

7.2: Classification of Chemical Bonds

To make a quantitative assessment of the type of binding present in a particular molecule it is necessary to have a measure of the extent of charge transfer present in the molecule relative to the charge distributions of the separated atoms. This information is contained in the density difference or bond density distribution, the distribution obtained by subtracting the atomic densities from the molecular charge distribution. Such a distribution provides a detailed measure of the net reorganization of the charge densities of the separated atoms accompanying the formation of the molecule.

The density distribution resulting from the overlap of the undistorted atomic densities (the distribution which is subtracted from the molecular distribution) does not place sufficient charge density in the binding region to balance the nuclear forces of repulsion. The regions of charge increase in a bond density map are, therefore, the regions to which charge is transferred relative to the separated atoms to obtain a state of electrostatic equilibrium and hence a chemical bond. Thus we may use the location of this charge increase relative to the positions of the nuclei to characterize the bond and to obtain an explanation for its electrostatic stability.

In covalent binding we shall find that the forces binding the nuclei are exerted by an increase in the charge density which is shared mutually between them. In ionic binding both nuclei are bound by a charge increase which is localized in the region of a single nucleus.

Covalent Binding

The bond density map of the nitrogen molecule (Fig. 7-2) is illustrative of the characteristics of covalent binding.

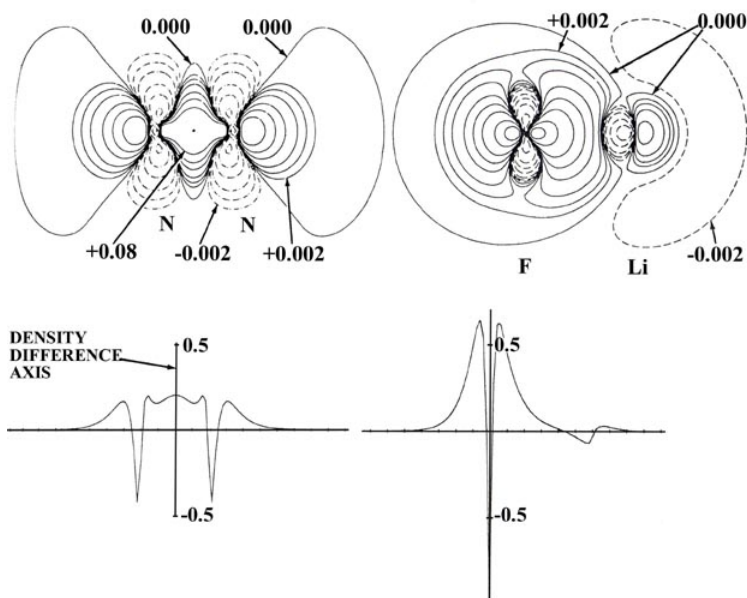


Fig. 7-2. Bond density (or density difference) maps and their profiles along the internuclear axis for N_2 and LiF . The solid and dashed lines represent an increase and a decrease respectively in the molecular charge density relative to the overlapped atomic distributions. These maps contrast the two possible extremes of the manner in which the original atomic charge densities may be redistributed to obtain a chemical bond. [Click here for contour values.](#)

The principal feature of this map is a large accumulation of charge density in the binding region, corresponding in this case to a total increase of one quarter of an electronic charge. As noted in the study of the total charge distribution, charge density is also transferred to the antibinding regions of the nuclei but the amount transferred to either region, $0.13 e^-$, is less than is accumulated in the binding region. The charge density of the original atoms is decreased in regions perpendicular to the bond at the positions of the nuclei. In three dimensions, the regions of charge deficit correspond to two continuous rings or roughly doughnut-shaped regions encircling the bond axis.

The increase in charge density in the antibinding regions and the removal of charge density from the immediate regions of the nuclei result in an increase in the forces of repulsion exerted on the nuclei, forces resulting from the close approach of the two atoms and from the partial overlap of their density distributions. The repulsive forces are obviously balanced by the forces exerted on the nuclei by the *shared* increase in charge density located in the binding region.

A bond is classified as covalent when the bond density distribution indicates that the charge increase responsible for the binding of the nuclei is shared by both nuclei. It is not necessary for covalent binding that the density increase in the binding region be shared equally as in the completely symmetrical case of N_2 . We shall encounter heteronuclear molecules (molecules with different nuclei) in which the net force binding the nuclei is exerted by a density increase which, while shared, is not shared equally between the two nuclei.

The pattern of charge rearrangement in the bond density map for N_2 is, aside from the accumulation of charge density in the binding region, quite distinct from that found for H_2 (Fig. 6-10), another but simpler example of covalent binding. The pattern observed for nitrogen, a charge increase concentrated along the bond axis in both the binding and antibinding regions and a removal of charge density from a region perpendicular to the axis, is characteristic of atoms which in the orbital model of bonding employ p atomic orbitals in forming the bond. Since a p orbital concentrates charge density on opposite sides of a nucleus, the large buildup of charge density in the antibinding regions is to be expected.

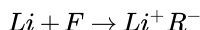
In the orbital theory of the hydrogen molecule, the bond is the result of the overlap of s orbitals. The bond density map in this case is characterized by a simple transfer of charge from the antibinding to the binding region since s orbitals do not possess the strong directional or nodal properties of p orbitals. Further examples of both types of charge rearrangements or polarizations will be illustrated below.

Ionic Binding

We shall preface our discussion of the bond density map for ionic binding with a calculation of the change in energy associated with the formation of the bond in LiF. While the calculation will be relatively crude and based on a very simple model, it will illustrate that the complete transfer of valence charge density from one atom to another in forming a molecule is in certain cases energetically possible.

Lithium possesses the electronic configuration $1s^2 2s^1$ and is from group IA of the periodic table. It possesses a very low ionization potential and an electron affinity which is zero for all practical purposes. Fluorine is from group VIIA and has a configuration $1s^2 2s^2 2p^5$. It possesses a high ionization potential and a high electron affinity. The following calculation will illustrate that the $2s$ electron of Li could conceivably be transferred completely to the $2p$ shell of orbitals on F in which there is a single vacancy. This would result in the formation of a molecule best described as Li^+F^- , and in the electron configurations $1s^2$ for Li^+ and $1s^2 2s^2 2p^6$ for F^- .

We can calculate the energy change for the reaction



in stages. The energy which must be supplied to ionize the $1s$ electron on the Li atom is:



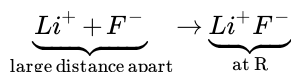
with $E_1 = I_1 = 5.4 \text{ eV}$.

The energy released when an electron combines with an F atom is given by the electron affinity of F:



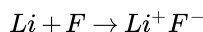
with $E_2 = -3.7 \text{ eV}$.

The two ions are oppositely charged and will attract one another. The energy released when the two ions approach one another from infinity to form the LiF molecule is easily estimated. To a first approximation it is simply $-e^2/R$ where R is the final equilibrium distance between the two ions in the molecule:



with $E_3 \approx -4 \text{ eV}$.

The sum of these three reactions gives



and the overall change in energy is the sum of the three energy changes, or approximately -2 eV. The species Li^+F^- possesses a lower energy than the separated Li and F atoms and should therefore be a stable molecule.

The transfer of charge density from lithium to fluorine is very evident in the bond density map for LiF (Fig. 7-2). The charge density of the 2s electron on the lithium atom is a very diffuse distribution and consequently the negative contours in the bond density map denoting its removal are of large spatial extent but small in magnitude. The principal charge increase is nearly symmetrically arranged about the fluorine nucleus and is completely encompassed by a single nodal surface. The total charge increase on fluorine amounts to approximately one electronic charge. The charge increase in the antibinding region of the lithium nucleus corresponds to only 0.01 electronic charges. (The great disparity in the magnitudes of the charge increases on lithium and fluorine are most strikingly portrayed in the profile of the bond density map, also shown in Fig. 7-2) It is equally important to realize that the charge increase on lithium occurs within the region of the 1s inner shell or core density and not in the region of the valence density. Thus the slight charge increase on lithium is primarily a result of a polarization of its core density and not of an accumulation of valence density.

The pattern of charge increase and charge removal in the region of the fluorine, while similar to that for a nitrogen nucleus in N_2 , is much more symmetrical, and the charge density corresponds very closely to the distribution obtained from a single $2p$ electron. Thus the simple orbital model of the bond in LiF which describes the bond as a transfer of the 2s electron on lithium to the single $2p$ s vacancy on fluorine is a remarkably good one.

While the bond density map for LiF substantiates the concept of charge transfer and the formation of Li^+ and F^- ions it also indicates that the charge distributions of both ions are polarized. The charge increase in the binding region of fluorine exceeds slightly that in its antibinding region (the F^- ion is polarized towards the Li^+ ion) and the charge distribution of the Li^+ ion is polarized away from the fluorine. A consideration of the forces exerted on the nuclei in this case will demonstrate that these polarizations are a necessary requirement for the attainment of electrostatic equilibrium in the face of a complete charge transfer from lithium to fluorine.

Consider first the forces acting on the nuclei in the simple model of the ionic bond, the model which ignores the polarizations of the ions and pictures the molecule as two closed-shell spherical ions in mutual contact. If the charge density of the Li^+ ion is spherical it will exert no net force on the lithium nucleus. The F^- ion possesses ten electrons and, since the charge density on the F^- ion is also considered to be spherical, the attractive force this density exerts on the Li nucleus is the same as that obtained for all ten electrons concentrated at the fluorine nucleus. Nine of these electrons will screen the nine positive nuclear charges on fluorine from the lithium nucleus. The net force on the lithium nucleus is, therefore, one of attraction because of the one excess negative charge on F.

For the molecule to be stable, the final force on the lithium nucleus must be zero. This can be achieved by a distortion of the spherical charge distribution of the Li^+ ion. If a small amount of the 1s charge density on lithium is removed from the region adjacent to fluorine and placed on the side of the lithium nucleus away from the fluorine, i.e., the charge distribution is polarized away from the fluorine, it will exert a force on the lithium nucleus in a direction away from the fluorine. Thus the force on the lithium nucleus in an ionic bond can be zero only if the charge density of the Li^+ ion is polarized away from the negative end of the molecule.

A similar consideration of the forces exerted on the fluorine nucleus demonstrates that the F^- ion density must also be polarized. The fluorine nucleus experiences a net force of repulsion because of the presence of the lithium ion. The two negative charges centred on lithium screen only two of its three nuclear charges. Therefore, the charge density of the F^- ion must be polarized **towards** the lithium in order to exert an attractive force on the fluorine nucleus which will balance the repulsive force arising from the presence of the Li^+ ion. Thus both nuclei in the LiF molecule are bound by the increase in charge density localized in the region of the fluorine.

The charge distribution of a molecule with an ionic bond will necessarily be characterized not only by the transfer of electronic charge from one atom to another, but also by a polarization of each of the resulting ions in a direction counter to the transfer of charge, as indicated in the bond density map for LiF.

In a covalent bond the increase in charge density which binds both nuclei is shared between them. In an ionic bond both nuclei are bound by the forces exerted by the charge density localized on a single nucleus.

The bond density maps for N_2 and LiF are shown side by side to provide a contrast of the changes in the atomic charge densities responsible for the two extremes of chemical binding. **In a covalent bond the increase in charge density which binds both nuclei**

is shared between them. In an ionic bond both nuclei are bound by the forces exerted by the charge density localized on a single nucleus. It must be stressed that there is no fundamental difference between the forces responsible for a covalent or an ionic bond. They are electrostatic in each case.

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