
\]

\[
\text{Potential Energy} = K \frac{q_1q_2}{r} \quad K = \text{Coulomb's Constant}
\]

**High kJ at point:**

**Few Electrons**

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Analysis

Approach

Electrostatic potential maps may look intimidating at first, but they are not very complicated.
Here is an electrostatic potential map of benzene (left) with two dimensional molecular structure (right).

As you can see, the three dimensional model of the electrostatic potential map is very similar to the fundamental structure of the two dimensional molecular structure. As a general trend, an atom inside of a molecule creates a spherical shape when modeled three dimensionally. Following this trend, in the above electrostatic potential map, the semi-spherical blue shapes that emerge from the edges of the above electrostatic potential map are hydrogen atoms. Spherical protrusions are generally individual atoms. Series of bonded atoms can form a variety of shapes, but they are still composed of a number of individual spheres and their corresponding atoms.

Here is a nice illustration that conveys these concepts:

Now that you know how to approach these diagrams. It is time to analyze them.

**Electronegativity**

The most important thing to consider when analyzing an electrostatic potential map is the charge distribution. The relative distributions of electrons will allow you to deduce everything you need to know from these maps. Consequently, you will want to be very familiar with principles of electronegativity.
Recall the relationship between electrostatic potential and charge distribution. Areas of low potential, red, are characterized by an abundance of electrons. Areas of high potential, blue, are characterized by a relative absence of electrons. Oxygen has a higher electronegativity value than sulfur. Oxygen atoms would consequently have a higher electron density around them than sulfur atoms. Thus the spherical region that corresponds to an oxygen atom would have a red portion on it. Now note that there are two oxygen atoms in sulfur dioxide. There are two sphere shaped objects that have red regions. These areas correspond to the location of the oxygen atoms. The blue tainted sphere at the top corresponds to the location of the sulfur atom.

**Bond Characteristics**

Electrostatic potential maps can also be used to determine the nature of the molecules chemical bond. Consider this diagram again:
There is a great deal of intermediary potential energy, the non red or blue regions, in this diagram. This indicates that the electronegativity difference is not very great. In a molecule with a great electronegativity difference, charge is very polarized, and there are significant differences in electron density in different regions of the molecule. This great electronegativity difference leads to regions that are almost entirely red and almost entirely blue. Greater regions of intermediary potential, yellow and green, and smaller or no regions of extreme potential, red and blue, are key indicators of a smaller electronegativity difference. Note that the electronegativity difference is a key determinant in the nature of a chemical bond. Additionally, sulfur dioxide is characterized by covalent bonds.

Outside Links

- http://people.reed.edu/~alan/ACS97/elpot.html
- http://academic.reed.edu/chemistry/...atic_maps.html
- http://www.chem.ucsb.edu/~kalju/chem...ual_elpot.html
- http://academic.pgcc.edu/~ssinex/pol...y/polarity.htm

Problems

All figures follow the conventional color spectrum with blue indicating the area of highest electrostatic potential, and red being area of lowest electrostatic potential.

1. Indicate the area of greatest electron concentration:

2. The following diagram is an electrostatic potential map of phosphoric acid. What regions correspond to atoms of oxygen, hydrogen, and phosphorous respectively?
3. The following electrostatic potential diagram, the ball and stick model in the center is simply a convenience, depicts a molecule composed of chlorine and oxygen. What is the structural formula?

4. Indicate the region of greatest electronegativity:

5. Which molecule has a greater electronegativity difference?
Solutions

1. The red region corresponds to the region of greatest electron density. Recall that the area of lowest electrostatic potential corresponds to the area of greatest electron concentration.

2. You do not need to know the molecular structure to answer this question. You do need to know the relative electronegative values of these atoms. Oxygen has the greatest electronegative value, phosphorous the second most, and hydrogen has the smallest electronegative value. Simply by knowing this, you can deduce that oxygen would be affiliated with the red region or red-ish regions of the diagram, and hydrogen would be affiliated with the blue region. Phosphorous would fall in between these two extremes, in the green region.

Here is the molecular diagram of phosphoric acid:
3. The molecular formula of the diagram is \(\text{ClO}_2\). This can be deduced from the electronegativity values of the chlorine and oxygen.

4. The red region of this diagram corresponds to region of greatest electronegativity.

5. Molecule B has a greater electronegativity difference. The greater the electronegativity difference, the less intermediary values, represented as intermediary colors, there are.

References


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