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Theoretically Calculated Deformation Density of Small Molecules

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Analysis of the theoretical electron deformation density based on EHMO and ab initio calculations has been applied to the simple molecules F_2, H_2O and SO_2. The effects from varied basis sets for such deformation density were sought. The accumulation of electron density between the bonded atoms calculated from EHMO and ab initio methods with STO-3G is generally under-estimated. Such phenomena are significantly improved by using split-valence basis sets e.g. 3-21G and 4-31G. The addition of d polarization functions is apparently important for the sulfur atom in sulfur-related bonding. 3-21G or 3-21G* basis sets were found to provide not only valuable deformation density distributions of molecules but also comparable orbital energy states with respect to the experimental values.

INTRODUCTION

The experimental deformation density has been used as a probe of the bonding character of molecules for the past two decades.[1-5] Conventionally the deformation density[4] ($\Delta\rho$) is defined as the difference between the molecular density and the promolecular density. The promolecular density is composed of the sum of the densities from the superposition of spherical free atoms, each centered at its equilibrium position in the molecule.

$$\Delta\rho = \rho_{\mathrm{mol}} - \sum_{i} \rho_{i}^{\mathrm{atom}} \qquad i = 1,2,3\cdots N$$

Thus the deformation density map can reveal the overlap density in the internuclear regions and the lone pair regions around the atom.

The deformation density can be obtained both by X-ray diffraction, generally at low temperature, and by molecular-orbital calculations. However, the unavoidable experimental errors and the limited resolution of the diffraction measurements may hinder the quantitative description of chemical bonding from such studies. A multipole model[4,6] of the deformation density distribution was later developed to surpress such experimental errors and to give better resolved results. As both experimental and multipole density distributions are basically derived from X-ray diffraction measurements, the limitation on the resolution and the effect of molecular thermal motion still make impossible precise analyses of chemical bond. Thus concurrent studies of theoretical and experimental approaches are important for the understanding of chemical bonding. However, the details of bonding character e.g. σ or π bond description still rely on the orbital wavefunctions. Once the theoretical deformation density distribution is in good agreement with the experimental one, such molecular orbitals can be used to understand further the bonding character in detail.

There are many levels of approximation in procedures for molecular-orbital calculations. Generally the more sophisticated calculation yields better results for the total energy, spectral parameters and other chemical properties. Ab initio calculations are becoming popular recently, because of the available software and the rapid improvement of computer hardware, but calculations on a complicated molecule are still protracted if extended basis functions are required. Therefore the choice of proper basis sets to study certain problems becomes important. In practice, most popular computer programs for ab initio calculations contain internally defined standard basis sets.[8,9,10,13] In this article, we discuss the suitability of various calculations to study deformation density distributions. A series of theoretical analyses on the small molecules F_2, H_2O and SO_2 were made in order to seek the most economic and efficient way to obtain valid information about the chemical bond in terms of the deformation density distribution.

COMPUTATIONAL PROCEDURE

The molecular-orbital calculations discussed in this work include the simplest one-the extended Hückel method and the most sophisticated one-the ab initio method. According to both methods, the molecular orbitals are generated using exactly the same molecular

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Dedicated to Professor Sheng-Lieh Liu (劉盛烈) on the occasion of his eightieth birthday.

geometry as the experimental one. For extended Hückel calculations, a program ICON[7] was used. For ab initio calculation, programs HONDO[10] and Gaussian 90[8] were used. Various basis sets such as STO-3G, 3-21G, 4-31G, 6-31G were tested in order to compare the effects appearing in the deformation density maps. The molecular orbitals were generated at a single-point RHF level. The spherical atomic orbitals were generated at the ROHF/GVB level with the same basis sets as in the molecular-orbital calculations.

The total molecular electron density and promolecular electron density were generated by the MOPLOT program.[11] For closed-shell molecules, each occupied molecular orbital is assigned to have two electrons. For spherical atoms, each p orbital of an F, O and S atom is assigned to have 5/3, 4/3 and 4/3 electrons respectively.

The contours of deformation density maps or molecular wavefunctions were plotted by CPPLOT program.[12]

All computations and plots were performed on the Micro-Vax 3600 computer and with a DEC LNO3+ laser jet plotter.

RESULTS AND DISCUSSION

F_2 Molecule

The deformation density study of the F_2 molecule

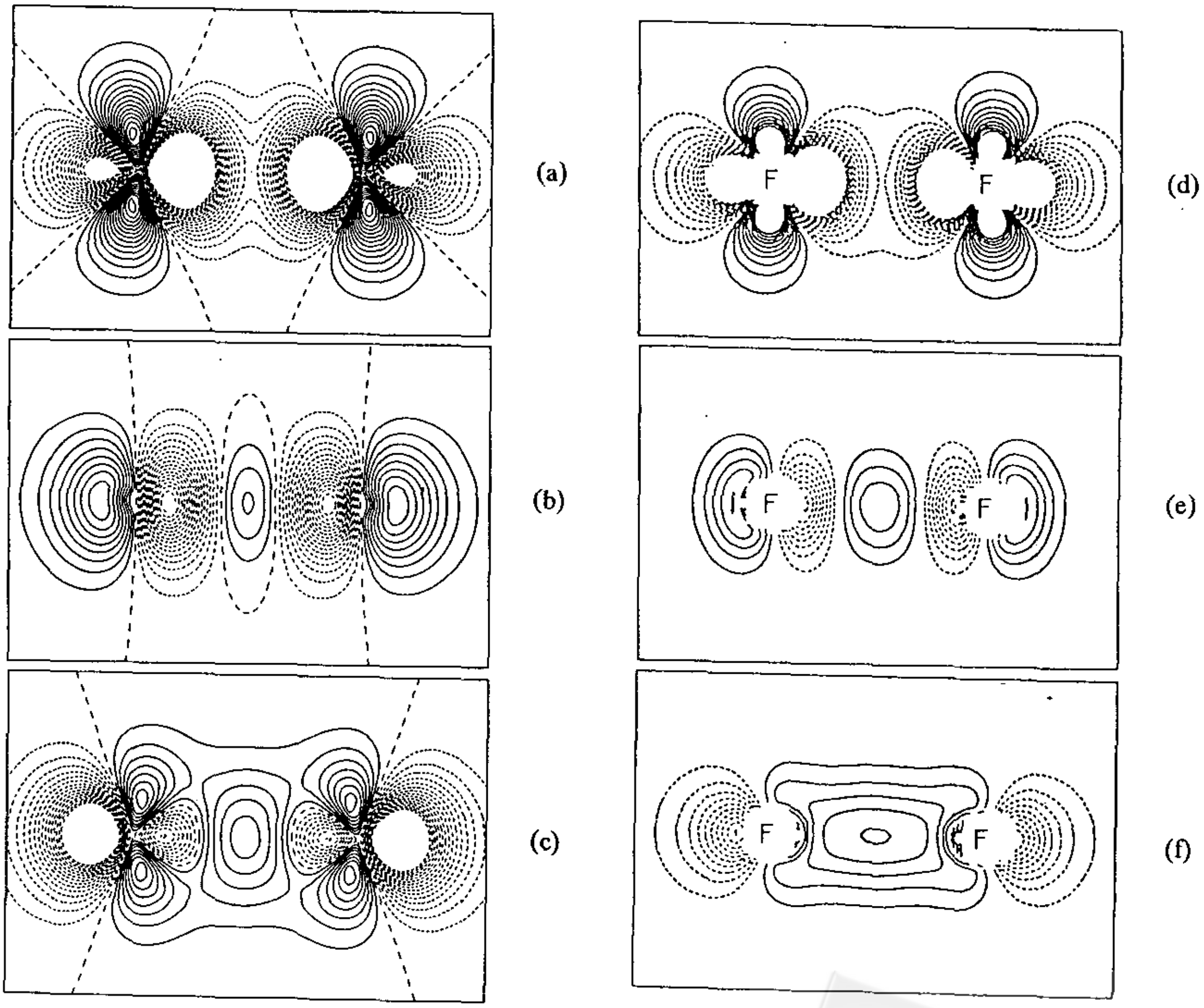

Fig. 1. Deformation electron density distributions of F_2 molecule; contour interval at 0.1eÅ^{-3}; solid line positive, dash line zero, dotted line negative. (a) atom in spherical condition; (b) atom in oriented condition; (c) atom in valence hybrid condition; (f) same map condition as in (a); (g) same map condition as in (b); (h) same map condition as in (c); (a)-(c) with EHMO method; (f)-(g) with ab initio method.

using ab initio calculations was published earlier.[14,17] In order to see whether we could reproduce these results using a much simpler approach, we undertook the deformation density study using EHMO. The F-F distance was fixed at 1.4177Å.[15] The atomic electron density of the *promolecule was investigated under several conditions* (assuming the interatomic axis is z): (a) a spherical condition ($s^2p_x^{5/3}p_y^{5/3}p_z^{5/3}$), (b) an oriented condition ($s^2p_x^2p_y^2\ p_z^1$), (c) a valence hybrid condition(($(sp_z)^1(sp_z)^2p_x^2p_y^2$). The resulting deformation density maps of the F_2 molecule are shown in Figs. 1(a), (b) and (c). Apparently they agree well with those generated by ab initio calculation[14] using a (9s5p/CGO 5s3p)triple-zeta basis set shown in Figs. 1(d), (e) and (f). The difference between (c) and (f) is probably due to the difference in the radial part of the wavefunctions. From the comparison, it is clear that, for such a simple molecule containing first-row elements, the deformation electron density has been suitably generated using the EHMO method. The "negative" deformation electron density along the bond in Fig 1(a) results from the fact that relatively large atomic densities in the Pσ orbitals are subtracted in the interatomic region. Along this direction there is less density in the molecule than that in the promolecule with an artificially spherical atom.[14,17] Such depletion of density along the internuclear axis disappeared in Fig. 1(b) when the oriented atom (p_z^1) and in Fig. 1(c) when a valence hybrid atom $(sp_z)^1$ were considered.

H_2O Molecule

H_2O molecule has been studied thoroughly in theoretical calculations.[16-18] Some experimental deformation density studies[19,20] are also available as solvent molecules in solids. Here we make a systematic comparison using EHMO and ab initio methods with various basis sets. We present first the deformation density maps of the molecular plane of H_2O in Fig. 2, in which the electron density of all atoms in the promolecule is considered to be spherical. Fig. 2(a) was produced using the EHMO method, Figs.(b)-(e) were produced using the ab *initio method with STO-3G, 3-21G, 4-31G, and 4-31G** basis sets respectively. A more sophisticated calculation including the double-zeta polarization MCSCF[17] result is shown in Fig. 2(f). The EHMO (Fig. 2(a)) and STO-3G (Fig. 2(b)) results greatly underestimate the density along the O-H bonds. Among the split valence basis sets, there are no significant differences between the results using 3-21G (Fig. 2(c)) and MCSCF (Fig. 2(f)).[17] The agreement between these theoretical deformation density maps and the experimental one (Fig. 2(g))[20] is good. The comparison of the deformation density of the plane normal to the molecular plane between the one based on the 3-21G single-point SCF and the one based on MCSCF[17] shown in Figs. 3(a) and 3(b) is also good.

In addition to the deformation density study, other properties of H_2O molecule derived from such theoretical studies are shown in Table 1. In general, the more numerous are the basis functions included in the calculation, the lower the total energy results. The inclusion of d polarization functions on the oxygen atom such as 3-21G*, 4-31G*, and 6-31G* decreases only slightly the energy (about 0.03 hartrees) relative to the values calculated from basis sets lacking polarization functions. The dipole moment computed from STO-3G basis set is near the experimental value,[21] but the dipole moments from the split-valence basis sets (3-21G, 4-31G, and 6-31G) seem to be overestimated. The addition of d functions tends to reduce the magnitude of the dipole moment. As for the geometry, the bond lengths and angles after geometry optimization

Table 1. Comparison of Properties of H_2O Molecule Based on Ab Initio Calculations

Method	Total Energy /hartrees	Dipole Moment /D	Predicted Bond Anlge /deg	Predicted Bond Length /Å	First I.E. /hartrees
STO-3G	-74.97	1.71	100.00	0.989	0.392
	(-74.97)[a]	(1.69)[a]	(100.0)[a]	(0.990)[a]	
3-21G	-75.59	2.39	107.7	0.967	0.477
3-21G*	-75.61	2.02	102.6	0.965	0.475
4-31G	-75.91	2.49	111.1	0.951	0.496
	(-75.91)[a]	(2.52)[a]	(111.0)[a]	(0.951)[a]	
4-31G*	-75.94	2.15	105.1	0.949	0.496
6-31G	-75.98	2.50	111.4	0.950	0.498
6-31G*	-76.01	2.17	105.3	0.949	0.498
	(-76.01)[a]	(2.19)[a]	(105.5)[a]	(0.948)[a]	
Experimental[a]	-76.48	1.85	104.5	0.957	0.463

[a] ref. 21.

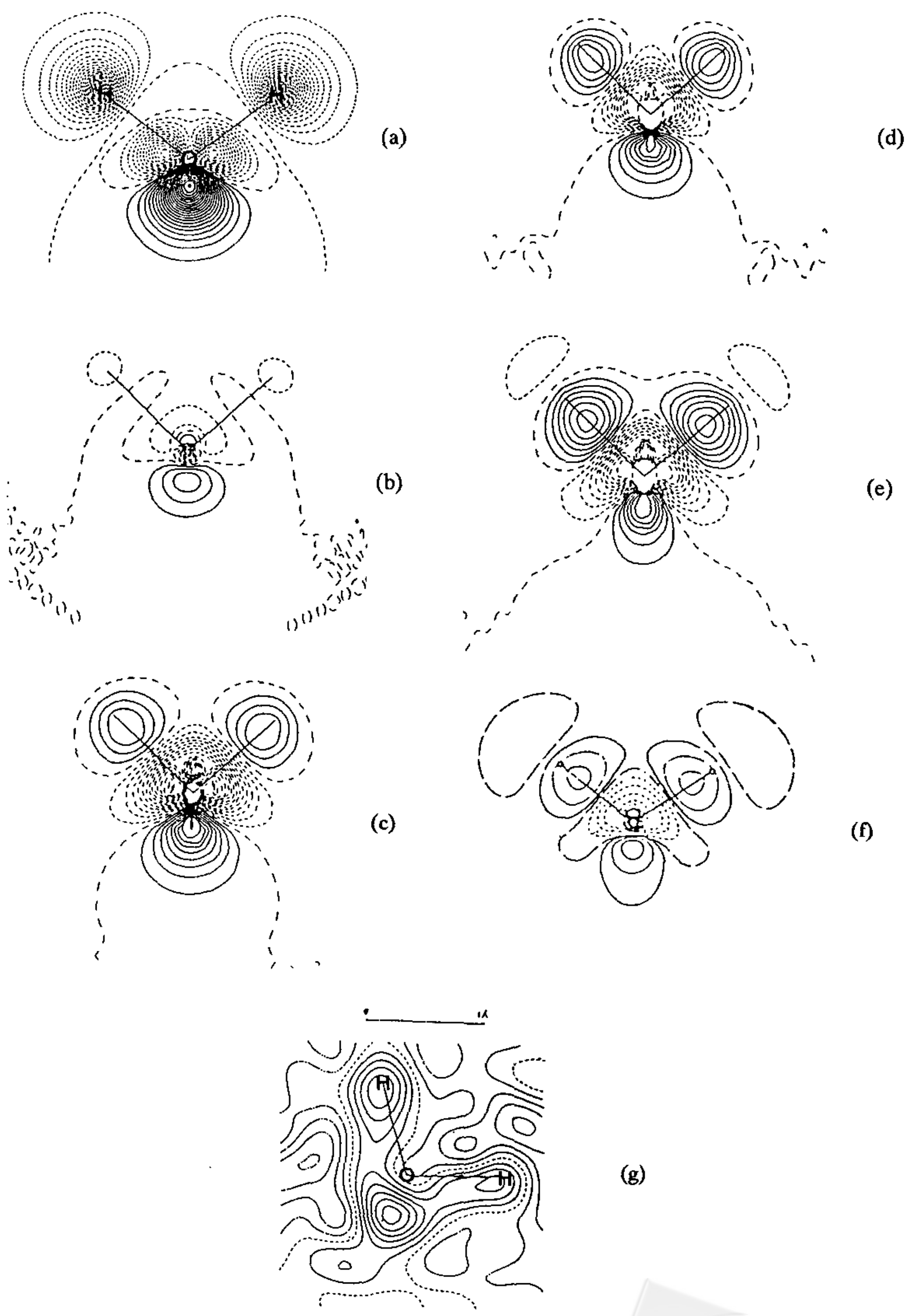

Fig. 2. Deformation electron density distributions of the H_2O plane; contour intervals etc. are as in Fig. 1 (a) from EHMO method; (b) ab initio using STO-3G basis set; (c) ab initio using 3-21G basis set; (d) ab initio using 4-31G basis set; (e) ab initio using 4-31G* basis set; (f) MCSCF results from ref.17; (g) experimental results from ref.20.

using 4-31G*, and 6-31G* are in better agreement with the experimental results[21]; the one using 3-21G* gives a somewhat smaller bond angle. However all O-H bond lengths are in good agreement with one another and are comparable with the experimental value.[21] The inclusion of d polarization on the oxygen atom generally decreases the H-O-H bond angle. The first ionization energy, i.e. the negative orbital energy of HOMO from the various calculations is listed in the last column of the table. The values from 3-21G* and 3-21G are in best agreement with experiment.

SO_2 Molecule

Split-valence level calculations produced results comparable to experimental ones for the first-row elements. Here we extend our investigation to second row elements. The sulfur atom has a large polarizability and possibly high coordination in molecules.

Again from the deformation density distribution of the SO_2 plane (Fig. 4), all calculations that exclude the d polarization functions of the sulfur atom (EHMO (Fig. 4(a)); 3-21G(Fig. 4(b)); 4-31G(Fig. 4(d)) underestimated greatly the S-O bonding effect. All corresponding calculations including the d polarization functions of the sulfur atom, e.g. 3-21G* vs 3-21G, significantly enhanced the S-O bonding effect. The inclusion of d polarization functions of the oxygen atom did not alter the feature significantly (see Fig. 4(f) vs 4(e)). A similar effect was found previously in the SO_2 plane of SO_3^- ion[18] shown in Fig. 5.

In Table 2 we compare the optimized geometries from various calculations with the experimental geometry.[22] The inclusion of d polarization functions of the sulfur atom is obviously important for the prediction of the correct geometry, but the size of the split-valence level basis sets is less important in this case. Therefore, it is necessary to in-

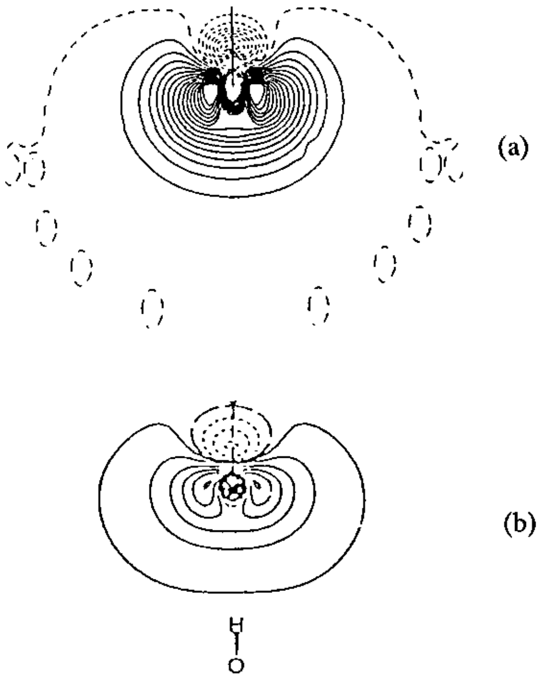

Fig. 3. Deformation density maps in the plane at the bisection of the H-O-H angle; contours as in Fig. 1. (a) calculated ab initio using 3-21G basis set; (b) MCSCF results from ref.17.

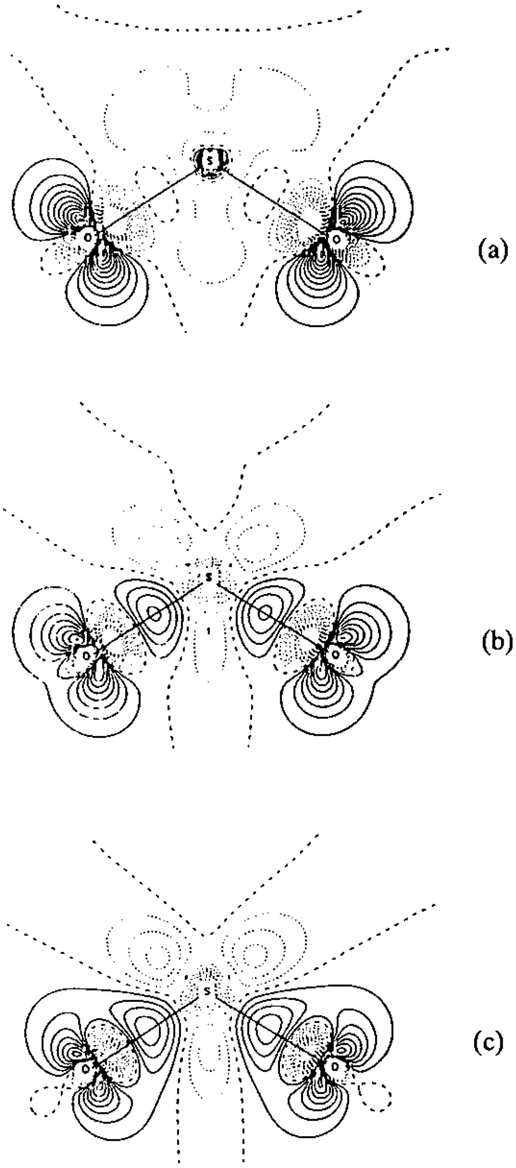

Fig. 5. Deformation density maps of SO_2 plane of H_3NSO_3 molecule from ref.18; contours as in Fig. 1. (a) using double-zeta calculation; (b) same as (a) plus d functions of S atom; (c) same as (a) plus d functions of S and O atoms.

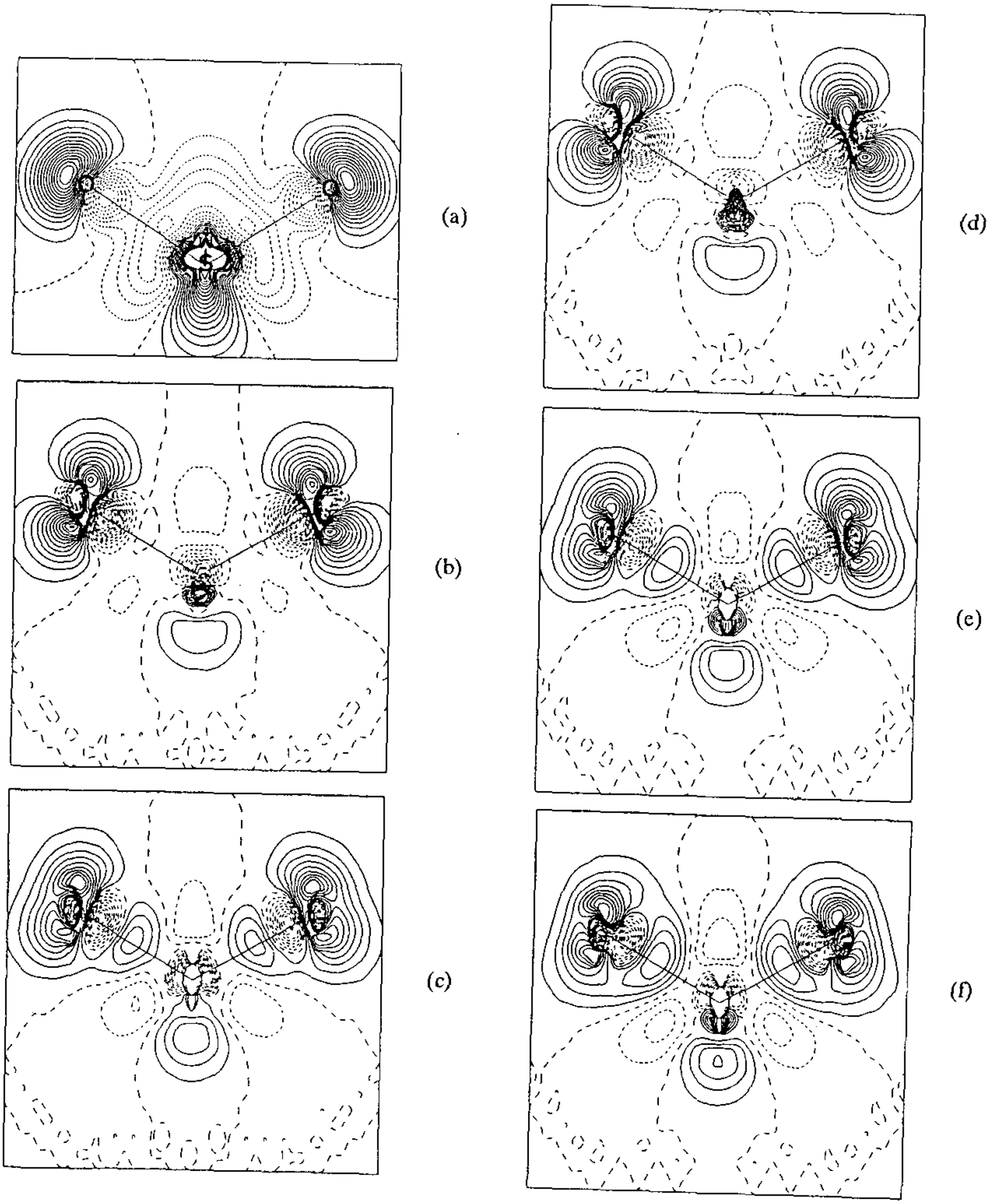

Fig. 4. Deformation electron density distributions of SO_2 plane; ontours as in Fig. 1. (a) ab initio using STO-3G basis set; (b) ab initio using 3-21G basis set; (c) ab initio using 3-21G* basis set; (d) ab initio using 4-31G basis set; (e) ab initio using 4-31G(*) basis set; (f) ab initio using 4-31G* basis set.

corporate d polarization functions for the study of compounds containing a sulfur atom. As the size of the basis sets seems less important to attain the correct geometry; considering the great saving on computational time[+], a cal-

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[+] : the computational time using 3-21G* basis set is about a half of that using 4-31G* and a quarter of that using 6-31G*

Table 2. Comparison of Optimized Geometries, Dipole Moment, Total Energy and CPU Time Used in Various Calculations on SO_2

		4-31G	4-31G$^{(*)}$	3-21G	3-21G*	6-31G*[23]	Exp.[22]
Net	S	+1.45	+1.03	+1.32	+1.00		
Charge/e	O	- 0.72	- 0.51	- 0.62	- 0.50		
$r_{S\text{-}O}$/Å		1.53	1.42	1.52	1.42	1.41	1.43
θ/deg		114.2	118.4	113.9	118.7	118.8	119.3
Dipole moment/D		3.31	2.61	2.98	2.29	2.19	1.63
Total Energy /hartrees		-546.352	-546.557	-544.270	-544.504	-547.169	
CPU time/s		1993	2949	1066	1451		

culation based on 3-21G* is the most economic way to provide valid deformation density results. In addition, the first six ionization energies were calculated based on 3-21G* and 4-31G(*) (Table 3); the linear relationship between the calculated values and the experimental values[24] shown in Fig. 6 implies the correctness of the calculations. As the Koopmans' ionization energy($-E_i$) neglects the correlation energy and relaxation energy ($IE = -E_i - E_{corr} + E_{rela}$), it tends to give a more positive ionization energy. However this deviation does not affect the relative orbital energies; thus the linear relationship between the experimental values and $-E_i$ still holds true. For the same reason, the slope of such a line is usually less than 1.[25,26] In this case, comparison of the two calculations (Table 3) with the experimental data[24] indicates that the results from the calculation using a 3-21G* basis set agree better with experimental data than those from the calculation using a 4-31G(*) basis set.

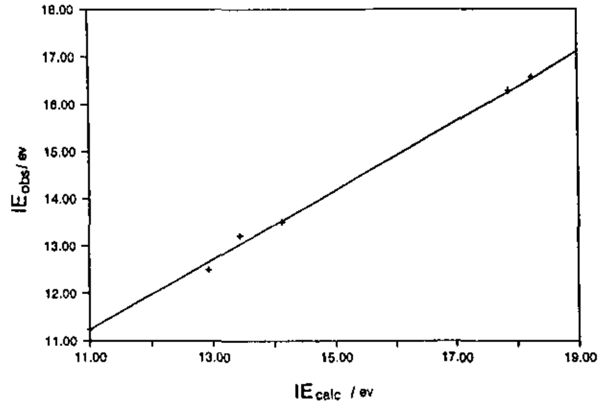

Fig. 6. Linear relationship between the Koopmans' ionization energy (IE_{calc}) and the experimental values (IE_{obs})
$IE_{obs} = 0.732(21)IE_{calc} + 3.19(13)$ for 3-21G*
$IE_{obs} = 0.739(21)IE_{calc} + 2.73(13)$ for 4-31G(*).

Table 3. Comparison of Koopmans' Ionization Energies/eV of SO_2

3-21G*	4-31G$^{(*)}$	Exp.[24]	Character
12.93	13.41	12.50	$\pi_{\|\|}$
13.45	13.97	13.21	n_O
14.12	14.58	13.50	$\pi_{d\text{-}p}$
17.88	18.28	16.31	$\pi_{\perp}$
18.26	18.70	16.60	σ
18.58	19.05	16.70	σ

CONCLUSION

Our results strongly indicate that the inclusion of d polarization functions is far more important for second-row elements such as sulfur atom than for first-row elements. The 3-21G* basis set is considered to be the most economic and appropriate basis set in terms of production of the deformation density distribution, optimized geometry and the orbital energies.

The deformation density study of F_2 molecule demonstrates that the results from the EHMO calculation are as good as those from the ab initio calculation. The interpretation of the deformation density must be referred to the atomic condition of the promolecule.

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Key Words
Deformation density; Theoretical study.

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