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Electron Correlation and the Charge Distribution in Lithium Hydride

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The redistribution of charge density as a consequence of electron correlation has been examined for LiH. Two correlated wave functions of differing complexity were analyzed. A natural orbital formulation allowed a first natural configuration to be considered as a noncorrelated limit. Thus, we minimized difficulties associated with different basis sets being used for correlated and noncorrelated calculations. In this way, by means of density difference maps, our examination of the changes in electron distribution concerned the influence of correlation introduced within the confines of each model. Both correlation maps indicated an expansion of the molecular charge cloud. The electron density increased at each nucleus and a reduction of charge occurred in the internuclear region. In a relatively extensive region around each nucleus, the density difference contours exhibited characteristics of split-shell correlation similar to those possessed by two-electron ions.

I. Introduction

Wave functions derived from Hartree-Fock-Roothaan calculations¹ have given rise to energies which are a close approximation to the true Hartree-Fock limit for many atoms and molecules. The preeminence of such independent-particle models lies in their physical and procedural simplicity. However, because the Hartree-Fock treatment itself makes no allowance for electron correlation² other than through the Fermi hole, the calculated energy can be in error by an amount comparable with the bond dissociation energy. In addition, electron correlation is usually necessary for a correct theoretical description of adiabatic dissociation.

With the advent of sophisticated computers, correlated wave functions are now becoming available for several small systems. Clearly, it is of considerable interest to examine the influence of electron correlation on the electronic structure. In this respect, although the determination of various one- and two-particle expectation values can be quite illuminating they are, of necessity, integrated properties of the wave function. Consequently, their sensitivity to localized changes in the density may well be limited. Therefore, it seems worthwhile to study the molecular charge distribution itself. Density maps and difference maps derived from noncorrelated wave functions for molecules have already been analyzed by several other workers.³⁻⁵ However, in this article, we examine the changes in the charge distribution which occur as a consequence of introducing some allowance for electron correlation at different levels of approximation. The need for such an investigation has been stressed by various workers.^{5,6}

As an example, we have considered the ground state of LiH at its equilibrium bond length. Two different treatments have been examined. Firstly, the wave function determined by Palke and Goddard⁷ and, secondly, the extensive configuration-interaction (CI) calculation of Bender and Davidson⁸ based on the use of

natural orbitals.⁹ Although other wave functions have been reported,^{10,11} the choice of the Bender and Davidson⁸ calculation was particularly pertinent since, at the time, it was energetically the best treatment of LiH. The result has only recently been improved upon by Boys and Handy,¹² who used a transcorrelated wave function. The Palke and Goddard wave function is of interest in its own right and also represents some intermediate step toward a CI function since it leads to significantly better energies than the Hartree-Fock method and yet retains an independent-particle interpretation.

II. Difference Maps, Wave Functions, and Electron Densities

The characteristics of a density difference map are

- (1) C. C. J. Roothaan, *Rev. Mod. Phys.*, **23**, 69 (1951).
- (2) An excellent discussion of electron correlation and correlation energy has been given by P. O. Lowdin, *Advan. Chem. Phys.*, **2**, 207 (1959).
- (3) See for example, T. Berlin, *J. Chem. Phys.*, **19**, 208 (1951); R. F. W. Bader, *J. Amer. Chem. Soc.*, **86**, 5070 (1964); A. C. Wahl, *Science*, **151**, 961 (1966); P. Politzer and R. E. Brown, *J. Chem. Phys.*, **45**, 451 (1966); R. F. W. Bader, W. H. Henneker, and P. E. Cade, *ibid.*, **46**, 3341 (1967); B. J. Ransil and J. Sinai, *ibid.*, **46**, 4050 (1967); P. E. Cade, R. F. W. Bader, W. H. Henneker, and I. Keaveny, *ibid.*, **50**, 5313 (1969); I. Cohn and K. D. Carlson, *J. Phys. Chem.*, **73**, 1356 (1969); D. B. Boyd, *J. Chem. Phys.*, **52**, 4846 (1970).
- (4) R. F. W. Bader, I. Keaveny, and P. E. Cade, *ibid.*, **47**, 3381 (1967).
- (5) C. W. Kern and M. Karplus, *ibid.*, **40**, 1374 (1964).
- (6) P. E. Cade and W. M. Huo, *ibid.*, **47**, 614 (1967).
- (7) W. E. Palke and W. A. Goddard, III, *ibid.*, **50**, 4524 (1969).
- (8) C. F. Bender and E. R. Davidson, *J. Phys. Chem.*, **70**, 2675 (1966).
- (9) P. O. Lowdin, *Phys. Rev.*, **97**, 1474 (1955); **97**, 1490 (1955); **97**, 1509 (1955); see also, P. O. Lowdin and H. Shull, *Phys. Rev.*, **101**, 1730 (1956).
- (10) For example, the separated electron-pair study of LiH by D. D. Ebbing and R. C. Henderson, *J. Chem. Phys.*, **42**, 2225 (1965). See also R. C. Sahni, B. C. Sawhney, and M. J. Hanley, *ibid.*, **51**, 539 (1969).
- (11) C. F. Bender and E. R. Davidson, *ibid.*, **49**, 4222 (1968).
- (12) S. F. Boys and N. C. Handy, *Proc. Roy. Soc., Ser. A*, **311**, 309 (1969).

obviously very dependent on the nature of the reference density from which the differences are measured. Since the amount of correlation energy contained within a calculation is normally measured as the improvement in energy over the Hartree-Fock result, the true Hartree-Fock density would be an ideal reference function for any study of electron correlation. Unfortunately, such densities exist for a very few systems. Although the Hartree-Fock-Roothaan (HFR) procedure can give rise to reliable energies, Kern and Karplus⁵ have shown that energetically comparable results based on different basis functions can possess variations in electron density equal in magnitude to those which arise from properties of chemical interest. To avoid this difficulty, we recall that the reformulation of a correlated wave function Ψ in terms of a natural spin orbital analysis⁹ helps to minimize the influence of the composition of the original basis set. Further, when the normalized Ψ is expressed as a sum of configurations built up from the natural spin orbitals, this natural expansion of the wave function is distinguished as the superposition of configurations of most rapid convergence toward the energy value E given by $\langle \Psi | H | \Psi \rangle$, where H is the Hamiltonian of the system. The first natural configuration has also been found¹³ to bear a striking resemblance to the Hartree-Fock result in terms of energy and total overlap. The relationship between natural orbitals and Hartree-Fock orbitals has been discussed by several workers:^{14,15} for example, Davidson and Jones¹⁴ showed for H_2 that the difference between such orbitals is almost equal to the f function introduced by Sinanoğlu¹⁶ in the expansion of an N -particle wave function. The f functions represent corrections to the Hartree-Fock orbitals as a consequence of correlation and, in general, their contribution to the energy is very small.¹⁵ Thus, for each correlated treatment of LiH, we used the first natural configuration to determine a corresponding noncorrelated reference density. By means of a density difference function, derived by subtracting this reference density from the associated correlated density, we can examine charge redistributions which arise from influences of correlation effects¹⁷ contained within each wave function.

We now discuss the wave functions considered in this analysis. For an N -particle system, Goddard¹⁸ expressed the total wave function as

$$\Psi(1, 2, 3, \dots, N) = G_i^\mu \Phi(1, 2, 3, \dots, N) \chi(1, 2, 3, \dots, N)$$

where Φ is a space function and χ is a product of one-electron spin functions. G_i^μ is a projection operator¹⁹ determined by the properties of a permutation group S_N such that $\Psi(1, 2, 3, \dots, N)$ is antisymmetric and also a spin eigenfunction. For LiH, Palke and Goddard⁷ used the G1 method and wrote

$$\Phi(1, 2, 3, 4) = \phi_1(1)\phi_2(2)\phi_3(3)\phi_4(4)$$

where each ϕ_j was a two-center molecular orbital (MO) given by

$$\phi_j = \sum_m C_{jm} \psi_m$$

The coefficients C_{jm} were determined by the variation method. The basis set $\{\psi_m\}$ was composed of Slater-type orbitals (STO's) 1s, 1s', 2s, 3s, 2p σ , 2p' σ , and 3d σ located on the Li nucleus and 1s, 2s, and 2p σ centered on H. The total wave function involved a linear combination of 24 possible products of four basis MO's and the coefficients in the linear combination were determined by the operator G_1^μ . Such a calculation corresponds to a variational valence bond approach in which electron correlation has been introduced, essentially, by means of a different-orbitals-for-different-spins (DODS) scheme.

The CI calculation of Bender and Davidson, which involved the direct use of natural orbitals (NO's), accounted for 89.1% of the correlation energy for LiH. Briefly, Bender and Davidson describe their CI-NO technique as follows: an estimation of the

Table I: Total Energies and Correlation Energies for LiH, Li⁺, and H⁻

System	Method	-Energy, au	- E_{corr} , au	% corr
LiH	CI-NO ^a	8.0606	0.0733	89.1
	G1 ^b	8.0173	0.0300	36.5
	HF ^c	7.9873		0 ^e
Li ⁺	Expt ^d	8.0696	0.0823	100 ^e
	CI	7.2792	0.0428	98.4
	HF	7.2364		0 ^e
H ⁻	Expt	7.2799	0.0435	100 ^e
	CI	0.5275	0.0395	99.2
	HF	0.4880		0 ^e
	Expt	0.5278	0.0398	100 ^e

^a Reference 8. ^b Reference 7. ^c The HFR value from ref 6. ^d Corrected for relativistic effects, see ref 6. ^e By definition, see ref 2 and 21. ^f Results quoted from ref 21.

(13) G. P. Barnett, J. Linderberg, and H. Shull, *J. Chem. Phys.*, **43**, 80 (1965); B. G. Anex and H. Shull, "Molecular Orbitals in Chemistry, Physics, and Biology," P. O. Lowdin and B. Pullman, Ed., Academic Press, New York, N. Y., 1964, p 227; G. V. Nazarov and J. O. Hirschfelder, *J. Chem. Phys.*, **39**, 715 (1963).

(14) E. R. Davidson and L. L. Jones, *ibid.*, **37**, 2966 (1962).

(15) O. Sinanoğlu, *Rev. Mod. Phys.*, **35**, 517 (1963). See also O. Sinanoğlu and D. F. Tuan, *J. Chem. Phys.*, **38**, 1740 (1963), and O. Sinanoğlu, *Advan. Chem. Phys.*, **6**, 315 (1964).

(16) O. Sinanoğlu, *J. Chem. Phys.*, **36**, 706 (1962).

(17) Within the present scheme of analysis, pair correlation terms will constitute the first, and dominant, correction for electron correlation interaction; see ref 15 and 16.

(18) W. A. Goddard III, *Phys. Rev.*, **157**, 81 (1967).

(19) G_i^μ is such that μ is the representation of S_N required by the spin state of the system and i indicates which of the f^μ -fold degenerate spin functions in μ is to be considered. For LiH, Palke and Goddard chose $i = 1$ and, hence, G1 is used as a label for both the method and the wave function.

NO's in terms of some chosen basis set, the construction of a reasonable number of configurations from these NO's and the optimization of the resulting CI wave function by variational means, a determination of the subsequent natural orbitals and the iteration of the procedure until the wave function and the natural orbitals converge. For the CI-NO treatment of LiH, the wave function Ψ consisted of 45 spatial configurations built up from an original basis set of 17 elliptical functions; the foci were located on the two nuclei.

In Table I, we quote the molecular and correlation energies²⁰ for LiH obtained from the calculations outlined above. For comparison, Table I includes the HFR energy for LiH determined by Cade and Huo;⁶ corresponding energies for Li^+ and H^- are also given. The correlation energies are defined as the energy improvement relative to the Hartree-Fock approximations.^{2,6,21}

The electron density $\rho(\vec{r})$ associated with a wavefunction $\Psi(1, 2, 3, \dots, N)$ which represents an N electron system can be defined as

$$\rho(\vec{r}) \equiv \rho(\vec{r}_1) = N \int \Psi^*(1, 2, 3, \dots, N) \Psi(1, 2, 3, \dots, N) d\tau_2 d\tau_3 \dots d\tau_N$$

where, in addition, integration is carried out over all spin coordinates. To obtain a noncorrelated reference density, the G_1 wave function of Palke and Goddard was analyzed in terms of natural orbitals χ_k : the transformation matrix $[A_{jk}]$ and the occupation numbers n_k are presented in Table II. As mentioned above, the

Table II: Transformation Matrix $[A_{jk}]$ and Occupation Numbers n_k for the NO Analysis of the G_1 Wave Function for LiH^a

ϕ_j/χ_k	x_1	x_2	x_3	x_4
ϕ_{1a}	0.50632	-0.07993	-0.11185	-2.68115
ϕ_{1b}	0.51038	-0.08054	-0.03191	2.73686
ϕ_{2a}	0.00719	0.54304	1.44508	-0.39132
ϕ_{2b}	0.00694	0.53560	-1.42928	0.18407
n_k	0.99959	0.98104	0.01802	0.00137

^a See ref 7 for details of the molecular orbitals ϕ_j .

CI-NO wave function of Bender and Davidson is already in a suitable form. Thus, the first natural configuration^{9,13} arising from each calculation for LiH was used to obtain a corresponding noncorrelated density. Such quantities, indicated by a subscript "n," are denoted by $\rho(\vec{r})_{Gn}$ for the Palke and Goddard (G) treatment and $\rho(\vec{r})_{Bn}$ when evaluated from the first natural configuration for the Bender and Davidson (B) wave function. For each correlated treatment of LiH, the electron density associated with the complete wave function^{7,8} is similarly designated $\rho(\vec{r})_{Gc}$ or $\rho(\vec{r})_{Bc}$.

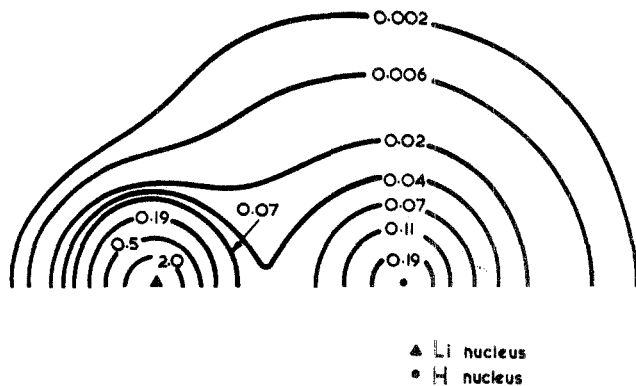


Figure 1. Contour map of the molecular charge density $\rho(\vec{r})$ in a plane containing the bond axis for the ground state of LiH when the internuclear separation $R = 3.015$ au, calculated from the CI-NO wave function of Bender and Davidson.

Each density was normalized to four electrons. The changes in electron density due to electron correlation effects contained within the framework of each treatment of LiH are given by

$$\delta\rho(\vec{r})_G = \rho(\vec{r})_{Gc} - \rho(\vec{r})_{Gn}$$

and

$$\delta\rho(\vec{r})_B = \rho(\vec{r})_{Bc} - \rho(\vec{r})_{Bn}$$

for the G_1 and CI-NO wave functions, respectively.²²

III. Discussion

The electron density for LiH shown in Figure 1, *i.e.*, $\rho(\vec{r})_{Bc}$, has the same general form as that obtained from an HFR wave function.⁴ The contour map for $\rho(\vec{r})_{Bc}$ reveals the existence of two extensive regions of density of almost spherical symmetry, one associated with each nucleus. Thus, as before,⁴ this suggests an Li^+H^- ionic interpretation of the density. This point is emphasized further by the steep gradient of the charge distribution behind the Li nucleus, a feature characteristic of an $\text{Li}^+(1s)^2$ core. A similar behavior was found for $\rho(\vec{r})_{Gc}$.

From the standpoint of our analysis, allowance for correlation effects contained within the wave functions of Palke and Goddard⁷ and Bender and Davidson⁸ cause density changes $\delta\rho(\vec{r})_G$ and $\delta\rho(\vec{r})_B$ shown, respectively, in Figures 2a and 2b. We see that the influence of electron correlation on the molecular charge distribution reveals several features of interest. Both difference maps indicate a reduction of charge density in the mid-bond region and an increase of charge at, and immediately around, each nucleus. Further, an increase in density also occurs in a toroidal outer

(20) Unless stated otherwise, all quantities are expressed in terms of Hartree atomic units.

(21) K. E. Banyard and C. C. Baker, *J. Chem. Phys.*, **51**, 2680 (1969); K. E. Banyard, *ibid.*, **48**, 2121 (1968).

(22) \vec{r} locates a network of grid points (in a plane containing the bond axis) relative to the Li nucleus as an arbitrary origin.

Table III: Electron Densities $\rho(\bar{r})$ Evaluated Along the LiH Molecular Axis (the Internuclear Separation R is 3.015 au and Positive x Is Measured from the Midpoint in the Direction of the H Nucleus)

Density	$x = -2.25$	-2.0	-1.75	-1.50 (\sim Li nucleus)	-1.25	-1.00	-0.75	-0.50	-0.25
$\rho(\bar{r})_{Be^a}$	0.237555	0.869109	3.38835	13.15237	3.04854	0.757670	0.205183	0.070139	0.042297
$\rho(\bar{r})_{Bn^a}$	0.237632	0.870326	3.39194	13.13822	3.05118	0.758401	0.205132	0.070145	0.042565
$\rho(\bar{r})_{Gc^b}$	0.237550	0.868993	3.39548	13.28063	3.05272	0.759684	0.205695	0.069519	0.040850
$\rho(\bar{r})_{Gn^b}$	0.238361	0.871189	3.39215	13.19209	3.04920	0.759786	0.205576	0.070069	0.042070
$\rho(\bar{r})_{HFR^c}$	0.238261	0.871422	3.39076	13.18966	3.04932	0.759721	0.205656	0.070005	0.041926

Density	$x = 0.00$	$+0.25$	$+0.50$	$+0.75$	$+1.00$	$+1.25$	$+1.50$ (\sim H nucleus)	$+1.75$	$+2.00$
$\rho(\bar{r})_{Be^a}$	0.044527	0.057826	0.079247	0.111735	0.162695	0.246134	0.388315	0.231830	0.137023
$\rho(\bar{r})_{Bn^a}$	0.045056	0.058529	0.079928	0.112051	0.162142	0.244089	0.384136	0.230011	0.136442
$\rho(\bar{r})_{Gc^b}$	0.042218	0.054789	0.075996	0.109036	0.160938	0.243554	0.376792	0.230428	0.138459
$\rho(\bar{r})_{Gn^b}$	0.043919	0.056488	0.077145	0.108685	0.158129	0.237925	0.367991	0.224947	0.135411
$\rho(\bar{r})_{HFR^c}$	0.043751	0.056431	0.077089	0.108597	0.157863	0.237432	0.369988	0.222505	0.132801

^a Derived from Bender and Davidson, ref 8. ^b Derived from Palke and Goddard, ref 7. ^c Derived from Cade and Huo, ref 6.

region around the bond axis at the position of the Li nucleus. Results of a similar nature have been observed from a corresponding analysis²³ for HeH⁺. The effect of electron correlation also gives rise to closed negative contours behind the Li nucleus. This implies that, in this region of space, a slight preferential increase of charge has occurred during molecular formation. Such a feature is in general accord with the description by Bader, *et al.*,⁴ of the charge movements associated with ionic bonding.

Some comparison of $\rho(\bar{r})_{Be}$, $\rho(\bar{r})_{Bn}$, $\rho(\bar{r})_{Gc}$, and $\rho(\bar{r})_{Gn}$ can be obtained from inspection of Table III where values of the densities are given for various positions along the LiH molecular axis: $x = 0$ locates the midpoint of the internuclear separation $R = 3.015$ au. As a reference, values for the HFR density are also included in Table III. We see that, in the immediate vicinity of the nuclei, the correlated wave functions yield a charge density which is larger than the appropriate noncorrelated value: also, this trend is carried over to a comparison between the $G1$ correlated results and the HFR values. However, in contrast, the CI-NO density $\rho(\bar{r})_{Be}$ at the Li nucleus is lower than the corresponding HFR result. From the comparisons available in Table III we also note that $\rho(\bar{r})_{Gn}$, rather than $\rho(\bar{r})_{Bn}$, has a better overall agreement with $\rho(\bar{r})_{HFR}$. At this point we recall that, although the HFR, $G1$, and CI-NO calculations each use different basis sets, the HFR and $G1$ results are derived from STO's, whereas the Bender and Davidson calculation was based on elliptical functions. Browne and Matsen²⁴ comment that STO's can give a better representation of the essentially spherical charge distributions near molecular nuclei than elliptical functions, but are not so well suited for a description of the valence electrons. These observations highlight difficulties associated with any direct interpretive comparisons between calculations involving the use of different basis

functions. The dependence of the present quantitative results on the nature of the basis set cannot, of course, be assessed with absolute accuracy. Certainly, this dependence has been minimized through our use of NSO analysis by the fact that the same basis set has been involved in determining the correlated and noncorrelated estimate for the electron densities within the bounds of each calculation examined here.

For each treatment of LiH, the correlated charge cloud is more diffuse throughout space than its noncorrelated counterpart. A measure of this effect was obtained from the shift of the 0.003 contour²⁵ for $\rho(\bar{r})$ at positions both along the LiH axis and perpendicular to it at the midpoint between the nuclei. For convenience, each result was expressed as a percentage of the "size" of the molecule given by the noncorrelated position of the contour. The Bender and Davidson wave function gave relative outward shifts of the 0.003 contour of 1.3% along the Li-H axis and 1.6% in the perpendicular direction: the $G1$ method gave an increase, due to correlation, of 1.6% and 1.8%, respectively. These results are, of course, only a rough guide. Ideally, it would be most instructive to consider how the spatial volume, associated with a fixed large fraction of the charge, changes as a consequence of electron correlation.

A detailed comparison of the correlation maps can be obtained from the $\delta\rho(\bar{r})$ profiles given in Figure 3. The amount of charge redistribution $\delta\rho(\bar{r})_G$ is seen to be greater and spatially more extensive than $\delta\rho(\bar{r})_B$. This behavior would seem to parallel the atomic situation, where the introduction of correlation by a DODS

(23) K. E. Banyard and C. C. Baker, *Int. J. Quan. Chem.*, **4**, 431 (1970).

(24) J. C. Browne and F. A. Matsen, *Phys. Rev.*, **135**, 1227 (1964).

(25) This contour generally contains well over 90% of the total electronic charge and hence provides some assessment of molecular size.

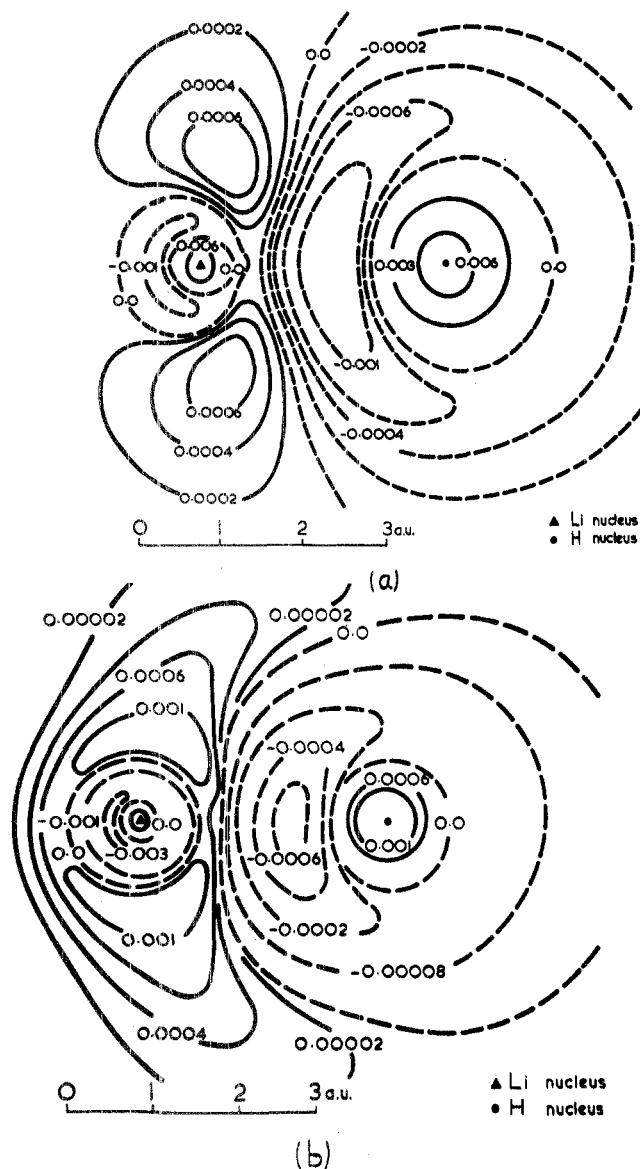


Figure 2. Correlation density difference maps for LiH. (a) $\delta\rho(\vec{r})_G$ arises from correlation effects contained in the $G1$ wave function of Palke and Goddard. (b) $\delta\rho(\vec{r})_B$ is due to correlation effects contained in the CI-NO wave function of Bender and Davidson.

scheme overemphasizes the density change by comparison with the results obtained from the analysis of a CI treatment.²¹ Figures 3b and 3c indicate that, around the Li nucleus, each calculation produces a correlated "split-shell" effect. A similar behavior, but more diffuse, occurs around the H nucleus. These features are also shown in Figure 3a; however, the decrease in charge density due to correlation effects in the internuclear region makes such an interpretation less obvious. An interesting extension of the present analysis would be to examine the behavior of $\delta\rho(\vec{r})$ for the ground state, and perhaps excited states, of LiH as we move from the separated atoms to the united-atom limit.²⁶ Such an examination, based on a dif-

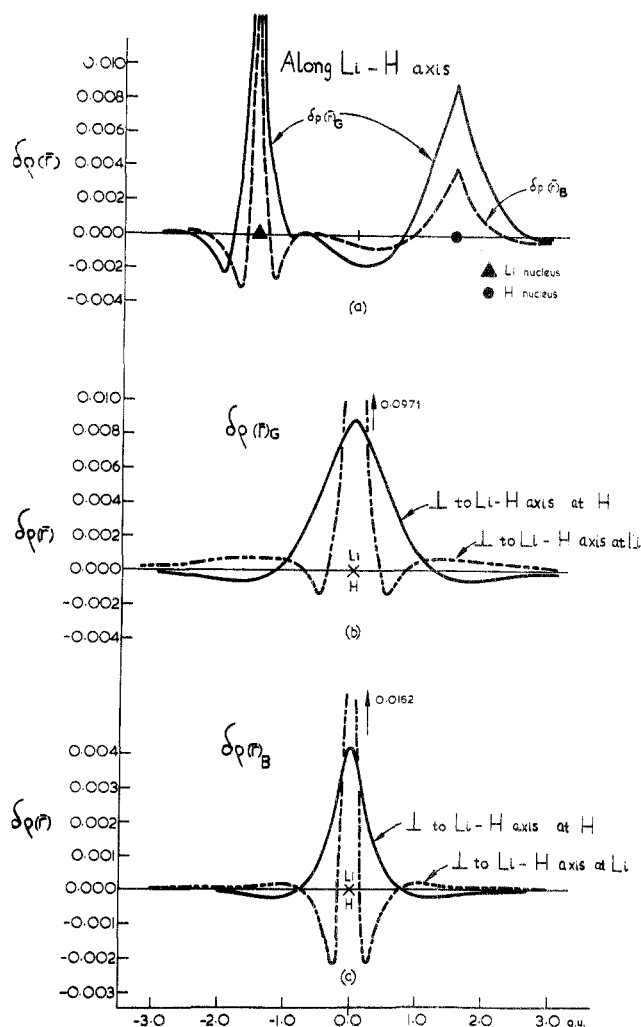


Figure 3. Profiles of $\delta\rho(\vec{r})_G$ and $\delta\rho(\vec{r})_B$. (a) Along the bond axis: solid line represents $\delta\rho(\vec{r})_G$, and the broken line is $\delta\rho(\vec{r})_B$. (b) Values of $\delta\rho(\vec{r})_G$ in a direction perpendicular to the bond axis at the Li nucleus (dashed line) and the H nucleus (solid line), and (c) shows corresponding results for $\delta\rho(\vec{r})_B$.

ferent model, has already been reported²³ for the ground state of HeH⁺.

Finally, a brief comment on the correlation energies² is appropriate. For LiH, E_{cor} is estimated to be 0.0823 au²⁰ where, in the absence of a Hartree-Fock energy, we have used the HFR value as our reference. The $G1$ method recovered only 36.5% of E_{cor} compared with 89.1% for the CI-NO treatment. The difference arises, essentially, from the representation of instantaneous correlation contained in the CI-NO scheme. The limitation of the $G1$ method was reflected, as seen, as an overdifuseness in the correlation map. In conclusion, we note that the value of 0.0823 au for E_{cor}

(26) Energies for LiH as a function of R have been reported recently by Bender and Davidson (ref 11) and Sahni, Sawhney, and Hanley (see ref 10). See also the separated pair calculations for LiH by E. L. Mehler, K. Ruedenberg, and D. M. Silver, *J. Chem. Phys.*, **52**, 1181 (1970). However, at $R = 3.015$ au, none of these calculations is energetically as accurate as the CI-NO wave function analyzed here.

(LiH) is quite close to the total E_{cor} of 0.0833 au associated with the Li^+ and H^- ions.

IV. Summary

The influence on the electron density of correlation effects inherent within each of two correlated wave functions has been investigated for LiH. A natural orbital analysis provided a first natural configuration which was used as a noncorrelated limit. Charge movements were illustrated by means of density difference maps and profile diagrams. The wave functions examined were those of Palke and Goddard and of Bender and Davidson which recovered, respectively, about 36% and 89% of the correlation energy for LiH.

Briefly, although the introduction of correlation effects caused the charge cloud to expand in both calculations, the Palke and Goddard calculation overemphasized the effect by comparison with the CI treatment. This conclusion parallels a similar situation found for atoms. Within the framework of our analysis, electron correlation increased the density at each nucleus and also reduced the charge in the internuclear region. Further, in the vicinity of the nuclei, the charge redistributions exhibited characteristics of split-shell correlation similar to those associated with two-electron ions. Although not part of this investigation, the study suggests some general support for an Li^+H^- interpretation of the bonding in LiH.

Nuclear Magnetic Resonance Spectra and Substituent Effects for Symmetrically Substituted Dihalobiphenyls

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Nmr spectra have been analyzed for the twelve symmetrically substituted dihalobiphenyls. Additivity of substituent effects has been observed for coupling constants and chemical shifts. The effects of substituents on the coupling parameters have been shown to correlate quite well with substituent electronegativity, in agreement with previous work on disubstituted benzenes. Substituent effects on the chemical shifts have been discussed in terms of ring current modification in the second ring and in terms of other well-known mechanisms. Downfield shifts at certain positions have been attributed to steric interactions. An inter-ring seven-bond H-F coupling has been observed in the case of 4,4'-difluorobiphenyl but no such inter-ring coupling was found for 3,3'- or 2,2'-difluorobiphenyl.

Introduction

Considerable interest has been directed toward obtaining and interpreting the nmr parameters of substituted benzenes.²⁻²⁴ Many of these studies have been concerned with additivity of substituent effects on coupling constants and chemical shifts, demonstrating the great utility of additivity values in the analysis and assignments of aromatic nmr spectra. Improvements in spectrometer performance and the availability of high-speed, iterative computer programs for nmr spectral analysis have greatly facilitated the study of these spectra and the resulting very precise values from these analyses have made the study of substituent effects much more reliable. Following the example of previous work,^{22,23,25-35} statistical correlations between substituent electronegativity and nmr coupling param-

eters were established in monohalo- and dihalobenzenes³⁶ where the changes in coupling values with sub-

(1) NDEA Fellow, 1967-1970; Tennessee Eastman Fellow, 1970-1971.

(2) (a) P. L. Corio and B. P. Dailey, *J. Amer. Chem. Soc.*, **78**, 3043 (1956); (b) J. B. Leane and R. E. Richards, *Trans. Faraday Soc.*, **55**, 707 (1959).

(3) I. Yamaguchi and N. Hayakawa, *Bull. Chem. Soc. Jap.*, **33**, 1128 (1960).

(4) P. Diehl, *Helv. Chim. Acta*, **44**, 829 (1961).

(5) H. Spiessicke and W. G. Schneider, *J. Chem. Phys.*, **35**, 731 (1961).

(6) J. C. Schug and J. C. Deck, *ibid.*, **37**, 2618 (1962).

(7) J. Martin and B. P. Dailey, *ibid.*, **37**, 2594 (1962).

(8) J. S. Martin and B. P. Dailey, *ibid.*, **39**, 1722 (1963).

(9) S. Castellano and C. Sun, *J. Amer. Chem. Soc.*, **85**, 380 (1963).

(10) T. K. Wu and B. P. Dailey, *J. Chem. Phys.*, **41**, 2796 (1964).

(11) S. Castellano and J. Lorenc, *J. Phys. Chem.*, **69**, 3552 (1965).