

## Electron densities from the Brueckner Doubles method

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**Summary.** The concept of the Brueckner orbital is examined, following a resurgence of interest in wavefunctions constructed from them. The distinction between Self Consistent Field, Natural and Brueckner orbitals are discussed. Total electron densities are calculated for several examples, and correlation densities are studied. It is found that the Brueckner orbitals are more localised than SCF orbitals. The total electron density constructed from the Brueckner reference determinant with Brueckner orbitals gives qualitatively similar pictures as other correlated methods. Brueckner orbitals are found to show dissociation well.

**Key words:** Electron densities – Molecular orbitals – Electron correlation – Coupled cluster approach – Highly correlated systems

### 1. Introduction

The concept of Brueckner orbitals in quantum chemistry has always been appealing, but because their determination needs iterations at the correlated level of calculation, their use has not been popular until recently. Brueckner [1] introduced the concept of these orbitals in physics and Nesbet [2] first suggested their use in chemistry. Given a basis set of  $m$  functions,  $m$  spatial orbitals  $\phi$  may be constructed, which may be split into  $n$  doubly occupied and  $m-n$  unoccupied orbitals (we shall discuss only closed shell systems here). The reference determinant is  $\Phi_0$ , from which it is possible to generate determinants with single excitations  $\Phi_i^a$ , double excitations  $\Phi_{ij}^{ab}$ , or higher excitations. The most accurate wavefunction which is possible to construct for a given basis is Full CI (FCI) which includes all excitations. Brueckner orbitals are defined to be those orbitals for which the coefficients of the single replacement determinants  $\Phi_i^a$  in the FCI expansion are zero. For any method which is an approximation to FCI, it is possible to define Brueckner orbitals as those for which the coefficients of the single replacements  $\Phi_i^a$  are zero.

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Kutzelnigg and Smith [3] and Larsson and Smith [4] argue that Brueckner orbitals are best overlap orbitals in the sense that they give the maximum overlap of a one-configuration approximation of the wavefunction with the true wavefunction,  $\langle \Phi_0 | \Psi_{\text{FCI}} \rangle$  is maximised by them. This can be seen by considering the variation  $\phi_i \rightarrow \phi_i + \epsilon \phi_a$  for which the first order variation of the overlap is  $\langle \Phi_i^a | \Psi_{\text{FCI}} \rangle$ . Brueckner orbitals from the FCI reference determinant are indeed those orbitals for which the reference determinant has maximum overlap with the FCI wavefunction.

We wish to compare Brueckner orbitals (BO) from the Brueckner Doubles (BD) method [5], for some many-electron systems, with Self Consistent Field orbitals (SCF) and Natural orbitals (NO). SCF orbitals are those for which the energy of the reference determinant  $\langle \Phi_0 | \hat{H} | \Phi_0 \rangle$  is minimised (or is stationary). Natural orbitals (NO) were introduced by Löwdin [6] as those orbitals which diagonalise the one particle density matrix  $\gamma$  of a correlated wavefunction. They give maximum overlap of the 1-determinant density with the Full CI density [3]. For a two-particle system, Brueckner and Natural orbitals are the same [3, 4, 7].

Löwdin argued that these Natural orbitals will give the most rapid convergence of a Configuration Interaction (CI) wavefunction to the FCI wavefunction. Bender and Davidson [8] reported their famous iterative natural orbital CI calculation on HeH and LiH. The correlating Natural orbitals were found to lie in the same region of space as the correlated occupied orbitals, in contrast to virtual SCF orbitals.

Shavitt et al. [9] performed Single plus Doubles Configuration Interaction (CISD) calculations on H<sub>2</sub>O, comparing SCF orbital calculations and iterative Natural orbital calculations. They examined  $\eta = \sum_{ai} C_i^a{}^2$ , where  $C_i^a$  is the coefficient of  $\Phi_i^a$  in the normalised wavefunction. They found that  $\eta = 0.000593$  for the SCF orbitals, and  $\eta = 0.000012$  for the Natural orbitals. They also found that the expectation value for one electron properties, predicted from the first natural configuration (i.e. the dominant term in the NO-CI calculation), was substantially close to the CI value than the corresponding SCF results. Dykstra [10] examined the Brueckner condition for a selection of molecular orbitals, and referred to Shavitt's [9] calculations, and deduced from the value of  $\eta$  that Natural orbitals were close to Brueckner orbitals. Dykstra also performed limited CI calculations with SCF and with Brueckner orbitals and showed that the CI energies obtained with Brueckner orbitals could either be slightly above or slightly below, when singly substituted configurations are important, those obtained with the SCF orbitals.

As methods for the calculation of correlated wavefunctions become increasingly accurate (and more sophisticated), they approach the FCI limit for a given basis set. Thus for these methods the BO approach the exact BO as defined above. It is probably agreed that the most accurate single reference based quantum chemistry methods nowadays are based on the Coupled Cluster approach [11]. Handy et al. [5] have recently reintroduced the idea of Dykstra [10] to formulate Coupled Cluster theory in terms of Brueckner orbitals. At the doubles level, the Coupled Cluster wavefunction is  $\Psi = \exp(T_2)\Phi_0$ , and the equation to determine the energy, the Brueckner orbitals and the doubles amplitudes  $a_{ij}^{ab}$  are:

$$\langle \Phi_0 | \hat{H} | (1 + T_2)\Phi_0 \rangle = E \quad (1)$$

$$\langle \Phi_i^a | \hat{H} | (1 + T_2)\Phi_0 \rangle = 0 \quad (2)$$

$$\langle \Phi_{ij}^{ab} | \hat{H} | (1 + T_2 + \frac{1}{2}T_2^2)\Phi_0 \rangle = a_{ij}^{ab} E \quad (3)$$

The wavefunction  $\Psi$  contains no single replacements  $\Phi_i^a$ , and the condition (2) defines the iterative procedure for finding these orbitals. Reference [5] describes the details of this approach, which has been called BD theory. It is contrasted with the usual CCSD theory [11], for which the wavefunction is  $\Psi = \exp(T_1 + T_2)\Phi_0$ , with  $\Phi_0$  being the SCF determinant. Recently, Hampel et al. [12] have shown that the BD method is marginally less expensive than the CCSD method.

It was suggested in [5] that the use of BO gives the most symmetrical form of the Coupled Cluster equations, because it can be argued that  $\exp(T_1)$  is present in both the bras and kets of the BD equations and has then been absorbed into the orbitals. In the CCSD equations  $\exp(T_1)$  only arises in the kets of the equations. In [5] an analysis of BD and CCSD theory was carried out in terms of the Møller–Plesset expansion of the energy, and it was shown that CCSD and BD contain the same fourth order terms, but that BD contains more fifth order terms than CCSD. Theoretically then BD theory should be superior to CCSD theory, but of course it depends upon the sign and magnitude of the missing terms in the methods.

It is of interest to look at the electron density arising from the reference determinant  $\Phi_0$  and the BD wavefunction  $\Psi = \exp(T_2)\Phi_0$ . It is not possible to calculate a one particle density matrix from  $\int \Psi^*(1, 2, \dots, n) \times \Psi(1', 2', \dots, n') d\tau_2 d\tau_3 \dots d\tau_n$  for this wavefunction. Rather we proceed through the derivative of the energy  $E$  with respect to one applied external electron perturbation  $\lambda \sum_i \hat{\mu}(i)$ :

$$\frac{dE}{d\lambda} = \sum_{pq} \gamma_{pq} \hat{\mu}_{pq} \quad (4)$$

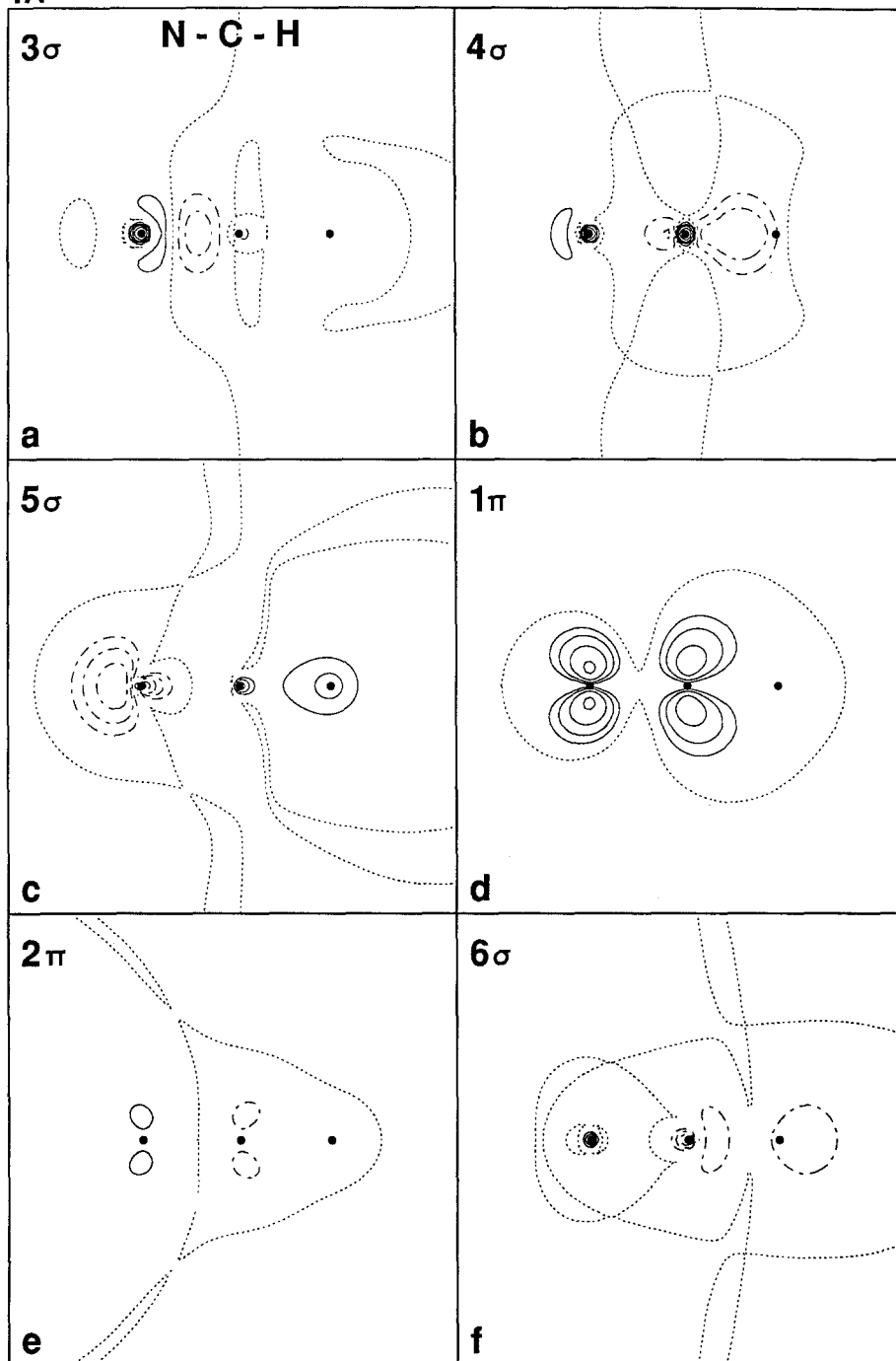
For wavefunctions which are fully stationary with respect to  $\lambda$ , Eq. (4) gives the same result as the expectation value  $\langle \Psi | \hat{\mu} | \Psi \rangle$ . In all other cases it is preferable to use the derivative based definition [13]. The matrix  $\gamma_{pq}$  is called the ‘relaxed’ density matrix. For non-variational methods this is how one calculates electron properties. We therefore shall use  $\gamma_{pq}$  as the one particle density matrix for BD theory. Formulae for  $\gamma_{pq}$  from the BD method are given by Kobayashi et al. [14], from MP2 by Simandiras et al. [15].  $\gamma_{pq}$  may be diagonalised to obtain the Natural orbitals for the BD method, the eigenvalues of  $\gamma_{pq}$  will be the occupation numbers. Both Brueckner orbitals and SCF orbitals have an occupation number 2 in the reference determinant.

In the following section we shall look at Brueckner orbitals through the orbital densities  $\phi^2$ , and compare them with corresponding SCF and Natural orbitals, which are obtained by diagonalising the BD ‘relaxed’ density matrix. Total densities ( $\rho = \sum \gamma_{pq} \phi_p \phi_q$ ) were calculated and difference densities were plotted.

## 2. Methods

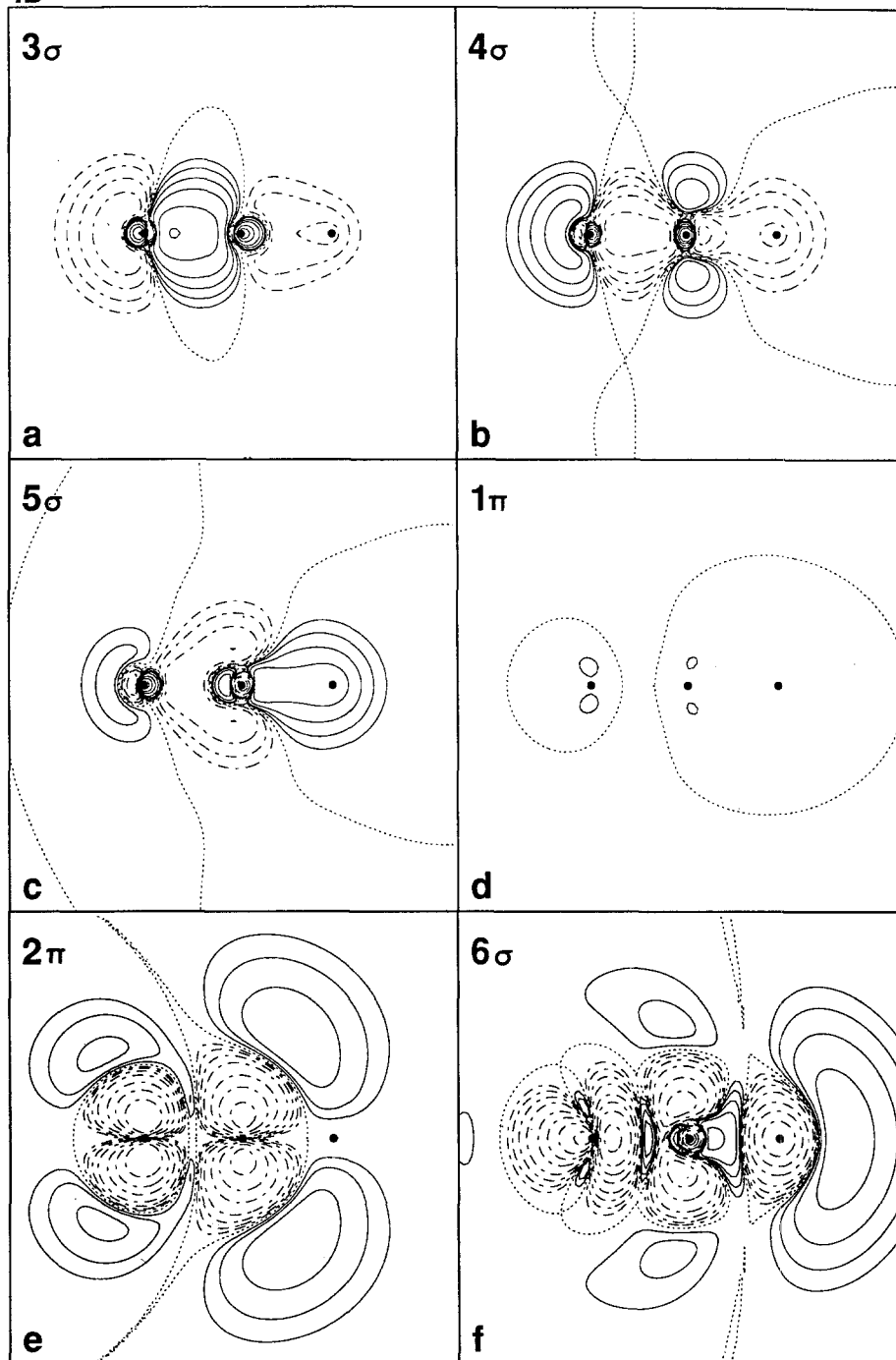
The molecules for which the Brueckner orbitals were studied are H<sub>2</sub>O, HCN, N<sub>2</sub>O and O<sub>3</sub>. The latter three were chosen because of their delocalised bonding and significant electron correlation effects. Ozone has been a problem for quantum chemists. It has been very difficult to obtain an energy surface which satisfactorily reproduces the experimental geometry and the harmonic frequencies. The groundstate may be thought of as two unpaired electrons, localised on

1A

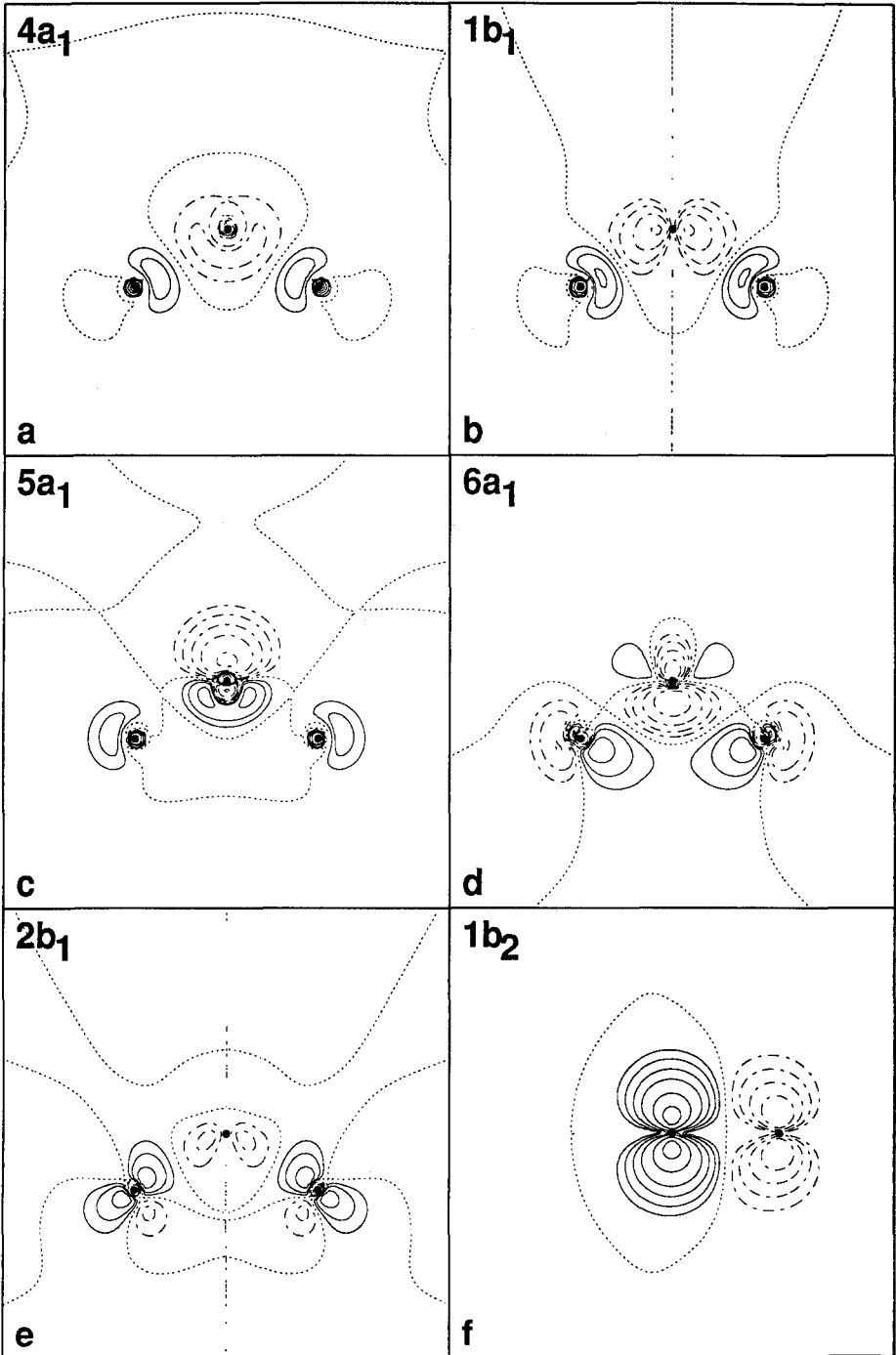


**Fig. 1A,B.** Difference density plots for the orbitals of HCN. **A:**  $\phi_{BR}^2 - \phi_{SCF}^2$ , **B:**  $\phi_{BR}^2 - \phi_{BD}^2$ . Contours are  $\pm 0.001, \pm 0.002, \pm 0.004, \pm 0.008, \pm 0.02, \pm 0.04, \pm 0.08, \dots$  etc  $e/\text{Bohr}^3$ . *Solid lines* indicate positive contours, *dashed lines* negative contours and *dotted lines* zero contours. [The same holds for all other plots]

1B



2A



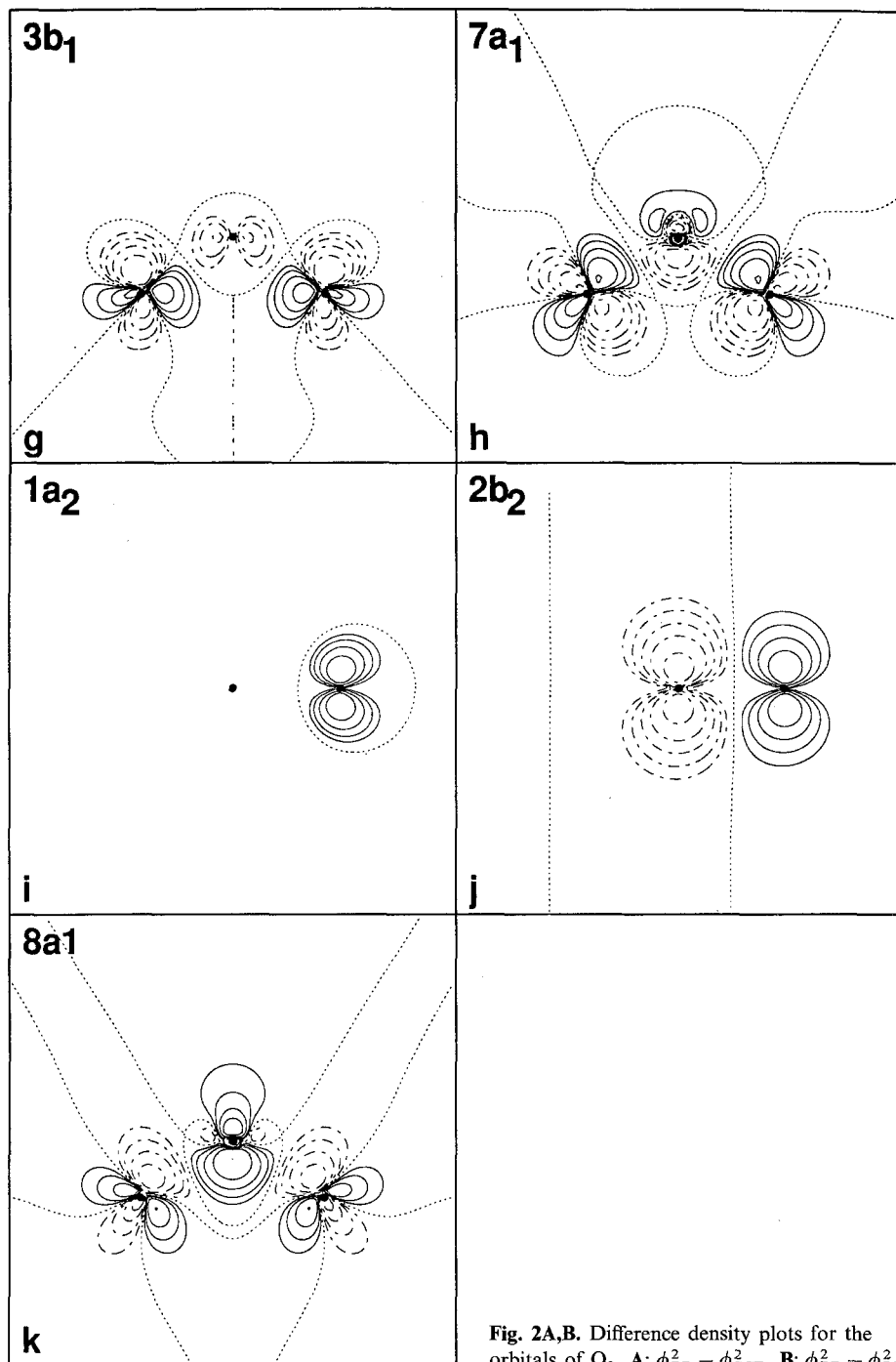


Fig. 2A,B. Difference density plots for the orbitals of O<sub>3</sub>. A:  $\phi_{BR}^2 - \phi_{SCF}^2$ , B:  $\phi_{BR}^2 - \phi_{BD}^2$

2B

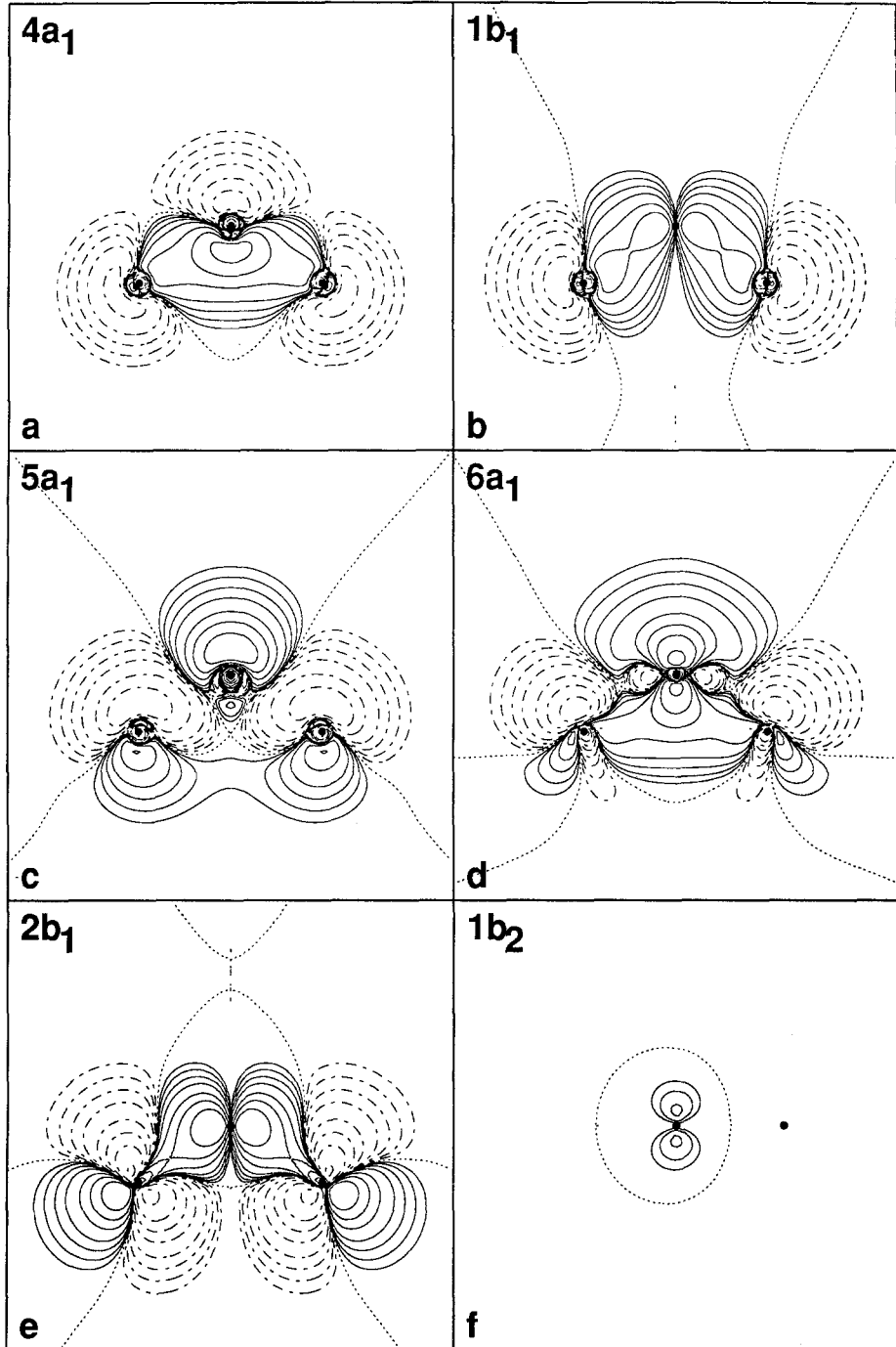


Fig. 2B.



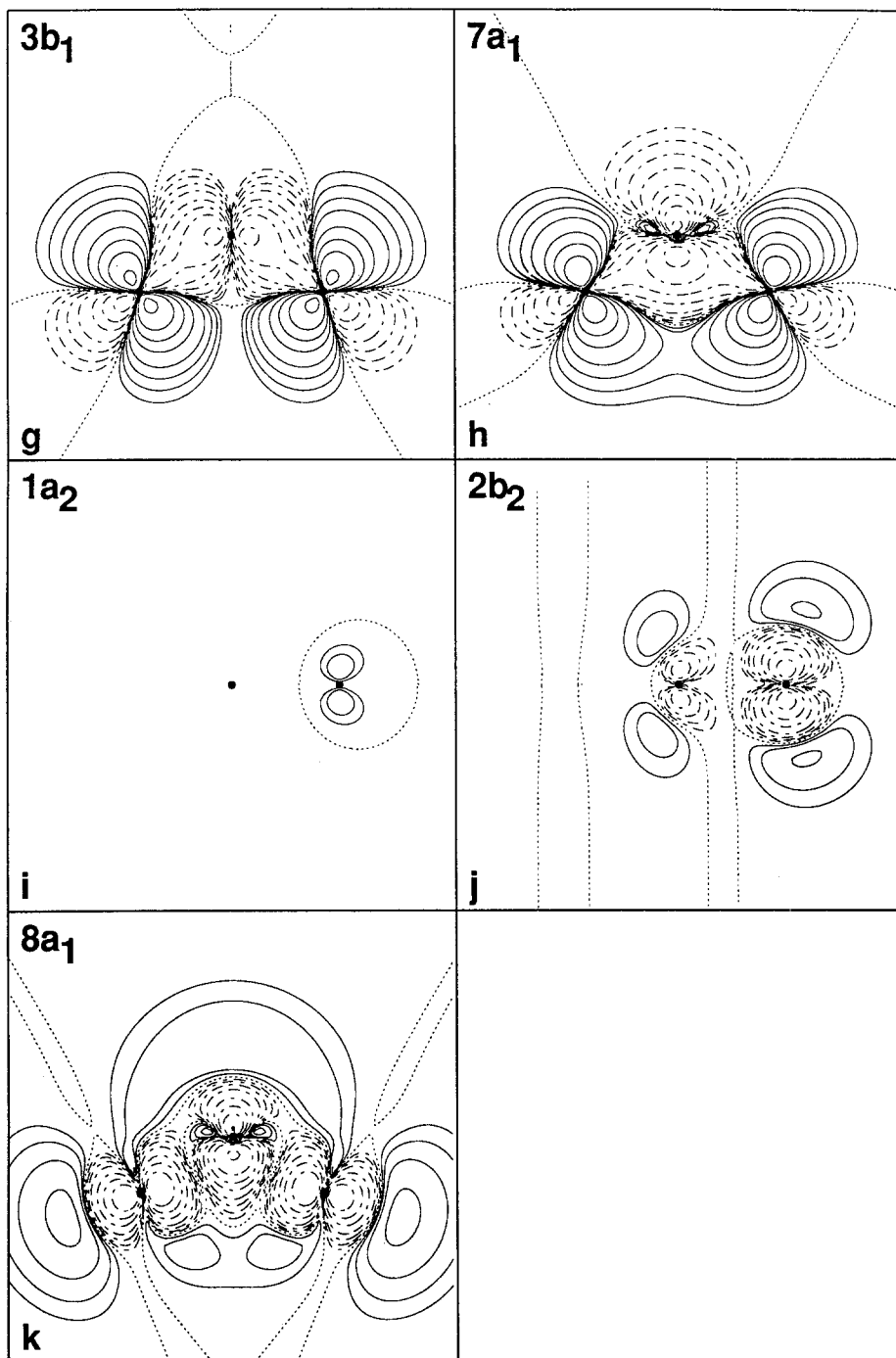


Fig. 2B (continued)

the end oxygen atoms. These two electrons are loosely coupled in a singlet state.  $N_2O$  also shows strong correlation effects and simple methods such as MP2 give the wrong sign for the dipole moment.

Calculations were performed using CADPAC [16] including a version of the BD method. SCF, MP2 and BD calculations were performed at the DZP level with Huzinaga and Dunning basis sets [17, 18, 19]. The geometries were held constant throughout at experimental geometries [20, 21, 22, 23]. The SCF and Brueckner orbitals, and the MP2 and BD relaxed densities were obtained for each system. Grids of charge densities, from which the contours were plotted, were calculated using  $100 \times 100$  points.

In the next section the subscript BR refers to the density of the one-determinant wavefunction, the Brueckner reference, with Brueckner orbitals. BD refers to the ‘relaxed’ density of the BD wavefunction ( $\Psi = \exp(\hat{T}_2)\Phi_0$ ). The MP2 density is also generated from the ‘relaxed’ density matrix, this is denoted with the subscript MP2. Natural orbitals where plotted, are those obtained by diagonalising the BD relaxed density.

### 3. Results

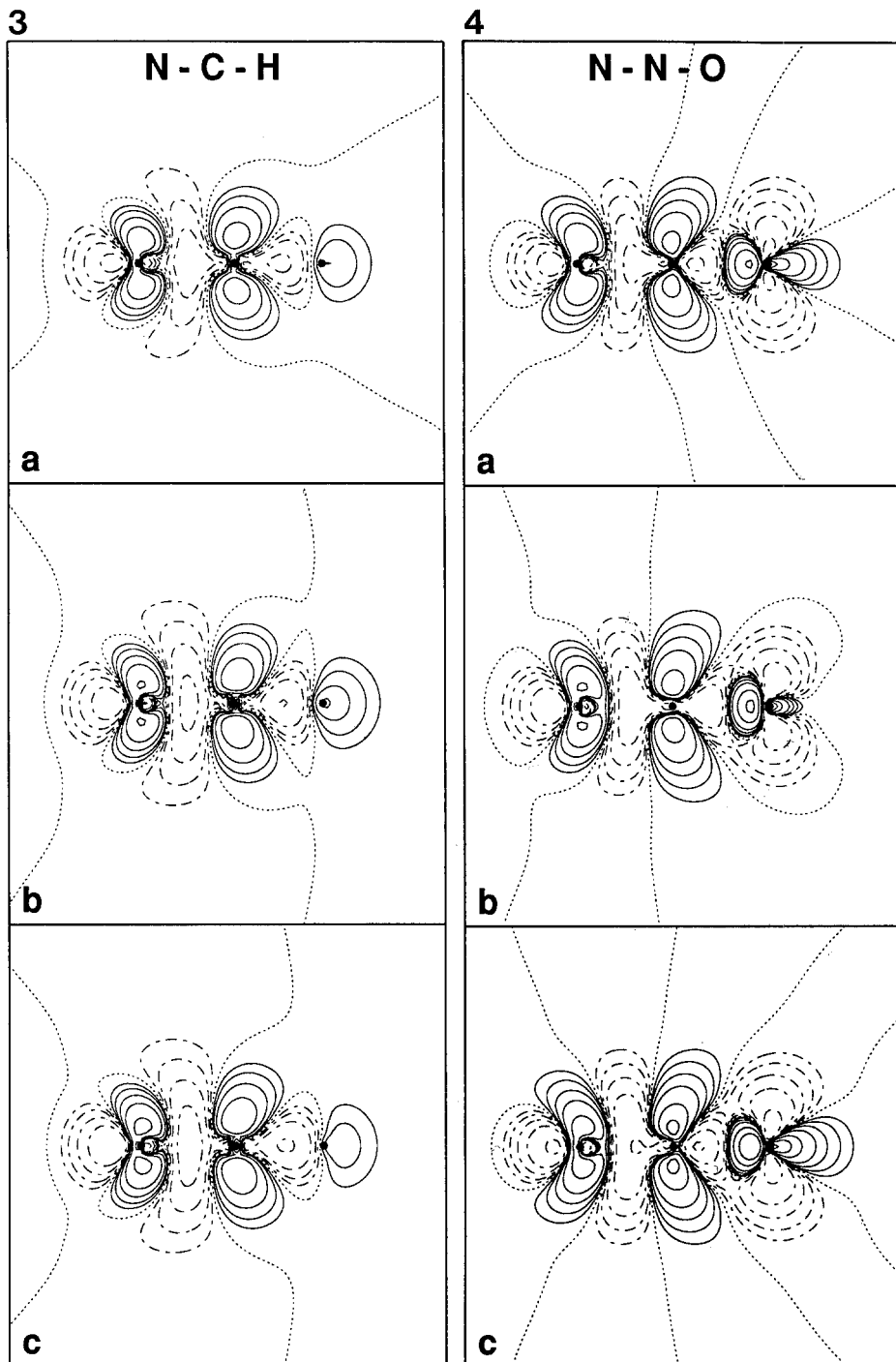
Figure 1A gives orbital density differences plots for HCN, for the difference between the Brueckner orbitals and the SCF orbitals. The first two orbitals have not been included as these, being basically  $1s$  atomic orbitals, show very little difference. The  $3\sigma$  and  $4\sigma$  orbitals also change relatively little, with difference only in the regions close to the nuclei. The  $5\sigma$  orbital changes more, with a shift of density towards the hydrogen, and the largest changes are in the  $\pi$ -orbitals which are noticeably more contracted than SCF – this seems to be a general feature which is noticed in other molecules. The first three virtual orbitals have also been plotted, which in HCN show relatively little change from SCF.

Figure 1B shows the differences between the Brueckner orbitals and the Natural orbitals of the relaxed BD density. As can be seen there are quite larger differences, despite the fact that the total density is not greatly different. For HCN it is certainly the case that Brueckner and Natural orbitals are not similar.

Figure 2A shows ‘Brueckner - SCF’ orbitals for ozone, including the first two virtual orbitals. The ‘ $\sigma$ -orbitals’ ( $a_1$  or  $b_1$  symmetry) have been plotted in the plane of the molecule, the ‘ $\pi$ -orbitals’ ( $a_2$  or  $b_2$  symmetry) are plotted in a plane perpendicular to the plane of the molecule and containing one bond. Overall the orbitals change by more than was the case with HCN, presumably because  $O_3$  is much less of a single-reference problem. In particular the  $\sigma$ -orbitals show a shift away from the central atom to the end atoms, and the orbitals are also more concentrated into the region of the atoms. Of the  $\pi$ -orbitals, the  $1b_2$  orbital shows a shift towards the central atom, and a general contraction of the orbital, and the  $1a_2$  orbital, which has no density on the central atom, just shows a contraction.

Figure 2B shows the differences between BO and NO for ozone. As with HCN there are large differences.

Figures 3, 4 and 5 show the total correlation densities (i.e. the differences from SCF) for HCN,  $N_2O$  and  $O_3$ . The correlation densities are for the Brueckner reference, the Full Brueckner relaxed density, and the MP2 relaxed



**Fig. 3a-c.** Correlation difference density plots for HCN. Plane of molecule: **a**  $l_{BD} - l_{SCF}$ , **b**  $l_{BD} - l_{SCF}$ , **c**  $l_{MP2} - l_{SCF}$

**Fig. 4a-c.** Correlation difference density plots for  $N_2O$ . Plane of molecule: **a**  $l_{BD} - l_{SCF}$ , **b**  $l_{BD} - l_{SCF}$ , **c**  $l_{MP2} - l_{SCF}$

## 5

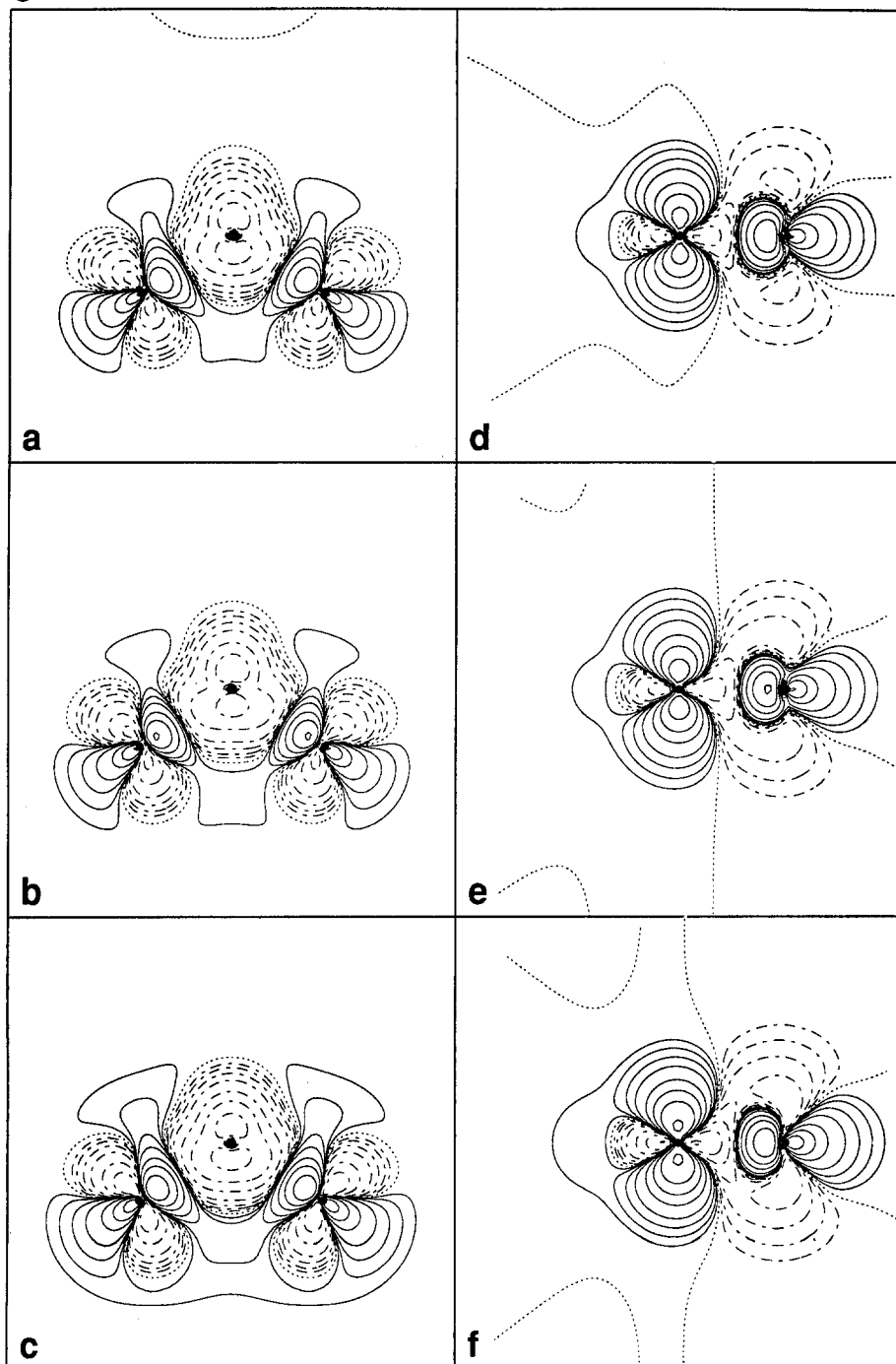


Fig. 5a-f. Correlation difference density plots for  $O_3$ . Plane of molecule: **a**  $\rho_{BR} - \rho_{SCF}$ , **b**  $\rho_{BD} - \rho_{SCF}$ , **c**  $\rho_{MP2} - \rho_{SCF}$ , plane through O-O bond, **d**  $\rho_{BR} - \rho_{SCF}$ , **e**  $\rho_{BD} - \rho_{SCF}$ , **f**  $\rho_{MP2} - \rho_{SCF}$

6

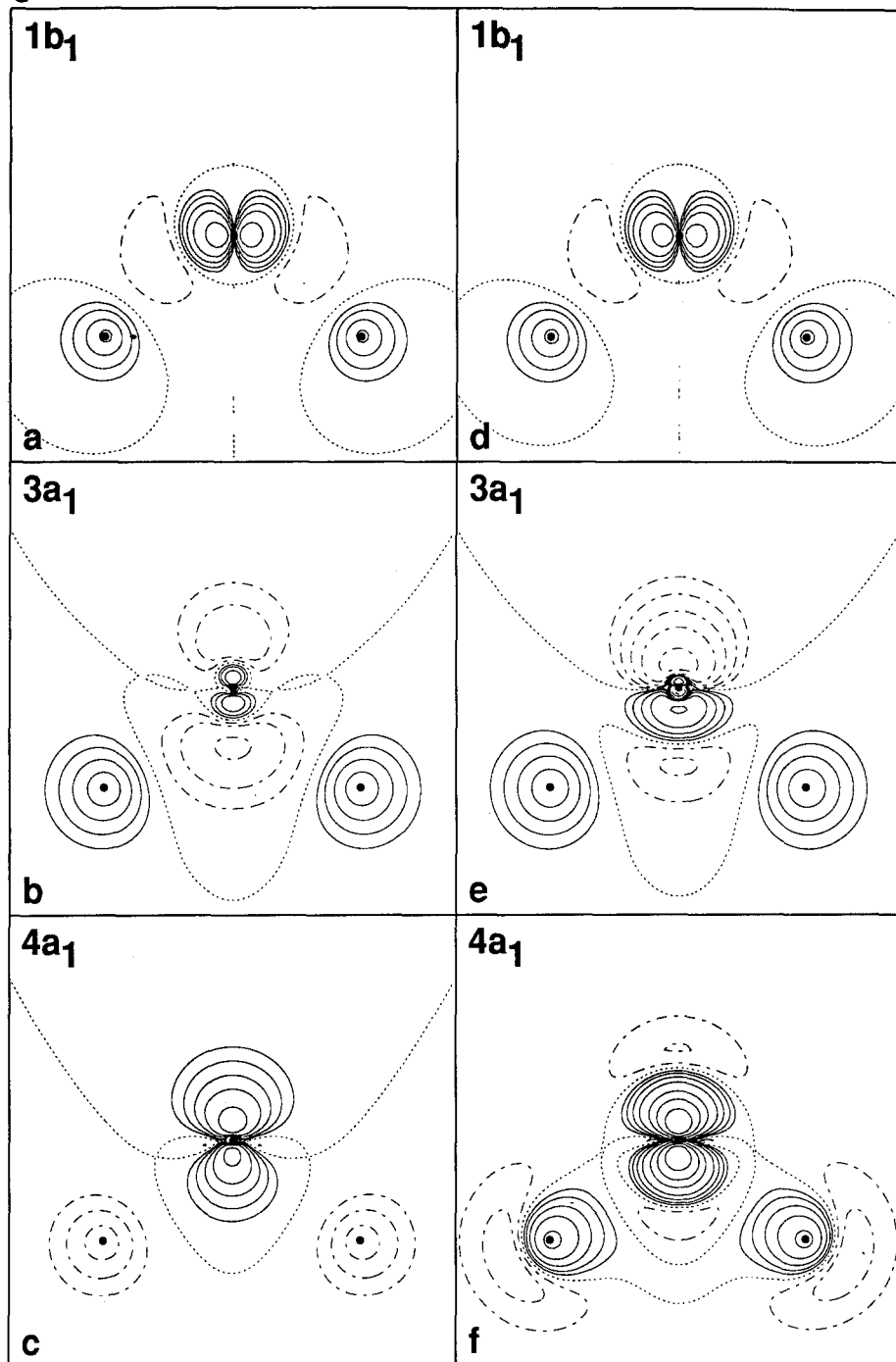


Fig. 6a–f. Difference density plots for the orbitals of H<sub>2</sub>O at 2.0  $R_e$ . a,b,c;  $\phi_{BR}^2 - \phi_{SCF}^2$ , d,e,f;  $\phi_{BD}^2 - \phi_{SCF}^2$

density. The plots all show the same qualitative features, particularly a greater localisation of the density towards the nuclei. This is in agreement with the work using CI of Wang and Boyd [24, 25]. Figures 5a, 5b and 5c show the difference plots for  $O_3$  viewed in the plane of the molecule. Figures 5d, 5e and 5f are in a plane perpendicular to the plane of the molecule, and containing one bond. All the plots are qualitatively the same, they show that the  $\sigma$ -electrons have been moved away from the central atom to the end atoms, whereas there is a build-up of electron density on the  $\pi$ -electrons of the central atom. There is also a small but definite enhancement of the electron density between the two non-bonded atoms. The Brueckner reference gives qualitatively a similar picture as the BD wavefunction. This shows that the effect of the single excitations on the electron density distribution (as in Brueckner orbitals) is much bigger than the effect of double excitations as is also known from Wang and Boyd [24, 25] and Meyer et al. [26]. Meyer et al. found that the effect of single and double excitations together in  $H_2O$  and  $N_2$  is around 80%, the other 20% were due to the triple and quadruple excitations. The BD wavefunction also includes double excitations, which are more pronounced close to the nuclei as Wang and Boyd concluded.

In  $N_2O$  we can see that the accumulation at the two outer atoms (especially on O) is a little more spread out for MP2 and Brueckner orbitals (BR). The nitrogen atom in the middle shows a distribution which is a little more spread out for BD orbitals and MP2. From the correlation difference plots we can see that MP2 still has a contribution in the outer regions whereas BR and BD drop off to zero faster. With a DZP basis, the dipole moment of  $N_2O$  at the SCF level is  $-0.663$  Debye (sign corresponds to the polarity  $+NNO-$ ), the MP2 value is  $0.068$  Debye and the BD value is  $-0.325$  Debye. The experimental value is  $-0.161$  Debye. A more detailed study of basis set and correlation effects on the dipole of  $N_2O$  is found in [28]. However, despite the fact that MP2 gives the opposite sign for the dipole moment, this is not really obvious from the density difference plots.

It is interesting to see how the Brueckner orbitals change when a molecule dissociates. This is studied with the dissociation of  $H_2O$ . Calculations were performed at the equilibrium structure (the O–H distance is  $R_e$ ), at  $1.5 R_e$  and at  $2 R_e$ . At  $2.0 R_e$ , the Brueckner orbitals (see Fig. 6, only the valence orbitals and the first virtual orbital are given) show more localisation of the electrons on the H-atoms. As the bond length increases the localisation becomes more, which is what we expect when a molecule dissociates to its atoms. In Fig. 6c, the orbital is emerging as an anti-bonding orbital. Again, the plots are similar to those of the difference densities of the BD orbitals but they are quite different from the MP2 orbitals.

#### 4. Conclusion

From the orbital densities we must conclude that the Brueckner orbitals are more similar to SCF orbitals than to the Natural orbitals of the Full BD wavefunction. They include however the majority of the electron correlation, comparable to the level of MP2 as the total electron densities show. They give qualitatively good pictures in the case of dissociation and are therefore useful for studying this feature.

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