A study of interaction in the lowest singlet and triplet states of H₂

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Abstract. The potential energy curves of the ground state and the first excited
state of H_2 are examined in terms of the electronic force acting on each nucleus.
The results reveal the detailed course of events that occur when two hydrogen atoms
with parallel and antiparallel electron spins approach one another from a large
internuclear separation.

Keywords. Potential energy curves; ground state; excited state; atomic polarisation;
orbital contraction.

1. Introduction

In our previous studies (Bader and Chandra 1968; Chandra and Sunder 1971;
Sunder and Chandra 1974; Chandra and Sebastian 1976a, b) we have presented
an interpretation of the process of bond–formation from two separated atoms as a
function of internuclear separation in terms of the electronic force acting on the
nuclei and the change in molecular charge distributions. Such studies reveal the
nature and origin of both the long-range and short-range interactions. Although
we have presented earlier the detailed course of events that occur during the forma-
tion of the ground state of H_2 (Bader and Chandra 1968) from two ground-state
hydrogen atoms, it is imperative to study how two ground-state hydrogen atoms
with their electron spins parallel behave when they approach each other from an
infinite separation. Since the triplet state of H_2 i.e. $^3\Sigma_u^+$ is unstable at all separa-
tions such study along with the studies of the $^1\Sigma_g^+$ state of H_2 may provide interesting
clues as to the nature of binding and are also relevant to theories of molecular
structure and intermolecular forces. The object of the present investigation is to
examine in terms of the electronic forces acting on the nuclei the potential energy
curves for both the ground state ($^1\Sigma_g^+$) and the first excited state ($^3\Sigma_u^+$) of H_2 which
were obtained with high precision by Bowman *et al* (1970). They employed
the extended Hartree–Fock approximation for the $^1\Sigma_g^+$ state and the usual single-
configuration Hartree–Fock approximation for the $^3\Sigma_u^+$ state. Both states of H_2
dissociate into two ground-state hydrogen atoms and their wave functions involve σ_g
and σ_u orbitals which are expressed by a basis set of Slater-type orbitals.

2. An analysis in terms of electronic forces

The total force acting on a nucleus A in a homonuclear diatomic for any inter-nuclear separation R is given by (Bader and Chandra 1968; Chandra and Sunder 1971; Sunder and Chandra 1974; Chandra and Sebastian 1976 a, b)

$$F_A(R) = \frac{Z}{R^2}(Z - f_A^\rho), \tag{1}$$

where

$$f_A^\rho = R^2 \int \rho(r) \frac{\cos\theta_{Ai}}{r_{Ai}^2} d\tau, \tag{2}$$

is called the charge equivalent of the net electronic force on nucleus A in the direction of the bond, Z is the nuclear charge and $\rho(r)$, the molecular electron density at a point r evaluated for the internuclear separation R. In order to understand the detailed course of events during the atomic interaction it is more useful to consider f_A^ρ than the total force $F_A(R)$. In figure 1 is shown the variation of f_A^ρ
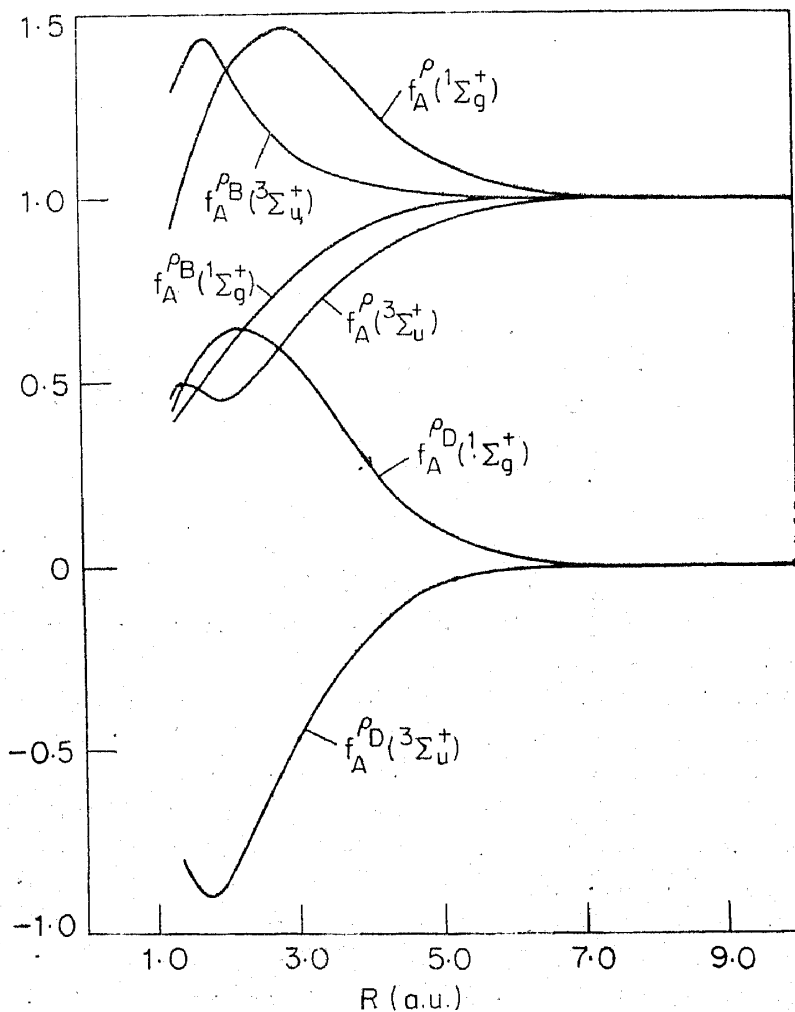

Figure 1. Variation with R of $f_A^\rho\ (^1\Sigma_g^+)$, $f_A^\rho\ (^3\Sigma_u^+)$, $f_{A}^{\rho_B}\ (^1\Sigma_g^+)$, $f_{A}^{\rho_B}\ (^3\Sigma_u^+)$ $f_{A}^{\rho_D}\ (^1\Sigma_g^+)$ and $f_{A}^{\rho_D}\ (^3\Sigma_u^+)$. All the quantities are in atomic units.

($^1\Sigma_g^+$) and f_A^p ($^3\Sigma_u^+$) with R. The limiting value of f_A^p for both the singlet and triplet states of H_2 is unity (Bader and Chandra 1968; Chandra and Sunder 1971; Sunder and Chandra 1974; Chandra and Sebastian 1976 a, b). Figure 1 shows that at large R the singlet and triplet states of H_2 behave identically and such situation persists for $R \approx 7a_0$. For $R < 7a_0$, the density in the $^1\Sigma_g^+$ state becomes more and more binding corresponding to a net force of attraction and the formation of a stable molecule, while in the $^3\Sigma_u^+$ state the charge distribution becomes anti-binding corresponding to a net force of repulsion. From the comparison of the potential energy curves of the singlet and triplet states of H_2, Bowman *et al* (1970) concluded that the near identity of these two states of H_2 persists for R as small as $5a_0$. Our analysis has however revealed that these two states of H_2 behave differently for $R > 5a_0$. This difference becomes more striking when we partition the electronic forces into three components as

$$f_A = f_A^{\rho_A} + f_A^{\rho_B} + f_A^{\rho_D}, \tag{3}$$

and analyse each term separately. The three terms of equation (3) are respectively called the atomic polarisation, screening and the overlap (or delocalisation) terms and their physical significance has been discussed in earlier publications (Bader and Chandra 1968; Chandra and Sunder 1971; Sunder and Chandra 1974; Chandra and Sebastian 1976a, b). In figures 1 and 2 are shown the variation of these three
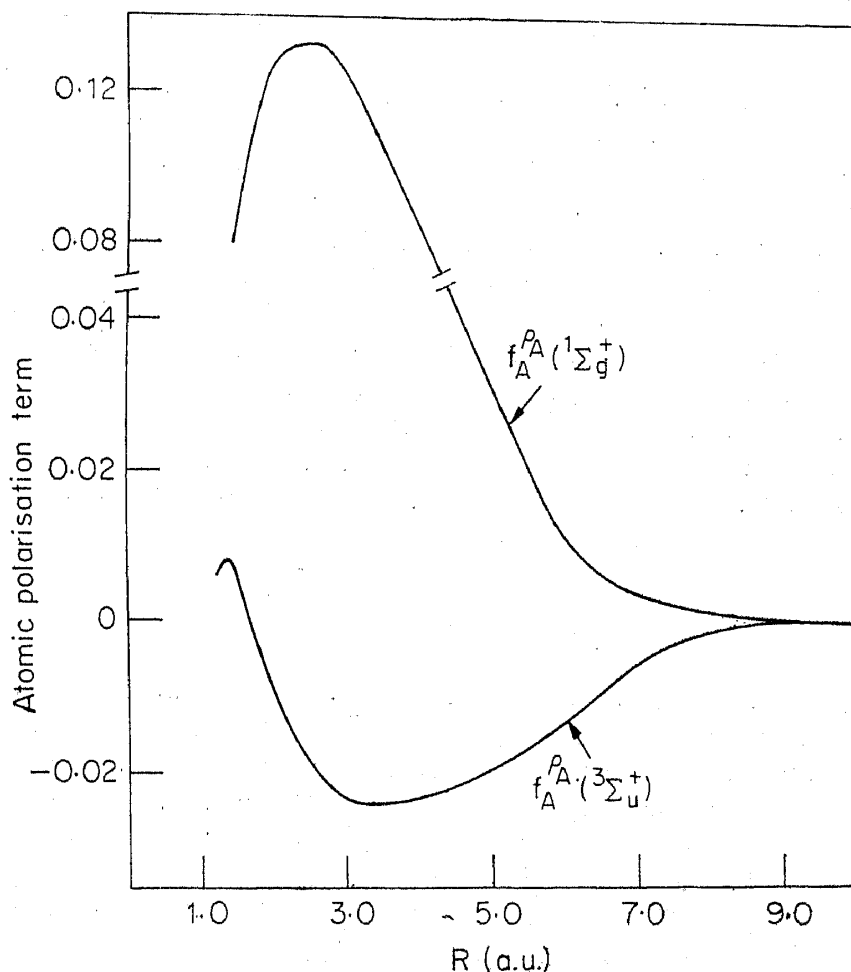

Figure 2. Variation with R of $f_A^{\rho_A}$ ($^1\Sigma_g^+$) and $f_A^{\rho_A}$ ($^3\Sigma_u^+$).

terms with R. It should be noted that all these three terms, i.e., $f_{A}^{\rho_A}$, $f_{A}^{\rho_B}$ and $f_{A}^{\rho_D}$ should converge to zero in the limit of the united atom. The variation of these terms with R in figures 1 and 2 shows this trend at a very small value of R.

The variation of $f_{A}^{\rho_A}$ with R for both the $^3\Sigma_u^+$ and $^1\Sigma_g^+$ states (figure 2) shows that even for $R \geqslant 5a_0$ when the overlap of two atomic orbitals is negligibly small, the electron cloud around each nucleus is polarised behind the nucleus in the $^3\Sigma_u^+$ state. On the other hand, in the $^1\Sigma_g^+$ state each atomic density is polarised towards the internuclear region resulting in an attractive force on each nucleus. But the variation of $f_{A}^{\rho_A}$ ($^3\Sigma_u^+$) with R for $R < 2a_0$ is somewhat surprising. Instead of going over directly to zero at $R = 0$, the value of $f_{A}^{\rho_A}$ ($^3\Sigma_u^+$) rises to a positive value and then decreases to zero. This can be understood when we discuss the behaviour of the component (σ_g and σ_u) orbitals for various R.

When R is decreased below $5a_0$, the variation of $f_{A}^{\rho_B}$ with R (figure 1) shows that in the singlet state each nucleus readily penetrates into the charge cloud of the other atom while in the triplet state there is no evidence of such penetration. The increase of the screening term for the $^3\Sigma_u^+$ state over the limiting value can be caused either by the contraction of the atomic orbitals or by a transfer of densities from the internuclear region or by both. This increase of the screening term beyond the limiting value implies an attraction between two atoms in the $^3\Sigma_u^+$ state but this increase is small and more than offset by the highly repulsive overlap term.

The variation of the overlap term, i.e. $f_{A}^{\rho_D}$ with R (figure 1) shows that as the two approaching atomic orbitals begin to overlap $f_{A}^{\rho_D}$ increases in the $^1\Sigma_g^+$ state implying transfer of charge in the internuclear region until it reaches a maximum. On further decrease of R, the charge density is transferred behind the nuclei causing a decrease in the value of $f_{A}^{\rho_D}$ ($^1\Sigma_g^+$) for $R < 2a_0$. On the other hand, in the $^3\Sigma_u^+$ state, the variation of $f_{A}^{\rho_D}$ with R implies a transfer of charge from the internuclear region to the region behind the nuclei and this charge density exerts a force which pulls the nuclei away from one another. At $R = 2a_0$ the force of repulsion exerted by the overlap density in the $^3\Sigma_u^+$ state corresponds to an increase of the nuclear charge by about $+0.85$ units. This sizable effect arises from the fact that two electrons with their parallel spins cannot occupy the same region of space simultaneously. On further decrease of R, the value of $f_{A}^{\rho_D}$ ($^3\Sigma_u^+$) increases. This may be due to the expansion of an orbital in which case the magnitude of the force on the nucleus should decrease or some charge density migrates to the internuclear region from the antibinding regions.

3. Behaviour of σ_g and σ_u orbitals

According to the simple concept of the molecular orbital theory for homopolar diatomics the σ_g and σ_u orbitals are respectively binding and antibinding. Since the antibinding character of the σ_u orbital density dominates, the $^1\Sigma_g^+$ state of H_2 with the predominant configuration of $|1\sigma_g^2|$ is stable and the $^3\Sigma_u^+$ state with the configuration of $|1\sigma_g^1 1\sigma_u^1|$ is unstable. This simple picture is however, only qualitatively valid when the force concept is used.

The total electronic force operative in the singlet and triplet states of H_2 may be broken down into the orbital components. Thus

$$f_{A}^{\rho} = f_{A}^{\sigma_g} + f_{A}^{\sigma_u}, \tag{4}$$

where f^i_A is the charge equivalent of the partial force exerted on the nucleus A by the density in the ith molecular orbital. For the separated atoms the density distribution corresponding to each non-degenerate molecular orbital φ_i may be written as

$$\varphi_i^* \varphi_i = \tfrac{1}{2}(\varphi_{iA}^2 + \varphi_{iB}^2), \tag{5}$$

where φ_{iA} and φ_{iB} are the centrosymmetric atomic orbitals on atoms A and B with which φ_i correlates for the separated atoms. At the limit of large R, f^i_A becomes (Bader and Chandra 1968; Chandra and Sunder 1971; Sunder and Chandra 1974; Chandra and Sebastian 1976a, b)

$$f^i_A (R = \infty) = n_i/2, \tag{6}$$

where n_i is the occupation number of the ith MO. In both the singlet and triplet states of H_2 at $R = \infty$ the occupation number of the σ_g and σ_u orbitals is unity and therefore the limiting value of each f^i_A is clearly $0\cdot5$. In figure 3 are shown the
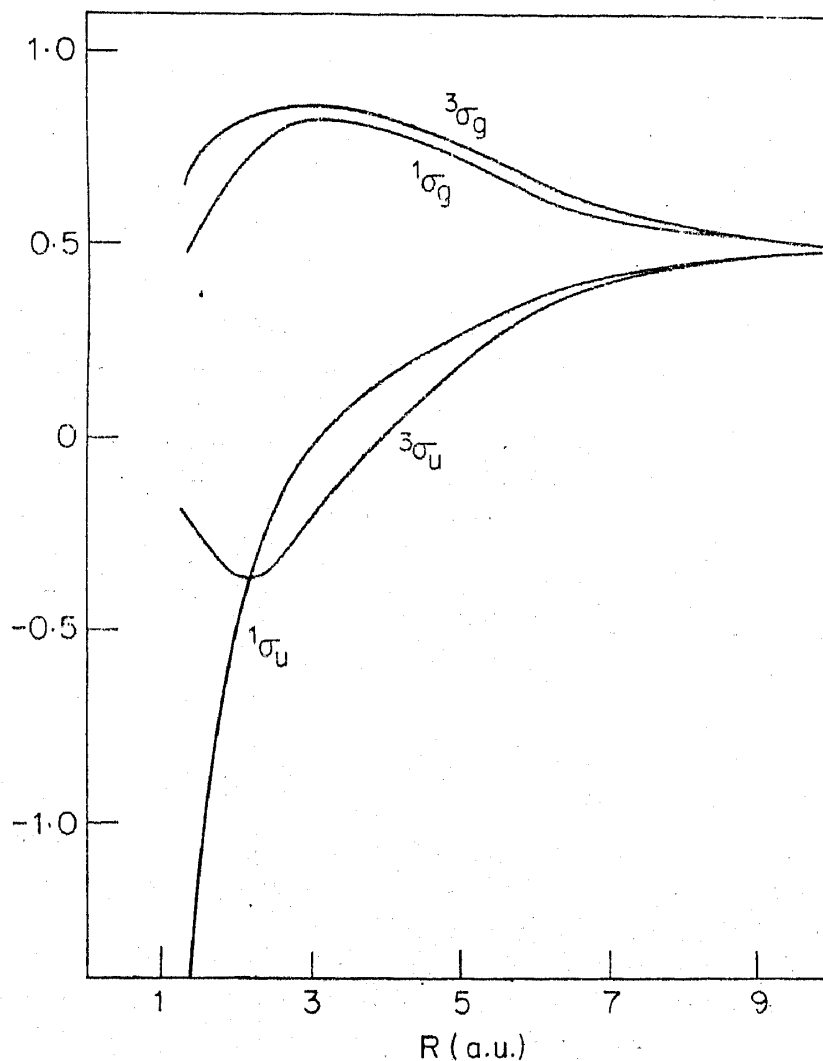

Figure 3. Variation with R of $f^{\sigma_g}_A$ and $f^{\sigma_u}_A$ per electron for the singlet and triplet states.

variations of $f_A^{\sigma_g}$ and $f_A^{\sigma_u}$ per electron with R for the singlet and triplet states. The results clearly show that ${}^1\sigma_g$ and ${}^3\sigma_g$ orbital densities are binding while ${}^1\sigma_u$ and ${}^3\sigma_u$ orbital densities are antibinding for $R < \infty$. The results further show that the properties of ${}^1\sigma_g$ and ${}^3\sigma_g$ orbital densities are similar for $R \geqslant 7a_0$. For $R < 7a_0$, the ${}^3\sigma_g$ orbital becomes more binding than the ${}^1\sigma_g$ orbital and this is possible if the ${}^3\sigma_g$ orbital contracts relative to the ${}^1\sigma_g$ orbital. This contraction of the ${}^3\sigma_g$ orbital is more marked for $R < 2a_0$. However, both the ${}^1\sigma_g$ and ${}^3\sigma_g$ orbitals converge to $1s$-orbital of helium at $R = 0$.

On the other hand, although ${}^1\sigma_u$ and ${}^3\sigma_u$ orbitals behave similarly at large R, the difference between these two orbitals become increasingly marked at lower R where the ${}^3\sigma_u$ orbital becomes more antibinding than the ${}^1\sigma_u$ orbital. For $R < 2a_0$ the antibinding ability of the ${}^3\sigma_u$ orbital density decreases while that of the ${}^1\sigma_u$ density continues to increase. Since both the ${}^1\sigma_u$ and ${}^3\sigma_u$ orbitals go over to the $2p$-orbital of helium at $R = 0$, it suggests that the ${}^3\sigma_u$ orbital expands relative to the ${}^1\sigma_u$ density for $R < 2a_0$. Such expansion of the ${}^3\sigma_u$ orbital relative to the ${}^1\sigma_u$ orbital at $R = 1 \cdot 5\, a_0$ has been strikingly shown in the orbital density diagrams of Bowman *et al* (1970). It is however to be noted from figure 3 that there is no indication of $f_A^{{}^1\sigma_u}$ converging to zero in the limit of the united atom.

If we measure the binding and antibinding abilities of the σ_g and σ_u orbitals by the magnitude of $(0 \cdot 5 - |f_A^i|)$ then we see from figure 3 that for $R < 7a_0$ the antibinding character of the σ_u orbitals dominates the binding abilities of the σ_g orbitals. Since in the ${}^3\Sigma^+$ state the occupation number of the ${}^3\sigma_u$ and ${}^3\sigma_g$ orbitals is always unity at all R while in the ${}^1\Sigma_g^+$ state the occupation of the ${}^1\sigma_u$ orbital decreases at lower R and has a value of approximately $0 \cdot 02$ (Bowman *et al* 1970) at $R = 1 \cdot 4a_0$, the ${}^1\Sigma_g^+$ state of H_2 becomes stable at $R = 1 \cdot 4a_0$ and the ${}^3\Sigma_u^+$ state remains unstable at all values of R. Therefore, the instability of the ${}^3\Sigma_u^+$ state at small R arises from the persistent tendency of its electrons to correlate while in the ${}^1\Sigma_g^+$ state such tendency of electrons is decreased so that two electrons can come close together on the average and exert a strong binding force on each nucleus.

One can now also understand why the atomic term in the triplet state increases to a positive value for $R < 2a_0$ and then decreases to zero as R tends to zero. Normally, the σ_u charge density exerts a negative atomic force which cancels the positive atomic term contributed by the σ_g density. On account of the expansion of the σ_u orbital the magnitude of its atomic term decreases while the positive atomic term of the σ_g density increases due to its contraction.

4. Changes in the charge distribution during the H + H interactions

The changing nature of the density distributions as the two H-atoms approach one another resulting in the formation of the stable H_2 molecule has already been illustrated in the $\triangle\rho$-contour maps (Bader and Chandra 1968) employing the extended Hartree–Fock wave functions of Das and Wahl (1966). Similar $\triangle\rho$-diagrams are obtained for the ground-state of H_2 from the wave functions of Bowman *et al* (1970) and are therefore not reported here. However, it will be of great interest to examine how the charge distribution changes in the triplet state of H_2 as a function of R. Figure 4 presents $\triangle\rho$-contour maps for the ${}^3\Sigma_u^+$ state of H_2 at a number of internuclear distances calculated from the wave functions of Bowman *et al* (1970).
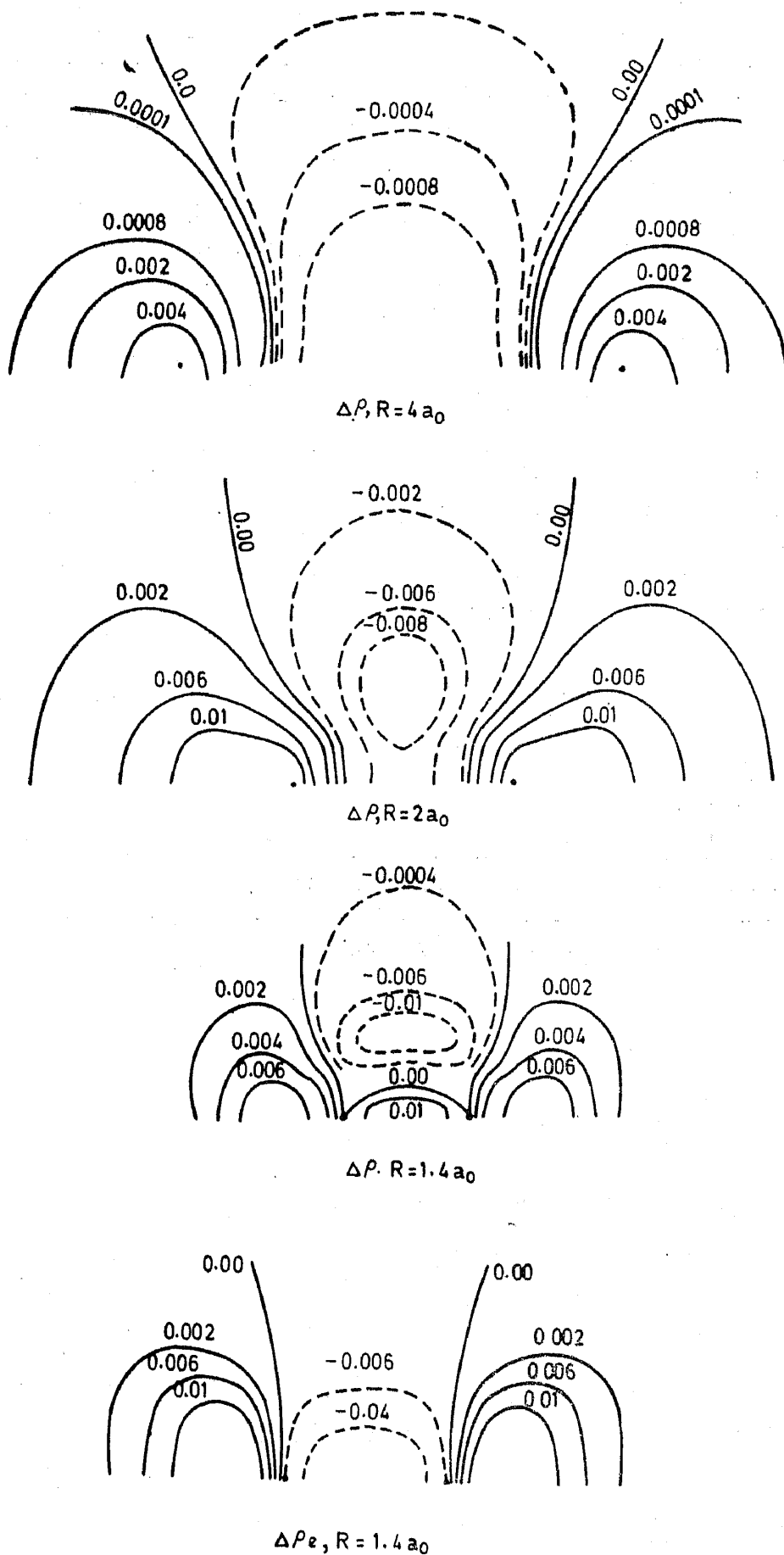
Figure 4. The $\triangle\rho$-contour maps for the $^3\Sigma_u^+$ state of H_2 at the indicated values of R and the $\triangle\rho_s$-map for $R = 1\cdot4a_0$.

These diagrams are the approximate opposites of the $\triangle\rho$-maps for the singlet state of H_2. The densities in the $^3\Sigma_u^+$ state increase in the regions behind the nuclei as well as in the vicinity around each nucleus at the expense of densities in the internuclear region as R is decreased. But, at $R = 1.4a_0$, figure 4 shows that there is an indication of slight increase in density in the internuclear region. This could arise from the simultaneous expansion of the $^3\sigma_u$ orbital and the contraction of the $^3\sigma_g$ orbital both having the occupation number of unity each in the $^3\Sigma_u^+$ state. In fact, the small positive atomic term at $R = 1.4a_0$ in figure 2 is consistent with the slight increase of density in the internuclear region. But this increase is very small and does not balance the nuclear repulsion, hence the $^3\Sigma_u^+$ state is unstable. Figure 4 also shows the plot of $\triangle\rho_e$ defined as

$$\triangle\rho_e = \rho\left(^3\Sigma_u^+\right) - \rho\left(^1\Sigma_g^+\right), \tag{7}$$

for $R = 1.4a_0$, where $\rho\left(^3\Sigma_u^+\right)$ and $\rho\left(^1\Sigma_g^+\right)$ are the molecular charge densities of the $^3\Sigma_u^+$ and $^1\Sigma_g^+$ states respectively for the same value of R. This shows that the charge density in the internuclear region is greater in the $^1\Sigma_g^+$ state than in the $^3\Sigma_u^+$ state.

It may be important to mention here that a similar study on the triplet state of HeH^+ which is isoelectronic with the $^3\Sigma_u^+$ state of H_2 as it dissociates into He^+ and H has been made earlier (Chandra and Sebastian 1976a). It was shown that the triplet state of HeH^+ shows a weak binding due to large polarisation of the electron cloud of the H atom caused by the unscreened positive charge of the He^+ ion.

References

Bader R F W and Chandra A K 1968 *Can. J. Chem.* **46** 953
Bowman J D, Hirschfelder J O and Wahl A C 1970 *J. Chem. Phys.* **53** 2743
Chandra A K and Sunder R 1971 *Mol. Phys.* **22** 369
Chandra A K and Sebastian K L 1976a *Mol. Phys.* **31** 1489
Chandra A K and Sebastian K L 1976b *Chem. Phys. Lett.* **41** 593
Das G and Wahl A C 1966 *J. Chem. Phys.* **44** 87
Sunder R and Chandra A K 1974 *Indian J. Chem.* **12** 145