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Original Investigations

Transferability of Some Properties of Localized Molecular Orbitals

II. Electric Moments

Ede Kapuy and Cornelia Kozmutza
Quantum Theory Group, Physics Institute, Technical University of Budapest Budapest, Hungary
and
Raymond Daudel
Centre de Mécanique Ondulatoire Appliquée Paris, France

The transferability of the first and second order electric moments of localized orbitals have been shown. Some moment characteristics have also been investigated. The standard deviation of first order localized moments is less than 2.0%. The standard deviation of second order electric moment components are larger: although they do not exceed 4.0% for bond orbitals, for lone pair ones they vary about 1.5–10.1%.

Key words: Localized MO's, Transferability of ~.

1. Introduction

In a series of papers we have investigated the various properties of localized charge densities [1–4]. The localized orbitals calculated by using basis sets including polarization functions have also been analyzed [5]. Then the transferable property of some quantities connected with localized charge distributions have been studied (Part I, [6]). The following ten and eighteen-electron systems were included in the investigation:

CH_4, CH_3CH_3, CH_3NH_2, CH_3OH,
NH_3, NH_2NH_2, NH_2OH,
H_2O, H_2O_2.

A uniform double-zeta basis set was used (more detail see in Refs. [1, 2]). The localized orbitals were obtained by the Edmiston–Ruedenberg procedure [7]. The actual geometries and the calculated total energies can be found in Part I, where we discussed the extent of transferability for the energy quantities connected with localized orbitals.

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In the present paper the transferability of the electric moments of localized orbitals are investigated. The electric charge distribution in a molecule is a characteristic of the molecule itself [8, 9]. For many purposes, however, a detailed knowledge of the charge density is not necessary. Instead, the electric multipole moments up to certain order (third or fourth) will suffice. The charge distribution of a molecule can be described using the electric moments of its LMO density.

2. First Order Electric Moments

The first order electric moment components for a localized orbital φ_k is defined as follows:

$$r_k(u)=\langle\varphi_k\,|u|\,\varphi_k\rangle \qquad u=x,\,y,\,z.$$

The center of the charge distribution is situated at the endpoint of vector $\boldsymbol{r}_k$, and $|\boldsymbol{r}_k|$, called centroid length, is:

$$|\boldsymbol{r}_k|=[\sum r_k^2(u)]^{1/2} \qquad u=x,\,y,\,z.$$

The origin of vector $\boldsymbol{r}_k$ is at the nucleus of the central atom. The non-vanishing total molecular dipole moments obtained for the 18-electron systems studied are the following in atomic unit:

CH_3NH_2 : 0.707
CH_3OH : 0.901
NH_2OH : 0.392
NH_2NH_2 : 1.036
H_2O_2 : 1.006

The values are expected to be close to those which can be obtained in the (sp) limit.

The first order electric moments for bond and lone pair localized orbitals in the systems considered are given in Table 1. Several regularities could be found. First, it is remarkable that the standard deviation for the centroid lengths of bond pair orbitals is not larger than 1.0%, while that for lone pair orbitals is about 1.5–2.0%. This means that the bond and lone pair localized moments seem to be transferable to a rather good approximation. It should be noted – as also mentioned in Part I – that the presence of polarization functions is expected to cause only small systematic changes in the overall transferability of the moments. Similarly to the energy contributions (see Part I [6]), the deviation between the centroid lengths of orbitals of a given type in the same molecule is not larger, than the deviation of the centroid lengths for same type of orbitals in different molecules.

It is also remarkable that the standard deviation for centroid lengths is decreasing both for bond and lone pair orbitals with increasing nuclear charge of the central heavy atom. From the results one can see that not only the

Table 1. Centroid lengths (in a.u.)

	Bond CH	
CH_4	1.36130	
CH_3CH_3	1.37756	
CH_3NH_2 (1)	1.40337	
(2)	1.37265	
CH_3OH (1)	1.39330	
(2)	1.37674	
Mean value	1.38052	
St. dev. (N%)	1.00	
	Bond NH	**Lone p.N**
NH_3	1.14778	0.71288
NH_2NH_2 (1)	1.16823	0.71155
(2)	1.14494	—
CH_3NH_2	1.15416	0.70115
NH_2OH	1.15292	0.73843
Mean value	1.15360	0.71603
St. dev. (N%)	0.70	1.91
	Bond OH	**Lone p.O**
H_2O	0.97796	0.60525
H_2O_2 (1)	0.97130	0.62614
(2)	—	0.62933
CH_3OH	0.97946	0.60306
NH_2OH	0.97339	0.62153
Mean value	0.97555	0.61706
St. dev. (N%)	0.34	1.75

standard deviations are small, but the values of centroid length for the series of studied C, N and O containing compounds are well-separated as well. This property can be useful in characterizing localized orbitals by their electric moments even for larger systems.

3. Second Order Electric Moments

The second order electric moment components for localized orbital φ_k can be defined in the following way:

$$Q_k(u, v) = \langle \varphi_k \, |uv| \, \varphi_k \rangle \qquad u, v = x, y, z.$$

The origin of second moment tensor is usually shifted into the endpoint of the corresponding centroid vector. In this case the second moment tensor has the components

$$\bar{Q}_k(u, v) = \langle \varphi_k \, |[u - r_k(u)][v - r_k(v)]| \, \varphi_k \rangle \qquad u, v = x, y, z.$$

In this section we analyze the shifted (located) second order electric moments for the systems considered.

The total quadrupole moments of the compounds studied are presented in Table 2. The values tabulated are given in atomic units. The eigenvalues–

Table 2. Principal values of the diagonalized quadrupole moment tensors (calculated relative to the center of mass)

	XX	*YY*	*ZZ*
CH_3CH_3	0.524	0.524	−1.048
CH_3NH_2	7.538	−8.079	0.541
CH_3OH	4.510	−2.873	−1.637
NH_2NH_2	3.626	−3.726	0.100
NH_2OH	5.502	−4.794	−0.708
H_2O_2	4.380	−3.865	−0.515

which characterize the second moment tensor for the individual localized orbital φ_k – can be obtained by diagonalizing $\bar{\mathbf{Q}}_k$. The diagonalized tensor has the components $q_x^2(k)$, $q_y^2(k)$, $q_z^2(k)$. The quantities q_x, q_y and q_z are called the dispersions in the given direction (for detail see [2]). If $\bar{\mathbf{Q}}_k$ has cylindrical symmetry the $q_y^2 = q_z^2$ equation will hold.

The second order electric moments for the bond orbitals are given in Table 3.a. As to the form of tensors $\bar{\mathbf{Q}}$ of bond pair charge densities it can be seen that $q_x \gg q_y > q_z$ in all cases. When the symmetry allows (CH_4, e.g.) then $q_y = q_z$, in all other cases q_y and q_z are different but their deviation does not exceed 5%

Table 3.a. Second order electric moments for bond orbitals[a]

Bond CH	q_x^2	q_y^2	q_z^2
CH_4	1.25470	0.70290	0.70290
CH_3CH_3	1.20412	0.69961	0.69461
Ch_3NH_2 (1)	1.14860	0.69156	0.68365
(2)	1.17881	0.68657	0.68233
CH_3OH (1)	1.12994	0.69037	0.67353
(2)	1.14624	0.68592	0.66291
Mean value	1.17705	0.69268	0.68330
St. dev. (N%)	3.59	0.85	1.91
Bond NH	q_x^2	q_y^2	q_z^2
NH_3	1.05596	0.55113	0.54942
NH_2NH_2 (1)	0.99822	0.55259	0.54725
(2)	0.99634	0.55030	0.54060
CH_3NH_2	1.03901	0.56165	0.54635
NH_2OH	0.97669	0.54240	0.53169
Mean value	1.01324	0.55160	0.54306
St. dev. (N%)	2.91	1.11	1.18
Bond OH	q_x^2	q_y^2	q_z^2
H_2O	0.92811	0.44453	0.44256
H_2O_2	0.85446	0.43046	0.42671
CH_3OH	0.90814	0.46797	0.44392
NH_2OH	0.88048	0.43734	0.43637
Mean value	0.89280	0.44508	0.43740
St. dev. (N%)	3.12	3.18	1.55

[a] in $(a.u.)^2$.

Table 3.b. Second order electric moments for lone pair orbitals[a]

Lone p.N	q_x^2	q_y^2	q_z^2
NH_3	0.90192	0.60622	0.60622
NH_2NH_2	0.86289	0.62319	0.57990
CH_3NH_2	0.93620	0.64952	0.59659
NH_2OH	0.77492	0.59151	0.58604
Mean value	0.86898	0.61760	0.59218
St. dev. (N%)	6.93	3.49	1.70
Lone p.O	q_x^2	q_y^2	q_z^2
H_2O	0.70506	0.45887	0.45628
H_2O_2 (1)	0.60074	0.45187	0.43914
(2)	0.60248	0.45663	0.44479
CH_3OH	0.69506	0.52082	0.45871
NH_2OH	0.63293	0.48035	0.44826
Mean value	0.64726	0.47370	0.44944
St. dev. (N%)	10.10	5.38	1.61

[a] in $(a.u.)^2$.

(see Table 3.a). The standard deviation of components q_x^2 for bonds CH, NH and OH vary between 2.9 and 4.6%. i.e., the deviations are much larger than those found for the first order localized moments. The standard deviations for the components q_y^2 and q_z^2 are smaller than those for q_x^2 in all of the three series.

It is interesting, that for the CH bond the standard deviation of q_y^2 is smaller than that of q_z^2, while for the NH bond they are nearly equal, and for the OH orbitals the standard deviation of components q_y^2 is much larger than that of q_z^2.

The second order electric moments for lone pair orbitals differ more within the same series from each other than those for bond orbitals. The results are presented in Table 3.b. The standard deviation for components q_x^2 for O containing series exceeds even 10.00% and the q_y^2 and q_z^2 are also rather large, varying between 1.6 and 5.4%. It is remarkable that while the components q_x^2 are always larger for bonds than for lone pair orbitals in the system studied, it does not hold the same for the values of q_y^2 and q_z^2 (see, e.g., NH bond and OH bond in Table 3.a, or N lone pair and O lone pair orbitals in Table 3.b).

The regularity generally holds that the first order electric moments for any type of localized orbitals are less sensitive to the change of molecular environment than the second order ones.

4. Moment Characteristics

Some quantities have been proposed recently [2] in order to characterize the charge distribution of bond and lone pair orbitals. First, the angles between the centroid vectors of bond orbitals are investigated. They are in all cases smaller than the corresponding valence angles. The deviation of bond centroid vector from the valence axis in degrees are given (under the heading α) in Table 4. The α values do not exceed the 3.0° for any of bond orbitals.

Table 4. Deviation angles for the centroid vectors (in degrees). Definition of α and β see in text

	Bond	CH
	α	β
CH_4	0.0	0.0
CH_3CH_3	0.4	0.8
CH_3NH_2 (1)	0.2	2.1
(2)	0.5	1.0
CH_3OH (1)	0.7	1.6
(2)	0.4	3.4
Mean value	0.4	1.5
St. dev. (*N*%)	60.3	72.7

	Bond	NH	Lone	p.N
	α	β	α	β
NH_3	0.6	3.2	—	8.5
NH_2NH_2 (1)	2.2	4.5	73.2	4.1
(2)	2.7	5.1	—	—
CH_3NH_2	1.7	5.2	73.2	11.0
NH_2OH	1.4	5.0	70.9	10.1
Mean value	1.7	4.6	72.4	8.4
St. dev. (N%)	41.5	16.1	1.5	31.5

	Bond	OH	Lone	p.O
	α	β	α	β
H_2O	0.6	2.4	—	6.4
H_2O_2 (1)	0.6	1.9	75.4	10.8
(2)	—	—	76.3	11.7
CH_3OH	1.6	5.2	77.1	11.7
NH_2OH	0.5	7.2	74.1	10.1
Mean value	0.8	4.2	75.7	10.1
St. dev. (N%)	54.5	51.6	1.5	19.4

In cases of lone pair orbitals under the heading α the deviation in degree of the given centroid vector and the molecular axis (i.e., the axis which connects the two heavy atoms) are presented. The standard deviation for both the nitrogen and oxygen lone pair orbitals is about 1.5%. The deviation angles are only slightly larger for the oxygen than for the nitrogen lone pair orbitals. The small standard deviations suggest that the orientation of lone pair centroid vectors are well defined in the 18-electron systems. Apart from the symmetric cases, the direction of major dispersion axis (q_x), which has its origin at the center of charge of the given localized orbital, does not coincide with the corresponding centroid vector. These non-zero angles are presented in Table 4 under the heading β. The standard deviation for the angles β are rather large both for bond and lone pair orbitals. The deviation angles β for a system containing similar orbitals were expected to be close to each other (see, e.g., NH_2NH_2(1) and (2) or H_2O_2 (1) and (2)).

In addition to the deviation angles, some further quantities have been defined for characterizing the main differences between bond and lone pair charge distributions (for all definitions see [2]). The asymmetry of bond orbitals (A_{orb}) is evidently decreasing as the nuclear charge of central heavy atom increases. The values are given in Table 5. The results parallel with those found for the centroid lengths – i.e. the CH, NH or OH bonds could be identified even by their LMO symmetry. It does not hold the same for the lone pair orbitals, as they vary between 0.72 and 0.84 for both nitrogen and oxygen containing systems.

The further moment characteristics, namely the effective solid angles (Ω_{eff}), the dispersion ratios (R_d) and dispersion products (P_d) of localized charge densities show similar regularities than the orbital asymmetries do. All of the three quantities form well-separated groups for CH, NH and OH bond orbitals (see Table 5). The values of two characteristics for the lone pair orbitals, however, do overlap in the nitrogen and oxygen containing series: the Ω_{eff} angles vary

Table 5. Moment characteristics

	A_{orb}	Ω_{eff} (sterad)	R_d	P_d (a.u.)^3
Bond CH				
CH_4	1.215	0.933	1.336	0.787
CH_3CH_3	1.256	0.908	1.316	0.763
CH_3NH_2 (1)	1.310	0.873	1.293	0.737
(2)	1.264	0.902	1.312	0.743
CH_3OH (1)	1.311	0.878	1.287	0.725
(2)	1.286	0.887	1.304	0.722
Bond NH				
NH_3	1.117	1.006	1.385	0.566
NH_2NH_2 (1)	1.169	0.978	1.347	0.549
(2)	1.147	1.003	1.352	0.544
CH_3NH_2	1.132	1.003	1.370	0.565
NH_2OH	1.166	0.981	1.349	0.531
Bond OH				
H_2O	1.015	1.090	1.447	0.427
H_2O_2	1.051	1.073	1.412	0.396
CH_3OH	1.028	1.110	1.411	0.434
NH_2OH	1.037	1.085	1.420	0.410
Lone p.N				
NH_3	0.751	2.040	1.220	0.576
NH_2NH_2	0.766	2.035	1.198	0.558
CH_3NH_2	0.725	2.108	1.226	0.602
NH_2OH	0.839	1.925	1.147	0.518
Lone p.O				
H_2O	0.721	2.103	1.237	0.384
H_2O_2 (1)	0.808	1.985	1.176	0.337
(2)	0.810	1.988	1.156	0.350
CH_3OH	0.723	2.180	1.192	0.408
NH_2OH	0.781	2.049	1.168	0.369

about 2.0 degree while the R_d ratios between 1.14 and 1.24. These results suggest that the charge distribution of lone pair orbitals have similar "form" for all systems considered, i.e. they are not too much dependent on the central atom nuclear charge or on the molecular environment. The dispersion product, however, even for lone pair orbitals is rather different in the series of oxygen and nitrogen containing molecules. The values are about 5.1–6.0 for the former, while 3.3–4.1 for the latter ones. This result confirms the regularity found earlier: while the "form" of lone pair orbital charge densities are similar, the "region" which they occupy are the larger the smaller is the nuclear charge of the central heavy atom.

The conclusion can be drawn that the moment characteristics for lone pair orbitals as well as for bonds are transferable to a rather good approximation.

5. Charge Displacements in the LMO's of 18-Electron Systems

The LMO's of the systems considered are slightly delocalized extending into regions away from the center of their charge clouds. We have found that in the LMO's of the valence shell beyond the contributions from the principal components (two-center bonds or one-center lone pairs) those from the basis functions of vicinal H atoms are also appreciable. Similar results were obtained by England *et al.* for acyclic hydrocarbons [10]. The comparison of our results with theirs is, however, not straightforward because they use INDO approximation with a minimal hybrid basis.

Our results have also shown that in the LMO of a given bond or a lone pair the coefficients of basis functions of a vicinal H atom are the largest if the H atom is coplanar (or nearly coplanar) to the principal components. In these cases the magnitude of some of the coefficients usually exceeds the value of 0.05. If the vicinal H atom is in the cis position the coefficients of its basis functions and those of the principal components are of opposite sign. If the vicinal H atom is in trans position, the coefficients of its basis functions in the corresponding LMO are of the same sign as those of the principal components. For vicinal H atoms in gauche position the magnitudes of the coefficients are usually smaller than 0.05. The position of the vicinal H atom manifests itself in the magnitude of the centroid length of the corresponding LMO. For example, in CH_3NH_2 the two equivalent CH bonds (denoted by (2) in Table 1) have nearly coplanar vicinal H atoms in trans position. As a consequence their centroid lengths are smaller than that of the other CH bond (denoted by (1) in Table 1). Similar situation occurs in NH_2NH_2 where the centroid length of the two NH bonds heaving nearly coplanar vicinal H atoms (denoted by (2) in Table 1) is smaller than that denoted by (1). In CH_3OH the centroid length of those CH bond is smaller (denoted by (2) in Table 1) which have a coplanar vicinal H atom in cis position.

The results obtained on the study of the charge displacement in the LMO's of 18-electron systems provided further information on the spatial distribution of localized charge densities (see, e.g., in [4]) in various molecules.

6. Conclusion

Several regularities have been found as investigating the localized moments and moment characteristics for some related ten- and eighteen-electron systems. The first order electric moments are transferable to a rather good approximation. As to the values of second order electric moments, they are more sensitive to the change of molecular environment. It is expected that results obtained for these quantities by the use of larger basis sets (including polarization functions) would not alter very much these conclusions.

The study of moment characteristics has shown that, in addition to their advantages pointed out in [2], they are even transferable to a fairly good approximation.

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