Field homogeneity errors are apparent in the measured centroids of single lines in undercycled and overcycled[4] fields, and a slightly overcycled field is the most likely source of the low-field average in Table I.

In many cases it should be possible to utilize the centroids of spectra to distinguish among alternative solutions to a chemical structure problem. To do so, it is necessary that some predictable difference in chemical shifts be of sufficient magnitude to deflect the average. For example, a detailed study of the proton magnetic resonance spectra of *trans*-norbornene dimers has established[10] that the pairwise interactions depicted below cause mutual, paramagnetic shifts of about 0.3 p.p.m. in the case of I and 0.6 p.p.m. in the

(10) D. R. Arnold, D. T. Trecker, and E. B. Whipple, *J. Am. Chem. Soc.*, 87, 2596 (1965).

case of III. Apart from these, the only shifts which vary appreciably with configuration are those resulting from exocyclic or endocyclic environments for the protons on the four-membered ring. In I there are four endocyclic protons and four interacting pairs of the first type, in III there are four exocyclic protons and four interacting pairs of the second type, while II has two protons and two interactions of each type. The shifts combine to displace the centroid of I to higher field than II and III to lower field than II by approximately $1.8/N$ p.p.m., where N is the number of protons per molecule.

This situation is not altered by substitution in positions not involved directly in the interactions I or III, so that the configurations of various dimers of substituted norbornenes could be assigned simply by comparing the centroids of their n.m.r. spectra.

The Ionic Bond

R. F. W. Bader[1] and W. H. Henneker

Contribution from the Burke Chemical Laboratories, McMaster University, Hamilton, Ontario, Canada. Received March 12, 1965

The model chosen to define the ionic bond is that of two oppositely charged spheres, each slightly polarized by the electric field of the other. The properties of the one-electron density distribution obtained from the Hartree–Fock wave function for LiF are compared with those of the model to determine how closely the bond in LiF approaches the ionic case. This comparison is carried out in terms of the forces exerted on the nuclei and by a direct comparison of the molecular density distribution with that of the ions Li^+F^-.

Introduction

An increasing number of Hartree–Fock wave functions are being made available for simple molecules. While the molecular binding energies predicted by these wave functions are too small by an amount equal to the correlation energy of the electrons, the derived one-electron density distribution and those properties which are determined by this distribution are correct to the second order.[2] Thus, a meaningful discussion of chemical bonding can be carried out in terms of Hartree–Fock one-electron density distributions and their dependent properties. The force acting on a nucleus in a molecule is an example of such a property, and, since this force is rigorously determined by classical electrostatics,[3] it provides an excellent basis for the discussion of chemical binding.[4] What is indeed available through these quantum mechanically determined density distributions is a classical description of the chemical bond.

We shall apply such an analysis to the bond in the lithium fluoride molecule.

The lithium fluoride molecule possesses a dipole moment of 6.284 D.[5] The separation of equal and opposite charges at the observed lithium fluoride bond length gives a dipole moment of 7.51 D. It is obvious that this molecule will possess a highly ionic bond by any previous definition of the work "ionic." According to Pauling's[6] definition of ionicity as the ratio of the observed dipole moment to that obtained for complete charge separation, the lithium fluoride molecule is 84% ionic and 16% covalent. With a Hartree–Fock density distribution available for this molecule, such useful but ambiguous definitions of bonding should be improved upon. The simplest physically realizable model of an ionic bond is that of two oppositely charged ions in contact, each necessarily polarized to a slight extent by the electric field of the other. We choose this as our definition of an ionic bond. This definition relates a purely ionic bond to the *complete transfer* of one or more units of negative charge. Slight distortions of the spherical charge distributions of the ions must be allowed for, or the ionic bond becomes a physically unrealizable situation. These small polarizations reduce the dipole moment due to the complete transfer of charge. Thus, as Rittner has pointed out,[7] the observation of a dipole moment less than that calculated for complete charge separation does not rule out the possibility that the transfer of one electronic charge from one atom to the other is complete. We shall investigate how closely the Hartree–

(1) A. P. Sloan Research Fellow.
(2) For a recent review of this matter see C. W. Kern and M. Karplus, *J. Chem. Phys.*, 40, 1374 (1964).
(3) R. P. Feynman, *Phys. Rev.*, 56, 340 (1939); H. Hellmann, "Einfuhrung in die Quantenchemie," F. Deuticke, Leipzig, 1937, p. 285.
(4) R. F. W. Bader, *Can. J. Chem.*, 41, 2303 (1963); R. F. W. Bader and G. A. Jones, *ibid.*, 41, 2251 (1963).

(5) L. Wharton, W. Klemperer, L. P. Gold, R. Strauch, J. J. Gallagher, and V. E. Derr, *J. Chem. Phys.*, 38, 1203 (1963).
(6) L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1960.
(7) E. S. Rittner, *J. Chem. Phys.*, 19, 1030 (1951).

Fock density distribution for LiF meets this definition by (a) comparing the forces acting on the nuclei calculated from the Hartree–Fock density with those predicted by the model and (b) by a direct comparison of the Hartree–Fock electron density distribution with that of Li^+F^-.

An SCF wave function has been obtained for the LiF molecule by McLean[8] using a basis set of 21 STO's for Li and F. At the equilibrium internuclear distance the forces acting on the Li and F nuclei are calculated to be -0.051 and -0.102 a.u., respectively.[9] The calculated dipole moment, another property dependent upon the one-electron density, is 6.2974 D. The small net forces and the small error in the dipole moment both indicate that the wave function is close to the Hartree–Fock limit.

An Interpretation of the Binding in Terms of the Forces Acting on the Nuclei

The force acting on a nucleus in a molecule is the sum of the electrostatic forces of repulsion due to the other nuclei and of attraction due to the electron density which is treated as a continuous distribution of negative charge. For a diatomic molecule A–B with an internuclear separation R, the force on nucleus A along the bond is (in a.u.)

$$F_A = Z_A Z_B / R^2 - Z_A \int [\rho(\vec{r}) \cos \theta_A / r_A^2] d\tau$$

where $\rho(\vec{r})$ gives the value of the negative charge density at each point in three-dimensional space and $\cos \theta_A / r_A^2$ is the operator which gives the component of force on nucleus A due to the density at $\vec{r}$. For an orbital approximation to a wave function the total electron density is given by

$$\rho(\vec{r}) = \sum_i n_i \phi_i^2$$

where the ϕ_i are the normalized molecular orbitals and the n_i are occupation numbers equal to 1 or 2. Each m.o. makes a separate contribution to the density, and thus the total electronic force may also be broken up into a sum of orbital contributions. It is convenient[4] to define a quantity f_{iA} for each orbital as the force exerted on nucleus A by the density in the ith m.o. multiplied by R^2/Z_A. This gives a dimensionless number, and the total force may now be expressed as

$$F_A = \frac{Z_A}{R^2}(Z_B - \sum_i f_{iA})$$

Division of an f_{iA} by R^2 gives the value of the electric field at A due to the charge density in the ith m.o. The electrostatic force on nucleus A is the charge at A (Z_A) multiplied by this electric field. The f_{iA} and f_{iB} values for a given orbital allow one to compare the electric fields at both A and B due to the density in the ith m.o. When R is very large or when it equals the equilibrium value R_e, F_A (and F_B) must be zero and $\sum_i f_{iA} = Z_B$ (and $\sum_i f_{iB} = Z_A$). To gain an understanding of the part each m.o. plays in the formation of a molecule, it is useful to compare the f_{iA} values for large R and R_e. A m.o. in a heteronuclear molecule may, at large values of R, correlate with an atomic orbital centered on just one of the nuclei, or it may correlate with a pair of a.o.'s, one centered on each nucleus. In either case the f_{iA} value, at large values of R, will reduce to the orbital occupation number n_{iB} of the correlated a.o. on B. This is a result of the fact that at this limit the charge density on B exerts a field at A equal to that obtained from an equivalent number of point charges located at the B nucleus. If the ith m.o. correlates with an orbital on A alone, then f_{iA} is zero for large values of R. For example, in LiF the most stable m.o., the 1σ, correlates with the doubly occupied 1s a.o. on F. For large values of R the Li nucleus is completely external to the 1s charge density on F. Consequently, $f_{1\sigma\ Li} = 2.00$ as the two electrons in this orbital screen two units of positive charge on the F nucleus. The force this density exerts on the Li nucleus is $-2(Z_{Li}/R^2)$. This same orbital density is symmetrically placed with respect to the F nucleus and exerts no force on it. Consequently, $f_{1\sigma\ F} = 0.00$. When the molecule dissociates into neutral atoms, the sum of the f_{iA} values will equal the total number of electrons on B, which in turn equals Z_B. Hence, $F_A = 0$ as it must for large values of R. For values of R encountered in molecules, however, the f_{iA} values give more information than do orbital occupation numbers. At R_e, the value of f_{iA} may be greater than, equal to, or less than n_{iB}. These three possibilities are termed binding, nonbinding, and antibinding, respectively, and are thus comparative measures of the role the density in each m.o. plays in the molecule relative to the simple screening effect it exerted for large values of R. For example, the value of $f_{1\sigma\ Li} = 2.00$ even at R_e. This indicates that the 1s electrons on F, which comprise the 1σ m.o., continue simply to screen an equivalent number of F nuclear charges from the Li nucleus and are not involved in or perturbed by the formation of the molecule. For a binding orbital, $f_{iA} > n_{iB}$ indicating that on the close approach of the atoms the electron density is transferred to the region between the nuclei where it exerts a force in *excess* of the simple screening effect. Similarly, when $f_{iA} < n_{iB}$, the density no longer shields an equivalent number of nuclear charges resulting in a *net* repulsive force as R is decreased.[10]

When the m.o.'s are constructed from a linear combination of atomic orbitals, the density expression for each m.o. will consist of a sum of products of atomic orbitals of the form $c_i c_j \phi_{iA} \phi_{jB}$, where c_i and c_j are the orbital coefficients and ϕ_i denotes the type of atomic orbital situated on nucleus A or B. We thus obtain three basic electron populations, the atomic population terms $\phi_{iA}\phi_{jA}$ or $\phi_{iB}\phi_{jB}$ and the overlap population $\phi_{iA}\phi_{jB}$. Each of these three electron populations gives rise to its own distinct contribution to the force acting on a particular nucleus.

Atomic Force. The atomic force is the force exerted on nucleus A by the density centered on A, $\phi_{iA}\phi_{jA}$. If $\phi_{iA}\phi_{jA}$ possesses a center of symmetry, then this density will not exert a force on nucleus A. However, the introduction of any asymmetry due to polarization (*i.e.*, sp or pd hybridization) gives rise to a force on nucleus A. Consequently, the atomic force

(8) A. D. McLean, *J. Chem. Phys.*, 39, 2653 (1963).
(9) The direction of a positive force on either nucleus corresponds to nuclear repulsion. 1 a.u. of force $= e^2/a_0^2 = 8.2378 \times 10^{-3}$ dyne.
(10) In the case of a homonuclear diatomic, the expression for the force is $F = (Z/R^2)\sum_i(1 - f_i)$. The limiting value of each f_i value is $n_i/2$ as each a.o. contributes to the formation of two m.o.'s, the g and u combinations.[4]

term is sensitive to the degree of charge polarization on a nucleus.

Screening Force. The screening force is the force exerted on nucleus A by the atomic charge density centered entirely on another nucleus, $\phi_{iB}\phi_{jB}$. It is a measure of the electronic shielding of nucleus B from nucleus A and the amount of this shielding is determined by the extent to which nucleus A penetrates the density around B. When $\phi_{iB}\phi_{jB}$ possesses spherical symmetry, the screening force has a particularly simple physical interpretation. According to Gauss' law, the field resulting from a spherical charge distribution acts as though all the charge were concentrated at its origin, and only that charge within the sphere defined by the bond length is effective. Thus, the screening contribution to an f_i value for spherical orbitals is numerically equal to the number of electrons contained in a sphere of radius equal to the bond length, and the corresponding force is the same number divided by R^2. The electron density in a p_σ orbital on B, since it places charge along the bond axis, exerts a screening force greater than the same amount of density spherically disposed. Electrons in p_π orbitals, on the other hand, are less effective than s electrons at shielding since their density is principally directed perpendicular to the bond axis.[11]

Overlap Force. The overlap force is the force on nucleus A due to the density in $\phi_{iA}\phi_{jB}$ which results from the overlap of two atomic orbitals. Such overlap results in the transfer of charge density to the region between the two nuclei, and the overlap force is a sensitive measure of the effectiveness of this transferred density in binding the two nuclei together.

In Table I the orbitals are listed in order of increasing energy. The m.o.'s are indicated opposite the a.o.'s with which they correlate for large values of R. The next column lists the f_i values for the forces acting on the Li nucleus for the case of large R, *i.e.*, a vanishingly small interaction between the atoms. At this limit the density on the Li atom does not contribute to the f_i values as this density is spherically disposed with respect to the Li nucleus. Thus, only the screening effect of the F electron density contributes to the f_i. The screening contribution equals the number of electrons in the correlated orbital on F regardless of the symmetry of the orbital in this limit of vanishingly small forces. The limiting value of $f_{4\sigma}$ is unity rather than 2 as it correlates with the singly occupied orbitals 2s on Li and $2p_\sigma$ on F. It will be seen that it is the redistribution of charge associated with the formation of the 4σ-orbital which is primarily responsible for the bond in LiF.

On the formation of the molecule $f_{1\sigma\text{ Li}}$ remains equal to 2.00, and this is due entirely to a screening contribution. This fact coupled with the absence of any atomic or overlap contribution shows that the 1σ m.o. is still primarily a 1s orbital on F and is nonbinding. The 1s orbital on Li is, however, perturbed at R_e. The small values of the screening and overlap contributions to $f_{2\sigma}$ show that no large amount of charge has been transferred from the 1s Li orbital, but the large atomic force term indicates a strong polarization of this density. The negative sign indicates that

density has been concentrated on the side of the Li nucleus away from F. Over-all, the 2σ-density exerts a net antibinding force as this density exerts no force on Li for large R. The 3σ-orbital is almost nonbinding in the molecule as the major contribution to the f_i value remains a screening effect of two nuclear charges. The small amount of 3σ-density on Li is again polarized away from F. The most striking change in force occurs for the 4σ-orbital. The value of $f_{4\sigma}$ is practically doubled, and the most important contribution is from a screening effect, *i.e.*, density situated entirely on F. The density on F in this orbital screens more than twice as many nuclear charges as it did for large values of R where there was but a single electron in the $2p_\sigma$ orbital. Charge has clearly been transferred from the Li 2s orbital to the F $2p_\sigma$. The completeness of the transfer is illustrated in the small value of the overlap contribution. While there is an overlap density, it is far from being equally shared and is close to the F nucleus. The density remaining on the Li nucleus is again back-polarized. The orbital is net binding by almost a factor of 2. The π-density is net antibinding due to the poor screening effect of this density on close approach of the atoms. The π-density does make the largest overlap contribution of all the orbitals to the force on the nuclei.

The electronic and nuclear forces acting on the Li nucleus in LiF come close to those predicted by the model chosen to define an ionic bond. In the case of complete charge transfer, the Li nucleus will experience a screening effect due to ten electrons and a nuclear repulsion due to only nine positive charges. Thus, to achieve electrostatic equilibrium, the density on Li$^+$ must be polarized *away* from the F$^-$ ion. In addition, for complete charge transfer there should be no overlap contribution to the force. The total atomic force contribution recorded in Table I shows that the density on Li is indeed back-polarized so as to overcome a net attractive pull by the F end of the molecule. The increase in the screening force from 9 (for large R) to 9.5 for $R = R_e$ indicates a net transfer of charge from Li to F. The fact that the screening contribution is less than 10 is due primarily to the ineffective screening of the π-density and not to a large transfer of charge to the overlap region. The total overlap contribution is, in fact, very small. In a covalent bond the reverse is found. For example, in a similar analysis[4] of Ransil's wave function[12] for N_2 the total screening contribution was found to *decrease* from 7 ($=Z_N$) for large R to 5.4 at R_e, and the overlap contribution of 3.0 was of comparable importance. The $3\sigma_g$-orbital, which is the principal binding orbital in N_2 can be contrasted with the 4σ-orbital in LiF. In LiF the screening contribution more than doubles while in N_2 it is decreased by almost the same factor. In LiF the overlap contribution to 4σ is negligible while in N_2 the overlap contribution for the binding orbital exceeds the screening contribution.

Table II lists a similar breakdown of the forces acting on the F nucleus. The f_i values of the 1σ- and 2σ-orbitals are now reversed from what they were for Li. The 1σ-orbital exerts only a small atomic force since it is primarily a slightly polarized 1s a.o. on F. The 2σ-orbital is primarily the 1s a.o. on Li, and thus the screening contribution is approximately 2. (It is less

(11) In previous publications[4] the screening contribution to the force was termed a penetration effect.

(12) B. J. Ransil, *Rev. Mod. Phys.*, **32**, 245 (1960).

Table I. Forces on the Li Nucleus

Li a.o.'s	F a.o.'s	LiF m.o.'s	f_{iLi} large R	f_{iLi} R_e	Atomic contribution	Overlap contribution	Screening contribution
1s²	1s²	1σ	2.000	2.000	0.000	0.000	2.000
		2σ	0.000	−0.289	−0.362	0.070	0.003
	2s²	3σ	2.000	1.956	−0.064	0.016	2.004
2s¹	2p_σ¹	4σ	1.000	1.984	−0.296	0.080	2.200
	2p_π⁴	π	4.000	3.494	0.010	0.180	3.304
		Totals	9.000	9.145	−0.712	0.346	9.511

Table II. Forces on the F Nucleus

Li a.o.'s	F a.o.'s	LiF m.o.'s	f_{iF} large R	f_{iF} R_e	Atomic contribution	Overlap contribution	Screening contribution
1s²	1s²	1σ	0.000	0.100	0.099	0.001	0.000
		2σ	2.000	2.007	0.007	0.028	1.972
	2s²	3σ	0.000	0.731	0.636	0.081	0.014
2s¹	2p_σ¹	4σ	1.000	−0.366	−1.148	0.739	0.043
	2p_π⁴	π	0.000	0.622	0.474	0.136	0.012
		Totals	3.000	3.094	0.068	0.985	2.041

than 2 owing to the back-polarization of the 2s orbital on Li). The small screening contribution for the 3σ-orbital again indicates that its density is mostly on F. The large atomic term shows that it is strongly polarized toward the Li nucleus. The forces on Li for the 4σ-orbital indicated that the transfer of charge from Li to F was almost complete as the contribution to the screening of the F nucleus from the Li nucleus was doubled. Thus, the same m.o. should *not* contribute to the screening of the Li nucleus from the F. This is indeed found as the 4σ-density remaining on Li screens only 0.04 unit of positive charge (as opposed to 1 unit for large R). There is a significant contribution to the force on the F nucleus in the 4σ-orbital from the overlap charge density. However, this overlap density is shared very unequally between the Li and F nuclei as this same overlap charge density exerted an electric field of only $0.08/R_e^2$ at Li compared to a field of $0.74/R_e^2$ at F. Thus, even the "shared" density in the bonding orbital is close to being completely transferred to the F nucleus. Very little of the π-electron density is transferred to the Li nucleus as the screening contribution from the π-orbital is very small. Again, however, as in the force on Li, there is a contribution to the force from the π-overlap density. Chemists have frequently speculated that in spite of the great electronegativity of F, π-electron density of the F atom may be transferred back into the molecule. This is precisely what is found for LiF. Furthermore, the overlap contribution to $f_{πLi}$ is almost the same as that for $f_{πF}$ indicating that this overlap density is almost equally shared by both nuclei. (Since the f_i values do not involve the nuclear charges, a contribution to the density distribution which exerts an equal electric field at each nucleus will make an equal contribution to both f_{iA} and f_{iB}.) According to the model defining the ionic bond, the nucleus of a *spherical* F⁻ ion should experience a net repulsive force of 1 unit exerted by the Li⁺ ion. Then, to achieve electrostatic equilibrium, the F⁻ density must polarize toward the Li nucleus. The net atomic force on F is in the direction required. In addition, the total screening force for F is approximately 2, indicating that the F nucleus sees the Li nucleus

and its associated charge density as a unit positive charge as required by the model.

Any chemical bond, ionic or covalent, results from the accumulation of negative charge density in the region between the nuclei to an extent sufficient to balance the nuclear forces of repulsion. However, the terms ionic and covalent are useful as they represent the two possible extremes of arriving at this state of electrostatic equilibrium. In a covalent bond this is accomplished by moving charge density off of both nuclei (decreasing the screening contribution to the force on each) and concentrating it symmetrically in the region between the nuclei (large and equal contributions to the forces from the overlap or "shared" density).[13] The ionic bond attains electrostatic equilibrium through a very asymmetric charge distribution. The screening experienced by the positive ion should increase by 1 unit, and that for the negative ion should decrease by 1 unit corresponding to the transfer of an electron from one atom to the other. In addition, the density on the positive ion must be polarized away from the negative ion and that on the negative ion must be polarized toward the positive ion. The overlap forces should ideally be zero. Even if small forces are present owing to density shared by both nuclei, the force this density exerts on the anion will be much greater than that on the cation illustrating again the highly unsymmetrical nature of the charge distribution.

The Electron Density Distribution

In Figure 1 the total electron density distribution is shown for a plane through the LiF molecule. In Figure 2 the difference between the density distributions of the molecule and the Li and F atoms (separated at a distance R_e) is shown.[14] Such a density difference map shows clearly the rearrangement in the charge density which accompanies the formation of the

(13) The atomic force could conceivably operate in either direction in a covalent bond. No accurate Hartree–Fock wave function for a covalent molecule has as yet been examined in this manner.

(14) The electron density distributions for the atomic cases were calculated from the wave functions given by E. Clementi, C. C. J. Roothaan, and M. Yoshimine, *Phys. Rev.*, **127**, 1618 (1962).
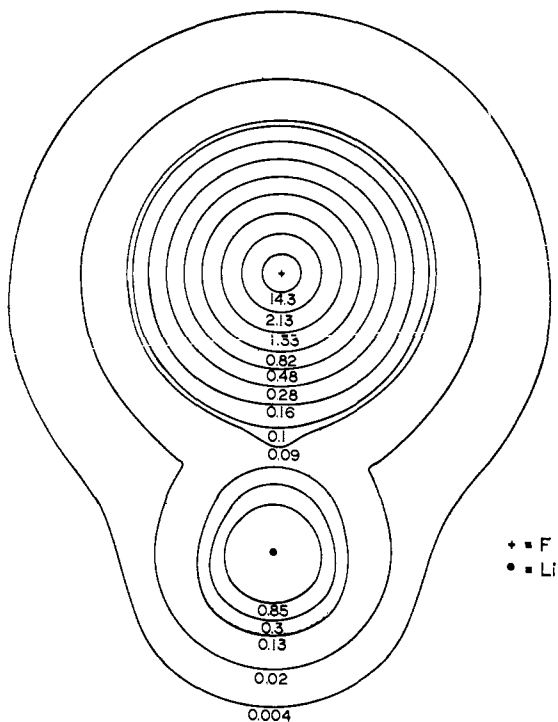
Figure 1. The electron density distribution in a plane for the LiF molecule. The density contours are in atomic units (1 a.u. = $e/a_0{}^3$).

molecule. The F atom density is that for the valence state corresponding to the configuration $1s^2 2s^2 2p_\sigma{}^1 2p_\pi{}^4$. The density around F has increased over that found in the isolated atom. This is clearly indicated by the large diameter of the zero contour line around F. It should be recalled that this plot shows only the migration of charge density, and thus the large area of increased charge density around F is not the result of the initially greater amount of charge at this center. The two lobes of negative values perpendicular to the molecular axis at F illustrate the decrease in the π-electron density. The force analysis indicated that this was transferred primarily to the region between the two nuclei. Charge has been removed from the region in front of the Li nucleus and slightly increased in the region behind it. Since the charge density in the Li+ ion is more contracted than in the Li atom, the charge density is increased in the vicinity directly behind and close to the Li nucleus. These positive contours extend only a short distance. Beyond the zero line the charge density is decreased, and over-all the density around Li is less than it was in the atom. This is most clearly indicated in Figure 3 where the density difference between the molecule and the ions Li+ and F⁻ (separated at R_e) is shown.[15] This map shows most clearly how close the LiF molecule approaches the ionic state. The contours in this difference plot are of smaller magnitude than those of Figure 2, illustrating that LiF approximates the ionic density quite closely. The charge polarizations are clearly indicated. Over-all, the F density is slightly more contracted than that of an isolated F⁻ ion and is polarized toward Li.

(15) The electron density distribution for the Li+ ion was calculated from the wave function given by C. C. J. Roothaan, L. M. Sachs, and A. W. Weiss, *Rev. Mod. Phys.*, **32**, 186 (1960), and that for the F⁻ ion from the work of L. C. Allen, *J. Chem. Phys.*, **34**, 1156 (1961).
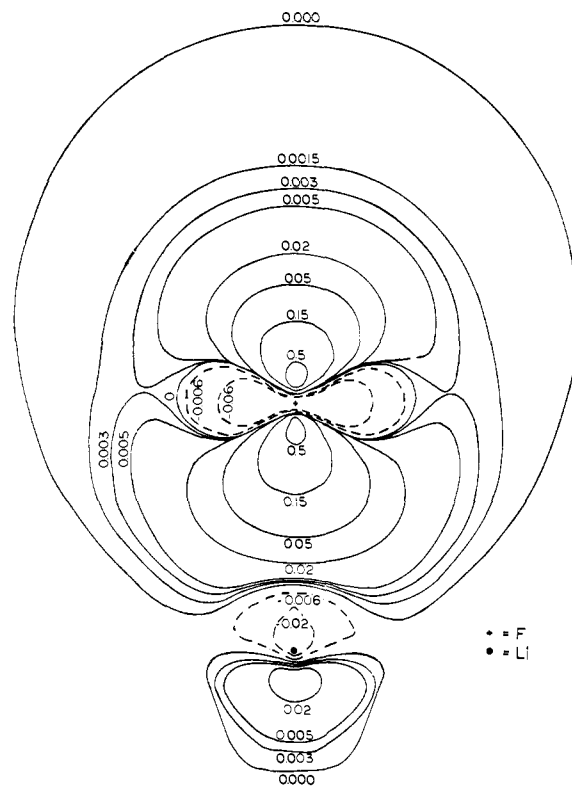
Figure 2. An electron density difference map between the LiF molecule and the Li and F atoms. A positive contour denotes an increase in the electron density.

The Li approximates quite closely a Li+ ion slightly polarized away from the F.

Figure 4 is a density difference plot (molecular minus atomic) calculated from a simple orbital wave function for the hydrogen molecule. The symmetrical movement of charge associated with the formation of a covalent bond is to be contrasted with the very asymmetrical charge migration depicted in Figure 2. Figure 4 shows clearly the decrease in the total density from the regions behind each nucleus and its symmetrical concentration in the overlap region. In LiF, while there is a slight preponderance of charge density on the Li side of the F, an almost equal amount has been transferred to the region behind the F nucleus. This difference in the two figures bears out the interpretation given to the covalent and ionic bonds in terms of the contributions to the electronic forces. The primary contribution to the force in a covalent bond is from the shared or overlap density. The density originally symmetrically placed around each nucleus (the screening contribution) is decreased. In the ionic bond, however, it is the increased screening of one nucleus which makes the primary contribution to the force binding the nuclei together. Thus, the transferred density in the ionic case should be almost symmetrically placed around one nucleus, rather than between the two nuclei.

While any breakdown of the density distribution or the electronic force is artificial, the concepts of screening, overlap, and atomic forces do reflect the most important characteristics of the redistribution of charge which can occur on the formation of a molecule. The analysis of the forces exerted on the nuclei by the electron density distribution allows one to draw the
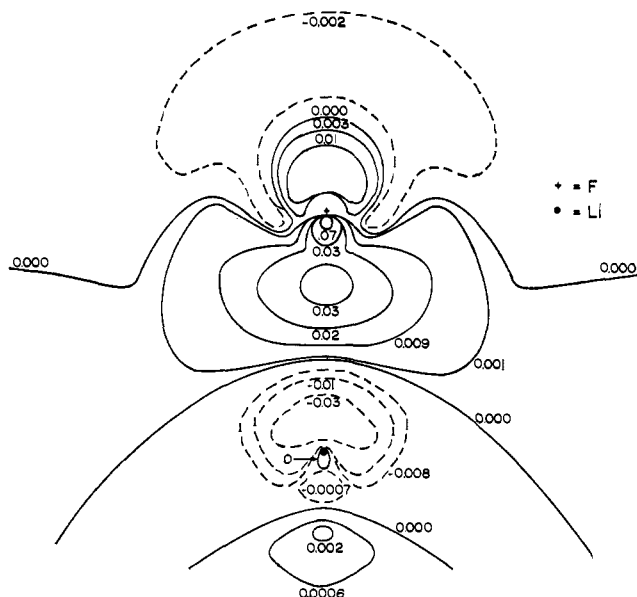
Figure 3. An electron density difference map between the LiF molecule and the Li⁺ and F⁻ ions.

Figure 4. An electron density difference map between the H₂ molecule and two H atoms.

following conclusions regarding the binding in LiF. The 1σ, 2σ, and 3σ m.o.'s are best described as polarized F 1s, Li 1s, and F 2s *atomic* orbitals, respectively. The polarizations are reflected in the atomic force contributions, particularly for the Li 1s and F 2s orbitals. Their essentially atomic character is illustrated by the fact that the density in each of these orbitals screens two units of nuclear charge as it does in the case of the separated atoms. Furthermore, the contributions to the forces from the overlap density is almost negligible. The Li 2s and F $2p_\sigma$ orbitals do interact strongly. The forces exerted by the density in the 4σ-orbital closely approximate those predicted for an ionic bond. The completeness of the charge transfer is evidenced by the decrease in the screening of the Li nucleus by approximately one unit and by a corresponding increase in the screening of the F nucleus by the same amount. Thus, charge is transferred primarily to the F atom itself and not to the overlap region. The charge transferred to the F is also strongly polarized away from the Li nucleus. The completeness of the charge transfer in the 4σ-orbital is again illustrated by the forces exerted by its overlap density. This density exerts an electric field on the F nucleus ten times greater than that on the Li nucleus. Thus, the overlap density binds the F nucleus much more than it does the Li
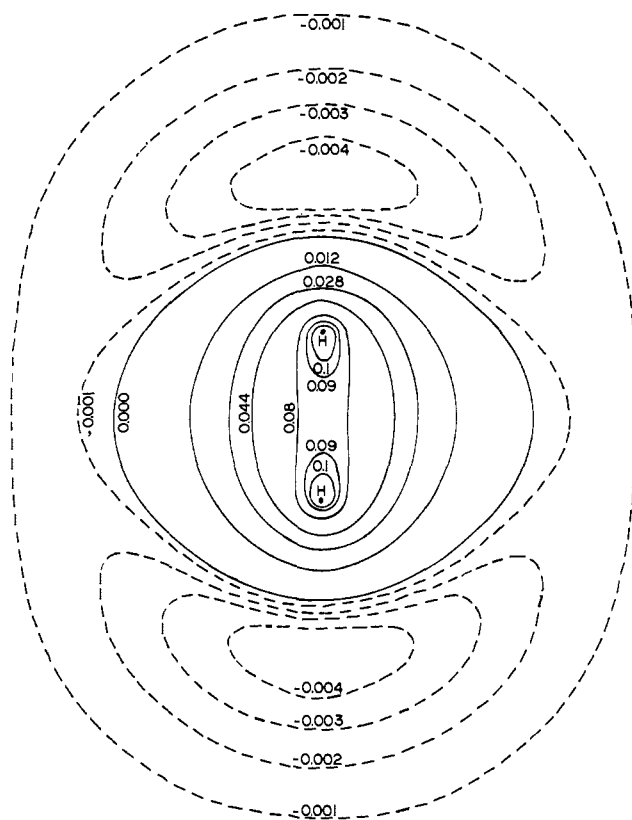
nucleus.[16] It is the density in the 4σ-orbital which exerts the net attractive force on the Li nucleus, but, owing to the strong polarization of the density on F, this same density exerts an antibinding force on F. This adverse force on F is counterbalanced by the polarization in the 3σ-orbital and by the π-bond in LiF. On the formation of the molecule the π-density on F is polarized toward Li and thus exerts a binding force on the F nucleus. In addition, charge density is transferred to the overlap region where it attracts both nuclei. Thus, while the σ-density is ionic in character, corresponding to almost complete transfer of charge to the F, the π-density, in addition to being polarized, exerts small but almost equal overlap forces on both nuclei in the manner of a weak covalent bond.

(16) A population analysis suffers from the defect that overlap populations are arbitrarily equally divided between the two nuclei. The force analysis clearly shows any asymmetry in the distribution of the overlap population by comparing the forces this density exerts on both nuclei.