A Difference Technique for the Study of Electronic Excitations

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A new method for the study of electronic excitations, Excited State Electron Density Differential (ESEDD), in which an excitation process is described as a difference in charge density between excited and ground states, has been developed and applied to the HOMO to LUMO and HOMO to antibonding $1b_{2g}$ transitions of ethylene.

In crystallography, the charge transfer process accompanying the formation of the chemical bonds within a molecule is obtained from Electron Density Deformation (EDD) maps. The differences between the magnitude of the atomic electron densities for the fixed arrangement of atoms in a molecule and the actual molecular charge density are obtained as contour lines. Several calculations of such data have been reported within the MS-X_{α}[1—7] and other molecular orbital methods.[8,9]

In this Communication, we introduce a new method, which we call the Excited State Electron Density Differential (ESEDD) in which we describe an excitation process as a difference in charge density between the excited state and the ground state.[10] We define the ESEDD according to equation (1), in which ψ_{1e}, ψ_{2e} · · · ψ_{re} are the respective molecular wavefunctions for the excited state and ψ_{1g}, ψ_{2g} · · · ψ_{rg} are such entities in the ground state; the HOMO being (ψ_{r-1}). It is important to note that according to this definition, the symmetry and the higher order orthogonality requirements

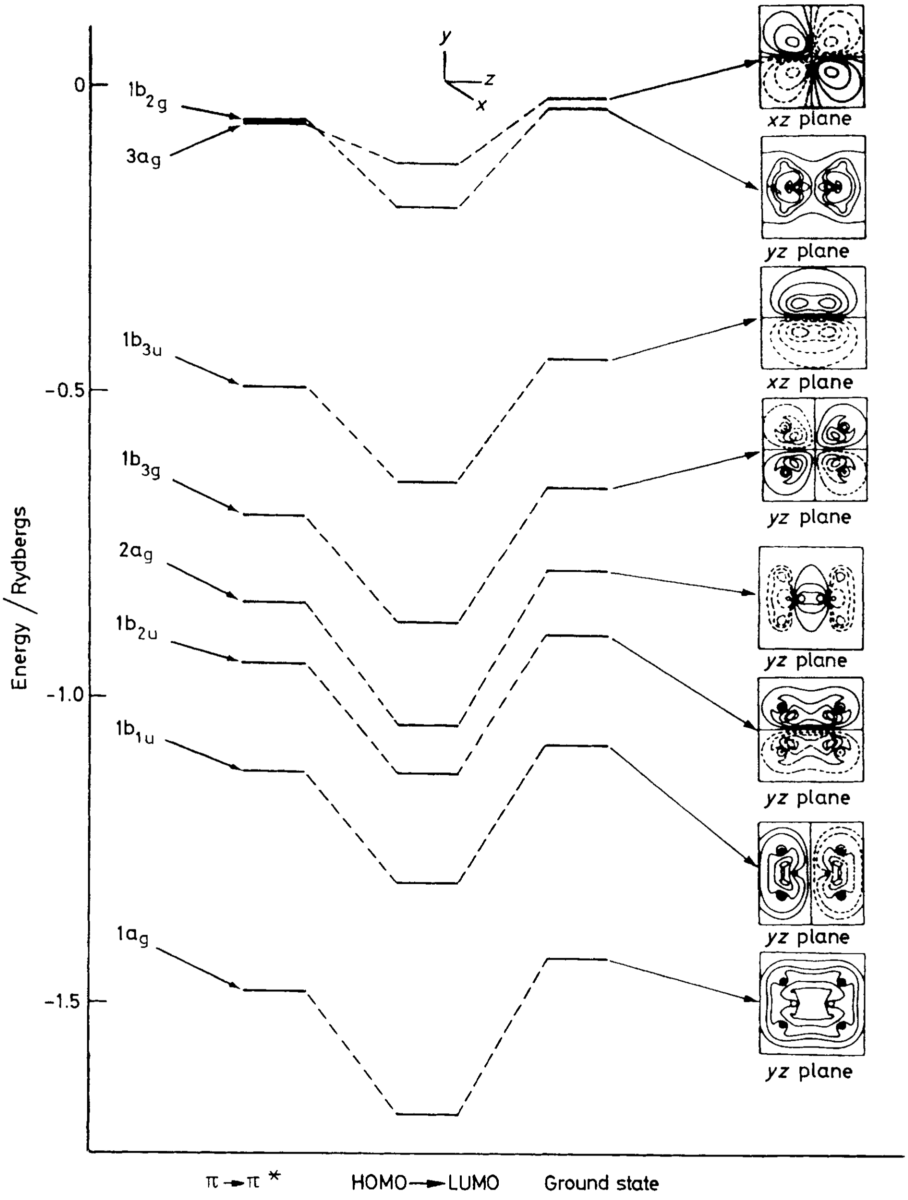

Figure 1.

must be preserved and that each of the non-singly degenerate molecular orbitals must be properly resolved into an appropriate combination of singly degenerate levels.

$$\Gamma^{\mathrm{ESEDD}} = \left\{ \sum_{i}^{r-1} 2(\psi_{ie}^2 - \psi_{ig}^2) \right\} + \psi_{re}^2 - \psi_{(r-1)g}^2$$

We apply this method to ethylene within the MS-X_α approximation in which we employ partial waves that correspond to an $l_{\mathrm{max.}}$ = 1, 0, and 3 around the C, H, and outersphere, respectively. In conducting the calculations, we have used an exchange potential parameterized with the Schwarz α values[11] and the amount of sphere overlap was determined by the Norman criteria.[12] According to our results, the ground state electronic configuration of ethylene is $(\mathrm{core})^4\,(1a_g)^2\,(1b_{1u})^2\,(1b_{2u})^2\,(2a_g)^2\,(1b_{3g})^2\,(1b_{3u})^2\,(3a_g)\,(1b_{2g})$ in which the $1b_{3u}$ π orbital is the HOMO. The $3a_g$ orbital is a non-bonding orbital that involves the s and p bases on the C atoms and is the LUMO whereas the b_{2g} is the anti-bonding π orbital perpendicular to the plane of the molecule. The two excitation processes that will be of interest to us involve a promotion of an electron from (a) the HOMO to the LUMO and (b) the HOMO to the antibonding $1b_{2g}$ orbital. Both of these excitations are allowed, being of the type $({}^1B_{3u} \leftarrow {}^1A_g)$ and $({}^1B_{1u} \leftarrow {}^1A_g)$, respectively. In Figure 1, we show the relative positions of the energies of the molecular orbitals in the ground and the two excited states of interest. Contour maps representing the respective molecular orbitals are also displayed in Figure 1. In Table 1, we report the orbital energies (in Rydbergs) for the ground state and the excited states in terms of the population of the C s and p bases.

In the case of the $\pi^* \leftarrow \pi$ transition, one expects to observe a flow of charge away from the C–C bond axis. An ESEDD map in the xz plane which contains the π bond under study would, therefore, properly describe this charge flow. Figure 2 represents the total charge density in the xz plane after and

Table 1. Orbital energies (in Rydbergs) of the ground state in ethylene in D_{2h} symmetry in which the starred orbital is the LUMO. The description of the orbitals is referenced to the carbon (2s) and (2p) bases in the ground state and the two excited states under study.

		Description of the orbitals in terms of the carbon (2s) and (2p) bases					
		Ground state		Excited State $1b_{2g} \leftarrow 1b_{3u}$		Excited State $3a_g \leftarrow 1b_{3u}$	
M.O. in D_{2h} symmetry	Energy/ Rydbergs	s	p	s	p	s	p
$1b_{2g}$	−0.014		0.500		0.500		0.500
$3a_g$*	−0.028	0.232	0.149	0.235	0.154	0.262	0.167
$1b_{3u}$	−0.444		0.500		0.500		0.500
$1b_{3g}$	−0.647		0.207		0.209		0.217
$2a_g$	−0.781		0.374		0.373		0.369
$1b_{2u}$	−0.892		0.264		0.266		0.273
$1b_{1u}$	−1.070	0.210	0.073	0.210	0.070	0.217	0.074
$1a_g$	−1.421	0.374	0.048	0.374	0.050	0.372	0.060

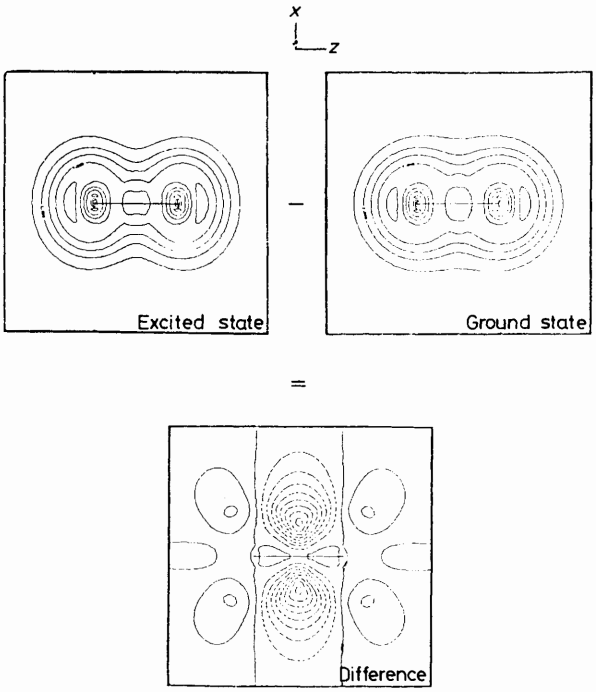

Figure 2.

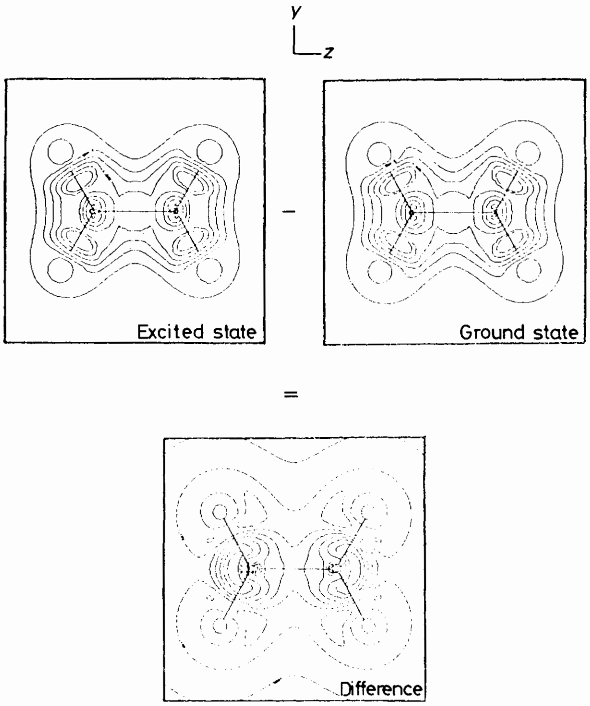

Figure 3.

before the excitation process and the difference thereof. The broken contours represent areas in which there is a depletion in the charge in contrast to the solid contours which represent areas in which there is a development of charge. This is in line with what one expects as a result of the excitation process. The construction of this map is particularly simple since the two orbitals under study are orthogonal to the rest of the occupied orbitals and, except for slight changes associated with the new potential environment that had ensued as a result of the excitation process, the population of the orbitals will not be expected to change drastically. Inspection of Table 1, in fact, indicates that the excitation process was not accompanied by appreciable changes in the charge composition of the occupied orbitals.

We now consider an excitation process that involves a promotion of an electron from the HOMO to the $3a_g$ orbital. Figure 3 is similar to Figure 2 and represents the flow of charge as a result of this excitation. The choice of this particular promotion is consequential since one is now dealing with a flow of charge from a π orbital to an essentially non-bonding orbital. One could argue that if such a process occurs without a relaxation of the charge in the molecular orbitals defined in the co-ordinate plane to which the electron has been promoted, the difference map should only show a development of charge. The difference map, however, shows that in addition to the development of charge around the C s and p_z bases, there are areas in which there is a depletion of charge around the H atoms. This result may be deduced from Table 1 by inspecting the $1b_{3g}$ and $1b_{2u}$ orbitals that represent σ interactions between the C p and the H s bases. The total charge contribution from the H atoms in these orbitals may be obtained by subtracting twice the charge contribution of the C p bases from unity. The percent charge composition of the H s bases in the $1b_{3g}$ orbital is calculated to be 58.6% and 56.5% in the ground and excited states, respectively, whereas in the case of the $1b_{2u}$ orbital it is calculated to be 47.2% and 45.4% in the ground and excited states, respectively. This would, of course, mean that the promotion of an electron to the $3a_g$ orbital had resulted in a redistribution of charge around the H atoms in order to accommodate the new set of conditions that had persisted as a result of the excitation process. The development of charge around the C atoms as a result of this excitation can likewise be deduced.

Application of this method would be particularly useful for the study of charge transfer processes in transition metal complexes, and we have started applying such a method to molybdenum species containing O and S ligands.

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