THE ELECTRON DENSITY DISTRIBUTION IN CN⁻, LiCN AND LiNC.
THE USE OF MINIMAL AND EXTENDED BASIS SET SCF MO CALCULATIONS

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Electron density maps are reported for the CN⁻ ion and the LiCN and LiNC molecules, calculated from molecular wavefunctions near the Hartree–Fock limit. The electron density distribution derived from CNDO/2 wavefunctions does not resemble the ab initio results. The ultimate ability of a minimal basis set to represent the electron density near the Hartree–Fock limit, has been tested. The requirement of N-representability of the trial electron density has been satisfied. It is found that the molecular valence density cannot be reproduced to a satisfactory extent by a minimal set of Slater orbitals, even when the exponents of the basis orbitals are optimized.

1. Introduction

The electron density distribution has been the subject of several quantum chemical studies [1–6].

The advances in X-ray and neutron diffraction, especially in the measuring techniques and the processing of the data, have resulted in an increasing accuracy in the experimental determination of the electron density distribution. The difference electron density, i.e. the molecular electron density minus the atomic electron densities, has been observed for a large number of compounds (for example refs. [7,8]). However, not much progress has been made in a quantitative analysis of the observed electron density in terms of parameters that are of direct significance in quantum chemistry. Coppens et al. [9] have developed a method in which the terms of the charge bond order matrix are used as parameters in a least-squares procedure to fit these terms to X-ray diffraction data. In order to remain significant, the number of parameters should be limited to avoid correlation. Consequently the electron density distribution has to be constructed from a limited number of basis functions. A faithful representation of the electron density was obtained with only a minimal set of Slater orbitals. However, in treating the terms of the charge bond order matrix as parameters to be fixed by experiment, Coppens et al. neglected the constraints imposed on this matrix by the requirement of N-representability, as proposed by Massa and Clinton [10,11]. Applying these constraints, a minimal basis set may no longer be able to give an accurate representation of the observed electron density distribution.

In section 2 of this contribution the difference electron density in the CN⁻ ion and the LiCN and LiNC molecules, is calculated from molecular and atomic wavefunctions near the Hartree–Fock limit. In section 3 the possibility is analysed to give an adequate description of the electron density in these molecules, with a state function based on a minimal basis set of Slater orbitals.

2. The difference electron density

The theoretical electron density distribution is given by

$$\rho(r) = \sum_\mu \sum_\nu P_{\mu\nu} \chi_\mu(r) \chi_\nu(r) , \tag{1}$$

where $P_{\mu\nu}$ is a term of the charge bond order matrix and $\chi_\mu(r)$ an atomic basis function.

A difference density map of the CN⁻ ion, calculated on basis of the results of Bonaccorsi et al. [12]
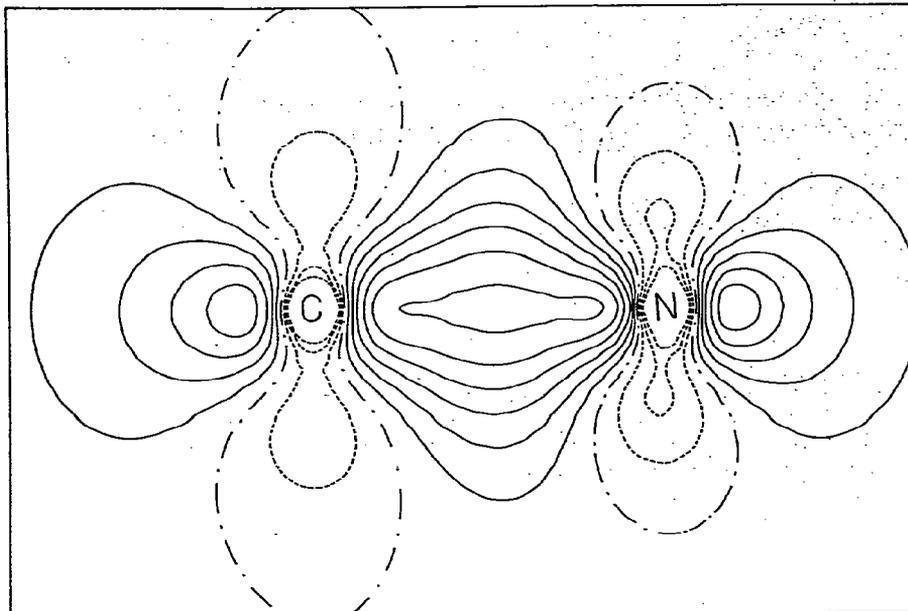
Fig. 1. The difference density in the CN⁻ion, using an extended basis set. Contour interval: 0.025 e/au^3.

and Clementi [13] for the molecular and atomic wave-functions respectively, is shown in fig. 1. The molecular wavefunction is based on a double zeta Slater basis including polarization functions and is supposed to lead to a close representation of the electron densi- ty at the Hartree–Fock limit [4,5]. Similar differ- ence density maps for LiCN and LiNC molecules, shown in figs. 2 and 3, are derived from the molecular wavefunctions given by Bak, Clementi and Kortze-born [14] which are based on 45 contracted gaussian
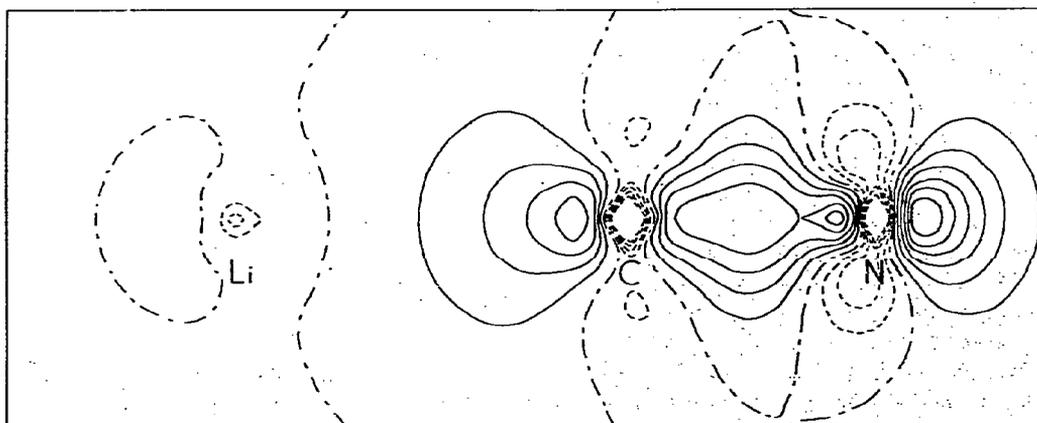

Fig. 2. The difference density in LiCN, using an extended basis set. Contours as in fig. 1.
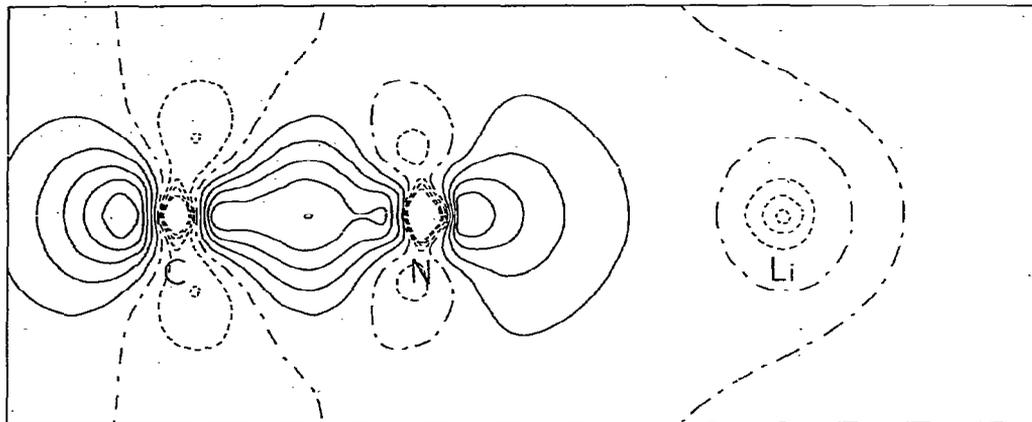
Fig. 3. The difference density in LiNC, using an extended basis set. Contours as in fig. 1.

orbitals. Subtracted are again atomic densities based on Clementi's atomic orbitals [13].

The lack of features near the Li atom in figs. 2 and 3 is a result of the very diffuse nature of the valence electron density of this atom. Comparison of figs. 1, 2 and 3 shows a striking resemblance of the electron density in the CN regions. Good correspondence is also found when compared with theoretical difference density maps of HCN and NCCN [15].

This apparent agreement is contradictory to the differences in Mulliken population analyses derived from the Hartree—Fock molecular wavefunctions and reported in table 1. This should not be surprising as it has been shown by Mulliken [17] and Politzer and Harris [18] that the Mulliken population analysis, based on an extended basis set Hartree—Fock calculation, often results in unrealistic net atomic charges.

Charges resulting from CNDO/2 calculations, however, have been found to be consistent with the electron density distribution near the Hartree—Fock limit [19]. They have been included in table 1. Following Giessner-Prettre and Pullman [20] and Shillady et al. [21] the coefficients resulting from the CNDO/2 calculations are assumed to be of the symmetric orthogonalized basis functions. A deorthogonalization procedure has been applied before performing the population analyses. The resulting net charges are almost identical to values obtained for the same compounds by integration over the Hartree—Fock electron densities and by estimations from core energies [22].

3. The minimal basis set

Minimal basis set quantum chemical calculations, both ab initio and semi-empirical, are generally found to give poor representations of the electron density distribution [6,9]. As example the difference density of CN⁻ based on a CNDO/2 calculation, using standard parametrization [23], is shown in fig. 4. The atomic electron density is assumed to be the spherically averaged density based on the same valence orbitals as used in the CNDO/2 calculation. Striking differences with fig. 1 can be noted in both the bonding and the lone pair regions: the latter regions seem to be stressed at the expense of the former.

It is clear that if the minimal basis set of Slater or-

Table 1
Net atomic charges according to Mulliken population analyses

	Hartree—Fock			CNDO/2 [c]		
	Li	C	N	Li	C	N
CN⁻		−0.502	−0.499 [a]		−0.39	−0.61
LiCN	0.475	−0.294	−0.180 [b]	0.43	−0.23	−0.19
LiNC	0.817	−0.004	−0.812 [b]	0.50	−0.09	−0.41

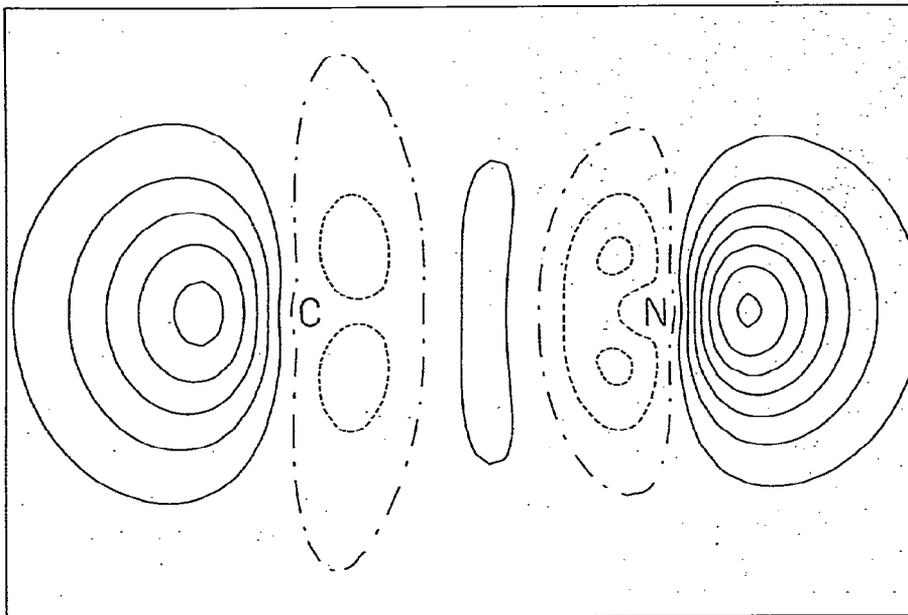[a] Ref. [16]. [b] Ref. [14]. [c] Results after deorthogonalization of basis functions.

Fig. 4. The difference density in the CN⁻ion, derived from a deorthogonalized CNDO/2 molecular wavefunction. Contours as in fig. 1.

bitals is too limited for our purpose, neither ab initio nor semi-empirical method for determining the coefficients of the basis functions in the molecular orbitals will give accurate results. It can be expected, however, that an improvement in the electron distribution will be obtained if the semi-empirical parameters are determined on basis of a comparison with accurate electron density distributions. In this case the density close to the nuclei will not play its dominant role as in the case of an energy minimization, with a beneficial effect on the bonding regions.

In order to assess the quality of a trial electron density distribution with respect to its ability to give a proper representation of a high quality reference electron density distribution, we introduce the error functional R, defined as

$$R = \int |\rho^{(ref)} - \rho^{(tr)}| \, dV / \int \rho^{(ref)} \, dV, \qquad (2)$$

where the superscripts (ref) and (tr) refer to the reference and trial quantities. This functional is easily calculated by numerical integration. Now the capability of a minimal basis set of Slater orbitals to represent the reference density can be found by minimizing R. In order to be physically significant, the trial electron density has to be restricted to satisfy N-representability [10,11].

The procedure we used is basically different from the one suggested by Clinton et al. [11]. The trial electron density can be interpreted in terms of a set of orthonormal molecular orbitals. Furthermore, such a set of functions can be regarded as the eigenvectors of a real symmetric matrix H. We assumed a starting matrix of the right order, i.e. the Fock matrix of a CNDO/2 calculation and varied the matrix terms one at a time, keeping the matrix symmetric. Subsequently we diagonalized the matrix and calculated the trial electron density from the deorthogonalized eigenvectors. The value of the error functional R was minimized by the steepest descent procedure. By repeating this procedure, the trial electron density converged in about ten cycles.

The relative deviation of the trial electron density,

based on a minimal set of 1s, 2s and 2p Slater functions, from the high quality density was considerable: the minimum in R was 12% for CN⁻. Restriction to a fit of the valence density using only 2s and 2p basis functions (as applied in the semi-empirical methods) made the results worse: $R = 16\%$ for CN⁻, $R = 9\%$ for LiCN.

It is interesting to note that no real improvement is obtained over the CNDO/2 wavefunctions which give $R = 16.4\%$ and $R = 10.6\%$ for CN⁻ and LiCN, respectively. So the CNDO/2 method results in almost the best electron density possible with a minimal set of 2s and 2p Slater orbitals with standard exponents.

In order to test the ultimate capability of a minimal set of Slater orbitals, the exponents ζ of these orbitals were varied as well. Ransil's work on C_2 and N_2 [24] indicates the sensitivity of the energy on the value of ζ. Electron density maps of these molecules, using Ransil's wavefunctions, however, did not show much improvement as result of the energy-optimization of the exponents when compared with the

Hartree—Fock densities of Bader et al. [1]. Full optimization of the trial electron density by varying both exponents and the values of the H-matrix was achieved by a similar procedure as described above. A fit of the valence density of CN⁻ with a minimal set of 2s and 2p Slater orbitals, optimizing three exponents per atom ($\zeta_{2s}, \zeta_{2p_\sigma}, \zeta_{2p_\pi}$) lowered the value of R to 9.7%. A similar fit of the valence density of LiCN reduced the value of R to 6.6%. The exponents showed an overall reduction during the refinement, indicating an average increase of the distance of the electrons from the nuclei. No attention has been paid to the uniqueness of the individual exponents.

The effect of the optimization can be seen in fig. 5, where the electron density contours of CN⁻ are drawn after the final refinement. Atomic valence densities calculated from Clementi's atomic orbitals have been subtracted. The massive lone pair regions of the CNDO/2 results are considerably reduced. The qualitative features of the Hartree—Fock difference map have not been reproduced to a satisfactory extent.

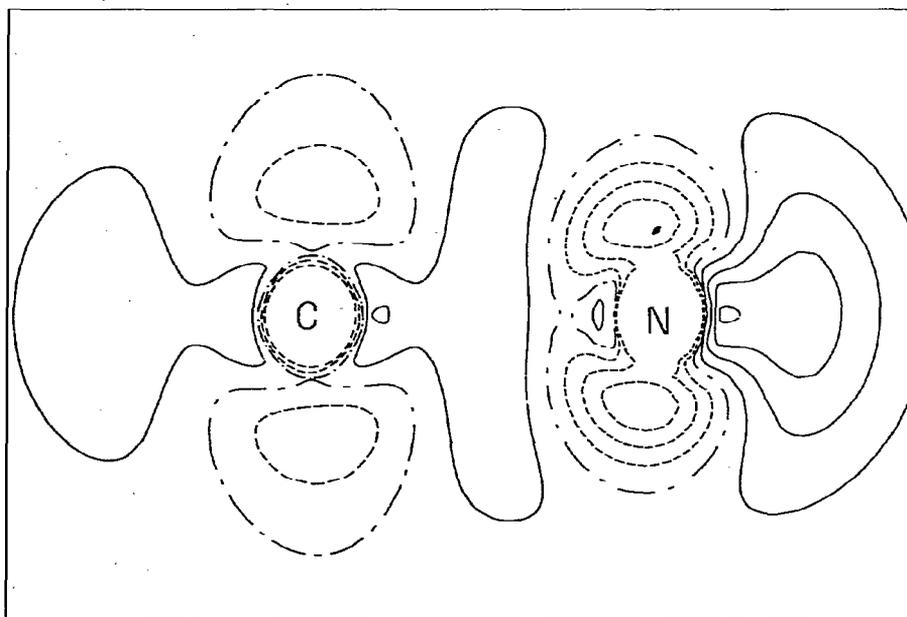The unsatisfactory description of the difference

Fig. 5. The difference density in the CN⁻ion: the ultimate optimized molecular valence density with a minimal basis set minus accurate atomic valence densities. Contours as in fig. 1

density of CN⁻ in the final map could be expected as the optimized valence density of CN⁻ still shows a deviation of about 10% of the high quality density, or in absolute terms, the deviation is still one electron, which equals about the electron change on molecule formation.

4. Conclusion

Summarizing this work the following conclusion can be made: quantum chemical calculations based on a minimal basis set of Slater orbitals are inadequate to lead to electron density maps with the same qualitative features as calculations near the Hartree—Fock level.

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