

MOLECULAR CHARGE DISTRIBUTION OF CO

G. DE WITH and D. FEIL

Chemical Physics Laboratory, Twente University of Technology, Enschede, The Netherlands

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The difference electron density of CO is studied by comparison of several calculations. It is shown that the Hartree-Fock-Slater and Hartree-Fock methods yield equally good charge-distributions and that the use of minimal basis sets should be avoided.

1. Introduction

In order to get a better understanding of what type of wavefunction is needed for the calculation of scattering amplitudes in X-ray diffraction of molecular crystals, we have compared several wavefunctions of CO. The criterion by which an approximate wavefunction is judged is not usually the energy but the electron density associated with the wavefunction. So we have studied the charge distribution difference function introduced by Roux [1]

$$\Delta\rho(\mathbf{r}) = \rho_M(\mathbf{r}) - \rho_A(\mathbf{r}),$$

where $\rho_M(\mathbf{r})$ is the electron density at the point \mathbf{r} for

the molecular charge distribution and $\rho_A(\mathbf{r})$ is the electron density appropriate to the non-interacting atoms at the same internuclear separation. As is customary, $\rho_A(\mathbf{r})$ is computed using the spherically averaged p orbitals of the atoms in the ground state. According to Smith and Richardson [2] we used the same basis of atomic orbitals for both molecular and atomic calculation for obtaining $\Delta\rho(\mathbf{r})$. Except for the minimal basis calculations all wavefunctions were calculated using Clementi's exponents [3].

2. Results and discussion

The different calculations on CO which we want to

Table 1
Specification of the wavefunctions used to calculate the molecular charge distribution

No.	Ref.	R (au)	E (au)	Basis ^{c)}	Identification ^{d)}
1	[4]	2.132	-112.7891	(22, 12)	HF limit
2	[4]	2.132	-112.7790	(16, 8)	DZ + D + F
3	a)	2.12	-112.6754	(12, 4)	DZ
4	b)	2.12	-112.8086	(12, 4)	DZ + CI
5	[6]	2.132	-112.3260	(6, 2)	SZ - BA
6	[6]	2.132	-112.3436	(6, 2)	SZ - Slater
7	[8]	2.12	-	(12, 4)	DZ, HFS

a) Calculation with the program "New Alchemy".

b) This is a 217-term CI on "New Alchemy" which lowered the total energy 0.0332 au. Notice that the energy is beneath the Hartree-Fock limit.

c) (a, b) means a σ -type and b π -type basis functions.

d) HF Hartree-Fock, HFS Hartree-Fock-Slater, DZ double zeta, SZ single zeta, CI configuration interaction, BA best atom.

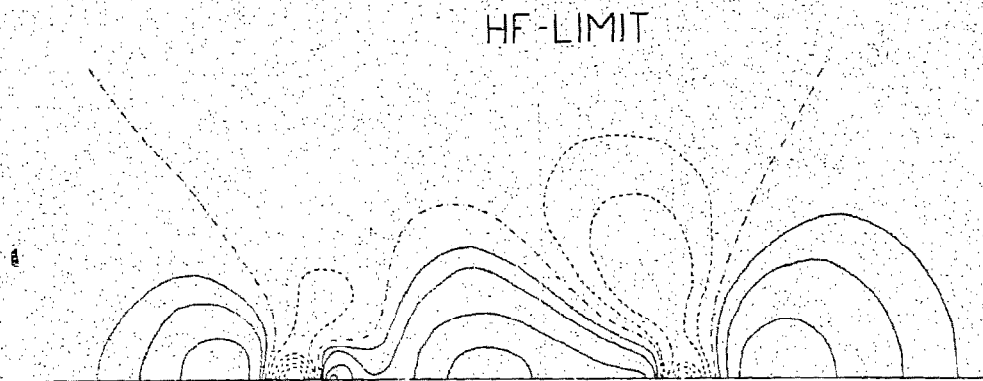


Fig. 1. Difference density map for HF-limit calculation. In this and the following figures contours are drawn at 0, ± 0.025 , ± 0.050 , ± 0.100 and $\pm 0.150 e/a_0^3$. The representations are positive contours (—), negative contours (- - -), null contour (- · -).

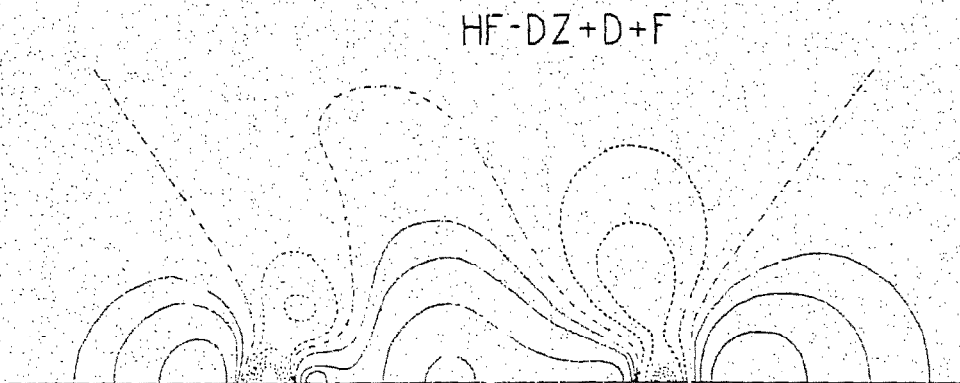


Fig. 2. Difference density map for HF + d + f calculation.

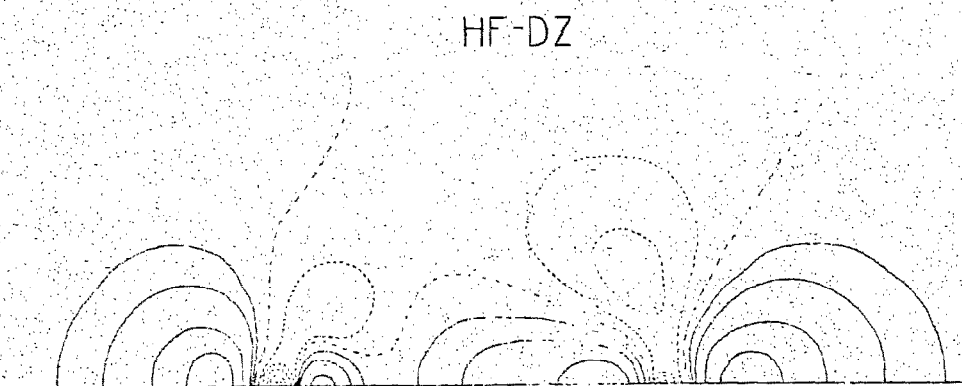


Fig. 3. Difference density map for HF - Dz calculation.

compare are given in table 1. In the following part we will discuss the different wavefunctions and their dif-

ference densities. The numbering is according to table 1.

HF-DZ-CI

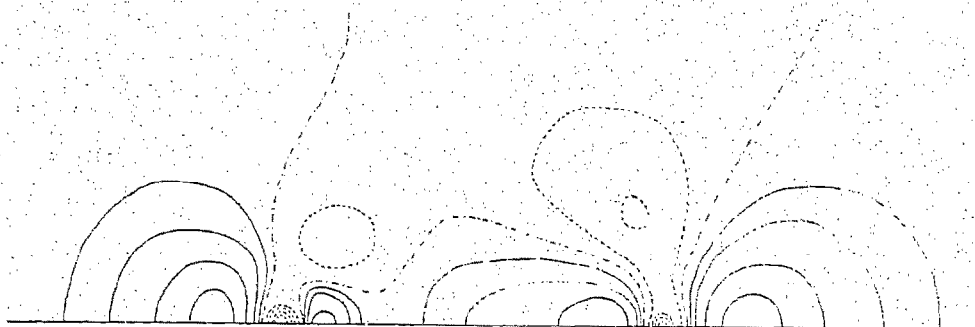


Fig. 4. Difference density map for HFS - DZ - CI calculation.

HF-SZ-BA

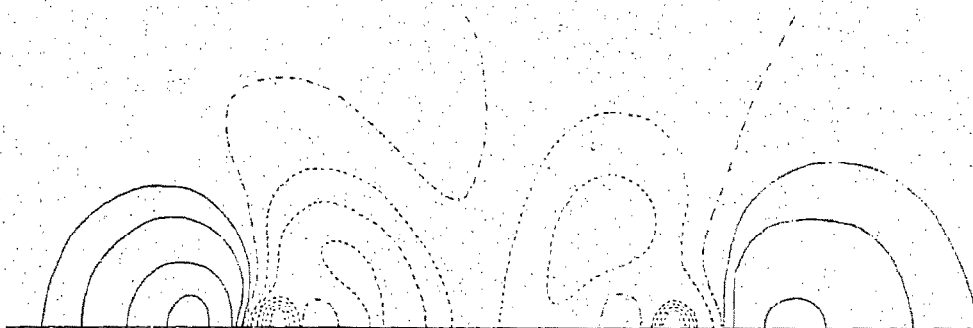


Fig. 5. Difference density map for HF - SZ calculation.

HFS-DZ

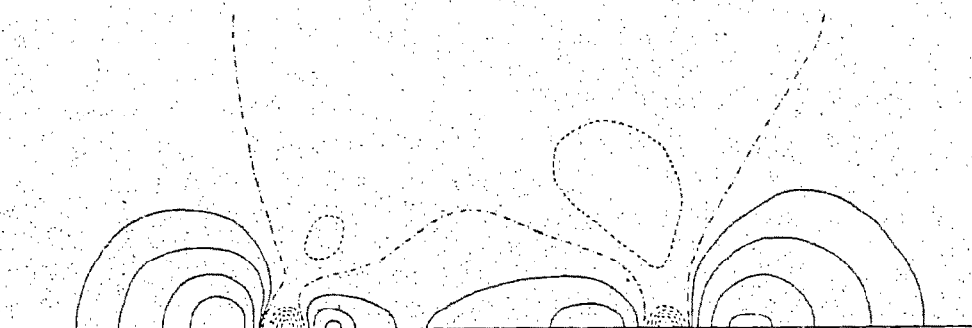


Fig. 6. Difference density map for HFS - DZ calculation.

1. A very sophisticated calculation is the one very near to the Hartree-Fock limit due to McLean and Yoshimine [4] (figs. 1 and 7). In the absence of ex-

perimental data on the charge density of CO we use this calculation as a reference.

2. One step backwards in theoretical accuracy is a

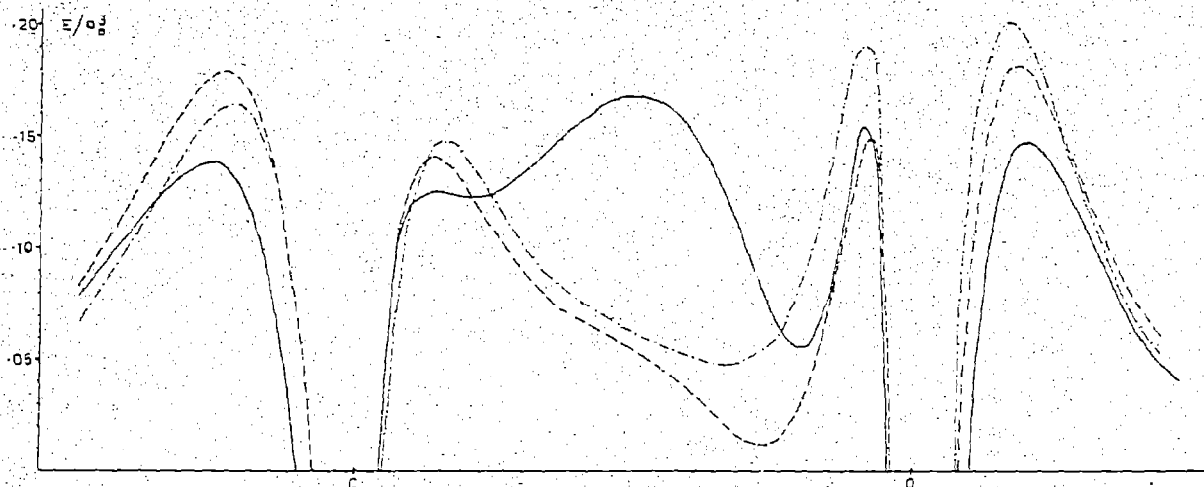


Fig. 7. Difference density along the molecular axis of CO. The representations are HF-limit (—), HF - DZ (---), HFS - DZ (-.-).

near Hartree-Fock limit calculation (double zeta basis plus a d and an f type function on each atom [4]) (fig. 2). There is a small difference in electron density as compared with the reference (on the molecular axis: bond density $\approx 0.01 e/a_0^3$ lower, lone pair density $\approx 0.01 e/a_0^3$ higher) suggesting the relative unimportance of the extra s and p basis functions of the reference in comparison with this calculation.

3. The next wavefunction considered is taken from a double zeta basis calculation (with the program "New Alchemy"). The difference in charge distribution is considerable (figs. 3 and 7) as compared with the reference. On the molecular axis: bond density $\approx 0.05 e/a_0^3$ lower, lone pair density $\approx 0.05 e/a_0^3$ higher. This shows that polarization functions are indispensable for an accurate description of the charge distribution.

4. The inclusion of configuration interaction* (fig. 4) makes a difference of less than $0.01 e/a_0^3$ as compared with no. 3 (as expected [5]).

5. A minimal basis set calculation using best-atom exponents [6] does not resemble at all no. 3. The greater part of the bond density is lower than the sum of the atomic densities in that region (fig. 5). This is

* This is a 217-term CI on "New Alchemy" which lowered the total energy 0.0332 au. Notice that the energy is beneath the Hartree-Fock limit.

in agreement with the results of others [2,7].

6. A slight improvement is obtained by the use of exponents calculated according to Slater's rules in the minimal basis calculation [6] (difference map not shown). In the nitrogen molecule the wavefunction with best-atom exponents described the bonding region somewhat better [2].

7. Last but not least we compared the charge distribution as calculated with the Hartree-Fock-Slater model [8] (figs. 6 and 7). This is a double zeta basis calculation. The electron density difference map is very much the same as obtained from no. 3.

This is strong evidence for the statement that the Hartree-Fock-Slater method (as used in ref. [8]) can yield wavefunctions as good as the normal Hartree-Fock method. (This is probably due to the use of the LCAO expansion instead of the use of the muffin-tin approximation, the first approximation being better in molecules, the latter in solids [9].) This statement is already supported by atomic calculations made with a double zeta basis, e.g. for the C, N and O atoms, the greatest difference being less than $0.01 e/a_0^3$ [10].

3. Conclusion

We might say that in an electron density analysis

one should use at least a double zeta basis calculation, preferably extended with some polarization functions. Inclusion of configuration interaction seems not to compensate for polarization. The use of minimal basis set calculations should be avoided.

However, there seems to be no objection in using a Hartree-Fock-Slater wavefunction (with the same quality of basis set) instead of a normal Hartree-Fock calculation. This gives rise to an enormous saving of computer time.

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References

- [1] M. Roux, S. Besnainon and R. Daudel, *J. Chim. Phys.* 54 (1956) 218.
- [2] P.R. Smith and J.W. Richardson, *J. Phys. Chem.* 71 (1967) 924.
- [3] E. Clementi, *IBM J. Res. Develop.* 9 (1965) suppl., table 45-01.
- [4] A.D. McLean and M. Yoshimine, *IBM J. Res. Develop.* 11 (1967) suppl.
- [5] R. McWeeny and B.T. Sutcliffe, *Methods of molecular quantum mechanics* (Academic Press, New York, 1969) p. 138.
- [6] B.J. Ransil, *Rev. Mod. Phys.* 32 (1960) 239.
- [7] A.F. Van-Catledge, *J. Phys. Chem.* 78 (1974) 763.
- [8] E.J. Baerends, D. Ellis and P. Ros, *Chem. Phys.* 2 (1973) 1.
- [9] J.M. Ziman, *Principles of the theory of solids* (Cambridge Univ. Press, London, 1972) ch. 3.
- [10] G. de With and D. Feil, unpublished results.