Theoret. Chim. Acta (Berl.) 50, 31–38 (1978)

THEORETICA CHIMICA ACTA

Basis Set Dependence of Localized Orbitals

Ede Kapuy and Cornelia Kozmutza

Quantum Theory Group, Physical Institute of the Technical University of Budapest, Budapest, Hungary

Raymond Daudel and Michael E. Stephens

Centre de Mécanique Ondulatoire Appliquée, CNRS, Paris, France

The effects of Gaussian basis set contraction and addition of polarization functions on H_2O localized orbitals have been studied at the experimental geometry. It is shown that the electric moments and moment features of localized orbitals are not influenced very much by basis set quality variations, as going from medium size to enlarged basis sets. The difference between bond pair and lone pair charge densities was found to be larger on approaching the Hartree–Fock limit. A minimal basis set, however, does not suitably characterize the localized charge distributions.

Key words: Localized molecular orbitals, basis dependence of ~, moments of ~

1. Introduction

In the framework of the independent particle model of molecular systems, Gaussian basis functions are often found more convenient than Slater type ones. Using Gaussian functions, rather large basis sets are necessary in order to obtain wavefunctions of near Hartree-Fock limit quality. Atomic basis sets alone are not sufficient, the introduction of polarization functions is also required for an accurate representation of bonding regions in molecules. Recently, various calculations have been carried out to study the influence of polarization functions on different molecular properties. The ground state energies, core ionization potentials and excitation energies for small molecules have been investigated using various basis sets [1]. The basis set dependence of molecular orbital hydrogenation energies has also been studied [2]. The effect of polarization functions on one-electron properties of some hydrides has been analyzed [3]. Using (*sp*/*s*) basis sets, then enlarging them by addition of *d* and *f* type functions on the heavy atoms, these studies have

0040-5744/78/0050/0031/$01.60

shown that the dipole and octupole moments are greatly (but the quadrupole moments less) affected by the presence of polarization functions.

Exhaustive investigations have been carried out on the molecular properties of H_2O using a large number of Gaussian and Slater bases [4–10]. It appears that for one-electron properties, the addition of $3d$ functions to the oxygen is more important than of $2p$ functions to the hydrogens. From Dunning's results it follows that the total dipole moment decreases rapidly as the basis set becomes less and less contracted. No monotonic improvement was found for the dipole moment, however, with enlarging basis set [8, 10] below the Hartree–Fock level. As to the quadrupole moments, they converge with oscillation to certain values with contraction [6] as well as basis set size variation [8, 10].

No systematic investigation has yet been reported how localized orbital multipole moments are changing with variation of the basis set. In this paper we analyze the basis set influence on the H_2O localized charge densities. The Coulomb and exchange interaction energies and especially the first and second order electric moments of the localized charge distributions are studied.

2. Method of Calculation

In order to investigate the contraction effects we used the following basis sets (exponents and contraction coefficients were taken from [4]):

I. $(9s5p/4s) \rightarrow [4s3p/2s]$
II. $(9s5p/4s) \rightarrow [5s3p/2s]$
III. $(9s5p/4s) \rightarrow [5s3p/3s]$
IV. $(9s5p/4s)$ non-contracted.

The localized orbitals of H_2O were studied by a minimal basis set as well: a $(6s3p/3s)$ contracted to $[2s1p/1s]$ Gaussian set with exponents and coefficients using the values as given in [11]. For a comparison, the results obtained by a $(13s7p/4s)$ contracted to a $[4s2p/2s]$ Gaussian basis set are also given (more detail see in [12–14]).

Earlier studies have shown that in the case of first row atoms, the most important part of the polarization effects can be described using $3d$ functions [15]. A previous investigation of H_2O concluded that one $2p$ function on the proton suffices to account for the charge polarization [16]. Accordingly, and in order to be consistent with bases I to IV, the polarization functions were added to the same (sp/s) basis set and the contraction as that for basis I was used in the calculations (d exponent taken from [6], the $2p$ exponent of hydrogen being equal to 0.9). Thus the improvement of basis set was as follows:

V. $(6s3p/3s) \rightarrow [2s1p/1s]$
VI. $(13s7p/4s) \rightarrow [4s2p/2s]$
VII. $(9s5p1d/4s) \rightarrow [4s3p1d/2s]$
VIII. $(9s5p1d/4s1p) \rightarrow [4s3p1d/4s1p]$.

The experimental geometry $R_{\text{exp}} = 1.809$ bohr, HOH$\measuredangle = 104.52°$) was used. The canonical orbitals were obtained by the IBMOL IV program. The localized molecular orbitals (LMO's) were computed from each canonical set using the Edmiston–Ruedenberg criterion [17], yielding the various interaction energies.

The electric moments for the sets of localized charge densities (localized moments) were calculated via the POLYATOM/2 system subroutines. The first order moment of a given LMO φ_i is the centroid of charge vector $\langle r \rangle_i$, with components $\langle x \rangle_i$, $\langle y \rangle_i$, $\langle z \rangle_i$. The second order moment of LMO φ_i can be identified as a tensor θ_i, whose components (after diagonalization denoted as $\langle x'^2 \rangle_i$, $\langle y'^2 \rangle_i$, $\langle z'^2 \rangle_i$) can be related to the orbital dispersions pointing to the main axes directions [12]. In actual calculations the origin of $\langle r \rangle_i$ is taken at the central heavy atom nucleus while that of θ_i is shifted to the endpoint of the charge centroid of i'th localized charge distribution.

The ground state total energies for the eight different basis sets at the experimental geometry can be compared to those of earlier studies. The [$4s3p/2s$], [$5s3p/2s$], [$5s3p/3s$] and the uncontracted ($9s5p/4s$) values are rather close to one another (Table 1). The values obtained from severely contracted sets (I and II) differ more from those of the less contracted (III) or uncontracted (IV) [4] than from each other. The contraction does not influence much the total energies (from basis I to IV, the energy decrease is less than 0.01 a.u.). The total energy obtained by minimal basis set is quite high while that of basis set VI is close to the total energy obtained by basis III or IV. Introducing the polarization functions $3d$, the total energy differs about 0.017 a.u. from basis IV, and including the hydrogen $2p$ functions (basis VIII), it shows a further decrease of 0.0135 a.u. It should be noted that the interpolated equilibrium geometry for the largest basis VIII is in a good agreement with the experimental values ($R_{\text{calc}} = 1.7883$ bohr, HOH$\measuredangle = 105.81°$), the energy lowering being 0.000367 a.u. (see in [14]).

3. Basis Set Influence on LMO Interaction Energies

It is known that a rather large basis including polarization functions is necessary to come close to the Hartree–Fock limits of physical properties (even then, however, the rapid convergence is not guaranteed [18]. Apart from degeneracy, the contributions of the individual canonical orbitals do also converge to certain values on a suitable enlarging of the basis set. It is plausible thus to assume – in cases where a unique set of LMO's exists – that even the contributions of the individual LMO approach certain values on nearing the Hartree-Fock limit.

The calculated Coulomb and exchange interaction energies between electrons on H_2O localized orbitals do not show large changes with variation of the contraction of basis IV (Table 1). All changes are less than 0.2% for the Coulomb energies, while the exchange interaction variations are about 1–2% on going from basis I to IV. The degree of contraction influences the bond pair/bond pair exchange ($\sim 2\%$ increase) interactions most, the bond pair/lone pair ($\sim 1\%$ increase) less, and the lone pair/lone pair ones still less. The results obtained with

Table 1. Basis set dependence of Coulomb and exchange interaction energies of electrons on localized orbitals (in atomic units)

Basis set	I	II	III	IV
Total energy	−76.00209	−76.00321	−76.01039	−76.01111
Core self	4.85146	4.85236	4.85213	4.85133
Bond pair self	0.82118	0.82111	0.82114	0.82150
Lone pair self	0.88214	0.88223	0.88180	0.88189
Core/bond pair[a]	0.89481	0.89488	0.89587	0.8958
	0.01479	0.01479	0.01482	0.01490
Core/lone pair	1.04029	1.04059	1.03996	1.04019
	0.02065	0.02067	0.02064	0.02074
Bond pair/bond pair	0.56502	0.56501	0.56696	0.56694
	0.03430	0.03430	0.03481	0.03480
Bond pair/lone pair	0.61123	0.61123	0.61186	0.61191
	0.04505	0.04505	0.04546	0.04544
Lone pair/lone pair	0.66609	0.66609	0.66543	0.66557
	0.05658	0.05655	0.05645	0.05646

Basis set	V	VI	VII	VIII
Total energy	−74.96381	−76.01081	−76.02882	−76.04172
Core self	4.85612	4.85250	4.85014	4.85003
Bond pair self	0.80447	0.81276	0.83368	0.83627
Lone pair self	0.99702	0.90471	0.87313	0.87071
Core/bond pair[a]	0.83617	0.88381	0.89658	0.89913
	0.00911	0.01468	0.01474	0.01498
Core/lone pair	1.09115	1.05406	1.03943	1.03810
	0.01627	0.02064	0.02063	0.02059
Bond pair/bond pair	0.54022	0.56531	0.56908	0.57182
	0.03115	0.03422	0.03416	0.03502
Bond pair/lone pair	0.62112	0.61271	0.61365	0.61508
	0.04518	0.04598	0.04505	0.04564
Lone pair/lone pair	0.72559	0.67668	0.66444	0.66349
	0.06244	0.05674	0.05771	0.05750

[a] The upper figure of each pair corresponds to the Coulomb, the lower one to the exchange integral.

basis sets I and II, and III and IV, respectively, are very close to each other for all off-diagonal matrix elements.

The core self-repulsions change also little with enlarging basis set. The bond pair self-interactions show a rather large increase as going from the minimal to the extended basis set: the increase exceeds 4%. The lone pair self-repulsions, on the other hand, have a larger (about 15%) value obtained by a minimal basis set than by basis sets including polarization functions (see Table 1). Similarly, the core/bond pair Coulomb interaction energies show a decrease while the core/lone pair ones show an increase with enlarging basis set. The Coulomb and exchange interaction energies vary the least between bond and lone pair localized orbitals. The bond pair/bond pair and lone pair/lone pair interactions are, however, more sensitive to basis set quality: the former interactions decrease (about 6%) while the latter ones increase (about 10%) comparing basis V to basis VIII both for Coulomb and exchange interactions. It is remarkable that especially the lone pair charge densities seem to be represented in an unsuitable way using minimal basis set (see Table 1). The results suggest that the principal effect on lone pair LMO distributions is their displacement away from the oxygen, while the bond pair LMO densities approach the heavy atom with improving basis set. This is in agreement with earlier results [14] that on approaching the Hartree–Fock limit, the bond and lone pair localized orbital densities differ more and more (becoming more compact and diffuse, respectively).

4. Basis Set Dependence of LMO Moments

A consequence of Brillouin's theorem assures that molecular one-electron properties can be calculated quite well even within the independent-particle model [19]. Previous investigations have pointed out that systematic variations of the contraction do cause while that of the size of basis set does not cause systematic changes in the total dipole moment of H_2O [4, 6, 8, 10]. Similar conclusions could have been drawn for the quadrupole moments. It is interesting to study how the contributions of the localized charge densities to the first and second moment vary with basis set quality.

The first order localized moments (as defined in [12, 20]) for bond and lone pair LMO's show little changes against the variation of the basis set contraction (Table 2). The results for I, II, III and IV are close to each other. Improving the basis set as well as including polarization functions the moment for bond and lone pair orbitals change less than 2%. The lone pair orbital first moments have a systematic decrease as going from basis I to IV and also from VI to VIII. It is to be emphasized that the results obtained by a minimal basis set do not show these variations. The valence orbital second order localized moments also change little on going from basis I to IV. The second order moments for bond pair orbitals decrease while those for lone pair charge densities increase with enlarging basis set. The presence of $3d$ functions on oxygen and of $2p$ functions on the hydrogens causes changes of less than 3%. It is to be noted, however, that the second order electric moments for lone pair charge distributions are too small being determined by a minimal basis set.

As to the degeneracy of the diagonalized second order tensor, it becomes larger for bond as well as lone pair charge densities on approaching the Hartree–Fock limit. From the results of Table 2 it can be concluded that the changes in the first and second localized moments against basis set variation are smaller than those of total dipole and quadrupole moments. These variations suggest a more compact form for bond LMO's and a more diffuse one for the lone pair localized orbitals on going to enlarged basis set.

Table 2. Basis set dependence of localized orbital multipole moments (in atomic units)

Basis set	I	II	III	IV	V	VI	VII	VIII
Total dipole moment[a]	1.014	1.013	1.040	1.040	0.717	1.044	0.853	0.840
First order localized moments								
$\langle r \rangle$ bond pair	0.99695	0.99689	0.98139	0.98138	1.07505	0.97796	1.00280	0.99067
lone pair	0.60323	0.60311	0.60432	0.60420	0.58704	0.60525	0.58246	0.57520
Total quadrupole moment[b]								
θ_{xx}	1.662	1.663	1.739	1.736	0.948	1.538	1.695	1.679
θ_{yy}	−1.779	−1.778	−1.852	−1.850	−1.119	−1.647	−1.859	−1.824
θ_{zz}	0.117	0.115	0.113	0.114	0.171	0.110	0.165	0.145
Second order localized moments								
$\langle x'^2 \rangle^{1/2}$								
bond pair	0.93464	0.93480	0.93959	0.93979	0.92127	0.96338	0.91755	0.91373
lone pair	0.87770	0.87776	0.87785	0.87751	0.67038	0.83968	0.88555	0.88576
$\langle y'^2 \rangle^{1/2}$								
bond pair	0.65434	0.65435	0.66104	0.66072	0.67193	0.66673	0.65401	0.65803
lone pair	0.68890	0.68889	0.68935	0.68915	0.60411	0.67740	0.69319	0.69980
$\langle z'^2 \rangle^{1/2}$								
bond pair	0.65378	0.65380	0.65857	0.65820	0.66820	0.66525	0.65236	0.65416
lone pair	0.68860	0.68858	0.68917	0.68896	0.60076	0.67548	0.69192	0.69121

[a] Experimental value: 0.728 a.u. [7]

[b] Experimental value: 1.859, −1.956 and 0.097 a.u., respectively [7]

5. Basis Set Dependence of LMO features

Several well-defined quantities [12, 13] derived by combining the first and second order localized moments summarily characterize the orbital charge distributions. The quantity A_{orb} measures the asymmetry of a given LMO, while the solid angle Ω_{eff}, and R_d dispersion ratio succinctly describe the spatial extent of the densities. The dispersion product P_d also has been shown to characterize LMO volume, but was found to be dominated by central atom nuclear charge and not simply related to molecular geometry.

The changes in A_{orb} and Ω_{eff} (which have different values for bond and lone pair LMO's) obtained by any of bases I to IV are very much similar to those of first order localized moments. The values obtained from sets VI to VIII show that the bond pair and lone pair charge distributions differ the more, the closer the Hartree–Fock limit is approached (see Table 3). The systematic enlarging of the basis set causes a decrease for lone pair orbital A_{orb} and bond pair orbital Ω_{eff} values, but an increase for the effective angles of lone pair charge densities. These values thus suggest that the bond pair LMO's are more compact than are the lone pair ones, in agreement with the conclusions of Sects. 3 and 4. The minimal basis set, however, yields values (especially for lone pair orbital characteristics) differing by about 10% from those obtained by other basis sets investigated. The R_d ratio quantities show similar changes, but their variations are rather small with increasing number of polarization functions (Table 3).

Table 3. Basis set dependence of localized orbital characteristics

Basis set		I	II	III	IV	V	VI	VII	VIII
A_{orb}	bond pair	1.0667	1.0664	1.0445	1.0442	1.1669	1.0151	1.0929	1.0842
	lone pair	0.6873	0.6871	0.6884	0.6885	0.8757	0.7208	0.6577	0.6494
$\Omega_{\mathrm{eff}}{}^{a}$	bond pair	1.0297	1.0298	1.0687	1.0681	0.9510	1.0899	1.0184	1.0447
	lone pair	2.1434	2.1439	2.1409	2.1407	1.8982	2.1026	2.2390	2.2788
R_d	bond pair	1.4290	1.4292	1.4240	1.4251	1.3749	1.4465	1.4047	1.3927
	lone pair	1.2743	1.2745	1.2736	1.2735	1.1128	1.2365	1.2787	1.2735
$P_d{}^{b}$	bond pair	0.3998	0.3999	0.4090	0.4087	0.4136	0.4273	0.3915	0.3933
	lone pair	0.4165	0.4164	0.4170	0.4166	0.2433	0.3853	0.4247	0.4284

[a] in steradian
[b] in $(\mathrm{a.u.})^3$

It is remarkable that the P_d values for basis sets V to VIII are quite different. For bases V and VI the bond pair orbitals, while introducing the polarization functions (bases VII and VIII), the lone pair orbitals have a larger dispersion product. These results suggest (contrary to those obtained by [21]) that there are some "volume" quantities – e.g. P_d – which are very sensitive to basis set variation so they are not suitable for characterizing bond and lone pair charge distributions. A geometry dependence study of LMO interaction energies and moments has also shown that the A_{orb} and Ω_{eff} quantities are useful to characterize LMO charge variations [14].

The conclusion could be drawn that the first and second moments of localized charge distributions of H_2O are not highly sensitive to basis set variation. The change of any of the quantities discussed above, even in the presence of polarization functions, does not exceed the 5% relative to the medium size (*sp*/*s*) basis set. A minimal basis, however, does not suitably reflect the main characteristics of localized orbitals. Apart from this, the variations of the moment features against increasing basis set size show regular differences for bond and lone pair LMO densities. The small basis set dependence increases the hope for their suitability for characterizing localized charge distributions of larger molecules.

Acknowledgements. Thanks are due to M. R. Peterson for assistance with the calculations. M.E.S. thanks the National Research Council of Canada for Postdoctoral Fellowship funding and C.M.O.A. for use of its facilities.

References

1. Deutsch, P. W., Curtiss, L. A.: Chem. Phys. Letters **39**, 588 (1976)
2. Hariharan, P. C., Pople, J. A.: Theoret. Chim. Acta (Berl.) **28**, 213 (1973)
3. Poirier, R. A.: M.Sc. thesis, Sudbury, Canada (1976)
4. Dunning, T. H.: J. Chem. Phys. **53**, 2823 (1970)
5. Dunning, T. H.: J. Chem. Phys. **55**, 716 (1971)
6. Dunning, T. H.: J. Chem. Phys. **55**, 3958 (1971)
7. Dunning, T. H., Pitzer, R. M., Aung, S.: J. Chem. Phys. **57**, 5044 (1972)
8. Rosenberg, B. J., Shavitt, I.: J. Chem. Phys. **63**, 2162 (1975)
9. Rosenberg, B. J., Ermler, W. C., Shavitt, I.: J. Chem. Phys. **65**, 4072 (1976)
10. Clementi, E., Popkie, H.: J. Chem. Phys. **57**, 1077 (1972)
11. Hehre, W. J., Stewart, R. F., Pople, J. A.: J. Chem. Phys. **51**, 2657 (1969)
12. Kapuy, E., Kozmutza, C., Stephens, M. E.: Theoret. Chim. Acta (Berl.) **43**, 175 (1976)
13. Kozmutza, C.: thesis submitted for the degree of candidate in physical sciences (in Hungarian), Budapest (1976)
14. Kozmutza, C., Kapuy, E., Stephens, M. E.: to be published
15. Cade, P. E., Sales, K. D., Wahl, A. C.: J. Chem. Phys. **44**, 1973 (1966)
16. Cade, P. E., Huo, W. M.: J. Chem. Phys. **47**, 614 (1967)
17. Edmiston, C., Ruedenberg, K.: Rev. Mod. Phys. **35**, 457 (1963)
18. von Niessen, W., Diercksen, G. H. F., Kraemer, W. P.: Proceedings of the SCR Atlas Symp. No. 4, Oxford, 1974, eds. Saunders, V. R., Brown, G., p. 221 (1975)
19. Møller, C., Plesset, M. S.: Phys. Rev. **46**, 618 (1934); Kapuy, E., Török, F.: Quantum theory of atoms and molecules (in Hungarian), Akadémiai Kiadó, Budapest, 1975
20. Robb, M. A., Haines, W. J., Csizmadia, I. G.: J. Am. Chem. Soc. **95**, 42 (1973)
21. Daudel, R., Goddard, J. D., Csizmadia, I. G., in: Theoretical organic chemistry, vol. 2. Amsterdam: Elsevier, 1977

Received March 1, 1977/March 6, 1978