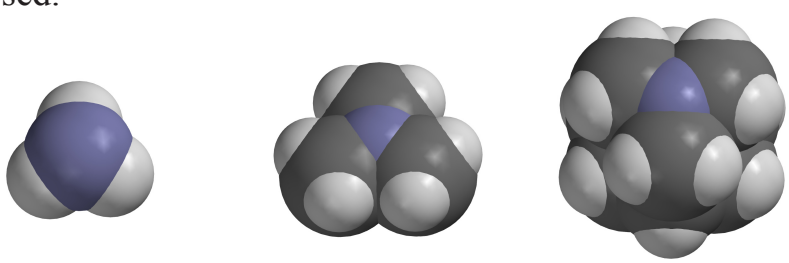
ELECTRON DENSITIES: SIZES AND SHAPES OF MOLECULES

How big is an atom or a molecule? Atoms and molecules require a certain amount of space, but how much? We know that gases can be compressed into a smaller volume but only so far, and that liquids and solids are very difficult is not nearly impossible to compress. While the individual atoms or molecules in a gas are widely separated and can be pushed into a much smaller volume, the atoms or molecules in a liquid or a solid are already close together and cannot be squeezed much further. Atoms can be talked about as having well-defined size. What is it?

Space-Filling Models

Chemists have long tried to answer the size question by using a special set of molecular models known as space-filling or CPK models. The space-filling model for an atom is simply a sphere of fixed radius. A different radius is chosen for each element in order to reproduce certain experimental observations, such as the compressibility of a gas, or the spacing between atoms in a crystal. Space-filling models for molecules consist of a set of interpenetrating atomic spheres. This reflects the idea that the chemical bonds that hold the molecule together cause the atoms to move closer together than the sum of the radii for the individual space-filling models. Interpenetration can be used as a criterion for chemical bonding. If two atomic spheres in a space-filling model strongly interpenetrate then the atoms must be bonded. Space-filling models not only show how big molecules are, but also show which parts of the molecule are shielded and which are exposed.

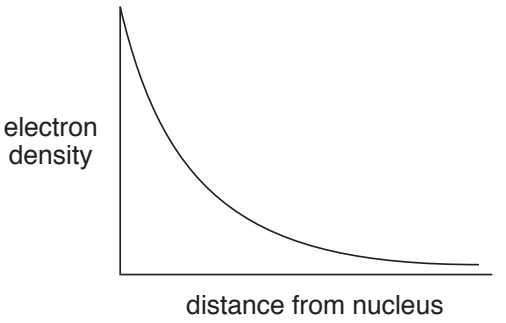


space-filling models for ammonia (left), trimethylamine (center) and 1-azaadamantane (right)

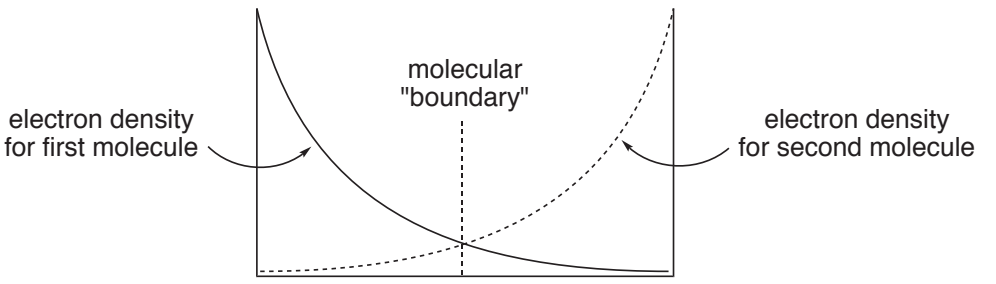
Open ***amines space filling*** in the ***topics*** directory. Space-filling models for ammonia, trimethylamine and 1-azaadamantane all appear on screen. Carbon atoms are colored dark grey, hydrogen atoms white and nitrogen blue. Note that the models clearly reveal the extent to which the nitrogen is exposed. Close ***amines space filling*** when you are finished.

Electron Density Surfaces

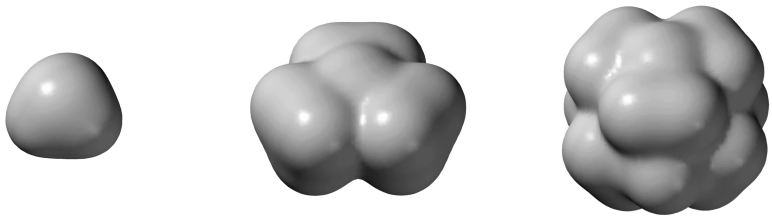
An alternative technique for portraying molecular size and shape relies on the molecule's own electron cloud. Atoms and molecules are made up of positively-charged nuclei surrounded by a negatively-charged electron cloud, and it is the size and shape of the electron cloud and not that of the nuclear skeleton that defines the size and shape of an atom or molecule. The size and shape of an electron cloud is described by the electron density (the number of electrons per unit volume). Consider a graph of electron density in the hydrogen atom as a function of distance from the nucleus.



The graph brings up a problem for chemists seeking to define atomic and molecular size, in that the electron cloud lacks a clear boundary. While electron density decays rapidly with distance from the nucleus, nowhere does it fall to zero. Therefore, when atoms and molecules rub up against each other, their electron clouds overlap and merge to a small extent.



This suggests that molecular size and shape is ill defined and that the best that can be done is to pick a value of the electron density, and to connect together all the points that have this value. The criteria for selecting this value is exactly the same as that for selecting atomic radii in space-filling models, the only difference being that only a single parameter (the value of the electron density) is involved (rather than a different radius for each element). The result is an electron density surface which, just like a space-filling model, is intended to depict overall molecular size and shape.



electron density surfaces for ammonia (left), trimethylamine (center) and 1-azaadamantane (right)

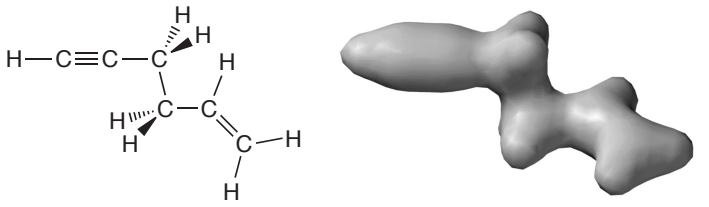
Open ***amines electron density*** in the ***topics*** directory. Electron density surfaces for ammonia, trimethylamine and 1-azaadamantane all appear on screen. Switch to a mesh or transparent surface in order to see the underlying skeletal model. *Click* on one of the surfaces, and select **Mesh** or **Transparent** from the menu which appears at the bottom right of the screen. With mesh selected, change the model to **Space Filling** (**Model** menu). This allows you to see how similar the electron density representation is to that offered by a simple space-filling model. Close ***amines electron density*** when you are finished.

Both space-filling models (atomic radii) and electron density models can be chosen to yield similar molecular volumes, and both show differences in overall size among molecules. Because the electron density surfaces provide no discernible boundaries between atoms, the surfaces may appear to be less informative than space-filling models in helping to decide to what extent a particular atom is exposed. This raises an important point. Electrons are associated with a molecule as a whole and not with individual atoms. The space-filling representation of a molecule with its discernible atomic boundaries does not reflect reality.

Bond Density Surfaces

More closely representing a conventional Lewis structure is a so-called ***bond density surface***, where the boundary corresponds to a much higher value of the electron density*. As such a surface is located much closer to the atomic nuclei, it encloses a relatively small volume, and does not give a correct impression of molecular size.

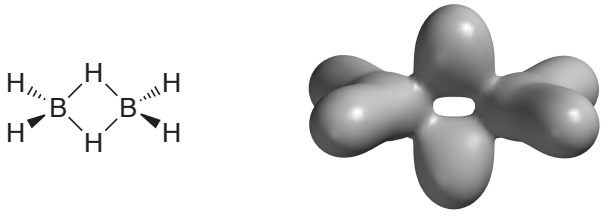
The bond density surface for hex-5-ene-1-yne clearly shows which atoms are connected, although it does not clearly distinguish single, double and triple carbon-carbon bonds.



bond density surface for hex-5-ene-1-yne

Open ***hex-5-ene-1-yne bond density*** in the ***topics*** directory, and switch to a mesh or transparent surface to see the connection between the chemical bonds in a conventional model and the electron density. Close ***hex-5-ene-1-yne bond density*** when you are finished.

The usefulness of the bond density surface is more apparent in the following model of diborane. The surface clearly shows that there is relatively little electron density between the two borons, suggesting the absence of a boron-boron bond. This is information extracted from the bond density surface model, and has been obtained without reference to any preconceived ideas about the bonding in diborane.

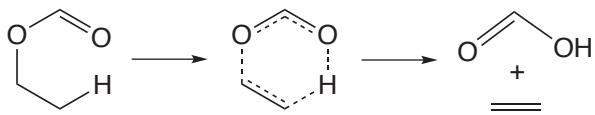


bond density surface for diborane

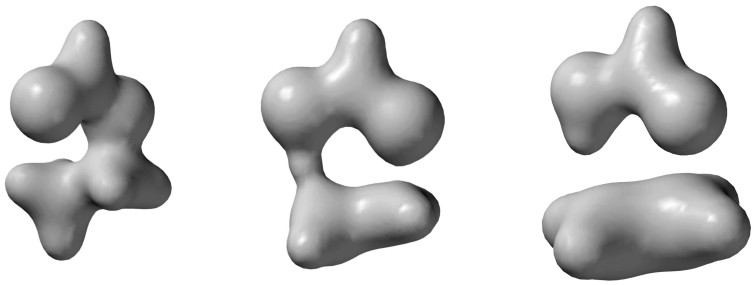
* An even higher value of the electron density leads to a surface in which only nearly spherical regions of electron density around the non-hydrogen atoms are portrayed. This serves to locate the positions of these atoms and is the basis of the X-ray diffraction experiment.

Open ***diborane bond density*** in the ***topics*** directory, and switch to a mesh or transparent surface to see how few electrons actually accumulate in the region between the two borons. Close ***diborane bond density*** when you are finished.

Bond density surfaces can also be informative in describing changes in bonding in moving from reactants to products through a transition state in a chemical reaction. For example, heating ethyl formate causes the molecule to fragment into two new molecules, formic acid and ethylene. A line drawing can show which bonds are affected by the overall reaction, but it cannot tell us if these changes occur all at once, sequentially, or in some other fashion.



On the other hand, the bond density surface is able to provide quantitative information.



bond density surfaces for the reactant, ethyl formate (left), pyrolysis transition state (center) and for the products, formic acid and ethylene (right)

Comparison of the bond density surface in the pyrolysis transition state with those of the reactant and the products suggests that the CO single bond of the reactant is clearly broken in the transition state and that the migrating hydrogen seems more tightly bound to oxygen (as in the product) than to carbon (as in the reactant). It can be concluded that the transition state more closely resembles the products than the reactants, and this provides an example of what chemists refer to as a late (product-like) transition state.

To see the smooth change in electron density throughout the course of the ethyl formate pyrolysis reaction, open ***pyrolysis bond density*** in the ***topics*** directory. *Click* on ▶| at the bottom left of the screen to animate the graphic (*click* on ⏸ to stop the animation). Switch to a mesh or transparent surface to follow the change in bonding. Close ***pyrolysis bond density*** when you are finished.