DEPENDENCE ON THE GEOMETRY AND ON THE BASIS SET OF LOCALIZED ORBITAL ENERGY AND MOMENT CONTRIBUTIONS

I. ENERGY QUANTITIES

By

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In a series of papers we investigate the localized orbital contributions at the molecular experimental and theoretical equilibrium geometries using various basis sets. The present study deals with some energy quantities obtained from localized charge densities: the kinetic, the (effective) potential and the selfinteraction energies are discussed. Several regularities were found for the systems considered, namely the molecules HF, H_2O, NH_3 and CH_4, respectively.

1. Introduction

As the simplest antisymmetric wavefunction of a closed-shell system, a single determinant of one-particle functions is invariant under any unitary transformation [1], the tranformations could be chosen to obtain new orbitals localized as much as possible [2]. Several localization procedures have been published as well as many advantages of using localized orbitals have been pointed out recently [3—7]. In a series of papers we also investigated various properties of localized charge densities for some ten- and eighteen-electron systems [8—11].

It is known that in any quantum-chemical calculation the problem arises which type of basis set and which geometry data are to be used for the study of the given molecular system. As to the choice of a suitable basis set, there are usually the computer time and/or size which make a limit for the number of basis functions. It has been pointed out, e.g., that at least one d function on the oxygen is necessary to take for the molecule H_2O in order to obtain an acceptable value for the total energy as well as for the electric moments (more details on basis set dependence see in [12—14]). An exhaustive analysis of the effect of basis set variation on the localized charge distribution of H_2O has also been done [1]. From the results it follows that in the presence of polarization functions (at least one d-type on the oxygen) the energy contributions as well as the electric moment components provide regular differences for bond and lone pair localized orbitals. The change of energy contributions parallels with that of total energy and similarly the first and second order moment components (localized moments) with that of the corresponding total molecular

values [10]. These results confirm — together with those obtained for the transferable property [11] — that the localized orbital energy contributions and the localized moments are suitable for characterizing even larger molecules.

It is interesting to investigate how the choice of geometry data influence the values for the localized orbital energy and moment contributions. The molecules are often investigated at their experimental equilibrium geometry (if available). In many cases — for simplicity — standard [15] or model [8] preferable. for the determination of harmonic force constants which geometry geometrical values are taken for the calculations. It is known that there are not too many differences between the total molecular properties whether calculated at the experimental or theoretical (or nearby) geometries. In spite of this, many authors argue (see, e.g., [16] and reference therein), which geometry data are preferable for the determination of harmonic force constants. In this paper we summarize our results obtained for HF, H_2O and NH_3 core, bond and lone pair localized orbitals and those obtained for CH_4 core and bond pair localized orbitals. We investigated the localized charge densities at the molecular experimental and calculated equilibrium geometries by the use of different basis sets.

2. Total energies and total kinetic energies

For a systematic study a suitable basis set is necessary. Various basis sets were chosen for the molecule H_2O in order to investigate it at the experimental and the calculated equilibrium geometry. The results are given in Table I the values suggest that the so-called 6-31G/d basis set seems to be the more convenient as the total energy is quite acceptable (the p-type polarization functions on hydrogens do not give large contributions to the total energy) and also the virial coefficient is one of the best. The detailed description of the basis sets considered are given in the corresponding papers: STO-3G [17], 4-31G [18], 6-31G [19] while 6-31G/d and 6-31G/d+p [20]. In order to investigate similar results as well, for a comparison the values obtained by the so-called DUNNING' basis sets are also given [12]. From the values one can see that the resulting total energy by basis 6-31G/d is better than any of (sp/s) type but worse than, e.g., DUNNING's contracted Gaussians of [4s3pld/2s]. The calculations, however, are rather effective, as pointed out in [18—20] with basis sets of split-valence types. Therefore we made our geometry dependence study by the use of basis 6-31G/d. For a comparison the corresponding values which we obtained by using 6-31G basis are also given. All calculations were performed on a CDC 3300 computer (Hungarian Academy of Sciences, Budapest).

The experimental geometry data were taken as those used in an earlier work [7]. The theoretically obtained values for basis 6-31G were as given in

Table I

Total energies calculated for H_2O (in hartree)

		Total energy	Total kinetic energy
STO-3G	Exp	−74.96381	74.53346
	Calc	−74.96543	74.46618
4-31G	Exp	−75.90847	75.87753
	Calc	−75.90987	75.89167
6-31G	Exp	−75.98480	75.91439
	Calc	−75.98628	75.93238
6-31G/d	Exp	−76.01205	75.76360
	Calc	−76.01231	75.80832
6-31G/d + p	Exp	−76.02318	75.74601
	Calc	−76.02365	75.80347
[4s3p/2s]	Exp	−76.00209	—
[4s3p1d/2s]	Exp	−76.02882	—
[4s3p1d/2s1p]	Exp	−76.04172	75.98016
	Calc	−76.04209	76.02276

Table II

Total energies calculated using basis 6-31G and 6-31G/d (in hartree)

		Basis 6-31G	
		Total energy	Total kinetic energy
HF	Exp	−99.98341	100.06277
	Calc	−99.98343	100.05384
H_2O	Exp	−75.98480	75.91439
	Calc	−75.98628	75.93238
NH_3	Exp	−56.16146	56.12776
	Calc	−56.16632	56.18475
CH_4	Exp	−40.18035	40.17622
	Calc	−40.18060	40.24605
		Basis 6-31G/d	
		Total energy	Total kinetic energy
HF	Exp	−100.00326	99.84123
	Calc	−100.00333	99.85858
H_2O	Exp	−76.01205	75.76360
	Calc	−76.01231	75.80832
NH_3	Exp	−56.18513	56.01449
	Calc	−56.18536	56.06068
CH_4	Exp	−40.19585	40.10471
	Calc	−40.19602	40.14709

[19], except for HF, where the $R = 1.7403$ a.u. was calculated (not given in the above reference). As to basis set 6-31G/d — even they have already been calculated [21] — we also were looking for the theoretical equilibrium geometries. This was necessary because in the calculations (as reported in [21]), an average value of 0.8 was used for the exponent of d-type functions, while we performed the calculations by using optimized exponents for each compound (values taken from [20]). The calculated equilibrium geometry data (only slightly different from those given in [21], are the following:

HF	$R = 1.7183$ a.u.
H_2O	$R = 1.7876$ a.u., $\alpha = 105.51°$
NH_3	$R = 1.8943$ a.u., $\alpha = 107.13°$
CH_4	$R = 2.0512$ a.u. (tetr.)

The results obtained for these molecules are given in Table II. The total energies are rather different obtained by basis 6-31G at the experimental and the calculated equilibrium: the largest difference was found for NH_3 (≈ 0.005 a.u.), that for H_2O is about 0.0015 a.u. while for HF and CH is less than 0.0003 a.u. The case is not the same for the total kinetic energies: the larger differences were found for CH_4 and NH_3. As to the results obtained by basis set 6-31G/d, they are rather close to each other at the experimental and the theoretical equilibrium, but only for the total energy. The kinetic energy result depends strongly on the geometry: the differences obtained at experimental and the calculated equilibrium are about 0.04—0.05 a.u., except for HF (less than 0.02 a.u.). The total energies and total kinetic energies obtained for these molecules suggest, that the inclusion of d-type function on the heavy atom is important. Although the use of a basis (sp/s) type may be sufficient for some cases, the geometry should then be chosen very carefully.

3. Energy contributions of core orbitals

Several quantities can be used for characterizing localized orbital densities (see, e.g., [7—9, 22]). In the present paper we investigate four quantities as energy contributions obtained from the individual localized orbitals. There are three different types of localized charge distributions for the systems considered: core, bond and lone pair orbitals. The energy contributions studied are the following: the kinetic, the potential, the self-interaction, and the so-called effective potential energy quantities. First the core orbitals are investigated.

The values obtained are given in Table III. In order to avoid the superfluous enlargement of the paper the results obtained only by basis 6-31G/d

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Table III

Energy contributions from core localized orbitals using basis 6-31G/d
(in hartree)

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		Kinetic energy	Potential energy
HF	Exp	39.3595	−79.9215
	Calc	39.3585	−79.9255
H_2O	Exp	30.6572	−63.4006
	Calc	30.6536	−63.4108
NH_3	Exp	23.0578	−48.8815
	Calc	23.0555	−48.8940
CH_4	Exp	16.5918	−36.3665
	Calc	16.5933	−36.3813

		Self-interaction	Effective potential
HF	Exp	5.48787	−65.1388
	Calc	5.48780	−65.1378
H_2O	Exp	4.84412	−50.8877
	Calc	4.84384	−50.8820
NH_3	Exp	4.20048	−38.3918
	Calc	4.20024	−38.3860
CH_4	Exp	3.56153	−27.6859
	Calc	3.56160	−27.6829

are presented. The kinetic energy contributions do not differ much whether obtained at the experimental or at the calculated equilibrium geometry. (They differ less from each other than the corresponding total kinetic energy values for all compounds studied). As the potential energy contributions do not involve the whole ("effective") potential energy for a given localized orbital, we calculated the effective ones for each type of localized orbital densities by the following equation:

$$V_{\text{eff}}^i = V_i + \sum_i \left(2 \langle ii|jj \rangle - \langle ij|ij \rangle \right),$$

where V_i = potential energy contribution of the i-th localized orbital, the expression in parentheses represents the interaction energy between the i-th and j-th localized orbital and so V_{eff}^i is the resulting effective potential energy contribution for the given i-th orbital. Both V_i and V_{eff}^i are given in Table III for the core orbitals. The results suggest that as the V_{eff}^i potentials show smaller differences between the experimental and the calculated equilibrium geometries, these contributions may be used as transferable quantities (similarly to the kinetic ones [23]) in a study of related large molecules.

The self-interaction energy contributions do not change much either as going from the experimental to the calculated equilibrium position of nuclei. It is remarkable that the signs of these changes parallel with those found for the kinetic energy contributions (see Table III). It generally holds that all deviations calculated for the core orbitals between the experimental and the theoretically determined equilibrium geometries are rather small, smaller than 0.05% in any cases.

4. Energy contributions obtained for bond and lone pair orbitals

The quantities discussed for core orbitals are given also for the bond orbitals: they are given in Table IV. The most remarkable results show that all quantities are larger at the calculated than at the experimental geometries. This may certainly be due to the shorter bond length at the theoretically

Table IV

Energy contributions from bond pair localized orbitals using basis 6-31G/d$_i$(in hartree)

		Self-interaction	Effective potential
HF	Exp	2.20646	−10.4503
	Calc	2.21469	−10.4828
H_2O	Exp	1.62373	−8.65182
	Calc	1.63501	−8.70041
NH_3	Exp	1.19079	−7.16050
	Calc	1.19847	−7.19583
CH_4	Exp	0.86508	−5.87136
	Calc	0.87018	−5.89695

		Kinetic energy	Potential energy
HF	Exp	0.91894	−3.31001
	Calc	0.92292	−3.32581
H_2O	Exp	0.83325	−2.57031
	Calc	0.83907	−2.59100
NH_3	Exp	0.75750	−2.00023
	Calc	0.76160	−2.01317
CH_4	Exp	0.68737	−1.53839
	Calc	0.69001	−1.54592

obtained total energy minima. As it is well known the shorter the bond distance the larger the nuclear potential, so the electron density becomes also more compact [24]. This fact is reflected even in the energy contributions obtained for bond pair localized orbitals.

As to the values of energy contributions resulting for lone pair orbitals (HF, H_2O and NH_3), similar conclusion could be found for the kinetic energy contributions. The self-interactions, however, are always larger at the experimental than at the calculated equilibrium geometry of nuclei (see Table V). The effective potential values do not change in the same direction for the studied systems. The general conclusion can be made that there are the kinetic energy terms which reflect the most suitably (i.e. for all of different types of localized orbitals) the increasing electron density as going from the experimental to the calculated equilibrium geometries. This result may well be used if the total energy of related larger systems is constructed by the use of the kinetic energy contributions of localized orbitals determined at the calculated equilibrium geometry of a small molecule.

5. Conclusion

Several energy quantities have been discussed using the localized decomposition of the total charge distribution for some small molecules. It can be seen that the kinetic, the self-interaction and the effective potential energy contributions characterize suitably the main differences for the various types of localized orbitals. There is an interesting question, however, to be further analyzed. It is a longstanding goal in the study of localized charge densities, to be able to determine whether a bond or a lone pair distribution is "larger" or "greater" in a given system [25]. There are the self-interaction energy con-

Table V

Energy contributions from lone pair localized orbitals using basis 6-31G/d (in hartree)

		Self-interaction	Effective potential
HF	Exp	2.78488	−11.6279
	Calc	2.78536	−11.6310
H_2O	Exp	1.98861	−9.34880
	Calc	1.99026	−9.35482
NH_3	Exp	1.37712	−7.43426
	Calc	1.37946	−7.43999

		Kinetic energy	Potential energy
HF	Exp	1.03012	−3.77782
	Calc	1.02991	−3.77834
H_2O	Exp	0.87860	−2.76981
	Calc	0.87753	−2.76867
NH_3	Exp	0.73644	−1.97108
	Calc	0.73485	−1.96911

tributions which could be related to the "extent" of an individual charge density. As one can see from the results (Table IV and Table V), there are the lone pair orbital self-interaction energies which are larger than the bond pair ones by about 10% (for HF) and 5% H_2O), but the opposite relation holds (bond pairs are larger than the lone pair one) for molecule NH_3 (approx. by 3 %). These results affirm that there is no reason to expect a larger extent for a bond or a lone pair localized charge distribution. These quantities do not depend only on the enlargement of the basis set but also, e.g., on the number of different types of localized orbitals (i.e. on the system) as well. It can also be noted that the effective potential energy contributions do show similar regularities for the studied molecules.

In the next paper of this series other types of energy quantities will be discussed: the interaction energy contributions between the localized orbitals. After that paper an analysis of the first and second order electric moments of localized charge distributions will follow. It is planned to publish a study on the geometry and basis set dependence of the localized moment characteristics as well.

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