

Transferability of Some Properties of Localized Molecular Orbitals

I. Energy Quantities

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The localized molecular orbitals of some related ten- and eighteen-electron systems have been studied. The transferability of the kinetic, self-interaction, Coulomb and exchange interaction energies on localized orbitals have been shown. The standard deviation of the kinetic and of the interaction energies (including exchange) are less than 2.5% except for lone pair orbitals of the oxygen atoms where the standard deviation is close to 4%.

Key words: Localized MOs, transferability of ~

1. Introduction

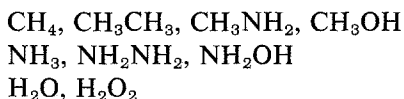
The notion of transferability may be interpreted in several ways. One can use directly the localized orbitals of small molecules for constructing the wavefunction of related larger molecules without further optimization. The orbitals are considered transferable if the molecular properties calculated with and without additional optimization are close together [1]. Another way to interpret transferability is through the use of the properties of the individual orbitals [2]. In this case actually certain properties of orbitals of the same type but in different environments are compared.

The transferability of certain molecular properties (bond energies, bond electric moments etc.) are considered as a long established fact in chemistry. For systems of certain types (e.g., aliphatic hydrocarbons) the bond energies are apparently transferable to an accuracy exceeding by an order of magnitude the accuracy of the results obtained by the Hartree–Fock method [3].

In the framework of the independent particle model the one-electron properties of the system (including the total energy at equilibrium geometry) can be written as the

sum of contributions from the individual orbitals [4]. This means that the transferability of the one-electron properties is implied by the transferability of the orbitals. As is well known, canonical molecular orbitals are nontransferable and even the localized molecular orbitals penetrating each other considerably [5] and having delocalized "tails" [6] cannot be considered as transferable in the strict sense. The transferability of localized orbitals is investigated in various papers [7–11]; the efforts in this direction are reviewed in [1].

In a series of papers we investigate the transferable property of quantities connected with localized charge densities of some related ten- and eighteen-electron systems. The following compounds have been studied:



These eighteen-electron systems have already been investigated by several authors [12–16]. Some of them have been the subject of many Hartree–Fock studies using different basis sets [17–20].

The purpose of the present study is to investigate the effects of the environment on

Table 1. Geometries considered in the calculations^a

| | Bond lengths (a.u.) | Bond angles (degree) |
|---------------------------------|--|---|
| CH ₄ | CH = 2.066 | HCH = tetr. |
| CH ₃ CH ₃ | CH = 2.066 CC = 2.890 | HCH = 109.7 |
| CH ₃ NH ₂ | CH = 2.066 CN = 2.786 NH = 1.916 | HCH = 109.5 HNH = 105.8 CNH = 112.2 tilt = 3.5 |
| CH ₃ OH | CH = 2.069 CO = 2.699 OH = 1.814 | HCH = 109.5 COH = 109 tilt = 3.3 |
| NH ₃ | NH = 1.912 | HNH = 106.69 |
| NH ₂ NH ₂ | NH = 1.931 NN = 2.738 | HNH = 108 HNN = 112 torsion = 90 |
| NH ₂ OH | NH = 1.946 NO = 2.759 OH = 1.833 | HNH = 107 HON = 102 HNO = 107 |
| H ₂ O | OH = 1.809 | HOH = 104.52 |
| H ₂ O ₂ | OH = 1.833 OO = 2.816 | HOO = 100 torsion = 111.5 |

^a Interatomic Distances, Special Publications No. 11 and No. 18. London: The Chemical Society 1958 and 1965

Table 2. Total energies calculated for the studied systems (in hartree)

| | Total energy |
|---------------------------------|--------------|
| CH ₄ | -46.18596 |
| CH ₃ CH ₃ | -79.20462 |
| CH ₃ NH ₂ | -95.17883 |
| CH ₃ OH | -115.00856 |
| NH ₃ | -56.17065 |
| NH ₂ NH ₂ | -111.13381 |
| NH ₂ OH | -130.95978 |
| H ₂ O | -76.01081 |
| H ₂ O ₂ | -150.76281 |

the localized orbitals. In this paper the energy quantities are discussed. The following paper will deal with the first and second-order electric moments.

For the calculations a rather large uniform basis set, a (13s7p/4s) Gaussian contracted to [4s2p/2s], is used (more details see in [21–23].) Except for CH₃OH the calculations have been carried out at the experimental geometries at which the properties studied are actually measured. The applied geometries are given in Table 1. The total energies obtained for the ten- and eighteen-electron systems are summarized in Table 2. All calculations were performed on an IBM 370/165 computer (CNRS, Orsay, France).

Recent investigations show that the inclusion of polarization functions is essential if we want to calculate the total electric moments or the equilibrium geometries to a good approximation [24]. The influence of polarization functions on the localized charge distributions of H₂O has been analyzed [25]. The results have shown that the presence of polarization functions cause systematic changes in the form of the bond and lone pair localized orbitals. It seems, however, to be highly improbable that the overall transferability of properties discussed in this paper would be affected by the inclusion of polarization functions or enlargement of the basis set.

2. One-Orbital Contribution

The canonical orbitals were transformed into the localized orbitals using the Edmiston–Ruedenberg method [26]. Let us denote the canonical orbitals by $\{\varphi_i\}_{i=1}^N$, the localized ones by $\{\bar{\varphi}_i\}_{i=1}^N$ (N = number of occupied orbitals). In the total electron-interaction energy expression

$$EI = 2 \sum_i \sum_j (\varphi_i^2 | \varphi_j^2) - \sum_i \sum_j (\varphi_i \varphi_j | \varphi_i \varphi_j) \quad (1)$$

the first part represents the Coulomb, the second one the exchange interactions. The diagonal terms

$$D(\varphi) = \sum_i (\varphi_i^2 | \varphi_i^2) \quad (2)$$

occur in both parts. The unitary transformations can be chosen so that the $D(\varphi)$ terms (self-repulsions) have their maximum value. According to the

Edmiston–Ruedenberg procedure the remainder of (1) will have a minimum when the desired transformation is found:

$$EI = \sum_{i \neq j} \sum_{\substack{\min \\ \max}} [2(\bar{\varphi}_i^2 | \bar{\varphi}_j^2) - (\bar{\varphi}_i \bar{\varphi}_j | \bar{\varphi}_i \bar{\varphi}_j)] + \sum_i (\bar{\varphi}_i^2 | \bar{\varphi}_i^2). \quad (3)$$

In the present paper we discuss the kinetic, the self-interaction, the Coulomb and the exchange interaction energies between electrons on localized orbitals. The self-interaction energies of electrons connected with localized orbitals for small molecules have already been studied in some recent works [25, 27]. No investigations have yet been reported, however, on the kinetic energy contributions obtained from localized orbitals.

As is well known [28], the total energy E of a system equals the negative of the kinetic energy, T , if the simple form of the virial theorem

$$-V/T = 2 \quad (4)$$

is satisfied.

Table 3a. Kinetic energies of electrons on localized orbitals

| | Core C | Bond CH | |
|-------------------------------------|---------|---------|----------|
| CH ₄ | 16.6363 | 0.86654 | |
| CH ₃ CH ₃ | 16.6377 | 0.88013 | |
| CH ₃ NH ₂ (1) | 16.6349 | 0.89079 | |
| (2) | — | 0.89532 | |
| CH ₃ OH (1) | 16.6360 | 0.89844 | |
| (2) | — | 0.90917 | |
| Mean value | 16.6362 | 0.89007 | |
| St. dev. (N%) | 0.01 | 1.53 | |
| | Core N | Bond NH | Lone p.N |
| NH ₃ | 23.1416 | 1.18132 | 1.45407 |
| NH ₂ NH ₂ (1) | 23.1295 | 1.20114 | 1.52250 |
| (2) | — | 1.21282 | — |
| CH ₃ NH ₂ | 23.1293 | 1.19252 | 1.49183 |
| NH ₂ OH | 23.1624 | 1.22482 | 1.50970 |
| Mean value | 23.1407 | 1.20252 | 1.49453 |
| St. dev. (N%) | 0.01 | 1.26 | 1.72 |
| | Core O | Bond OH | Lone p.O |
| H ₂ O | 30.7732 | 1.60487 | 2.04794 |
| H ₂ O ₂ (1) | 30.8447 | 1.67264 | 2.11198 |
| (2) | — | — | 2.09702 |
| CH ₃ OH | 30.7751 | 1.61729 | 2.07010 |
| NH ₂ OH | 30.8080 | 1.65632 | 2.08581 |
| Mean value | 30.8003 | 1.60487 | 2.08257 |
| St. dev. (N%) | 0.09 | 1.69 | 1.06 |

Table 3b. Self-interaction energies of electrons on localized orbitals for the studied systems

| | Core C | Bond CH | |
|-------------------------------------|---------|---------|----------|
| CH ₄ | 3.56701 | 0.67003 | |
| CH ₃ CH ₃ | 3.56708 | 0.67669 | |
| CH ₃ NH ₂ (1) | 3.56693 | 0.68095 | |
| (2) | — | 0.68188 | |
| CH ₃ OH (1) | 3.56711 | 0.68340 | |
| (2) | — | 0.68559 | |
| Mean value | 3.56703 | 0.67977 | |
| St. dev. (N%) | 0.00 | 0.76 | |
| | Core N | Bond NH | Lone p.N |
| NH ₃ | 4.20829 | 0.74202 | 0.77969 |
| NH ₂ NH ₂ (1) | 4.20731 | 0.74770 | 0.79081 |
| (2) | — | 0.75250 | — |
| CH ₃ NH ₂ | 4.20711 | 0.74584 | 0.77991 |
| NH ₂ OH | 4.21013 | 0.75431 | 0.80351 |
| Mean value | 4.20820 | 0.74846 | 0.78848 |
| St. dev. (N%) | 0.03 | 0.60 | 1.24 |
| | Core O | Bond OH | Lone p.O |
| H ₂ O | 4.85250 | 0.81276 | 0.90471 |
| H ₂ O ₂ (1) | 4.84777 | 0.83235 | 0.93558 |
| (2) | — | — | 0.93072 |
| CH ₃ OH | 4.85261 | 0.81649 | 0.90640 |
| NH ₂ OH | 4.84552 | 0.82690 | 0.92147 |
| Mean value | 4.84960 | 0.82215 | 0.91978 |
| St. dev. (N%) | 0.06 | 0.96 | 1.36 |

In the single-determinant approximation we have

$$E = -T \equiv \sum_{i=1}^N \langle \varphi_i | \Delta | \varphi_i \rangle. \quad (5)$$

In our case (4) is not satisfied exactly, and thus equality (5) does not hold; the difference of the quantities E and $-T$ is, however, always less than 0.2 a.u.

The kinetic energy contributions from the localized orbitals of the systems considered can be found in Table 3a. The standard deviations (in %) of quantities calculated with localized orbitals of the same type are also given. The standard deviations are smallest for cores, larger for bonds and largest for lone pair orbitals in the case of molecules containing nitrogen. As to the compounds with the oxygen atoms, the standard deviations for bonds are larger than for the lone-pair orbitals. None of the standard deviations exceed 1.8%.

The results obtained for the self-interactions have shown that they describe clearly the characteristics of the corresponding orbitals (core, bond-pair and lone-pair orbitals), and vary systematically with the heavy atom charge [22]. In Table 3b we summarized (given in atomic units) the self-interaction energies of electrons on localized orbitals for some ten- and eighteen-electron molecules. The standard deviation of the former quantities is increasing as going from core orbitals through bond-pair orbitals to lone-pair orbitals. It is remarkable that the standard deviations for the self-interactions of core orbitals are smaller than those for the other type of localized orbitals. This is in agreement with the results obtained for the kinetic energy contributions as well as with the fact that the "core" (inner-shell) orbitals are not much affected by the molecular environment. The standard deviation for core orbitals for the C, N, and O containing systems is less than 0.1%. The self-repulsions for bond orbitals are smaller than those for the core orbitals. The standard deviations for the bonds CH, NH and OH studied are, however, about 0.6–1.0%. Most sensitive to the molecular environment are the lone pair orbitals: their standard deviations are largest (about 1.2–1.4% for the N and O containing compounds).

3. Two-Orbital Contributions

The interaction energies of electrons on localized orbitals are grouped with respect to the nuclear charge of the heavy atom. In Table 4 we present (in atomic units) the interactions of electrons on core and bond orbitals and those on two bond orbitals

Table 4. Interaction energies for C-containing molecules

| | Coulomb | Exchange |
|-------------------------------------|---------|----------|
| Core C/Bond CH | | |
| CH ₄ | 0.64405 | 0.00857 |
| CH ₃ CH ₃ | 0.64610 | 0.00861 |
| CH ₃ NH ₂ (1) | 0.64613 | 0.00872 |
| (2) | 0.65157 | 0.00887 |
| CH ₃ OH (1) | 0.65025 | 0.00888 |
| (2) | 0.65511 | 0.00909 |
| Mean value | 0.64887 | 0.00880 |
| St. dev. (N%) | 0.58 | 2.08 |
| Bond CH/Bond CH | | |
| CH ₄ | 0.40469 | 0.01897 |
| CH ₃ CH ₃ | 0.40550 | 0.01877 |
| CH ₃ NH ₂ (1) | 0.40631 | 0.01845 |
| (2) | 0.40738 | 0.01873 |
| CH ₃ OH (1) | 0.40732 | 0.01838 |
| (2) | 0.40964 | 0.01884 |
| Mean value | 0.40681 | 0.01869 |
| St. dev. (N%) | 0.39 | 1.12 |

for the carbon-containing compounds. In all cases the interactions of electrons on joint localized orbitals are investigated in order to study the same type of interaction for the ten- and eighteen-electron systems. Several regularities can be found from the results.

As to the interaction energies corresponding to the core of carbon and the CH bond, the Coulombic parts differ less in the studied molecules than the exchange parts. A similar conclusion holds for the interactions of electrons on two joint CH bonds. It is also remarkable that the interactions between the electrons on the core and on the CH bonds, respectively, have a standard deviation larger than those on two joint CH bonds both for the Coulomb and the exchange parts. The differences between the Coulomb or the exchange interaction energies corresponding to the same localized orbital in different molecules are in general not larger than those in the same molecule corresponding to two similar orbitals (see, e.g., $\text{CH}_3\text{NH}_2(1)$ and $\text{CH}_3\text{NH}_2(2)$ in comparison with $\text{CH}_3\text{OH}(1)$ and $\text{CH}_3\text{OH}(2)$ in Table 4).

The results obtained for the interactions of electrons on localized orbitals in nitrogen-containing molecules are given in Table 5 (in atomic units). The regularities are similar to those found for the carbon series. The core and valence shell interactions differ more from each other in the series than the interactions of electrons on the valence shell orbitals. This fact may be due to the different magnitude of overlap of localized orbitals [5, 29]. It is to be noted that – in contrast to the case of self-repulsions – the sensitivity of interactions for lone-pair orbitals is close to that for bond orbitals (see the standard deviations in Table 5).

The above regularities are valid even for the series of molecules presented in Table 6 (given in atomic units). In this table the H_2O and some related eighteen-electron systems are shown, in order to see how similar the interaction energies of electrons

Table 5. Interaction energies for N-containing molecules

| | Coulomb | Exchange | Coulomb | Exchange |
|------------------------------|-----------------|----------|------------------|----------|
| | Core N/Bond NH | | Bond NH/Lone p.N | |
| NH_3 | 0.76128 | 0.01127 | 0.52304 | 0.03541 |
| NH_2NH_2 (1) | 0.76426 | 0.01144 | 0.52851 | 0.03589 |
| (2) | 0.77258 | 0.01170 | 0.53141 | 0.03620 |
| CH_3NH_2 | 0.76332 | 0.01131 | 0.52605 | 0.03586 |
| NH_2OH | 0.77445 | 0.01184 | 0.52784 | 0.03453 |
| Mean value | 0.76718 | 0.01150 | 0.52737 | 0.03558 |
| St. dev. (N%) | 0.69 | 1.82 | 0.53 | 1.64 |
| | Core N/Lone p.N | | Bond NH/Bond NH | |
| NH_3 | 0.89687 | 0.01619 | 0.48097 | 0.02647 |
| NH_2NH_2 | 0.91024 | 0.01715 | 0.48323 | 0.02675 |
| CH_3NH_2 | 0.90074 | 0.01669 | 0.48183 | 0.02629 |
| NH_2OH | 0.91391 | 0.01677 | 0.48716 | 0.02731 |
| Mean value | 0.90543 | 0.01670 | 0.48330 | 0.02671 |
| St. dev. (N%) | 0.76 | 1.94 | 0.49 | 1.44 |

Table 6. Interaction energies for O-containing molecules

| | Coulomb | Exchange | Coulomb | Exchange |
|-----------------------------------|-----------------|----------|-------------------|----------|
| | Core O/Bond OH | | Lone p.O/Lone p.O | |
| H ₂ O | 0.88756 | 0.01471 | 0.67668 | 0.05674 |
| H ₂ O ₂ | 0.90798 | 0.01548 | 0.67819 | 0.05194 |
| CH ₃ OH | 0.89031 | 0.01475 | 0.67826 | 0.05740 |
| NH ₂ OH | 0.90250 | 0.01528 | 0.67820 | 0.05467 |
| Mean value | 0.89710 | 0.01508 | 0.67783 | 0.05518 |
| St. dev. (N%) | 0.94 | 2.22 | 0.98 | 3.86 |
| | Core O/Lone p.O | | Bond OH/Lone p.O | |
| H ₂ O | 1.05432 | 0.02085 | 0.61430 | 0.04550 |
| H ₂ O ₂ (1) | 1.07117 | 0.02126 | 0.62206 | 0.04560 |
| (2) | 1.07570 | 0.02141 | 0.62354 | 0.04581 |
| CH ₃ OH | 1.05672 | 0.02101 | 0.61503 | 0.04540 |
| NH ₂ OH | 1.06528 | 0.02114 | 0.62005 | 0.04567 |
| Mean value | 1.06464 | 0.02214 | 0.61900 | 0.04560 |
| St. dev. (N%) | 0.77 | 1.01 | 0.56 | 0.31 |

on their localized orbitals are. From the results it follows that the extent of transferability does not seem to be dependent on the heavy atom nuclear charge, as similar regularities were found for all of the three series. The standard deviation for the exchange part for the lone pair orbital interactions – occurring only in the oxygen-containing series – is the largest, 3.8%. These deviations for the lone pair/lone pair interactions may certainly be due to the relatively large absolute and density overlap of these orbitals [5, 29].

4. Characterization of the Heavy Atom Bonds

In order to have a systematic study of all types of localized orbitals investigated, we present the results obtained for the heavy atom bonds as well. These are given in atomic units in Table 7. In addition to the self-interactions, the interactions of electrons on the heavy atom bonds and on the localized orbitals connected with only one of the heavy atom (core, hydrogen-containing bonds, lone pairs) have been studied.

First the self-interaction energies of the heavy atom bonds are investigated. It can be seen that the self-repulsions are increasing as going from CC through CN to CO bond (and similarly in the series CN, NN, NO or OO, NO and CO). This regularity is due to the systematic change of nuclear charge. In spite of the different orbitals, e.g. for the interactions between electrons on the heavy atom bonds and the core orbitals, the differences between the Coulombic parts are not too large: the deviations are less than 3% for core C, 6% for core N and 8% for core O orbitals. The deviations for the exchange interactions are about 10–15% for the several heavy atom bonds and core orbitals.

Table 7. Interaction energies of electrons on localized orbitals. Heavy atom bonds

| Heavy atom bond/ other orbital | Coulomb | Exchange |
|-----------------------------------|---------|----------|
| CC | 0.65489 | — |
| CN | 0.70536 | — |
| CO | 0.76453 | — |
| NN | 0.71209 | — |
| NO | 0.72397 | — |
| OO | 0.70611 | — |
| CC/Core C | 0.62975 | 0.00814 |
| CN/Core C | 0.61242 | 0.00730 |
| CO/Core C | 0.59857 | 0.00658 |
| CN/Core N | 0.73855 | 0.01060 |
| NN/Core N | 0.69745 | 0.00926 |
| NO/Core N | 0.65435 | 0.00792 |
| CO/Core O | 0.86047 | 0.01396 |
| NO/Core O | 0.79329 | 0.01205 |
| OO/Core O | 0.73540 | 0.01040 |
| CC/Bond CH | 0.39896 | 0.01777 |
| CN/Bond CH (1) | 0.39063 | 0.01452 |
| (2) | 0.39240 | 0.01474 |
| CO/Bond CH (1) | 0.38599 | 0.01285 |
| (2) | 0.38759 | 0.01240 |
| NN/Bond NH | 0.45339 | 0.02262 |
| CN/Bond NH | 0.47009 | 0.02616 |
| NO/Bond NH | 0.44177 | 0.02016 |
| OO/Bond OH | 0.50543 | 0.02737 |
| CO/Bond OH | 0.54960 | 0.03479 |
| NO/Bond OH | 0.52707 | 0.03068 |
| NN/Lone p.N | 0.49908 | 0.03054 |
| CN/Lone p.N | 0.51507 | 0.03528 |
| NO/Lone p.N | 0.47851 | 0.02635 |
| OO/Lone p.O (1) | 0.54735 | 0.03670 |
| (2) | 0.54714 | 0.03682 |
| CO/Lone p.O | 0.60218 | 0.04528 |
| NO/Lone p.O | 0.57325 | 0.04049 |

As to the Coulomb interactions of electrons on the various heavy atom bonds and the bond orbitals joint to a hydrogen, the following result was obtained. The smaller the nuclear charge of the heavy atom is, the smaller is the standard deviation: about 2% for the CH bonds, larger for the NH bonds (about 3%) and largest for the OH bonds (about 5%). This fact may be due to the increasing number of lone pair orbitals on the individual heavy atom. Similar regularity holds for the exchange interactions (see Table 7).

From the above results it follows that the differences for the Coulomb interactions between electrons on heavy atom bonds and on lone pair localized orbitals might be still larger. The values given in Table 7 show that the deviation for the nitrogen lone-pair orbitals is larger than 4% while that for the oxygen lone-pair orbitals is about 6%. The corresponding deviations for the exchange interactions are about 14%.

5. Conclusion

Some regularities have been found on comparing the corresponding quantities for ten- and eighteen-electron systems. The kinetic and the Coulomb interaction energies are transferable to a fairly good approximation; the standard deviations never exceed the value of 2%. This means that these quantities are not very sensitive to any changes in the vicinal groups.

The exchange interactions of electrons on localized orbitals differ always more from each other in any series than the Coulomb interactions. Even the largest standard deviation, for the lone-pair orbitals of oxygen, however, does not exceed 4%.

The differences between the sensitivity of the exchange and Coulombic parts can be interpreted in the following way. The localized orbitals are not completely localized, they contain the basis functions of atoms in vicinal position with coefficients of appreciable magnitude. These "tails" are characteristic of the vicinal groups (see next paper in this series). The exchange interactions are more sensitive to the changes in the "tails"; the larger standard deviations can be attributed to this greater sensitivity.

A study of transferability of several other quantities related to localized molecular orbitals will be the subject of our next paper.

References

1. O'Leary, B., Duke, B. J., Eilers, J. E.: *Advan. Quantum Chem.* **9**, 1 (1975)
2. Rothenberg, S.: *J. Chem. Phys.* **51**, 3389 (1969); *J. Am. Chem. Soc.* **93**, 68 (1971)
3. Allen, T. L.: *J. Chem. Phys.* **31**, 1039 (1959)
4. Kapuy, E., Török, F.: *Quantum theory of atoms and molecules (in Hungarian)*. Budapest: Akadémiai Kiadó, 1975
5. Daudel, R., Stephens, M. E., Kapuy, E., Kozmutza, C.: *Chem. Phys. Letters* **40**, 194 (1976)
6. Gordon, M. S., England, W.: *J. Am. Chem. Soc.* **94**, 5168 (1972)
7. England, W., Salmon, L. S., Ruedenberg, K.: *Topics in Current Chem.* **23**, 31 (1971)
8. von Niessen, W.: *Theoret. Chim. Acta (Berl.)* **31**, 111, 297 (1973); **33**, 7 (1974)
9. England, W., Gordon, M. S., Ruedenberg, K.: *Theoret. Chim. Acta (Berl.)* **37**, 177 (1975)
10. Adams, W. H.: *J. Am. Chem. Soc.* **92**, 2198 (1970)
11. Peters, D.: *J. Am. Chem. Soc.* **94**, 707 (1972)
12. Pedersen, L., Morokuma, K.: *J. Chem. Phys.* **46**, 3941 (1967)
13. Palke, W. E., Pitzer, R. M.: *J. Chem. Phys.* **46**, 3948 (1967)
14. Blom, C. E., Slingerland, P. J., Altona, C.: *Mol. Phys.* **31**, 1359 (1976)
15. Tel, L. M., Wolfe, S., Csizmadia, I. G.: *J. Chem. Phys.* **59**, 4047 (1973)
16. Flood, E., Pulay, P., Boggs, J. E.: *J. Am. Chem. Soc.* **99**, 5570 (1977)
17. Hariharan, P. C., Pople, J. A.: *Theoret. Chim. Acta (Berl.)* **28**, 213 (1973)

18. Dunning, T. H., Winter, N. W.: J. Chem. Phys. **63**, 1847 (1975)
19. Ryan, P. B., Todd, H. D.: J. Chem. Phys. **67**, 4787 (1977)
20. Cremer, D.: J. Chem. Phys. **69**, 4440 (1978)
21. Kapuy, E., Kozmutza, C., Stephens, M. E.: Theoret. Chim. Acta (Berl.) **43**, 175 (1976)
22. Kapuy, E., Ozoróczy, Zs., Kozmutza, C.: Acta Phys. Acad. Sci. Hung. **41**, 125 (1976)
23. Daudel, R., Stephens, M. E., Csizmadia, I. G., Kozmutza, C., Kapuy, E., Goddard, J. D.: Intern. J. Quantum. Chem. **11**, 665 (1977)
24. Bell, S.: J. Chem. Phys. **68**, 3014 (1978)
25. Kapuy, E., Kozmutza, C., Daudel, R., Stephens, M. E.: Theoret. Chim. Acta (Berl.) **50**, 31 (1978)
26. Edmiston, C., Ruedenberg, K.: J. Chem. Phys. **43** S, 97, (1965)
27. Robb, M. A., Csizmadia, I. G.: Intern. J. Quantum Chem. **4**, 365 (1970)
28. Allen, T. L., Shull, H.: J. Chem. Phys. **35**, 1644 (1961)
29. Stephens, M. E., Kapuy, E., Kozmutza, C.: Theoret. Chim. Acta (Berl.) **45**, 111 (1977)

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