Theoret. Chim. Acta (Berl.) 45, 111–120 (1977)

THEORETICA CHIMICA ACTA

The Spatial Distribution of Localized Molecular Orbital Densities

Michael E. Stephens

Centre de Mécanique Ondulatoire Appliquée,
23, rue du Maroc, F-75019 Paris, France

Ede Kapuy and Cornelia Kozmutza

Quantum Theory Group, Physical Institute of the Technical University of Budapest,
1111 Budapest, Budafoki ut 8, Hungary

The widely-employed "principal lobe" description of localized molecular orbitals is evaluated. Spatial decompositions of bond and lone pair LMO densities for a series of ten-electron hydrides are presented. "Tail" populations are $\simeq 10\%$ of the total. The 0.001 electron a.u.$^{-3}$ contour of the principal lobe contains $\simeq 90\%$ of the pair population. A recent statistically defined cone model of valence orbital distribution correctly locates the central 45–50% of the density. An earlier ellipsoidal model volume encompasses a much smaller fraction of the population, in agreement with its predictions on "ideal" Gaussian distributions.

Key words: Localized molecular orbitals, density distribution and spatial models of ~

1. Introduction

Spatial images yielding rationales of molecular electronic structure have preoccupied chemists since the last century. The culmination of the classical models was Lewis' hypothesis of grouping of atomic valence electron octets into four maximally separated (and static) pairs [1].

The same basic concept of the "electron pair" has since repeatedly appeared in many guises. Most recently, interpretations of quantum mechanical wavefunctions have defined electron "pairs" variously, through energetic [2, 3] or statistical [4, 5] considerations.

One of the more enduring schemes of retrieving from SCF calculations a pair description analogous to the intuitive Lewis picture is that yielding localized molecular orbitals (LMO) [6, 7]. To the extent that the one-particle (orbital) method is in principle *capable* of consistent and faithful description of important features of molecular electronic structure, orbital analyses may provide a useful rationale of molecular geometry and reactivity.

Whether LMO generated from orbital energetic separability [6] or spatial localizability [8] criteria are used, one can enquire as to the *degree* of spatial localization obtained [9]. Furthermore, of interest is the extent to which the orbital density distributions (approximated by volumes containing 90 % of the density, for instance) occupy non-overlapping regions of the molecule. That is, do the popular images of electronic structure, such as the VSEPR tangent-sphere model [10], find a parallel in the localized one-particle description?

Here we compare recently proposed ellipsoidal [11, 12] and cone [13] statistical descriptions of the valence LMO distribution to detailed breakdowns of the bond and lone pair orbital densities in a series of ten-electron hydrides. Orbital "tail" populations are computed. Conclusions are drawn about the suitability of such summary images of valence electron comportment.

2. Computations

The molecules considered were the neutral ten-electron hydrides, CH_4, NH_3, H_2O, HF and Ne. Previously computed IBMOL/4 wavefunctions at the equilibrium geometries in a double-ζ-equivalent Gaussian basis were used. The SCF canonical molecular orbitals were localized by the Edmiston-Ruedenberg procedure. These

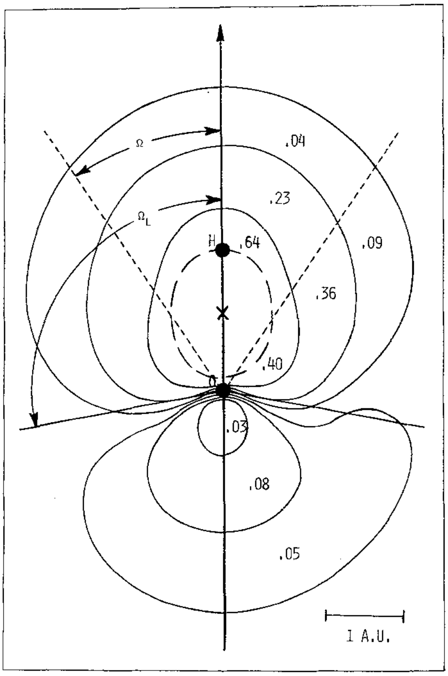

Fig. 1. Isodensity contour map for bond pair LMO of H_2O. Contours shown are (reading inwards) 0.001, 0.01, and 0.1 electrons a.u.$^{-3}$. Also shown are the ellipsoid (long dashed line), cone (short dashed line), and "tail" (solid line) model surfaces. The atoms are indicated by filled circles, orbital centroid by a cross. Region populations are indicated

calculations were performed at C.I.R.C.E., Orsay, France. Further details may be found in Ref. [12].

Region populations of the LMO distributions were computed by a contour-searching variant (written by one of us, M.E.S.) of the Gaussian quadrature numerical integration programme SUPER [14]. These calculations were carried out at C.C.P.N., University of Paris VI, France.

For the integrations, each orbital was assumed to have cylindrical symmetry about the heavy atom-orbital centroid axis. This assumption is quite justified, as can be seen from the plots of the bond and lone pair LMO of H_2O in Figs. 1 and 2. The H_2O orbitals have the most asymmetric environment, and hence will be the most distorted of the orbitals of the whole series of molecules. Isodensity contours, at densities of 1.0, 0.1, 0.01 and 0.001 electrons a.u.$^{-3}$ were plotted for each orbital (normalized to 2.000). The distribution was then further divided into three zones, defined by two cones centered on the symmetry axis. The first cone was fixed by "effective" angle Ω of the cone model [13] and the second by an angle Ω_L, a (visual) approximation of the zero density surface (necessarily present because of the orbital phase sign change) separating the two density lobes. A value of Ω_L variable by ± 10° is not crucial, as the density in the region of the partitioning surface is very low and use of a conical surface is an approximation in any case. The smallest regions considered then lie between adjacent pairs of the isodensity curves, and are delimited angularly by one or both of the zone cones.

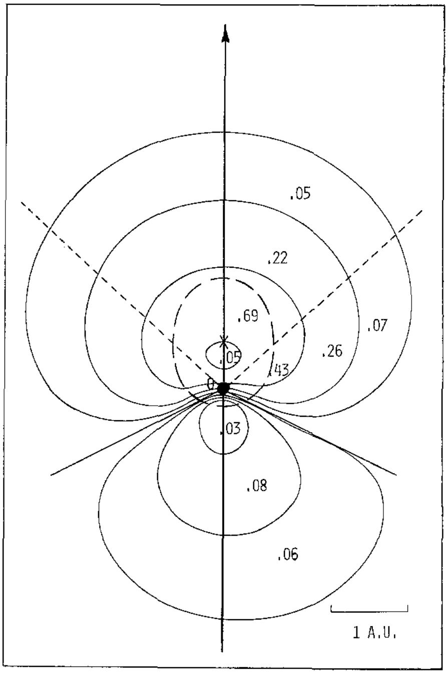

Fig. 2. Isodensity contour map for lone pair LMO of H_2O. Contours shown are (reading inwards) 0.001, 0.01, 0.1 and 1.0 electrons a.u.$^{-3}$. The symbols are the same as in Fig. 1

The cone of apex angle Ω and the central torus together define the "major lobe" of the orbital; the third zone, the cone of apex angle Ω_L, is taken to define the "minor lobe" or "tail".

Also shown on Figs. 1 and 2 are the ellipsoids (centered on the orbital centroid, and of dimensions defined by the standard deviations of the orbital distribution along the three principal axes of the second moment tensor) from the ellipsoid model [12], which will be discussed below.

The sum of the breakdown populations ranged from 1.91 to 1.98 for the various LMO, compared to the normalized orbital populations of 2.000. Small percentage, but cumulative, inaccuracies in the numerical integrations for each region, plus omission of regions with density less than 0.001 electrons a.u.$^{-3}$, account for the discrepancy. From previous experience, the individual regional populations may be expected to be accurate to ± 0.02 electrons, quite sufficient for the conclusions drawn. The toroidal region between the two cones is of rapidly varying density, at a constant distance from the central nucleus, with variation of the angle from the cylindrical symmetry axis. Thus determination of the multiple contour crossovers required by the integration program was more delicate than for the other two regions, but the individual region results should again be in error by less than 0.02 electron.

3. Discussion

Table 1 contains the complete regional breakdown of the bond and lone pair valence LMO distributions for the five species studied. The values of Ω computed from the cone definition of orbital extent [13] range between 47.5° and 48.6° for lone pairs, and between 32° and 36° for bond pairs. There was no consistent trend followed in the Ω_L angles chosen between major and minor lobes; they vary randomly between 95° and 115° for both bond and lone pairs, but as noted previously, a precise definition is unimportant. However, these values do define a major lobe confined almost exclusively to one half of the molecular volume.

Because of the opposing effects of increasing shell volume but decreasing density with distance from the heavy atom, all regions out of the 0.001 contour contain non-trivial portions of the orbital populations in all three zones. The effects of the contrary variation of volume and density with radial distance appear in the random difference in relative population between the 0.1 and 1.0, and the 0.01 and 0.1, contours in the three zones. The several regions of each cone defining an orbital "tail" individually contain very small fractions of the total.

These region results are combined in Tables 2 and 3 to show the population of variously-shaped approximations to effective orbital extent. Several conclusions can be drawn.

First, the cone model volumes (Table 2) are consistently found to contain a population of 0.91 ± 0.02 electrons (bond orbital), and 1.01 ± 0.02 electrons (lone pair orbital) of the "principal orbital" included. Thus the model cones, in correctly

Table 1. Regional breakdown of bond and lone pair LMO distributions

a) Bond orbital

	Ω	Ω_L	Orbital model cone				Torus between cones				"Tail" cone				Total[b]
	(degrees)	(degrees	→1.0[a]	→0.1	→0.01	→0.001	→1.0	→0.1	→0.01	→0.001	→1.0	→0.1	→0.01	→0.001	population
CH_4	31.62	107	—	0.58	0.31	0.05	—	0.20	0.56	0.15	—	0.00	0.03	0.05	1.93
NH_3	32.88	114	—	0.61	0.26	0.04	—	0.30	0.48	0.12	—	0.01	0.05	0.04	1.91
H_2O	34.26	100	—	0.64	0.23	0.04	—	0.40	0.36	0.09	—	0.03	0.08	0.05	1.92
HF	35.71	107	0.05	0.62	0.21	0.03	0.00	0.50	0.30	0.07	0.00	0.06	0.09	0.04	1.97

[a] Column heading indicates lower contour limit of integration; upper limit for each region is given by the preceding column heading; upper limit of first region is less than 10 (electrons a.u.$^{-3}$)

[b] Orbitals were normalized to 2.00; deviation from that value indicates accumulation of numerical integration errors

b) Lone pair orbital

	Ω	Ω_L	Orbital model cone				Torus between cones				"Tail" cone				Total
	(degrees)	(degrees)	→1.0	→0.1	→0.01	→0.001	→1.0	→0.1	→0.01	→0.001	→1.0	→0.1	→0.01	→0.001	population
NH_3	47.50	112	—	0.65	0.28	0.06	—	0.33	0.36	0.10	—	0.01	0.07	0.07	1.93
H_2O	47.99	115	0.05	0.69	0.22	0.05	0.00	0.43	0.26	0.07	0.00	0.03	0.08	0.06	1.95
HF	48.63	96	0.24	0.58	0.17	0.04	0.00	0.45	0.19	0.04	0.00	0.07	0.11	0.08	1.95
Ne	48.61	109	0.38	0.48	0.14	0.03	0.05	0.45	0.18	0.04	0.01	0.10	0.09	0.04	1.99

Table 2. "Principal Orbital" and "Other Orbital" populations in valence orbital model cones

a) Bond cones

	Orbital populations			
		Other		
	Principal	Core	Bond	Lone
CH_4	0.93	0.15	0.01	—
NH_3	0.91	0.16	0.02	0.03
H_2O	0.90	0.18	0.03	0.04
HF	0.91	0.19	—	0.04

b) Lone pair cones

	Orbital populations			
		Other		
	Principal	Core	Bond	Lone
NH_3	0.99	0.32	0.05	—
H_2O	1.01	0.33	0.07	0.08
HF	1.02	0.34	0.08	0.10
Ne	1.02	0.34	—	0.11

summarizing the important statistical characteristics of each distribution [13] contain (the central) 45–50% of the orbital density.

Table 2 also reports the population of each of the remaining LMO contained in each cone. It can be seen that the bond cones contain only 0.5 to 2.0%, and the lone pair cones 3 to 6%, of the remaining valence orbital populations. Each cone does contain a non-trivial fraction of the core orbital density. The core population contained varies from 8 to 10% for the bond cones, and 16 to 17% for the lone pair cones. These values all follow the relation $(1-\cos \Omega)$, applicable to a spherical distribution of total population 2, to ± 0.004 electrons in each case. Thus the core densities are spherical (and the integration programme yields accurate populations for such spatially compact densities). To eliminate such large "other-orbital" heavy-atom core contributions, the cone apices can be truncated by the cone intersection with a core sphere, of radius of the order of 0.3 to 0.5 a.u. for the first-row atoms considered [5].

The "major lobe" of each orbital (see Table 3) contains 86 to 92% of the principal orbital density. Thus the canonical orbitals *have* been substantially redirected from equipartition between the two halves of the molecule. *The 0.001 contour around the principal lobe hence realistically defines a volume containing consistently approximately 90% of the orbital density.*

The "minor lobe", or "tail", of each orbital, as defined, contains 5 to 10% of a bond LMO distribution, and 7–13% of a lone pair distribution. Comparing bond and

Table 3. Lobe- and isodensity contour-contained populations
a) Bond orbitals

	Lobe populations		Contour populations			
	Major	Minor (Tail)	Inside 1.0[a]	Inside 0.1	Inside 0.01	Inside 0.001
CH_4	1.84	0.09	0.00	0.77	1.67	1.93
NH_3	1.80	0.11	0.00	0.92	1.70	1.91
H_2O	1.76	0.15	0.00	1.06	1.74	1.91
HF	1.77	0.19	0.05	1.22	1.82	1.96

[a] electrons a.u.$^{-3}$ contour

b) Lone pair orbitals

	Lobe populations		Contour populations			
	Major	Minor (Tail)	Inside 1.0	Inside 0.1	Inside 0.01	Inside 0.001
NH_3	1.79	0.15	0.00	1.00	1.71	1.94
H_2O	1.77	0.18	0.05	1.20	1.77	1.94
HF	1.71	0.26	0.24	1.33	1.81	1.96
Ne	1.75	0.23	0.43	1.46	1.86	1.97

lone pair "tail" populations for each molecule, one sees that the bond orbitals are consistently, if only slightly more redirected than lone pair orbitals.

The populations contained within a given contour (combining both major and minor lobe results – see Table 3) show that for HF bond and lone pairs and the Ne lone pairs, the 0.01 contour suffices to account for 90 % of the density. For all other orbitals, regions of density down to the 0.001 contour must be added in. This trend is due, no doubt, to the greater density compactness, and hence to the rate of radial decrease around the most highly charged nuclei, F and Ne, in the series.

As well, for each molecule, greater "peaking" of lone than bond pair density was observed in the orbital plots. Thus, comparing Figs. 1 and 2, the H_2O lone pair has a 0.1 contour not present for the more dispersed bond pair density, which is distributed around two nuclei rather than one.

Explicit population calculations for the ellipsoid model volumes were not carried out. However, from the region calculations one can estimate that the bond pair ellipsoid for H_2O (Fig. 1) must contain substantially less than the 1.04 electrons within the 0.01 contour. A similar conclusion may be drawn for the lone pair (Fig. 2). Given the regular trends in orbital distribution and defined ellipsoid noted throughout the series of molecules [12], a low (but increasing with heavy atom charge) fraction of the orbital population may be expected to lie within the ellipsoids.

This result can be predicted on general theoretical grounds, given the approximately "normal" (Gaussian) form of the orbital distribution (around the density peak(s) at the one or two nuclei significantly involved in each LMO).

Thus, consider the general case of a three-dimensional normal distribution:

$$\rho(x,y,z)=(2\pi)^{-3/2}(\sigma_1\sigma_2\sigma_3)^{-1}\exp\left[-\frac{1}{2}\left(\frac{x^2}{\sigma_1^2}+\frac{y^2}{\sigma_2^2}+\frac{z^2}{\sigma_3^2}\right)\right]$$

(with centroid fixed at the coordinate axes origin and standard deviations σ_1, σ_2, and σ_3 in x, y, and z directions). If we define an ellipsoidal volume by the relation:

$$\frac{x^2}{\sigma_1^2}+\frac{y^2}{\sigma_2^2}+\frac{z^2}{\sigma_3^2}\leqslant\mu^2, \quad \mu>0$$

then the percentage q of the distribution population contained in the ellipsoid varies with μ as follows:

μ	0.1	0.5	1.0	1.5	2.0	2.5	3.0	5.0
q	0.02	3.09	19.87	47.78	73.89	90.00	97.06	99.99

(see Fig. 3). The 0.1 density contour is found at $\mu=1.66$ (the ellipsoid thus defined containing $\simeq 60\%$ of the density); the 0.01 contour is at $\mu=2.71$ (for an ellipsoid containing 90% of the density).

An ellipsoid centered on the orbital centroid, with semi-axes $\sigma_1=\langle x'^2\rangle^{1/2}$ and $\sigma_2=\sigma_3=\langle y'^2\rangle^{1/2}=\langle z'^2\rangle^{1/2}$, corresponds to the definition chosen for cone model orbital volume [12]. For this volume, a "normal" distribution would contain only 20% of the total density. Using the dispersions computed for the H_2O valence

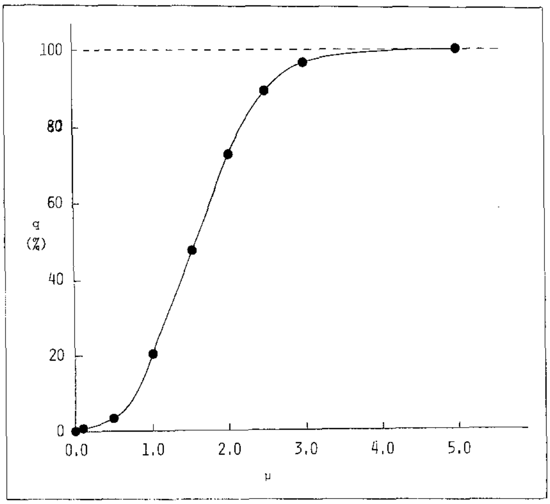

Fig. 3. Percentage of Gaussian distribution population contained within the ellipsoidal volume fixed by parameter μ

orbitals, the 0.1 contour is predicted to be an ellipse scaled up by a factor of 1.5 from the ellipse plotted in Figs. 1 and 2, and to contain about 47 % of the density. The 0.1 contour of each orbital does contain a population of 52 % of the bond pair, and 59 % of the lone pair. This reasonable agreement with such a simple approximate model shape is encouraging, perhaps the best that could be hoped for. The integration calculations show the model ellipsoids to contain a low fraction of the total orbital density. Expanding the ellipsoid principal axes by a factor of 2.5 gives the (almost innocuous) result that 90 % of each orbital density is to be found within 2.5 a.u. of its centroid. But one would then lose the information that the density actually has been substantially redirected by the localization process.

These lobe and cone integration results are directly paralleled by several other quantities: the relative ordering of orbital interaction energies [10, 15–16], orbital spatial overlapping [9] and statistical pair localizability [5] for Hartree-Fock wavefunctions. All of these approaches predict the Coulomb and exchange interactions to increase in the order: bond/bond, bond/lone and lone/lone.

Lower bond tail populations and greater "other orbital" populations of the wider lone pair cones and major lobes were computed. These results reflect the lone pair orbitals occupying a greater solid angle around, *and* being closer to, the heavy atom than the more redirected bond pairs. Thus overlapping more severely [9], lone pair mutual interaction is of necessity greater.

4. Conclusions

In summary, the orbital localizing procedure does relatively successfully project the major portions of the valence orbital distributions to different regions of the heavy atom periphery (at least relative to the constraints imposed by an *s-p* basis set lacking polarization functions). But these results also confirm earlier findings [9] of large local overlapping between still rather *diffuse* valence LMO distributions on the same heavy atom.

Intuitive contiguous volume models of atomic pairs tend to overemphasize the concentration of each density around its centroid. "Tail" lobe populations of the order of 5 to 15 % are implicitly ignored, and the 90 % contour of the major lobe is rather more extended than volumes of the order of the distribution standard deviations. The integrations reported here clearly reveal these deficiencies and correlate with previous measures of LMO interaction.

Acknowledgements. C.K. and M.E.S. wish to express their appreciation for access to the facilities of the Centre de Mécanique Ondulatoire Appliquée provided through its director, Professor R. Daudel. Receipt of funding from the National Research Council of Canada is gratefully acknowledged by M.E.S.

References

1. Lewis, G. N.: J. Am. Chem. Soc. **33**, 762 (1916)
2. Bader, R. F. W.: Accts. Chem. Research **8**, 34 (1975)

3. Rouse, R. A.: Theoret. Chim. Acta (Berl.) **41**, 149 (1976)
4. Daudel, R., Bader, R. F. W., Stephens, M. E., Borrett, D. S.: Can. J. Chem. **52**, 1310, 3077 (1974)
5. Bader, R. F. W., Stephens, M. E.: J. Am. Chem. Soc. **97**, 7391 (1975)
6. Edmiston, C., Ruedenberg, K.: Rev. Mod. Phys. **35**, 457 (1963)
7. Weinstein, H., Pauncz, R., Cohen, M.: Advan. At. Mol. Phys. **7**, 97 (1971)
8. Boys, S. F.: Rev. Mod. Phys. **32**, 296 (1960)
9. Daudel, R., Stephens, M. E., Kapuy, E., Kozmutza, C.: Chem. Phys. Letters **40**, 194 (1976)
10. Gillespie, R. J.: Molecular geometry. London: Van Nostrand Reinhold Co. 1972
11. Robb, M. A., Haines, W. J., Csizmadia, I. G.: J. Am. Chem. Soc. **95**, 42 (1973)
12. Daudel, R., Stephens, M. E., Kozmutza, C., Kapuy, E., Goddard, J. D., Csizmadia, I. G.: Intern. J. Quantum Chem., in press
13. Kapuy, E., Kozmutza, C., Stephens, M. E.: Theoret. Chim. Acta (Berl.) **43**, 175 (1976)
14. Runtz, G., Messer, R.: SUPER: A Slater/Gaussian basis LCAO wavefunction quadrature integration programme for the CDC/6000 series computer, Dept. of Chemistry, McMaster University, Hamilton, Ont. Canada. Written in the FORTRAN/4 language, SUPER computes one-electron operator expectation values over any desired region of the molecular space
15. Kaldor, U.: J. Chem. Phys. **46**, 1981 (1967)
16. Wilson, S., Gerratt, J.: Mol. Phys. **30**, 789 (1975)

Received January 1, 1977